DAIRY WASTEWATER TREATMENT BY PHYSICO-CHEMICAL METHODS AND SEQUENTIAL BATCH REACTOR

A THESIS

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **DAIRY WASTEWATER TREATMENT BY PHYSICO-CHEMICAL METHODS AND SEQUENTIAL BATCH REACTOR** in partial fulfilment of the requirements for the award of the Degree of Doctor of Philosophy and submitted in the Department of Chemical Engineering of Indian Institute of Technology Roorkee is an authentic record of my own work carried out during a period from August 2008 to February 2011 under the supervision of Dr. I. D. Mall, Professor, and Dr. V. C. Srivastava, Assistant Professor, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee.

The matter presented in the thesis has not been submitted by me for the award of any other degree of this or any other Institute.

(JAI PRAKASH KUSHWAHA)

This is to certify that the above statement made by the candidate is correct to the best of our knowledge.

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ABSTRACT

Dairy industries are involved in the manufacturing of various types of milk products. It is one of the most polluting industries not only in terms of volume of effluent generated as well as in terms of its characteristics too. Dairy wastewaters are treated using biological and physico-chemical methods. Most attention has been paid to anaerobic treatment process followed by aerobic and membrane methods. High energy requirement by aerobic biological treatment methods is the primary drawback of these processes, whereas, anaerobic treatment of dairy wastewater reflects very poor nutrient removal. Therefore, further treatment of anaerobically treated effluent is required. Among physico-chemical methods: adsorption, coagulation–flocculation and electro-chemical treatment (ECT) are reported for the treatment of dairy wastewater. Coagulation with inorganic coagulants reported in the literature lack studies on mechanism of treatment process. Moreover, coagulation studies using natural coagulants except for chitosan are not reported in the literature. Further studies have to be concentrated on these aspects of coagulation treatment. ECT using various types of electrodes also requires immediate attention. Disposal aspect of residues (scum and sludge), which are generated during the ECT have not been dealt in previous studies. Among physico-chemical methods, adsorption is an important treatment method for treatment of various types of wastewaters. However, only few studies are reported for the treatment of dairy wastewater by adsorption. Moreover, in these studies, mechanism of adsorption is lacking; kinetic, isotherm, and thermodynamics aspects have not been dealt with which are important for the design of any adsorption unit. Disposal aspects of the spent adsorbents were also not reported in these studies. Disposal of sludge during biological methods is also very important; however, only few investigators have dealt this aspect of wastewater treatment. Present study has been undertaken with endeavor to study the treatment of dairy wastewater by following methods:

1. Treatment by coagulation process using inorganic coagulants such as poly aluminum chloride (PAC), $FeSO_4$ and potash alum; and organic coagulants such as guar gum, sodium alginate and sodium salt of carboxy methyl cellulose (Na-CMC).
2. Treatment by electro-chemical method.
3. Treatment by adsorption process using commercial activated carbon and bagasse fly ash.
4. Treatment by aerobic sequential batch reactor.

To avoid the change in COD and nutrients during storage, simulated dairy wastewater (SDW) was used in the present study. SDW was generated in the laboratory by dissolving 4 g of milk powder (Amulya brand, manufactured by Banaskantha District Cooperative Milk producer's Union Ltd., Palanpur, Uttarakhand, India) per litre of distilled water. Several investigators used same method for making SDW (Ramasamy et al., 2004b; Balannec et al., 2005; Leal et al., 2006).

Inorganic coagulants like poly aluminum chloride (PAC), ferrous sulphate ($FeSO_4$) and potash alum ($KAl(SO_4)_2.12H_2O$) were used for the treatment of SDW. Batch coagulation experiments were conducted to evaluate the influence of initial pH (pH_{i-in}: 5-10) and coagulant dosage (m_{in}: 100-5000 mg/l) on COD removal from SDW. Residual COD and system pH were observed as function of time. Optimum pH_{i-in} ($pH_{i-in.op}$) was found to be 8.0 for all the three coagulants. Optimum m_{in} (m_{in-op}) was found to be 300, 800 and 500 mg/l for PAC, $FeSO_4$ and $KAl(SO_4)_2.12H_2O$, respectively, giving 69.2, 66.5 and 63.8% COD removal efficiency in 30 min at $pH_{i-in.op}$≈8.0. COD removal mechanism by the coagulants was mainly due to charge neutralization and adsorption (Kushwaha et al., 2010b). Slurry produced by PAC and $KAl(SO_4)_2.12H_2O$ showed good settling characteristics. Organic coagulants such as guar gum, sodium salt of carboxy methyl cellulose (Na-CMC) and sodium alginate (Na-alginate) were also tested for their efficiency of COD removal at pH_i (pH_{i-na}) range of 3-10 and dosage range (m_{na}) of 10-200 mg/l. Maximum COD removal efficiency of 66%, 67% and 74% for gar gum, Na-CMC and Na-alginate respectively, was obtained at $pH_{i-na}=4$ and $m_{na}=100$ mg/l.

Response surface methodology with four-factor and five-level full factorial central composite (CC) design has been used to design the experiments for batch ECT of SDW using aluminum (Al) and iron (Fe) electrode. Cuboid shape batch reactor of dimension 108 mm×108 mm×130 mm having working volume 1.5 litre of Perspex sheet was used to conduct the ECT experiments. Magnetic stirrer was used to agitate the SDW. Two pairs of Al and Fe electrodes of thickness 1 mm and 1.5 mm, respectively, each having dimensions of 10 cm × 8.5 cm with inter-electrode spacing of 1 cm were used. Four operational parameters, namely J: 61.7–308.6 A/m^2; m (weight of NaCl): 0-2 g/l; t: 10–90 min and pH_i: 5–11, were taken as input parameters and percentage COD removal (Y_1) and specific energy consumed (KWh per kg of COD removed) (Y_2) were taken as a responses of the system. Multi-response

optimization technique was applied to find values of operational parameters which maximize the Y_1 and simultaneously minimize Y_2. The optimum values of operational parameters were found to be J=123 A/m^2, m=2.0 g/l, t=74 min and pH_o=6.5 with Y_1 and Y_2 were found to be 68% and 1.22 kWh/kg COD removed by Al electrode (Kushwaha et al., 2010c). Whereas, corresponding values for Fe electrode were 270 A/m^2, 0.0, 50 min, and 7.0, respectively, with Y_1 =70% and Y_2=2.76 kWh/kg of COD removed (Kushwaha et al., 2010d). TS, TN and turbidity at optimum condition by Al electrode were found to be 54%, 919% and 99%, respectively. Fe electrode showed TS, TN and turbidity removal efficiency of 48%, 93% and 99%, respectively. Electro-coagulation (charge neutralization of anionic colloids present in the SDW by monomeric cationic aluminum species and sweep coagulation), electro-floatation and electro-oxidation by hypochlorite were found to be the real mechanism of SDW treatment.

Adsorptive treatment of SDW was done by means of adsorption onto activated carbon-commercial grade (ACC) and bagasse fly ash (BFA). Dosage study was carried out by varying the dosages (m_{ad}) in the range of 0.5-25 g/l for both the adsorbents at the optimum pH_i (pH_{i-opt}) and 303 K. The adsorption of SDW by the adsorbents was studied over a pH_i range of 3–10 at 303 K. For SDW treatment by adsorption, optimum pH (pH_{i-opt}) was found to be ≈4.8. Optimum adsorbent dose (m_{ad-opt}) were found to be 20 g/l for ACC and 10 g/l for BFA. Equilibrium contact time was found to be 8 h for both the adsorbents. Pseudo-second order kinetic model was found to fit the kinetic data and Redlich–Peterson isotherm model was generally found to best represent the equilibrium data for SDW treatment by ACC and BFA. The change in entropy and enthalpy for SDW adsorption onto ACC and BFA were estimated as 126 kJ/mol K and 92 kJ/mol; and 26 kJ/mol K and 18 kJ/mol, respectively. The negative values of change in Gibbs free energy indicate the feasibility and spontaneous nature of the adsorptive treatment (Kushwaha et al., 2010e).

Aerobic sequential batch reactor (SBR) technology was used for the biological treatment of SDW. The experimental set-up consisted of a well-mixed cylindrical glass reactor having maximum volume of 10 litre and a working volume of 5 litre. A stirrer was used to keep reactor contents homogeneous. Temperature and SRT were maintained constant 28±2 °C and 20 d, respectively, during the study. The reactor was operated on a fill-and-draw basis, with a cycle time (t_C) of 12 h, while, settle time (t_S), decant time (t_D) and idle time (t_I)

were 1, 0.5 and 0.5 h, respectively. React time (t_R) were varied according to the fill and anoxic phases strategies to degrade the carbonaceous materials and nitrogen present in SDW. For this four phases study was carried out. In the phase-I of SBR operation, instantaneous filling strategy, t_F=0, was implemented with varying volume exchange ratio (VER) and hydraulic retention time (HRT) from 0.40-0.80 and 0.625-1.25 d, respectively. Aeration was started at the start of the reaction time and closed when settle phase started. Phsae-II was initiated by varying t_F in the range of 0.5-2 h at optimum VER (VER$_{opt}$) and HRT (HRT$_{opt}$) obtained from phase-I study. The filling of SDW to SBR was carried out under aerated and mixed fill strategy. In phase-III and IV, an anoxic zone (t_A) were introduced to enhance the nitrogen removal just after fill phase and react phase, respectively, at optimum t_F ($t_{F,opt}$), VER$_{opt}$ and HRT$_{opt}$. t_A after fill (t_{A-F}), varied in the range of 0.5-2 h, was introduced in phase-III. The effect of t_A after reaction (t_{A-R}), which was varied in the range of 1-3 h, was studied in phase-IV at optimum t_{A-F} ($t_{A,opt-F}$).

An increase in HRT from 0.625 to 1.25 d decreased the final liquid effluent COD. This was due to increased biological conversion at higher HRT. Optimum HRT (HRT$_{opt}$) was found to be 1.0 d giving 97% COD removal efficiency and 65% TKN removal efficiency. $t_{F,opt}$=1.0 h was found to be sufficient to treat SDW of C_o=3900 mg/l. With an increase of t_F from 0.5-1.0 h, more and faster nitrification was observed. Optimum t_{A-F} ($t_{A,opt-F}$) was found to be 1.0 h giving 77% TKN removal at the end of reaction, while introduction of t_{A-R} showed no effect on TKN removal.

Heating values of the sludge generated by the coagulants PAC, $FeSO_4$ and $KAl(SO_4)_2.12H_2O$ were found to be 20.7, 29.6 and 17.3 MJ/kg, respectively. Sludge generated in other treatment methods also showed heating values in the range of 16.5-19.2 MJ/kg. Due to the high heating value of residues generated during various treatment processes, they can be dried and used as a fuel in the boilers/incinerators, or can be used for the production of fuel-briquettes.

Comparison of various treatment methods shows that treatment in SBR removes highest amount of COD, however, it requires higher treatment time as compared to ECT or coagulation.

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JAI PRAKASH KUSHWAHA

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NOMENCLATURE

ABBREVIATIONS

ACC	Activated carbon-commercial
ADU	Anaerobic digestion unit
AF	Anaerobic filter
AFBR	Anaerobic filter bioreactor
ALE	Anaerobic lagoon effluent
ANOVA	Analysis of variance
AS	Activated sludge
ASBR	Anaerobic sequencing batch reactor
BDD	Boron doped diamond
BDE	Biodigester effluent
BFA	Bagasse fly ash
BNR	Biological nitrogen removal
BOD	Biological oxygen demand (mg/l)
CC	Central composite
CF	Cheese factory
CFA	Coal fly ash
CI	Cheese Industry
CNTs	Carbon nanotubes
COD	Chemical Oxygen Demand (mg/l)
CP	Cheese production
CST	Continuos stirred tank reactor
CTMP	Chemi-thermo-mechanical pulping
CW	Cooling Water
DAF	Dissolved air flotation
DF	Degree of freedom
DI	Dairy industry
DID	Dairy industry and domestic
DO	dissolved oxygen

DS	Detergents and sanitizing agents
DTA	Differential thermal analysis
DWW	Dairy wastewater
EC	Electro-coagulation
ECT	Electro-chemical treatment
EDX	Energy dispersive X-ray
EF	Electro-flotation
EO	Electro-oxidation
EP	Egg processing
GAC	Granular activated carbon
GAS-SBR	Aerobic granular activated sludge SBR
HDTMAB	Hexadecyltrimethylammonium bromide
HRT	Hydraulic retention time
HTST	High temperature short time
HUASB	Hybrid upflow anaerobic sludge blanket
IC	Ice-cream
LL	Landfill Leachate
LMG	Leachate from municipal garbage landfills
MB	Milk bottling
MBBR	Membrane bioreactor
MCB	Milk and cream bottling
MF	Micro filtration
MLSS	Mixed Liquor suspended solids (mg/l)
MLVSS	Mixed Liquor volatile suspended solids (mg/l)
MSBR	Membrane sequencing batch reactor
Na-CMC	Sodium salt of carboxy methyl cellulose
NEB	Non-enzymatic browning
NF	Nanofiltration
OLR	Organic loading rate
OM	Olive mill
PAC	Poly aluminum chloride
PCM	Potato chips manufacturing

PVC	Poly vinyl chloride
RM	Raw Milk
RO	Reverse-osmosis
ROW	Refectory oily wastewater
R-P	Redlich-Peterson isotherm
RSM	Response surface methodology
SBR	Sequencing batch reactor
SD	Synthetic dairy
SDW	Simulated dairy wastewater
SEM	Scanning electron microscope
SIC	Synthetic ice-cream
SRT	Solid retention time (d)
SS	Suspended solids concentration (mg/l)
ST	Steam
SVI	Sludge volume index (ml/g)
SW	Saline wastewater
TDS	Total dissolved solids
TG	thermo-gravimetry
TGA	Thermo-gravimetric analysis
TKN	Total Kjeldahl Nitrogen (mg/l)
TMP	Thermo-mechanical pulping
TN	Total nitrogen (mg/l)
TOC	Total organic carbon
TP	Total Phosphates
TS	Total solids
TSS	Total suspended solids (g/l)
UASB	Up flow anaerobic sludge blanket
UF	Ultra filtration
UFAF	Upflow anaerobic filter
UW	Urban wastewater
VER	Volume exchange ratio
VS	Volatile solids

VSS	Volatile suspended solids (mg/l)
WM	Whole milk
WP	Whey permeate
WW	Wash water
XRD	X-ray diffraction
YB	Yoghurt and buttermilk

NOTATIONS

N	Nitrogen
n_m	Number of measurements
$1/n$	Heterogeneity factor
a_R	R–P isotherm constant (l/mg)
C_0	Initial COD concentration of SDW (mg/l)
C_e	Equilibrium COD concentration (mg/l)
C_f	Final COD concentration (mg/l)
C_t	COD concentration (mg/l) at time t
D	Overall desirability
d_i	Desirability of response i
E	Activation energy (kJ/mol)
F	Faraday's constant (96486 C/mol)
h	initial sorption rate (mg/g min)
J	Current density (A/m^2)
k	Number of responses
k_0	Frequency factor
K_F	Freundlich constant (l/mg)
k_f	Pseudo-first order rate constant
k_{id}	Intra-particle diffusion rate constant (mg/g min$^{1/2}$)
K_L	Langmuir adsorption constant (l/mg)
K_R	R–P isotherm constant (l/g)
k_s	Pseudo-second order rate constant
K_T	Tempkin equilibrium binding constant (l/mol)
m	Weight of NaCl (g/l)

m_{ad}	Dosage of adsorbents (g/l)
$m_{ad\text{-}opt}$	Optimum adsorbent dosage (mg/l)
m_{in}	Inorganic coagulant dosage (mg/l)
$m_{in\text{-}op}$	Optimum inorganic coagulant dosage (mg/l)
m_{na}	Natural organic coagulant dosage (mg/l)
$m_{na\text{-}op}$	Optimum natural organic coagulant dosage (mg/l)
N_C	Number of cycles per day
n_p	Number of parameters in the model
pH_f	Final pH
$pH_{f\text{-}in}$	Final pH of SDW by the inorganic coagulants
$pH_{f\text{-}na}$	Final pH of SDW by the natural organic coagulants
pH_i	Initial pH
$pH_{i\text{-}in}$	Initial pH for the coagulation of SDW by the inorganic coagulants
$pH_{i\text{-}in,op}$	Optimum initial pH of SDW by the inorganic coagulants
$pH_{i\text{-}na}$	Initial pH for the coagulation of SDW by natural organic coagulants
$pH_{in\text{-}effective}$	Effective pH_i for the coagulation of SDW by inorganic coagulants
$pH_{i\text{-}opt}$	optimum pH_i
pH_{iso}	Isoelectric pH
Q	Daily waste water flow rate (l/d)
q_e	Adsorbate adsorbed on the adsorbent at equilibrium (mg/g)
$q_{e,calc}$	Calculated value of q_e (mg/g)
$q_{e,exp}$	Experimental value of q_e (mg/g)
q_m	Adsorption capacity (mg/g)
q_t	Adsorbate adsorbed at any time t (mg/g)
R	Universal gas constant (8.31541 J/(mol K))
r	Weight and a positive constant used to determine scale of desirability
t	Time (min)
T	Absolute temperature (K)
T_{If}	Final temperature of exothermicity
T_{Ii}	Onset temperature of the exothermic reaction
t_{AE}	Aerobic react time (h)
t_{AN}	Anaerobic react time (h)

t_A	Anoxic react time (h)
t_{A-F}	t_A after fill (h)
t_{A-R}	t_A after reaction (h)
t_D	Decant time (h),
t_F	Fill time (h),
t_I	Idle time (h)
T_{max}	Temperature at which maximum rate of weight loss occurred
t_R	React time (h)
t_S	Settle time (h)
V_F	Filled volume (l)
V_T	Total volume (l)
V_W	Waste sludge volume (l)
Y_1	Percentage COD removal
Y_2	Specific energy consumed (KWh per kg of COD removed)
Y_i	Response values of response *i*
Y_{i-max}	Maximum acceptable value of response *i*
Y_{i-min}	Minimum acceptable value of response *i*

GREEK LETTERS

ΔG^0	Gibbs free energy change (kJ/mol)
ΔS^0	Entropy change (kJ/mol)
ΔH^0	Heat of adsorption (kJ/mol K)

Chapter – 1

INTRODUCTION

1.0. GENERAL

Steady rise in demand of milk and milk products in many countries has led to advancements in veterinary science which has subsequently led to steady growth in the production of milk per head of cattle (Poompavai, 2002). This has caused enormous growth of dairy industries in most countries of the world. Consequently, amount of wastewater generated and discharged from these industries has also increased. According to Ministry of Agriculture, Government of India, the average rate of milk production in India increased at an average rate of 3.56% annually in the period of 2001-2007 (http://www.indiastat.com/table/agriculture/2/milkanddairyproducts/167/3858/data.aspx). It is estimated that about 110 million tonne of the milk and about 275 million tonne of wastewater will be generated annually from the Indian dairy industries by the year 2010.

The dairy wastewaters are characterized by high chemical oxygen demand (COD) and biochemical oxygen demand (BOD) (Omil et al., 2003) and by high concentrations of nutrients and organic contents (USDA-SCS, 1992). If dissolved oxygen is not available in sufficient quantity for oxidation of organic matter present in the dairy wastewater, the lactose present in dairy wastewater gets converted into lactic acid which decreases the pH of wastewater and causes precipitation of casein present in the wastewater. This leads to formation of foul-smelling substances that do not support the aquatic life. Moreover the dairy wastewater contains high amount of nutrients which causes the eutrophication problem to the receiving streams. Hence, it is highly essential to reduce the organic and nutrient load of the dairy wastewater.

1.1. MILK PRODUCTS AND PROCESS

1.1.1. Various Fluid Milk Products

Milk is subjected to a range of processing operations before being sold in the market in many forms such as whole milk, flavoured milk, skimmed milk and low-fat milk. Low fat milk requires the removal of the fat portion as cream. Flavoured milk has the addition of flavours and colouring agents, which are sometimes added post-pasteurisation (Fig. 1.1.1).

Cheese is defined as the product made from the curd obtained from milk (by coagulating the casein with the help of rennet or similar enzymes in the presence of lactic acid) from which part of the moisture has been removed by cutting, cooking and /or pressing and which has been shaped in a mould, and then ripened by holding it for some time at suitable temperature and humidity. The clotting of milk by rennet is a key passage in cheese making that, markedly, affects the characteristics of produced cheese. Different types of rennet produced by (animal, vegetable, microbial and recombinant from genetically modified microorganism) are used (Addis et al., 2008).

Yoghurt is fermented product of milk. For producing yoghurt, desired quantity of milk is weighed and heated to 80-90°C for 15-20 min, then it is cooled to 45-48°C. Two to three percent of yoghurt culture is added to the milk and mixed well so as to produce lactic acid from milk lactose. When the desired acidity is reached, yoghurt is quickly cooled to a temperature around 20°C in order to stop lactic fermentation. After cooling, yoghurt is packed and stored at a temperature between 2-5°C (Staff, 1998; Tamine and Robinson, 1988). Whole (full cream) milk contains, typically, about 87% water whereas skim milk contains about 91% water. For producing milk powder, this water is removed by boiling the milk under reduced pressure at low temperature in a process known as evaporation. The resulting concentrated milk is then sprayed in a fine mist into hot air to remove further moisture and so give a powder.

1.1.2. Various Common Process Operations in Dairy Industry

The initial operations of clarification, pasteurization, homogenisation and deodorisation are common to most plants and products.

Clarification: Milk is clarified through centrifugal devices or mechanical filters to remove suspended matters, body cells from the udder and bacteria in the milk but bacteria not completely removed.

Pasteurization: The clarified milk is pasteurised to remove disease-producing bacteria (pathogens) present in milk. The target micro-organism is *mycobacterium tuberculosis*. Pasteurization is done by two methods; (1) batch method (2) high temperature short time (HTST) method. In batch method, milk is heated at temperature of 63 °C for 30 min, and in HTST method not less than 72 °C for 15 s.

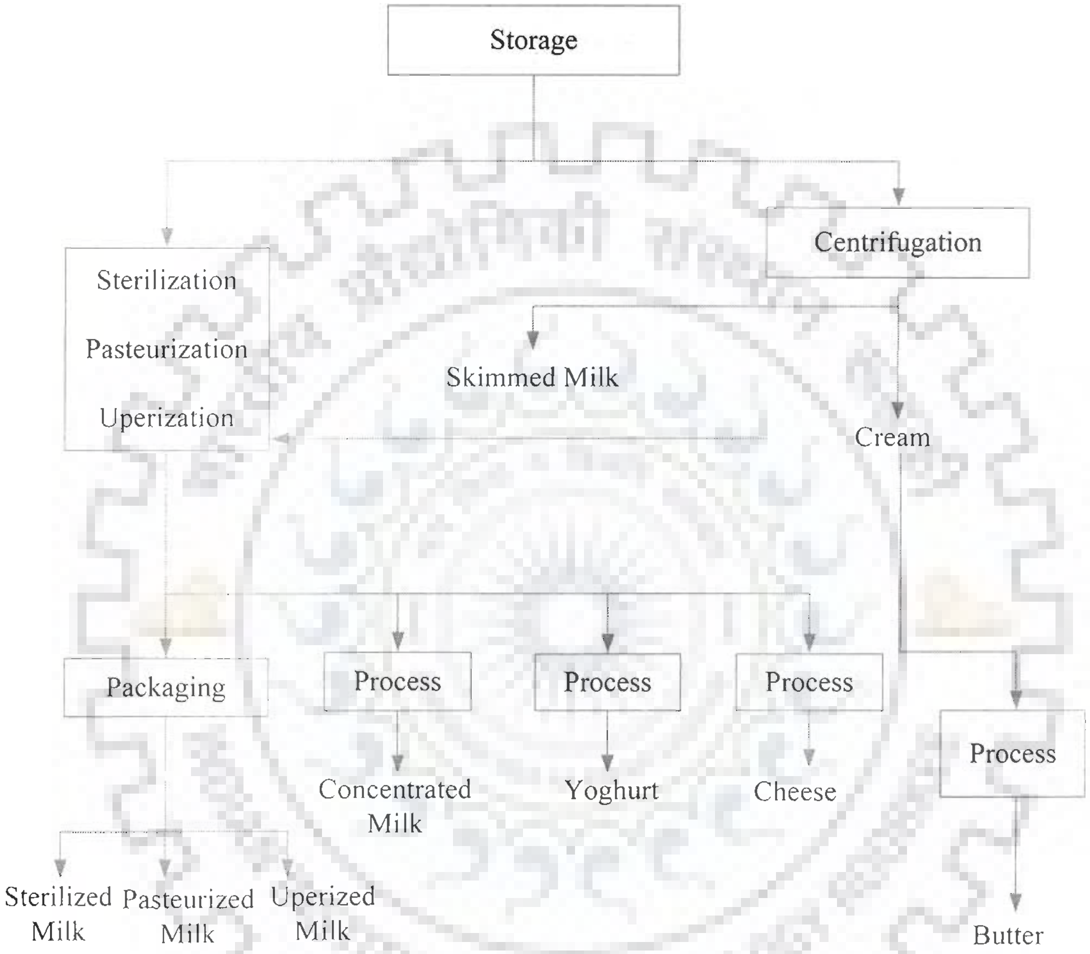


Fig. 1.1.1. Flow sheet for manufacturing of various milk products.

Source: Gutierrez et al., 1991.

Homogenisation: The pasteurised milk has fat globules. These fat globules may combine together to form lumps and being lighter make a layer at surface of milk. The reason of homogenisation is to divide the fat globules in such a smaller particles that they could not rise up to the surface. This makes the milk more uniform and richer taste.

Deodorization: Homogenised milk is deodorised by vacuum steam injection treatment to eliminate off-flavours and odors. Where flavours and odors are not serious matter, only vacuum treatment is used.

1.2. WASTEWATER DISCHARGE QUALITY

Dairy wastewaters are characterized by high BOD and COD concentrations; and generally contain fats, nutrients, lactose as well as detergents and sanitizing agents (USDA-SCS, 1992). Nutrients lead to eutrophication of receiving waters, and detergents affect the aquatic life. Due to high pollution load of dairy wastewater, milk processing industries discharging untreated/partially treated wastewater cause serious environmental problems (Montuelle et al., 1992). Therefore, to protect the environmental quality for sustainable development different legislations (Acts, Rules and Regulations) have been rectified and clear stipulations have been made. It is mandatory for the industries to meet the discharge standards of the effluents. In India, the Water (Prevention and Control of Pollution) Act, 1974 and the Environment (Protection) Act, 1986 bound the total discharge of wastewater and the water quality discharge standards set down which are to be met before the effluents are discharged either on land/in surface waters/in to sewers.

The Ministry of Environment and Forests (MoEF), Govt. of India, and the Central Pollution Control Board (CPCB) are authorized under the law to impose the standards and to monitor and regulate the effluent being discharged. There are two types of standards set by CPCB:

(a) Environment(Protection) Rules, 1986, (Schedule VI) - General standards for discharge of environmental pollutants, Part - A: Effluents

(b) Industry Specific Standards - General standards are based on the nature of the receiving body whether the treated effluent is being discharged to inland surface water, public sewers, land (for irrigation) or marine coastal areas (Table 1.2.1). These standards include usual pollution parameters, standards for nitrogen and related compounds, heavy metals, oil and grease, radioactive compounds, etc. Industry specific standards are the wastewater discharge standards for the specific industries.

The wastewater generation and wastewater effluents discharged standards from dairy industry set by CPCB and World Bank are shown in Table 1.2.2. Also, CPCB imposed stricter standards for dairy wastewater discharge depending on type of receiving water body. BOD may be made stringent up to 30 mg/l, if the recipient fresh water body is a source for drinking water supply. BOD shall be up to 350 mg/l for the chilling plant effluent for applying on land provided the land is designed and operated as a secondary treatment system with suitable monitoring facilities. The drainage water from the land after secondary treatment has to satisfy a limit of 30 mg/l of BOD and 10 mg/l of nitrate expressed as 'N'. The net addition of the groundwater quality should not be more than 3 mg/l of BOD and 3 mg/l of nitrate expressed as 'N'. The limit for applying on land is allowed subject to the availability of adequate land for discharge under the control of the industry BOD value is relaxable up to 350 mg/l, provided the wastewater is discharged into a town sewer leading to secondary treatment. Suspended solids is relaxable up to 450 mg/l, provided the wastewater is discharged into town sewer leading to secondary treatment of the sewage.

1.3. WASTEWATER TREATMENT

Dairy wastewaters are generally treated usually using biological methods such as activated sludge process, aerated lagoons, trickling filters, sequencing batch reactor (SBR), anaerobic sludge blanket (UASB) reactor, anaerobic filters, etc. (Demirel et al., 2005). Physico-chemical treatment methods consisting of coagulation/flocculation by various inorganic and organic natural coagulants, electro-chemical treatment (ECT) adsorption and membrane processes like nanofiltration (NF) and/or reverse osmosis (RO) have also been reported. Occasionally, pre-treatment strategies like wetlands are used to improve the treatment efficiency (Arvanitoyannis and Giakoundis, 2006).

Fig. 1.3.1a and b shows the number of research publications and citations for the various processes employed for the treatment of dairy wastewater for last 20 years (1990-2009). It is clear that researchers gave most attention to anaerobic treatment process followed by aerobic and membrane methods. Very few studies are reported for coagulation and adsorption treatment processes.

Table 1.2.1. General standards for discharge of environmental pollutants.

Parameter (mg/l)	Inland surface water	Public sewers	Land for irrigation	Marine/coastal areas
Suspended solids,	100	600	200	(a) For process wastewater (b) For cooling water effluent 10 per cent above total suspended matter of influent.
Particle size of suspended solids	shall pass 850 micron IS Sieve	-	-	(a) Floatable solids, solids max. 3 mm (b) Settleable solids, max 856 microns
pH value	5.5 to 9.0	5.5 to 9.0	5.5 to 9.0	5.5 to 9.0
Temperature	shall not exceed 5°C above the receiving water temperature			shall not exceed 5°C above the receiving water temperature
Oil and grease, max	10	20	10	20
Total residual chlorine	1.0	-	-	1.0
Ammonical nitrogen (as N)	50	50	-	50
Total kjeldhal nitrogen (as N)	100	-	-	100
Free ammonia (as NH_3)	5.0	-	-	5.0
BOD (3 d)	30	350	100	100
COD	250	-	-	250
Arsenic (as As)	0.2	0.2	0.2	0.2
Mercury (as Hg)	0.01	0.01	-	0.01
Lead (as Pb)	0.1	1.0	-	2.0

Parameter (mg/l)	**Inland surface water**	**Public sewers**	**Land for irrigation**	**Marine/coastal areas**
Cadmium (as Cd)	2.0	1.0	-	2.0
Hexavalent chromium (as Cr^{+6})	0.1	2.0	-	1.0
Total chromium (as Cr)	2.0	2.0	-	2.0
Copper (as Cu)	3.0	3.0	-	3.0
Zinc (as Zn)	5.0	15	-	15
Selenium (as Se)	0.05	0.05	-	0.05
Nickel (as Ni)	3.0	3.0	-	5.0
Cyanide (as CN)	0.2	2.0	0.2	0.2
Fluoride (as F)	2.0	15	-	15
Dissolved phosphates (as P)	5.0	-	-	-
Sulphide (as S)	2.0	-	-	5.0
Phenolic compounds (as C_6H_5OH)	1.0	5.0	-	5.0
Radioactive materials:				
(a) Alpha emitters micro curie mg/l	10 -7	10 -7	10 -8	10 -7
(b) Beta emitters micro curie mg/l	10 -6	10 -6	10 -7	10 -6
Bio-assay test	90% survival of fish after 96 h in 100% effluent	90% survival of fish after 96 h in 100% effluent	90% survival of fish after 96 h in 100% effluent	90% survival of fish after 96 h in 100% effluent
Manganese	2	2	-	2
Iron (as Fe)	3	3	-	3
Vanadium (as V)	0.2	0.2	-	0.2
Nitrate Nitrogen	10	-	-	20

Table 1.2.2. Minimal standards for discharge of effluents from the dairy industry.

Parameter	Maximum value (mg/l)	
	World Bank [#]	CPCB, India[$]
pH	6-9	6.5-8.5
BOD_5	50	100 (based on BOD_3)
COD	250	-
Total suspended solids	50	150
Oil and grease	10	10
Total nitrogen	10	-
Total Phosphorus	2	-
Temperature increase	≤ 3 °C	-
Coliform bacteria	400 Most Probable Number/100 ml	-
Wastewater generation		3 m^3/m^3 of milk

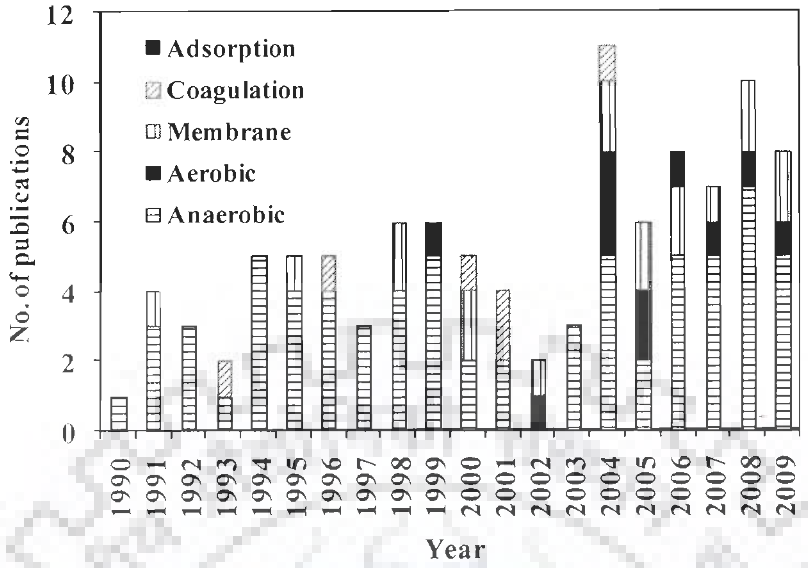
[#]**Source:** Pollution Prevention and Abatement. Fruit and Vegetable Processing. "Pollution Prevention and Abatement: Dairy Industry". January 31, 1996 P 621, World Bank, Environment Department 1996.

[$]**Source:** http://www.cpcb.nic.in/Industry-Specific-Standards/Effluent/DiaryIndustry.pdf

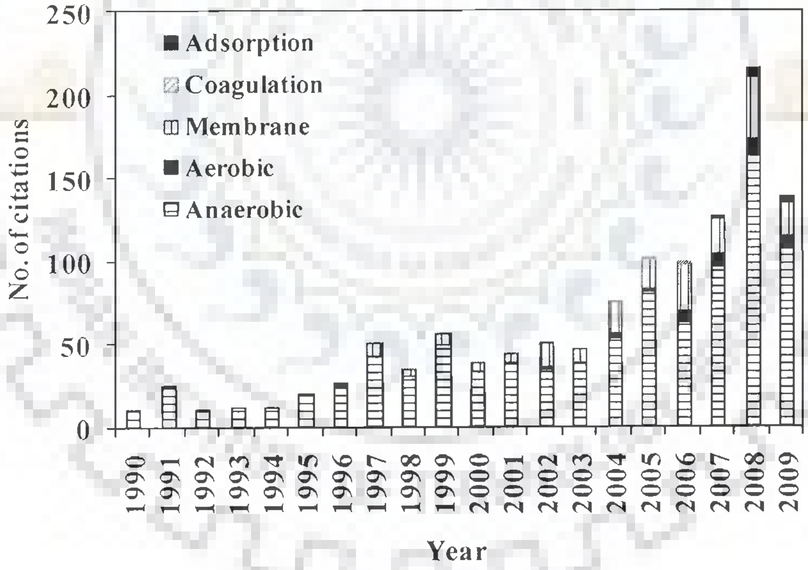
Table 1.3.1 shows various physico-chemical methods as reported in open literature for dairy wastewater treatment. Few studies are reported for the coagulative treatment and only two studies are reported for electro-chemical treatment (ECT) and adsorptive treatment of dairy wastewater in open literature. Moreover, treatment mechanism and disposal aspects of the sludge generated during the treatment are lacking. Literature review and research gaps are given in detail in chapter 2 in section 2.2 and 2.3, respectively.

Table 1.3.1. Physico-chemical treatment studies for dairy wastewater treatment as reported in open literature.

Treatment Method			references
Coagulation	Coagulants	Fe^{3+} /Cr^{3+} sludge	(Namasivayam and Ranganathan, 1992)
		Ferric chloride	(Namasivayam and Ranganathan, 1992; Hamdani et al., 2004)
		Ferrous sulphate	(Namasivayam and Ranganathan, 1992)
		Chitosan	(Selmer-Olsen et al., 1996; Mukhopadhyay et al., 2003; Sarkar et al., 2006)
		Aluminum sulphate	(Hamdani et al., 2004)
		Calcium hydroxide	(Hamdani et al., 2004)
Electro-coagulation	Electrodes	Iron	(Sengil and Ozacar, 2006)
		Aluminum	(Tchamango et al., 2010)
Adsorption	Adsorbents	Bagasse, straw dust, saw dust, coconut coir, fly ash and Powdered activated Carbon	(Rao and Bhole, 2002)
		Powdered activated Charcoal	(Sarkar et. al., 2006)



(a) Publications



(a) Citations

Fig. 1.3.1. **Number of publications and citations from 1990-2009 for the various processes for the treatment of dairy wastewater.**

1.4 OBJECTIVES

In view of the literature survey presented in Chapter 2 and the necessity of studying treatment of dairy wastewater by physico-chemical methods and SBR, the following aims and objectives have been set for the present work:

(a) Treatment of dairy wastewater by coagulation process using inorganic coagulants potash alum, $FeSO_4$, poly aluminum chloride (PAC) and organic coagulants (guar gum, sodium alginate, Na-CMC)

- To study the effect of coagulant dosage and initial pH of dairy wastewater on COD removal.
- To study the settling characteristics of treated effluent.
- To perform the sludge disposal study.

(b) Treatment of dairy wastewater by electro-chemical method

- To study the effect of type of electrodes (aluminum and iron) on COD removal.
- To study the effect of current density, detention time, initial pH of dairy wastewater and electrical conductivity on COD removal.
- To perform the sludge disposal study.

(c) Treatment of dairy wastewater by adsorption process using commercial activated carbon and bagasse fly ash.

- To study the effect of adsorbent dosage, initial pH, time, and temperature on COD removal.
- To do kinetic and equilibrium modelling of adsorption process, and check the disposal of spent-adsorbent.

(d) Treatment of dairy wastewater by aerobic sequential batch reactor.

- To study the effect of HRT, filling time and anoxic length on COD and nitrogen removal.
- To perform the sludge disposal study.

Chapter – 2

LITERATURE REVIEW

2.0. GENERAL SCOPE

This chapter presents a review of the research work available in the open literature for the dairy wastewater treatment by various technologies. Various sections in this chapter focus on the dairy wastewater generation and its characteristics, and its treatment by various biological and physico-chemical methods. In biological treatment, aerobic and anaerobic treatments with combined aerobic-anaerobic treatment processes are discussed. Finally, areas where further research and attention are required have been identified.

2.1. DAIRY WASTEWATER GENERATION AND CHARACTERISTICS

Dairy industries are involved in the manufacturing of various types of milk products such as fluid milk, butter, cheese, yogurt, condensed milk, flavoured milk, milk powder, ice cream, etc. Typical by-products obtained include buttermilk, whey, and their derivatives. A chain of operations involving receiving and storing of raw materials; processing of raw materials into finished products; packaging and storing of finished products; and a group of other ancillary operations (e.g., heat transfer and cleaning) are examples of some of the great variety of operations performed in the dairy products industries. The initial operations of homogenisation, standardisation, clarification, separation and pasteurization are common to most plants and products. Clarification (removal of suspended matter) and separation (removal of cream for milk standardization to desired butterfat content), generally, are accomplished by specially designed large centrifuges. Drying, condensing, etc. are also used in dairy industries for production of various products. Types and size of processes and equipment used are determined by raw material inputs and the finished products manufactured (Carawan et al., 1979).

Dairy industry is one of the most polluting industries not only in terms of volume of effluent generated but also in terms of its characteristics too. It is estimated that about 2% of total milk processed is wasted into drains (Munavalli and Saler, 2009). It generates about 0.2-10 litre of effluent per litre of processed milk (Vourch et al., 2008) with an average generation of about 2.5 litre of wastewater per litre of the milk processed (Ramasamy et al., 2004).

In the dairy industry, some amount of wastewater gets produced during starting, equilibrating, stopping and rinsing the processing units (flushing water, first rinse water, etc.) (Vourch et al., 2008). However majority of wastewater gets produced during cleaning operations, especially between product changes when different types of product are produced in a specific production unit and clean-up operations (Fig. 2.1.1). Wastewaters generated from milk processing can be separated into two groups: first group concerns wastewater having high flow rates and the second concerns the effluents produced in small milk transformation units (cheese production for instance) (Castillo et al., 2007). Dairy processing effluents is generated in an intermittent way and the flow rates of these effluents change significantly (Kolarski and Nyhuis, 1995). Also the quality and quantity of product content in the dairy wastewater at a given time changes with the application of another technological cycle in the processing line (Janczukowicz et al., 2008). Moreover, because the dairy industry produces different products, the characteristics of these effluents also vary widely both in quantity and quality, depending on the type of system and the methods of operation used (Vidal et al., 2000; Rico et al., 1991). Dairy wastewater contains milk solids, detergents, sanitizers, milk wastes and cleaning water. It is characterized by high concentrations of nutrients, organic and inorganic contents (USDA-SCS, 1992). Significant variations in COD (80-95,000 mg/l) and BOD (40-48,000mg/l) have been reported by various investigators of dairy wastewater (Table 2.1.1). Total COD of dairy wastewater is mainly influenced by the milk, cream or whey (Wildbrett, 1988). The pH varies in the range of 4.7-11 (Passeggi et al., 2009) whereas the concentration of suspended solids (SS) varies in the range of 0.024-4.5 g/l. Significant amount of nutrients, 14-830 mg/l of total nitrogen (Rico-Gutierrez et al., 1991) and 9-280 mg/l of total phosphorous (Gavala et al., 1999) are also found in dairy wastewater. Nitrogen in dairy wastewater originates mainly from milk proteins, and is either present in organic nitrogen form such as proteins, urea, nucleic acids or as ions such as NH_4^+, NO_2^- and NO_3^-. Phosphorus is found mainly in inorganic forms such as orthophosphate (PO_4^{3-}) and polyphosphate ($P_2O_7^{4-}$) as well as in organic forms also (Demirel et al., 2005).

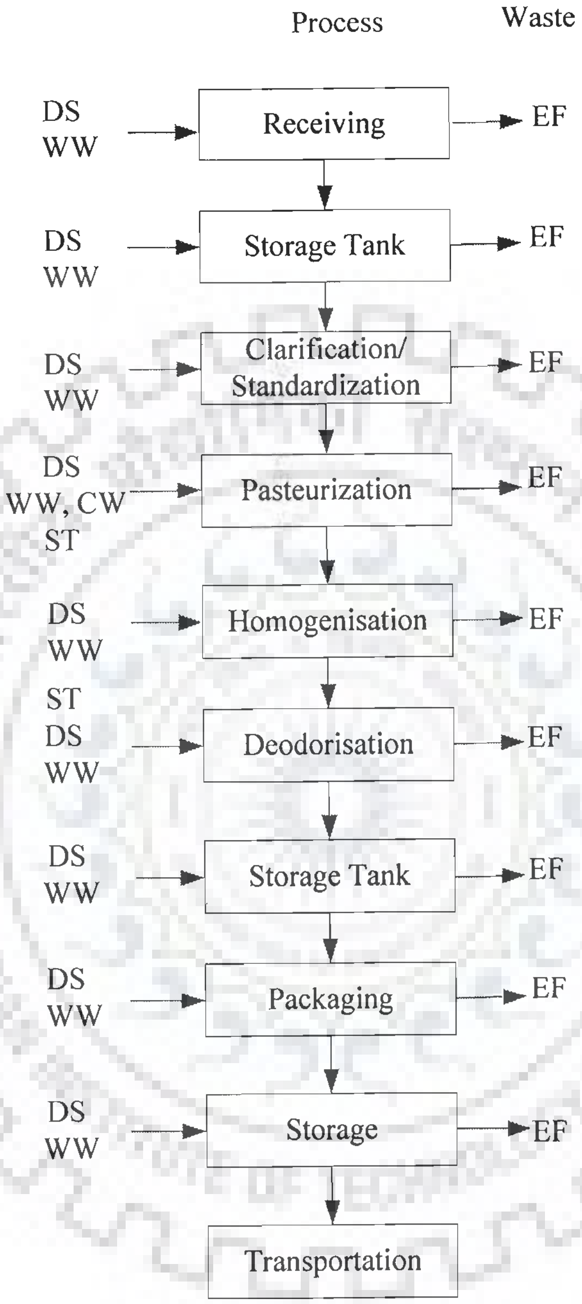


Fig. 2.1.1. Effluent generation from various units of milk processing. DS-Detergents and Sanitizing Agents, WW-Wash Water, ST-Steam, CW-Cooling Water.

Table 2.1.1. Characteristics of dairy industry wastewaters (composition in mg/l, except for pH).

Waste Type	COD	BOD	pH	TSS	VSS	TN	TP	Cl	Fats	Reference
DI$^{\neq}$	80-95 000	40-48 000	4.5-9.4	24-4500	-	15-180	12-132	48-559	-	(Rico et al., 1991)
DI$^{®}$	4000	2600	8.0-11.0	-	635	55	35	-	400	(Kasapgil et al., 1994)
DI	4500	2300	-	800	-	60	50	-	350	(Koyuncu et al., 2000)
DI	4000	2000	-	800	-	60	-	-	-	(Koyuncu et al., 2000)
YB	1500	1000	7.2	191	-	63	-	-	-	(Koyuncu et al., 2000)
CI	4430	3000	7.32	1100	-	18	14	-	-	(Monroy et al., 1995)
DI	1745	-	-	400	355	75	9.1	-	-	(Koyuncu et al., 2000)
DI	980-7500	680-4500	-	300	-	-	-	-	-	(Kolarski and Nyhuis, 1995)
CI	-		4.7	2500	-	830	280	-	-	(Gavala et al., 1999)
DI	18045	8239	-	7175	-	329	-	593	4890	(Arbeli et al. 2006)
DI	2000-6000	1200-4000	8.0-11.0	350-1000	330-940	50-60	-	-	-	(Ince, 1998a)
DI	430-15200	650-6240	4.7-11	250-2750	210-1890	14-90	-	-	160-1760	(Passeggi et al., 2009)
DI	2800	1600	-	-	-	140	30	-	-	(Schwarzenbeck et al., 2005)

≠TS = 135-18500, ® TS = 675DI: Dairy Industry; CI: Cheese Industry; YB: Yoghurt and buttermilk.

The detergents and their additives are also present in small quantities in dairy wastewater. They may be alkaline or acid, and very often contain additives like phosphates, sequestering agents, surfactants, etc. (Grabhoff. 1997). Significant amount of Na, Cl, K, Ca, Mg, Fe, CO, Ni, Mn are also always present in dairy wastewater. The presence of high concentration of Na and Cl is due to the use of large amount of alkaline cleaners in dairy plant (Demirel et al., 2005).

2.2. DAIRY WASTEWATER TREATMENT

Common techniques for treating dairy industry wastewaters include grease traps, oil water separators for separation of floatable solids; equalization of flow; clarifiers to remove SS. Biological treatment includes aerobic and anaerobic process. Sometimes anaerobic followed by aerobic treatment is employed for reduction of soluble organic matter (BOD) and biological nutrient removal (BNR) is employed for reduction of nitrogen and phosphorus.

2.2.1. Physico-Chemical Treatment Process

Physico-chemical treatment processes like coagulation/flocculation, adsorption and membrane process are required to remove suspended, colloidal and dissolved constituents.

2.2.1.1. Coagulation: Coagulation and flocculation is a frequently applied process in the primary purification of industrial wastewater (in some cases as secondary and tertiary treatment). Coagulation using chemical coagulants consists of combining insoluble particles and/or dissolved organic matter present in dairy wastewater into large aggregates, thereby facilitating their removal in subsequent sedimentation, floatation and filtration stages.

Migo et al. (1993) studied the removal of colour and total organic carbon (TOC) from DWW, biodigester effluent (BDE), and the anaerobic lagoon effluent (ALE) by using various inorganic coagulants like $FeCl_3$, $AlCl_3$ and poly-ferric hydroxyl sulfate. Poly-ferric hydroxyl sulfate was found to be the best giving 32, 87, 94% colour reduction and 21, 73, 73% TOC reductions for DWW, BDE and ALE, respectively. Increased dosage of the flocculants beyond optimum, increased turbidity, colour and reduced the TOC removal efficiency.

Chaudhari et al. (2007) reported the treatment of BDE by coagulation/flocculation using $FeCl_3$, $AlCl_3$ and PAC coagulants. The COD reductions at optimum conditions were

55, 60 and 72.5%; colour reductions were 83, 86 and 92% for coagulation with 60 mmol Al^{3+} (as $AlCl_3$), 60 mmol Fe^{3+} (as $FeCl_3$) and 1820 mg/l Al^{3+} (as PAC), respectively, at optimum pH of 5.5 for $AlCl_3$ and PAC and 3 for $FeCl_3$. They concluded that the pH affected the flocculation/coagulation process tremendously for COD/BOD/colour removal. The slurry generated during the process was found to have very poor filtrability.

Singh and Dikshit (2010) studied decolourization of pretreated anaerobically digested molasses spent wash by PAC without dilution of wastewater by Aspergillus niger isolate IITB-V8 using Plackett–Burman design for screening the important parameters and Box–Behnken design to determine their optimum values. They showed maximum decolourization of 86.8% and reported that fungal decolourization after pretreatment with PAC is a feasible option for the treatment of anaerobically digested molasses spentwash.

The precipitation of dissolved lignin and other matters form textile wastewater by using different coagulants such as alum, $FeCl_3$, PAC and lime has been reported by several researchers (Dugal et al., 1976; Stephenson and Duff, 1993, 1996a,b; Srivastava et al., 2005).

Stephenson and Duff (1993) have shown that no benefits will build up in using combined dosage of $FeCl_3$, $CaCl_2$ and $AlCl_3$ on the coagulation of a combined chemi-thermo-mechanical pulping/thermo-mechanical pulping (CTMP/TMP) effluent from a pulp and paper mill. They concluded sturdy effect of pH on the efficiency of the chemical precipitation with metal salts. The metal coagulant precipitated solids were also found to depend strongly on pH for their solubility. They reported that the metal precipitates formed under acidic conditions with the addition of metal salts go back to colloidal suspension form after increasing pH to alkaline.

Stephenson and Duff (1996a) studied the coagulation of effluent from mechanical pulping having a COD value in the range of 2520 - 7930 mg/l on the removal of carbon, colour and turbidity using metal salts like $FeCl_3$, $FeSO_4$, $AlCl_3$ and $Al_2(SO4)_3$. These salts were found to be very effective with removal efficiencies up to 88, 90 and 98%for total carbon, colour and turbidity, respectively. Also, they showed that the pH of the wastewater participated a crucial role on the effectiveness of coagulants. The optimum pH range was found to be above 7.4 for $FeSO_4$, 5.8 to 6.8 for $Al_2(SO4)_3$, 5.0 to 6.0 for $AlCl_3$ and 4.0 to 6.5 for $FeCl_3$.

Stephenson and Duff (1996b) also observed the toxicity removal and metal salt recovery from a combined bleached CTMP and TMP effluent. They prepared wastewaters of different strengths (3/4, 1/2, 1/4) by diluting the full strength effluent with tap water. It was observed that the micro toxicity could be removed completely for 1/4 strength effluent at lower coagulant dose, but after an optimum dose, toxicity was found to have increased. Ferric chloride was found to be the best among all the coagulants used from the point of view of coagulant recovery, with a fixed solids recovery of around 82%.

Physico–chemical treatability of pulp and paper mill effluents with an alum dosage of 100 mg/l was reported by Dilek and Gökçay (1994). They reported COD removal efficiency of 96, 50 and 20% for the effluents of the paper mill, alkali extraction and bleaching plant, respectively. They also showed 80% colour removal from the alkali extraction effluent.

The use of various inorganic coagulants like alum, $FeCl_3$ and $FeSO_4$ were also reported by Al-Malack et al. (1999) for the treatment of polymeric (acrylic) wastewater. $FeCl_3$ was found to be the best with 96 and 97% COD and turbidity removal efficiency, respectively, at pH = 8.5. The $FeCl_3$ was also found to be effective at a wide range of pH (6.5 to 9.0), while alum was effective only at pH = 8.5. $FeSO_4$ reduces 70% COD and turbidity at pH = 9.0.

Sundin (2000) has studied the influence of metal ions on the lignin removal from pulp mill wastewater. Metal cations used for the lignin precipitation were Na^+, Ca^{2+}, Mg^{2+}, Al^{3+} but only Ca^{2+} and Mg^{2+} ions showed considerable lignin precipitation at a pH range of 11-13. For the Na^+ ions, pH = 9.0 was found to be the optimum at 25 °C.

A pilot plant study has been reported for the treatment of cotton textile wastewater using lime and $FeSO_4$ (Georgiou et al., 2003). The treatment with lime alone proved to be very effective in removing the colour (yellow, red and blue) by 70-90% and COD by 50-60%. $FeSO_4$ gave similar results. However, the large volume of the precipitated sludge was the drawback of this process. Sometimes two stage coagulation may be very effective. Srivastava et al. (2005) showed two stages chemical coagulation – adsorption method for the removal of COD and colour from the alkaline black liquor and acidic wastewaters from different sections of the small agri-based pulp and paper mills which do not have chemical recovery units. PAC as the chemical coagulant and bagasse fly ash (BFA) were used as the adsorbent. They concluded that the coagulation-flocculation gave 80 and 90% removals of COD and colour, respectively, at pH≈3 at a PAC dosage of 3000 mg/l. The second stage treatment with BFA at pH≈4 and BFA dosage of 2000 mg/l increased the total removal efficiency of COD and colour to 87 and 95%, respectively.

Only few studies are reported in open literature for the coagulation of dairy wastewater (Namasivayam and Ranganathan, 1992; Selmer-olsen et al., 1996; Mukhopadhyay et al., 2003; Hamdani et al., 2004; Sarkar et al., 2006a). Table 2.2.1 shows the comparison of the work carried out by these researchers.

Table 2.2.1. Parameters reported for the treatment of dairy wastewater by coagulation.

Waste Type	Coagulant	COD_i (mg/l)	%COD Removal	%BOD Removal	%TN Removal	%TP Removal	Reference
DI	Fe^{3+} / Cr^{3+} sludge	2000	70 ±5	68	-	70	(Namasivayam and Ranganathan, 1992)
	Ferric chloride	-	73	57	-	64	(Namasivayam and Ranganathan, 1992)
	Ferrous sulphate	-	61	57	-	79	(Namasivayam and Ranganathan, 1992)
DI	Chitosan	1160-2690	60	-	-	60	(Selmer-Olsen et al., 1996)
Whey	Chitosan	-	-	87	-	-	(Mukhopadhyay et al., 2003)
DI	Ferric chloride	6140	-	-	40	-	(Hamdani et al., 2004)
	Aluminum sulphate	-	-	-	40	-	(Hamdani et al., 2004)
	Calcium hydroxide	-	-	-	40	89	(Hamdani et al., 2004)
DI	Chitosan	1500-3000	57	-	-	-	(Sarkar et al., 2006a)

DI = Dairy industry, COD_i = Initial COD, TP = Total phosphates

Rusten et al. (1993) studied on different combinations of coagulants for the treatment of dairy wastewater. They found that $FeClSO_4$ removed 2-3% more COD than H_2SO_4 combined with CMC, and 4-6% more COD than lactic acid combined with CMC. Feofanov and Litmanova (2001, 2001) studied removal of organic impurities from contaminated wastewater of a dairy plant by coagulation with aluminum oxychloride and aluminum oxochloride at pH 2-12. Hamdani et al. (2004) found that the treatment of dairy wastewater by coagulation-decantation with iron chloride ($FeCl_3.6\ H_2O$), aluminium sulfate ($Al_2(SO_4)_3.18\ H_2O$) and calcium hydroxide ($Ca(OH)_2$) removed only 40% of organic matter and nitrogen content. However, this treatment considerably reduced the suspended matter (94%) and total phosphorus (89%) with calcium hydroxide. Sarkar et al. (2006a) employed coagulation by chitosan followed by adsorption with powdered activated carbon as pre-treatment steps before treating the dairy wastewater by membrane separation method and found 57% reduction in COD at 10–50 mg/l chitosan dosage. Selmer-olsen et al. (1996) used various types of chitosan as coagulants for the treatment of dairy wastewater. Mukhopadhyay et al. (2003) isolated lactose from whey by treatment with chitosan followed by alcohol precipitation. They reported BOD removal efficiency of 87%.

A look into the literature shows that there is no description regarding the variation of COD removal efficiencies with change in pH. Moreover, these studies don't give information about settleability of treated effluent and disposal aspects of the sludge generated during coagulation. These aspects are very important from industrial and designing point of view.

2.2.1.2. Electrochemical treatment: Various researchers have utilized electrochemical treatment (ECT) for the treatment of varieties of industrial wastewater (Jiang et al., 2002; Holt et al., 2002; Stephenson and Tennant, 2003; Mahesh et al., 2006a,b; Feng et al., 2007; Raju et al., 2008; Thella et al., 2008; Kumar et al., 2009).

Kumar et al. (2009) reported COD reduction of BDE by ECT using iron electrode. They concluded maximum COD and colour reduction of 50.5% and 95.2%, respectively, at optimum conditions. Ahlawat et al. (2008) also investigated the removal efficiency of an acid dye, cotton blue (chemical name: aniline blue WS) dye, from aqueous solution by an ECT in batch mode using aluminum electrodes and reported the 97% removal efficiency at the optimized conditions.

Feng et al. (2007) studied treatment of tannery wastewater by electro-coagulation using mild steel and aluminum electrodes. The removal rates of COD, ammonia, TOC, sulfide and colority were 68.0, 43.1, 55.1, 96.7 and 84.3%, respectively, with the initial concentrations 2413.1, 223.4, 1000.4 and 112.3 mg/l, respectively.

Nutrient rich wastewater like restaurant wastewater has also been very successful treated by ECT (Chen et al., 2000). Also, there are few studies in the literature utilizing ECT successfully for food industries wastewaters (Bejankiwar et al., 2003; Gotsi et al., 2005; Bellakhal et al., 2006; Khoufi et al., 2006).

Lakshmipathiraj et al. (2010) reported the arsenic removal from aqueous solutions by using mild steel electrodes. Effect of electrolytes such as NaCl, $NaNO_3$ and Na_2SO_4 on anodic dissolution of iron was investigated. 98% arsenic removal was reported in the presence of NaCl, whereas 75% in the presence of Na_2SO_4 and $NaNO_3$. Almost 95% of the total arsenic was removed within 5 min from its initial concentration of 10 mg/l. Table 2.2.2 shows the utilization of ECT process for treatment of various types of wastewaters.

However, only two studies are available in open literature for the ECT of dairy wastewater (Sengil and ozacar 2006; Tchamango et al., 2010). Tchamango et al. (2010) studied the ECT of dairy wastewater with aluminium electrodes and reported COD, nitrogen content and turbidity removal efficiencies of 61%, 81% and 100%, respectively. Sengil and ozacar (2006) used iron electrode and focused the study on COD and oil-grease removal. Moreover, disposal aspect of residues (scum and sludge), which are generated during the ECT, were not dealt in any of the above two studies which are very important from the environmental point of view.

Table 2.2.2. Various applications of ECT process.

Waste Type	Reactor/ Operation	Electrode material		% Removal	Current/Voltage/Current density	Reference
		Anode/Cathode	Surface area			
OM	cylindrical, batch	Al/Fe/	35 cm^2	COD: 42% Colour: 90-97%	-	(Inan et al., 2004)
LMG	Batch,	Fe-Cu and Al-Cu	80 cm^2	COD: 30-50%	2 V	(Tsai et al., 1997)
Zinc from aqueous solutions	continuous	Pt-5 mm and Stainless Steel mesh	-	96%	15 V	(Casqueira et al., 2006)
PCM	cylindrical, batch	Al/Fe	78 cm^2	COD: 60% Turbidity: 98%	25-300 A/m^2	(Kobya et al., 2006)
EP	Cuboidal	Al/Fe/ Stainless Steel	30 cm^2	COD: 92-97% Turbidity: 99%	-	(Xu et al., 2002)
SW	Cylindrical cell	Peripheral Ti (coated), Central Stainless Steel	87.1 cm^2	Total Coliforms: 99.9%	0-2.5 A.	(Li et al., 2002)
ROW	cuboidal, continuous	Fe/Fe	20 x 10 cm	Oil and grease: 95% COD: 75%	10-14 A/m^2	(Xu and Zhu, 2004)

Waste Type	Reactor/ Operation	Electrode material		% Removal	Current/Voltage/Current density	Reference
		Anode/Cathode	Surface area			
UW	continuous	Al	0.15 m^2	TP: 80%	8A	(Pouet and Grasmick, 1995)
Textiles	cuboidal, batch,	Ti/RuO_2, SS/08	11 cm x 9.5 cm	-	-	(Hyun Kim et al., 2003)
Water disinfection	batch and continuous	BDD (peripheral) anode, Stainless Steel cathode	30 cm^2 anode, 20 cm^2 central cathode	Reduced to detection limit at 5 mA in 5 min	15-133 A/m^2	(Polcaro et al., 2007)

DAF: Dissolved Air Flotation; UW: Urban Wastewater; LMG: Leachate from municipal garbage landfills; SW: Saline wastewater; PCM: Potato chips manufacturing; OM: Olive mill; ROW: Refectory oily wastewater; EP: Egg processing

BDD: Boron doped diamond; Ti: Titanium; CI: Cast Iron.

2.2.1.3. Adsorption: Amongst various physico-chemical treatment methods, adsorption has been found to be attractive for the removal of organic compounds in wastewaters. There are many adsorbents in use. All surfaces contain unsaturated bonds and this bond causes the reactant molecules to get attached to the adsorbent surface. The degree of interaction between adsorbate and adsorbent obviously depends on the nature of adsorbate and the adsorbent. Table 2.2.3 shows the adsorption capacities of various adsorbents. Various adsorbents reveal different adsorption capacities. Activated carbon-commercial (ACC) seems to be excellent adsorbent giving maximum adsorption capacity. Activated carbon (AC) is the most widely used for the removal of a variety of organics from varieties of wastewaters. But the disadvantage associated with it is the high regeneration cost and the generation of carbons fines, due to the brittle nature of carbons used for the removal of organic species. Table 2.2.4 describes the various types of activated carbons for the adsorption of phenol and it derivatives. Granular AC is considered as one of the best adsorbent for furfural having highest adsorption capacity. Sulaymon and Ahmed (2008) have studied the competitive adsorption of furfural and phenolic compounds with activated carbon in a fixed-bed and developed mathematical modelling to describe the mass transfer. They concluded that the external mass transfer and pore diffusion well described the adsorption process. Orshansky and Narkis (1997) used powdered activated carbon to remove organic toxic pollutants. They suggested Langmuir isotherm for adsorption process. Adsorption of resorcinol and other phenolic derivatives on multi-walled carbon nanotubes (CNTs) and HNO_3-treated multi-walled CNTs has been also studied to explore the possibility to use multi-walled CNTs as efficient adsorbents for pollutants. The multi-walled CNTs showed higher adsorption ability in a rather wide pH range of 4.0–8.0 for resorcinol, while decreased adsorption capacity was found for acid-treated multi-walled CNTs.

Zeolites are a naturally occurring crystalline aluminosilicates. Zeolites contain a wide variety like clinoptilolite and chabazite, in which clinoptilolite is most abundant in nature and is readily available from more than 40 natural zeolite species (Vaca-Mier et al., 2001). An important property of zeolites is the capacity to be easily regenerated while keeping their initial properties (Khalid et al., 2004). Li et al. (2000) reported the adsorption of ionizable organics on a natural zeolite modified with a cationic surfactant, hexadecyltrimethylammonium bromide (HDTMAB).

Phenol adsorption using HDTMAB-modified zeolite was affected by solution pH. Razee and Masujima (2002) also reported the adsorption of phenolic compounds including phenol, 4-aminophenol, 2-aminophenol, 4-Nitrophenol, 2- Nitrophenol, and 2-methyl-4-nitrophenol by natural zeolites, natrolite, and clinoptilolite. 45 to 64% of pollutants were removed from aqueous solution in 4 h. Modification of zeolites with cyclo-dextrins, especially a-cyclo-dextrin, considerably improved the adsorption efficiency to 65–74% for clinoptilolite. Hobday et al. (1994) reported the coal to be a suitable adsorbent for 4-nitrophenol. HNO_3-pretreatment significantly enhanced the surface properties that were confirmed by pore structure characterization and phenol adsorption capacities. They reported the Freundlich equation best fits the experimental isotherm data. However, pre-treated coal was found to be better than the original coal as an adsorbent for phenol removal (Ahsan et al., 1994). Ahmaruzzaman and Sharma (2005) studied coal, residual coal and the treated residual coal by H_3PO_4 for the adsorption of phenol from wastewater. Low-cost adsorbents such as petroleum coke, rice husk and rice husk char and BFA have also been used for treatment of various wastewaters. The parameters influencing the system of adsorbate and adsorbent, such as pH, contact time, and temperature were studied. Srivastava et al. (2006) have studied the adsorption of phenol on BFA. They reported that the optimum conditions for phenol removal were pH = 6.5, adsorbent dosage =10 g/l of solution, and equilibrium time = 5 h. Redlich–Peterson isotherm best fitted the experimental isotherm data. The removal of phenol and 4-Nitrophenol using BFA was also reported by Gupta et al. (1998). They concluded that the adsorption data followed both the Langmuir and Freundlich isotherms, and adsorption process as exothermic in nature. Coal fly ash (CFA) has also been used as adsorbent, which is produced as a fine, non-combustible residue carried with the flue gas during burning of coal. The disposal requires large quantities of land and water. The use of CFA as an adsorbent for phenolic compounds was found to be cost effective and thus can be considered as an alternative to activated carbon. Ravikumar et al., (2005) reported 100% removal of basic blue 69 and acid blue 125 by a hybrid adsorbent prepared from pyrolysing mixture of carbon and fly ash. Sarkar and Acharya (2006) studied and reported the adsorption of phenol and its analogs from water with CFA. Langmuir isotherms best fitted the equilibrium experimental data and the process was endothermic and spontaneous in nature. The increased randomness was confirmed by positive value of entropy change. CFA was also effective for the removal of 2-sec-butyl-4, 6-dinitrophenol from wastewater (Wang and Jiang, 2007). The high adsorption capacity and removal efficiency of 2-sec-butyl-4, 6-dinitrophenol from solutions can be achieved at pH 4.0.

Pan et al. (2008) studied adsorptive removal of phenol from aqueous solution by porous acrylic ester polymer (Amberlite XAD-7) and reported that acidic pH was favorable for the adsorption. Langmuir and Freundlich isotherms well correlated the data. Pseudo-second-order kinetic model best fits the adsorption process. Adsorption of phenol onto XAD-7 was reported to be exothermic in nature and intraparticle diffusion was found to be rate controlling. Al-Ghouti et al. (2009) studied the adsorption of methylene blue onto Jordanian diatomite and concluded that pseudo-second order model best fitted the data. Equilibrium time was found at 50min and on increasing pH from 4 to 11, adsorption capacity was found to increased from 75 to 105 mg/g. Complete removal of methylene blue was reported at 1.7 g of diatomite.

Pokhrel and Viraraghavan (2006) reported adsorptive removal of arsenic from aqueous solution by iron oxide coated non-viable *Aspergillus niger* biomass. 95% of As(V) and 75% of As(III)) removal was observed at pH 6.

Table 2.2.3. Adsorption capacities of various adsorbents.

Adsorbent	Adsorption capacity (mg/g)
Commercial activated carbon	980.3
Activated carbon produced from New Zealand coal	588
Filtrasorb 400	476
Activated carbon	400
Activated carbon produced from Venezuelan bituminous coal	380
Peat	324
Coal	323.68
Filtrasorb 400	299
Norit	276
Picacarb	246
Filtrasorb 300	240
Activated carbon	238
Coal	230
Commercial activated carbon	200
Bituminous coal	176
Charcoal	62.7
Activated carbon	9.81
BFA	6.46
Red mud	2.49
Spent tea leaves	300.5
Zeolite	10.82
Papaya seeds	555.55
Pineapple stem	119.05

Source: Rafatullaha et al., 2010

Table 2.2.4. Comparison of various commercial activated carbons for the adsorption of phenol and its derivatives.

Adsorbent	Solute	pH	T (°C)	Isotherm Model used	Capacity (mg/g)	Reference
GAC	Furfural	8.1	–	Langmuir	374.4	(Sulaymon and Ahmed, 2008)
GAC	Phenol	5.7	–	Langmuir	350	(Sulaymon and Ahmed, 2008)
GAC	4-CP	5.7	–	Langmuir	319.9	(Sulaymon and Ahmed, 2008)
APET	Phenol	5	–	Langmuir	262	(Laszlo, 2005)
APET	Phenol	11	–	Langmuir	184.2	(Laszlo, 2005)
APET	Aniline	5	–	Langmuir	243.6	(Laszlo, 2005)
APET	Aniline	11	–	Langmuir	283.6	(Laszlo, 2005)
CCM200 (carbon cryogel)	Phenol	–	–	Langmuir	140	(Kim et al., 2006)
G-BAC	Phenol	–	–	Langmuir	235.4	(Kim et al., 2006)
PACT (power activated carbon treatment)	Phenol	–	25	Langmuir	135.7	(Orshansky and Narkis, 1997)
PACT	Aniline	–	25	Langmuir	126.6	(Orshansky and Narkis, 1997)
PAC	Phenol	–	–	–	303	(Ania et al., 2002)
Steam-PAC (from coal)	Phenol	–	–	–	226	(Ania et al., 2002)
Chemical-PAC (from coal)	Phenol	–	–	–	98	(Ania et al., 2002)
GAC (F400) F-DI	Phenol	–	–	Freundlich	75.2	(Leng and Pinto, 1997)
GAC(F400) F-HCl	Phenol	–	–	Freundlich	75.5	(Leng and Pinto, 1997)

Adsorbent	Solute	pH	T (°C)	Isotherm Model used	Capacity (mg/g)	Reference
F400-N_2	Phenol	–	–	Freundlich	96	(Leng and Pinto, 1997)
F400-Air	Phenol	–	–	Freundlich	54	(Leng and Pinto, 1997)
CNTs	Phenol	–	–	–	15.9	(Liao et al., 2008)
CNTs	Catechol	–	–	Langmuir	14.2	(Liao et al., 2008)
CNTs	Pyrogallol	–	–	Langmuir	33.6	(Liao et al., 2008)

Source: Su-Hsia et al., 2009.

AC: Activated carbon; BFA: Bagasse fly ash; CNTs: Carbon nanotubes; CP: Chlorophenol; GAC: Granular activated carbon; PAC: Powdered activated carbon.

Only two studies are reported for adsorptive treatment of dairy wastewater in open literature. Rao and Bhole (2002) used some low cost adsorbents along with powdered activated carbon (PAC). PAC was found to be better in lowering total dissolved solids (TDS) than other pretreated adsorbents like bagasse, straw dust, saw dust, coconut coir and fly ash. Sarkar et al. (2006) employed coagulation by chitosan followed by adsorption with PAC as pre-treatment steps before treating the dairy wastewater by membrane separation method. During adsorption step, PAC showed a maximum COD removal of 68% at pH = 4, adsorbent dose of 1.5 g/l, contact time of 1.5 h for dairy wastewater having an initial COD of 2000 mg/l.

Moreover, in the above two studies, mechanism of adsorption is lacking; kinetic, isotherm, and thermodynamics aspects have not been dealt with which are important for the design of any adsorption unit. Disposal aspects of the spent adsorbents were also not studied in the previous studies.

2.2.1.4. Membrane treatment process: Membrane treatment process includes microfiltration (MF), ultrafiltration (UF), naofiltration (NF), reverse osmosis (RO), dialysis, and electrodialysis. These methods are very promising where product recovery is feasible and produce high quality effluent suitable for direct reuse. NF membrane treatment is a viable alternative to the conventional treatment by RO because it can operate at lower pressures, lower energy consumption and higher permeate recoveries than RO (Owen et al., 1995). Frappart et al. (2006) reported the recovery of lactose and milk proteins as well as COD and ionic concentration reduction of dairy process waters having initial COD of 36,000 mg/l by NF using high shear rate dynamic filtration systems. Vourch et al. (2008) used RO treatment until 90-95% water recovery was achieved with an average permeate flux around 11 l/h m^2. Vourch et al. (2005) studied the performance of one-stage and two-stage (NF + RO and RO + RO) membrane treatment process. They evaluated the performances in terms of permeate flux, milk components rejection, purified water characteristics. They concluded that both TOC and conductivity of water treated by a single RO or NF + RO operations were suitable for reuse as heating, cooling, cleaning and boiler feed water. In another study, milk house and milking parlour dairy wastewater treatment was reported by wheat straw biofilter (Shah et al., 2002). The biofilter was found to be very effective removing 89% TSS and 76% of oil and grease but its effectiveness in COD removal was only 37%. The biofilter was ineffective in attenuating nitrate, while its effectiveness in attenuating ammonium (20% removal) and total Kjeldahl nitrogen (TKN) (15% removal) was low. They concluded that the biofilter performance could be enhanced by using residual heat in the wastewater to raise the operating temperature of the biofilter and by removing oil and grease prior to applying the wastewater to the biofilter.

2.2.2. Biological Treatment (Kushwaha et al., 2010a)

2.2.2.1. Aerobic process: Aerobic biological treatment involves microbial degradation and oxidation of waste in the presence of oxygen. Conventional treatment of dairy wastewaters by aerobic processes includes processes such as activated sludge, trickling filters, aerated lagoons, or a combination of these (Carta-Escobar et al., 2004). All compounds of dairy wastewater are biodegradable except protein and fats which are not easily degraded (Omil et al., 2003). Owing to the presence of high organic matter, dairy wastewaters are well suited for biological treatment, especially anaerobic treatment (Rico et al., 1991). However, the presence of fats shows the inhibitory action during anaerobic treatment of dairy wastewaters (Vidal et al., 2000). This inhibition is due to the presence of long chain fatty acids formed during the hydrolysis of lipids, which causes retardation in methane production (Hanaki et al., 1981). Long chain fatty acids were reported to be inhibitory to methanogenic bacteria (Koster, 1997) but lipids do not cause serious problems in aerobic processes (Komatsu et al., 1991). Table 2.2.5 summarizes the reported conditions of aerobic treatment of dairy wastewater by various authors. Amongst the various aerobic technologies, sequential batch reactor (SBR) seems to be the most promising technology for treatment of dairy wastewater. It is a fill- and draw activated sludge system. In this system, wastewater is added to a single batch reactor, treated to remove undesirable components, and then discharged. Equalization, aeration, and clarification can all be achieved using a single batch reactor. Hence savings on total cost are obtained by elimination of clarifiers and other equipment (U.S. Environmental Protection Agency, 1999). The treatment efficiency of SBR depends on the operating parameters such as phase duration, hydraulic retention time (HRT) and organic loading, temperature, mixed liquor suspended solid (MLSS), pH, dissolved oxygen concentration and the strength of wastewater.

Mohseni-Bandpi and Bazari (2004) used a bench-scale aerobic SBR to treat the industrial milk factory wastewater. More than 90% COD removal efficiency was achieved when COD concentration was varied from 400 to 2500 mg/l. The optimum dissolved oxygen in the reactor was 2 to 3 mg/l and mixed liquor volatile suspended solids (MLVSS) was around 3000 mg/l.

Sometimes membrane is coupled to SBR and the reactor is named as membrane sequencing batch reactor (MSBR). Bae et al. (2003) used MSBR for BNR. Nitrogen and phosphorus removal were found to be 96 and 80%, respectively; whereas BOD removal was found to be in the range of 97-98%. Stable SS free effluent was obtained by membrane separation. Compared to SBR, MSBR performed better even at higher organic loadings. Sirianuntapiboon et al. (2005) reported that high organic loading of 1.34 kg BOD_5/m^3 d; the COD, BOD_5, TKN and oil and grease removal efficiencies were found to be 89.3±0.1, 83.0±0.2, 59.4±0.8 and 82.4±0.4%, respectively. The respective removal efficiencies in the conventional SBR system were only 87.0±0.2, 79.9±0.3, 48.7±1.7 and 79.3±10%, respectively. The bio-sludge generated in MSBR was also three times lower as compared to conventional SBR. Neczaj et al. (2008) studied about dependency of removal efficiency on the operating parameters using two SBR for the treatment of dairy wastewaters having initial COD concentration in the range of 400-7500 mg/l. Aeration time of 19 h and anoxic phase of 2 h gave 98.6% COD and 80.1% TKN removal. The removal efficiencies of the SBRs decreased with increasing organic loading or decreasing HRT. The best effluent quality was observed under organic loading of 0.8 kg BOD_5/m^3 d and HRT of 10 d. Combined biochemical, ultrafiltration (UF) and reverse osmosis (RO) treatment technology has been proposed for the rayon grade paper mills waste effluent (Bhattacharya et al., 2005). Biochemical treatment showed 50% of the dissolved reducing sugar and COD from the liquor and RO showed almost complete removal of the remaining sugar.

Nitrogen is the main source of eutrophication. In this regard, complete oxidation of ammonia during the treatment is favorable. Li and Zhang (2002) studied about biological nitrogen removal using single-stage and two-stage SBR systems. In single-stage SBR system, the removal efficiencies for TKN, total nitrogen (TN), COD, total solids and volatile solids were found to be 75, 38.3, 80.2, 63.4 and 66.2%, respectively. For complete ammonia oxidation in single-stage SBR system, 4 d HRT was required. However, $1/3^{rd}$ HRT was required in two-stage system (SBR and a complete-mix biofilm reactor) for complete ammonia oxidation as compared to the single SBR system. Torrijos et al. (2004)

found a SBR giving the good results (99.5% COD, 95% TKN and 87% of total phosphorus) with excess sludge produced in only very low amounts with 0.2 g of SS/g of COD and sludge volume index (SVI) of 30 ml/g.

In recent trends, aerobic granular activated sludge SBR (GAS-SBR) have been reported to give very high-rate aerobic treatment and better settling (Wichern et al., 2008). Schwarzenbeck et al. (2005) reported removal efficiencies of 90% COD, 80% TN and 67% total phosphorous in a GAS-SBR.

Although the mixed culture activated sludge is widely used by the researchers for the treatment of dairy wastewaters but the bioaugmentation (addition of external microorganisms with high degradation capacity for specific wastewater) has been successfully used to give better performance by the various authors (Fantroussi and Agathos, 2005). Loperena et al. (2007) reported that although the commercial and mixed activated-sludge inocula gave similar COD removal in batch experiments for the treatment of a dairy industrial effluent, however the COD degradation rate was greater for the commercial inoculum.

2.2.2.2. Anaerobic treatment: Despite various studies and some advantages of the aerobic biological treatment of dairy wastewater (Table 2.2.6.), there are number of drawbacks associated with these studies. High energy requirement by aerobic treatment methods is the primary drawback of these processes. Dairy effluents have high COD and organic content and are warm, enabling them ideal for anaerobic treatment (Wheatley, 1990). Furthermore, no requirement for aeration, low amount of excess sludge production and low area demand are additional advantages of anaerobic treatment processes in comparison to aerobic processes (Table 2.2.6.). Consequently, a number of studies have been reported in open literature for the treatment of dairy wastewater by anaerobic methods. Table 2.2.7 summarizes the reported conditions of anaerobic treatment of dairy wastewaters by various authors.

Table 2.2.5. Reported conditions for the aerobic treatment of dairy industry wastewaters.

Waste type	Reactor Type	% BOD Reduction	% COD Reduction	% TKN reduction	SVI (ml/g)	HRT (d)	BOD /COD Loading kg/m^3 d	Reference
DI	MSBR	97-98	-	96	-	-	-	(Bae et al. 2003)
DI	Bioreactor supported with plastic mesh		92-98 CODs	-	-	-	-	(Carta-Escobar et al., 1999)
MF	MSBR	83.0 ± 0.2	89.3 ± 0.1,,	59.4 ± 0.8	< 100	-	1.340 (BOD)	(Sirianuntapiboon et al., 2005)
MF	SBR	79.9 ± 0.3,	87.0 ± 0.2,	48.7 ± 1.7	-	-	-	(Sirianuntapiboon et al., 2005)
MF	MSBR	97.9 ± 0.1	97.9 ± 0.0,	79.3 ± 1.0	44 ± 3.4	-	0.680 (BOD)	(Sirianuntapiboon et al., 2005)
MF and LL	SBR 1	97.9	98.6	80.1	-	-	-	(Neczaj et al., 2008)
	SBR 2	97.3	98.4	79.2	-	10-7	-	(Neczaj et al.. 2008)
MF	SBR		90-92	-	-	-	-	(Mohseni-Bandpi and Bazari, 2004)
Diluted WM	Batch Reactor		57-63	-	-	-	-	(Loperena et al.. 2009)
CP	MBBR		> 80	-	-	-	5.0 (COD)	(Andreottola et al., 2002)
DI	AS Reactor	99	-	91	-	0.82	-	(Fang, 1990)
WP	Batch Reactor		> 90	-	40-50 at	0.41-	-	(Bickers and bhamidimarri,

Waste type	Reactor Type	% BOD Reduction	% COD Reduction	% TKN reduction	SVI (ml/g)	HRT (d)	BOD /COD Loading kg/m^3 d	Reference
					10 h HRT	0.833		1998)
Diluted WM	SBR		90-99	90-99	-	-	-	(Gutierrez et al., 2007)
DI	Granular Sludge SBR		-	Nearly Complete	-	-	9.0 (COD)	(Wichern et al., 2008)
Diluted DI	Bioreactor		78-81	-	-	-	-	(Loperena et al., 2007)
CP	SBR		99.5	95	-	-	-	(Torrijos et al., 2004)
Anaerobically treated DI and SD	SBR		97	98	-	-	-	(Benitez et al., 2006)
DI	Granular Sludge SBR#		90	-	-	-	-	(Schwarzenbeck et al., 2005)
DI	SBR@		80.2	75	-	-	-	(Li and Zhang, 2002)

 # 80% total nitrogen removal and 67% total phosphorous, @ 38.3% Total nitrogen

SD-Synthetic dairy, CP-Cheese production, MF-milk factory, WM-Whole milk, LL-Landfill Leachate, DI-Dairy Industry, WP-Whey permeate, MBBR-Membrane bioreactor.

Table 2.2.6. Comparison of advantages and disadvantages of aerobic and anaerobic treatment of dairy industry wastewaters.

Factors	Aerobic Process	Anaerobic Process
Reactors	Aerated lagoons, oxidation ditches, Stabilization ponds, Trickling filters and Biological discs	UASB, Anaerobic filter, Upflow packed bed reactor, CSTR, Down flow fixed film reactor, Buoyant Filter Bioreactor,
Reactor size	Aerated lagoons, oxidation ditches, Stabilization ponds, Trickling filters and Biological discs requires larger land area but SBR needs comparatively lower area.	Smaller reactor size is required.
Effluent Quality	Excellent effluent quality in terms of COD, BOD and nutrient removal is achieved.	Effluent quality in terms of COD is fair but further treatment is required. Nutrient removal is very poor.
Energy	High energy is required.	These processes produce energy in the form of methane.
Biomass yield	In comparison to anaerobic process, 6-8 times greater biomass is produced (Metcalf and Eddy, 2003).	Lower biomass is produced
Loading rate	Maximum 9000 g COD/m^3 d (Wichern et al., 2008) is reported in literature.	Very high Loading rate of 31kg COD/m^3 d has been reported (Rico Gutierrez et al., 1991). This is the reason for smaller reactor volume and lesser area.
Oil and grease removal	These do not cause serious problems in aerobic processes (Komatsu et al., 1991).	Fats in wastewater shows the inhibitory action during anaerobic treatment of dairy wastewaters (Vidal et al., 2000)
Shock loading	Excellent performance in this regard.	Anaerobic processes showed not good responses to this shock loading.
Alkalinity addition	No need.	There is need for alkalinity addition to maintain the pH because pH changes during the digestion of lactose.

Table 2.2.7. Reported conditions for the anaerobic treatment of dairy industry wastewaters.

Waste type	Reactor type	% COD reduction	COD Loading (Kg COD /m^3 d)	HRT (d)	Biomass Yield (mg-VSS/mg-COD)	Methane Yield (m^3CH4/kg $COD_{removed}$)	Reference
CP	UASB	90.00	31.0	-	-	-	(Rico Gutierrez et al., 1991)
SD	UASB Control Reactor	82-88	-	-	-	-	(Leal et. al., 2006)
	Hydrolysed Reactor	90-91	-	-			(Leal et. al., 2006)
CP	UASB	98-85	6.2-7.5	-	-	-	(Gavala et al., 1999)
RW	Intermittent UASB	-	-	-	-	-	(Nadais et al.,2005)
DID	UASB and AS*	98.9	-	1.08	-	-	(Tawfik et al., 2008)
SD	Continuous and intermittent UASB	64-78 (intermittent) 65-88 (continuous)	-	-	-	-	(Nadais et al.,2006)
DI	Two UASB in parallel	90	5.5	0.70	-	-	(Passeggi et al., 2009)
CW	UASB	> 90	-	-	-	-	(Yan et al., 1989)
WP	UASB	99-64.2	-	0.4-5	-	-	(Hwang and Hansen. 1992)
CP	UASB	90	-	-	-	-	(Cammarota et al., 2001)
SD	Two phase HUASB	97-99	10.7-19.2	-	-	-	(Banu et al., 2007)
IC	AFBR I Two phase	65-90	1.1-6.6	8.11-1.13	-	-	(Motta-marques et al., 1990)

Waste type	Reactor type	% COD reduction	COD Loading (Kg COD /m^3 d)	HRT (d)	Biomass Yield (mg-VSS/mg-COD)	Methane Yield (m^3CH4/kg $COD_{removed}$)	Reference
	AFBR II Calcium Amended	75	1.5-9.4	6.67-1.11	-	-	(Motta-marques et al., 1990)
	AFBR III Biopolymer system		1.5-9.4	6.67-1.11	-	-	(Motta-marques et al., 1990)
	AFBR IV Control System	65-70	1.5-9.4	6.67-1.11	-	-	(Motta-marques et al., 1990)
IC	AF	85	6		-	0.32-0.34	(Ince, 1998b)
RM	AF	90	5-6		-	-	(Omil et al., 2003)
SD	BFBR	96.25	10		-	-	(Haridas et al.,2005)
IC	UFAF	70	9		-	0.35	(Moronoy et al., 1994)
MCB	UFAF two phase	90	5	2 d	-	-	(Ince, 1998a)
MB	UFAF	80	21	0.50 d	-	-	(Ince et al., 2000)
SD	Hybrid	90-97	0.82-6.11	4.1-1.7 d	-	0.354 (at 1.7 d HRT)	(Ramasamy et al., 2004)
CW	Hybrid	> 95	Up to 11	2 d	-	-	(Strydom et al., 1995)
IC	ASBR#	62		0.25 d	-	-	(Calli and Yukselen.2002)
DI	ASBR	> 80	($1.6x10^{-3}$)-	(40-5) d	0.196-	-	(Goblos et al., 2008)

Waste type	Reactor type	% COD reduction	COD Loading (Kg COD /m^3 d)	HRT (d)	Biomass Yield (mg-VSS/mg-COD)	Methane Yield (m^{3}CH4/kg COD$_{removed}$)	Reference
			(12.8x10^{-3})		0.276		
RW	ADU	90.4	-	-	-	0.342	(Borja et al.1992)
SD	Two upflow packed-bed reactor in series	93.8-98.5 for I and 72.5-84 for II reactor	14.9 max. for I 5.0 max. for II reactor	-	-	-	(Venkataraman et al., 1992)
Not given	Upflow packed-bed	93.8-98.5. 72.5-84	5-14.29	-	-	-	(Morgan et al., 1991
SD	up flow reactor	59.4		0.5 d	0.32	-	(Yu and Fang, 2002a)
SD	Batch reactor	-		-	0.19-0.25	-	(Yu and Fang, 2002b)
DI	Anaerobic Reservoir @	> 75		-	-	-	(Arbeli et al., 2006)
CW	Downflow fixed-film	75	13	4.9 d		0.28	(van den Berg and Kennedy, 1992)

Waste type	Reactor type	% COD reduction	COD Loading (Kg COD /m^3 d)	HRT (d)	Biomass Yield (mg-VSS/mg-COD)	Methane Yield (m^{3}CH4/kg COD$_{removed}$)	Reference
SIC	CSTR	98-97-96-94-92 (SCOD)[$]	-	7.45-5.99-4.60-3.76-2.99 (d)	-	-	(Ramasamy and Abbasi, 2000)
MP	-		9.3	0.5 d	-	-	(Demirel and Yenigun, 2004)
CW	Multi-chamber bioreactor	83	-	2 d	-	-	(Patel and Madamwar, 1998)

[#]75%BOD reduction, [@]> 75% BOD reduction, 99.6% BOD and 98.9% oil and grease reduction. [$]Soluble COD.

CF-Cheese factory, SD-Synthetic dairy, RM-Raw Milk, DID-Dairy industry and Domestic, CW-Cheese whey, WP-Whey permeate, CP-Cheese production, IC-Ice-cream, MCB-Milk and cream bottling, MB-Milk bottling, SIC-Synthetic ice-cream. MF-milk factory, WM-Whole milk. DI-Dairy Industry. CSTR-Continuos stirred tank reactor, ASBR-Anaerobic sequencing batch reactor, UFAF-Upflow anaerobic filter, BFBR-Buoyant filter bioreactor, AFBR-Anaerobic filter bioreactor, HUASB-Hybrid upflow anaerobic sludge blanket, UASB-Upflow anaerobic sludge blanket, AS-Activated sludge, AF-Anaerobic filter, ADU-Anaerobic Digestion Unit.

UASB reactors have been widely used for the dairy wastewater treatment in full-scale applications (Rico Gutierrez et al. 1991; Gavala et al., 1999; Yan, Lo and Liao, 1989; Hwang and Hansen, 1992). The basic elements of a typical UASB reactor are a sludge blanket, influent distribution system, gas-solid separator and the effluent withdrawal system. In UASB reactor, the influent is distributed at the bottom and travels in up-flow mode (Metcalf and Eddy, 2003). In one of the study, COD reduction of 90% at organic loading rate of 0.031 kg COD/m^3 d (t = 0.07 d) was achieved operating in steady-state conditions using a wastewater with a COD influent of 2050 mg/l.

Dairy wastewater contains fats and the inhibitory action of the fat to the anaerobic treatment does not allow fast and increased removal efficiency (Vidal et al., 2000). Various authors reported that the enzymetic hydrolysis of fats as pre-treatment may remove this problem. Cammarota et al. (2001) found that treatment of dairy wastewaters containing elevated fat and grease levels (868 mg/l) in UASB reactor resulted in effluents of high turbidity (757 NTU), volatile suspended solids (VSS) up to 944 mg/l and COD removal below 50%. However, same dairy wastewater pre-treated with 0.1% (w/v) of fermented babassu cake containing Penicillium restrictum lipases showed higher COD removal efficiency of 90% when treated in same UASB reactor. In another study, Leal et al. (2006) used synthetic dairy wastewater containing high levels of oil and grease (200, 600 and 1000 mg/l) using two identical UASB reactors one fed with wastewater from enzymatic hydrolysis step and the other with raw wastewater. 90 and 82% COD removal efficiencies were achieved in the reactors fed with the hydrolysed effluent and with raw wastewater, respectively. Passeggi et al., (2009) combined two anaerobic UASB reactors in parallel with internal fat-separation by flotation, external lamella- settler and floated material digester for the treatment of wastewaters containing high fats. 90% of COD removal was found using loading rates up to a maximum 5.5 kg COD/m^3.d, HRT of 17 h. Average sludge digester efficiency using a loading rate of 3.5 kg VS/m^3.d, showed 87% of lipid removal.

Many authors have reported reduced efficiency of continuous UASB reactors due to the build up of organic matter in the reactor (Morgan et al., 1991; Motta Marques et al., 1990). Nadais et al. (2005) studied the intermittent operation of mesophilic UASB reactors to over come the build up of organic matter and the influence of cycle duration in the reactor. They reported that 96 h cycle (48 h feed+48 h feed less) reflected highest conversion to methane.

Anaerobic filter reactors are generally suitable for dairy effluents containing low concentrations of SS. The anaerobic filter reactors capture SS and provide sufficient retention time for biosolids. Hence, the SS retention time and the HRT necessary become satisfying. A laboratory-scale plastic medium anaerobic filter reactor provided average COD removal rates between 78 and 92% at a HRT of 4 d (Viraraghavan and Kikkeri, 1990, 1991). Monroy et al. (1994) investigated the performance of an upflow anaerobic filter reactor treating a high solid-containing dairy waste at 0-18 kg COD/m^3 d organic loading. The mean COD removal was found to be 70%.

The type of support media (porous or non-porous) greatly affects the reactor's performance in anaerobic filter reactors. The ideal packing media for the anaerobic filter is that which maximizes both surface area and porosity. Large surface area of the media enhances the attachment of the biomass and increased porosity decreases the overall reactor volume required and minimizes the filter clogging. The performances of porous and non-porous support media in anaerobic filter reactors on mesophilic anaerobic treatment of milk bottling plant wastewater were investigated and It was concluded that the reactor with non-porous packing showed instability above an organic loading of 4 kg COD/m^3 d, whereas the reactor with the porous packing was stable at very high organic loading of 21 kg COD/m^3 d (Anderson et al., 1994). In an another study, strength and performance of a porous media in an upflow anaerobic filter (UFAF) were investigated up to an organic loading rate of 21 kg COD/m^3 d with a HRT of 0.5 d. The highest quantity of attached biomass (103 mg VSS/media ring) was found at the bottom and lowest (23 mg VSS/media ring) at the top. After 8 months of operation, reduction in compressive strength was 50% of the media; and during this time, 80% COD removal efficiency was achieved (Ince et al., 2000).

Borja et al. (1992) studied about anaerobic digestion for the treatment of raw- milk based wastewater. The reactor contained suspensions of micronized clays (sepiolite, saponite and bentonite) of different chemical compositions on which the anaerobes were adhered. They found the methane yield coefficient 0.342 m^3 CH_4/kg $COD_{removed}$. The COD removal was efficiency was found to be 90.4%. Table 2.2.8 describes the comparison of various anaerobic reactors with retention time and organic loading rates. It can be seen in the table 1.2.4 that fluidized bed reactor can withstand very high COD loading rate of 2-50 kg COD /m^3 d giving 70–80% COD removal, while CSTR with high retention time of 1-5 d.

Yu and Fang (2002b) studied acidogenesis of a dairy wastewater in batch reactors at pH = 5.5 and 55 °C with reactors fed COD of 8000 mg/l. At the start the concentration of acetate and butyrate increased rapidly and reached maxima at some points, then declined. Increase in substrate concentration, increased the butanol and propanol fractions. Beyond 8000 mg/l of COD the metabolism shifted to the alcohol-producing pathways.

Due to the gas generation, all types of anaerobic reactors are well mixed but the reactor performance gets affected by the degree of mixing and the solid content in the waste. The fluidized bed reactors remove the problem of mixing and give better mass transfer characteristics; however they require very long time for stable biofilm establishment (Rockey and Forster, 1985).

Table 2.2.8. Typical operating conditions for anaerobic digester.

Anaerobic digester type	COD Loading (kg /m^3 d)	Retention (d)	%COD removal
CSTR	0.5–2.5	1–5	80–90
Anaerobic filter	2–10	0.41–2.08	70–80
UASB	2–15	0.33–2.08	70–90
Fluidized bed	2–50	0.02–1	70–80

Source: Demirel et al., 2005.

The ‘two-stage’ reactor concept improves process stability and efficiency and is particularly suitable for dairy wastewaters containing high concentrations of organic SS (Demirel et al., 2005). In a two-stage system, acidogenic and methanogenic phases can be operated separately under respective optimum conditions. In the first stage, hydrolysis and degradation of lipids and proteins into amino acids and fatty acids take place (Schroder and Haast, 1998; Malaspina et al., 1995). This degradation gives a high-energy yield to the microorganisms. In the second stage, the end-products of the fermentation process (acetate, butyrate, propionate, formic acid, carbon dioxide and hydrogen) are produced by methanogenic microorganisms into methane and carbon dioxide. Table 2.2.9 describes the performances of various two stage anaerobic reactor types with various dairy waste types. It can be seen in the table that how various operating parameters affect the methane yield and COD/BOD removal.

Temperature and pH are important parameters in treatment with two-stage anaerobic reactors. Degradation efficiency is generally more at higher temperatures (Ghosh, 1991). Thus, the thermophilic operation facilitates the treatment at higher loading rates, and therefore requires smaller treatment plants than the mesophilic systems. Yu and Fang (2002a) reported that degradation of dairy wastewater pollutants increased with an increase in pH from pH 4.0 to 5.5. 48.4% of COD was converted into volatile fatty acids and alcohols, 6.1% into hydrogen and methane and the remaining 4.9% into biomass. On increasing the pH up to 6.5, there was very slight increase in degradation.

HRT is also an important variable in two-stage anaerobic treatment processes. The effects of HRT on anaerobic acidogenesis have been investigated earlier (Ghosh et al., 1975; Yilmazer and Yenigun, 1999; Horiuchi, 2002). In a recent study, the performance of mesophilic acidogenic reactor was evaluated in terms of volatile fatty acid production, with respect to HRT variations between 1-0.5 d with organic loading rate of about 9.3 kg COD/m^3 d, in a continuous flow-completely mixed anaerobic reactor, coupled with a conventional gravity settling tank and a continuous recycling system. It was shown that, acid production increased proportionally to the organic loading rate with decrease in HRT. The highest degree of acidification and the rate of acid production were 56% and 3.1 kg/m^3 d, respectively, at 0.5 d of HRT. Variations in HRT affected volatile fatty acid production (Demircl and Yenigun, 2004).

Anaerobic processes treat only carbonaceous pollutant with subsequent production of methane, while nitrogenous organic material is partly converted to ammonia which is also not desirable. The removal of phosphorous is also low. So a complete treatment, compatible with a good quality discharge to the natural environment, needs an additional process (Montuelle et al., 1992). A hybrid system comprising of both anaerobic and aerobic reactor are used to treat dairy wastewaters. The combination of a UASB and activated sludge (AS) gave an overall removal efficiency of 98.9% for COD, 99.6% for BOD_5 and 98.9% for oil and grease at a total HRT of 1.08 d and 1.9-4.4 kg COD/m^3 d of organic loading. TSS and VSS removal averaged above 72 and 75%, respectively (Tawfik et al., 2008). In another study, dairy wastewater was fed to anaerobic and anoxic reactors in series with an aerobic reactor. The overall system was operated at an HRT of 7 d. Overall COD and total nitrogen removal was more than 90 and 65% (Donkin and Russell, 1997).

Successful anaerobic treatment of wastewaters discharged by raw milk quality control laboratories was achieved in SBR with anaerobic filter (AF) without fat removal prior to the anaerobic reactor with COD removal being higher than 90% in AF and most of the fat was successfully degraded (Omil et al., 2003). The two-stage anaerobic treatment using HUASB (Hybrid-UASB) with polyurethane foam cubes and PVC has been reported to be a better alternative for the complete treatment of dairy wastewater giving 99% COD removal at 19.2 kg COD m^3/d loading with methane content of 70% in the biogas in stage I, and 66% in stage II (Rajesh Banu et al., 2007). In an another study, the HUASB was combined with photocatalytic oxidation reactor and resulted in 95% removal of COD from the dairy wastewater at very high organic loading rate (OLR) (19.2 kg COD/m^3) (Rajesh Banu et al., 2008)

Table 2.2.9. Two-stage anaerobic treatment process performances for dairy wastewater treatment.

Waste type	Reactor type	HRT (d)	COD Loading (kg /m^3.d)	Temperature (°C)	Methane yield ($m^3/kg\ COD_{removed}$)	Removal (%)	Reference
Cheese-fresh milk-powder milk/butter effluents	CSTR + upflow filter		2.82–2.44–0.97	35	0.359–0.327–0.287	97–94–91 (COD)	(Strydom et al., 1997)
Dilute milk waste	CSTR + upflow filter	4.4	-	-	-	92 -	(Li et al., 1984)
Dilute milk waste	Fluidized beds		9.4	-	-	76–92 (COD	(Tanaka et al., 1985)
Wastewater of a milk bottling plant	CSTR + upflow filter	2		35	-	90 (COD)	(Cohen et al., 1994)
Skimmed milk	CSTR + upflow filter	2		20	-	95.5 (COD)	(Anderson et al., 1994)
Wastewater of a milk and cream bottling plant	CSTR + upflow filter	2	5	33–36	-	90 (COD), 95 (BOD)	(Jeyaseelan et al., 1995)
Synthetic cheese whey	CSTR – upflow filter	5		35	-	95 (COD)	(Ince et al., 1998)

Source: Demirel et al. 2005

2.3. RESEARCH GAPS

It is clear from literature review most attention has been paid to anaerobic treatment process followed by aerobic and membrane methods. Very few studies are reported for coagulation and adsorption treatment processes.

Coagulation with inorganic coagulants reported in the literature lack studies on mechanism of treatment process. Moreover, coagulation studies using natural coagulants except for chitosan, are not reported in the literature. Further studies have to be concentrated on these aspects of coagulation treatment. ECT using various types of electrodes also requires immediate attention. Only two studies are available in open literature for the ECT of dairy wastewater (Sengil and ozacar, 2006; Tchamango et al., 2010). Tchamango et al. (2010) studied the ECT of dairy wastewater with aluminium electrodes while Sengil and ozacar (2006) used iron electrode. Moreover, disposal aspect of residues (scum and sludge), which are generated during the ECT, were not dealt in any of the above two studies which are very important from environmental point of view.

Among physico-chemical methods, adsorption is an important treatment method for treatment of various types of wastewaters. However, only two studies (Rao and Bhole, 2002; Sarkar et al., 2006) are reported for the treatment of dairy wastewater by adsorption. Moreover, in the above two studies, mechanism of adsorption is lacking; kinetic, isotherm, and thermodynamics aspects have not been dealt with which are important for the design of any adsorption unit. Disposal aspects of the spent adsorbents were also not reported in these studies.

Hybrid membrane systems with combination of RO, NF and UF are likely to become area of future research. Combination of membranes with biological and/or chemical methods is likely to achieve the target of zero water discharge in dairy industries.

In the field of aerobic biological treatment process, mixed culture activated sludge have been widely used by the researchers for the treatment of dairy wastewaters, however, future studies have to be more concentrated on bioagumented cultures which can specifically treat dairy wastewaters with high removal efficiencies in less HRT. Anaerobic processes treat only carbonaceous pollutant and partly degrade nutrients. So for complete treatment, more studies on anaerobic-aerobic combination are required. Disposal of sludge during biological methods is very important; however none of the investigators have dealt this aspect of wastewater treatment.

Chapter – 3

THEORY

3.0. GENERAL

In this chapter, theories related to coagulation, electro-chemical treatment (ECT), adsorption and treatment using sequential batch reactor (SBR) have been presented.

3.1. COAGULATION

Coagulation and flocculation is a frequently applied process in the primary treatment of industrial wastewater (in some cases as secondary and tertiary treatment) to remove suspended and/or colloidal particles and partially dissolved particles. Coagulation using chemical coagulants consists of combining insoluble particles and/or dissolved organic matter present in dairy wastewater into large aggregates, thereby facilitating their removal in subsequent sedimentation, floatation and filtration stages.

The colloids contained in the water are positively charged at $pH < pH_{iso}$ (isoelectric pH) and negatively charged at $pH > pH_{iso}$. These colloids are stable due to the repulsive forces between the negative charges. These colloids are, however, destabilized by positively charged ions formed from the hydrolysis of coagulants. Destabilization of colloidal particles can be influenced by the double layer compression, adsorption and charge neutralization, entrapment in precipitates (sweep flocculation) and interparticle bridging (Faust and Ally, 1998).

3.1.1. Mechanism of Coagulation

3.1.1.1. Double layer compression: The negative colloid and its positively charged atmosphere produce an electrical potential across the diffuse layer. This is highest at the surface and drops off progressively with distance, approaching zero at the outside of the diffuse layer and is known as Zeta potential. When a coagulant is added, it destabilizes the negatively charged particles. A cationic coagulant reduces the zeta potential of the particles by adding positive charge. This is usually accomplished by adding a metal salt to the water. Double layer compression involves adding salts to the system. As the ionic concentration increases, the double layer and the repulsion energy curves are compressed until there is no longer an energy barrier. Particle agglomeration occurs rapidly under these conditions because the colloids can just about fall into the van der Waals "trap" without having to surmount an energy barrier. The thickness of the double layer depends upon the concentration of ions in solution. A higher level of ions means more positive ions are available to neutralize the colloid. The result is a thinner double layer. Decreasing the ionic concentration (by dilution, for example) reduces the number of positive ions and a thicker double layer results.

3.1.1.2. Adsorption and charge neutralization: Inorganic coagulants (such as alum and ferrous sulphate) often work through charge neutralization. When these metal based coagulants are added to water, it dissociates and metal ions are formed. Fe^{2+}/Al^{3+} are liberated, if ferrous salt/alum is used. Liberated Fe^{2+}/Al^{3+} and OH^- ions react to form various monomeric and polymeric hydrolyzed species. The concentration of the hydrolyzed metal species depends on the metal concentration, and the solution *pH*.

The percentage of Fe^{2+} and Al^{3+} hydrolytic products can be calculated from the following stability constants (Benjamin 2002; Duan et al., 2004):

$Fe^{2+} + H_2O = Fe(OH)^+ + H^+ \quad pK_1 = 9.5$ (3.1.1)
$Fe(OH)^+ + H_2O = Fe(OH)_2 + H^+ \quad pK_2 = 11.07$ (3.1.2)
$Fe(OH)_2 + H_2O = Fe(OH)_3^- + H^+ \quad pK_3 = 10.43$ (3.1.3)

$Al^{3+} + H_2O = Al(OH)^{2+} + H^+ \quad pK_1 = 4.95$ (3.1.4)
$Al(OH)^{2+} + H_2O = Al(OH)_2^+ + H^+ \quad pK_2 = 5.6$ (3.1.5)
$Al(OH)_2^+ + H_2O = Al(OH)_3 + H^+ \quad pK_3 = 6.7$ (3.1.6)
$Al(OH)_3 + H_2O = Al(OH)_4^- + H^+ \quad pK_4 = 5.6$ (3.1.7)

The speciation diagram of Fe(II) and Al(III) as drawn using above stability constants is presented in Fig. 3.1.1 and Fig. 3.1.2.

It can be seen from speciation diagram of Fe(II) ions that the dominant soluble species are Fe^{2+} and $Fe(OH)_3^-$ at low and high pH, respectively. The hydrolysis constants for aluminum cover a very narrower range, and all of the aluminum deprotonations are 'squeezed' into an interval of less than 2 unit. Therefore, apart from a narrow pH region approximately 5.5–6.5, the dominant soluble species are Al^{3+} and $Al(OH)_4^-$ at low and high pH, respectively.

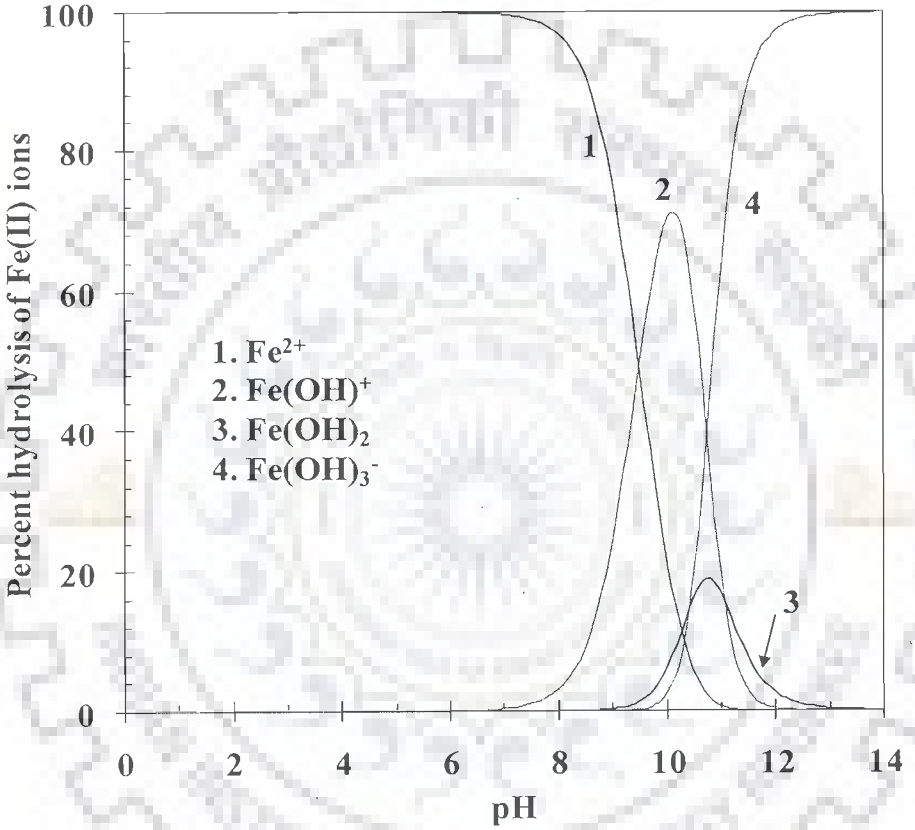


Fig. 3.1.1. Speciation diagram of Fe(II).

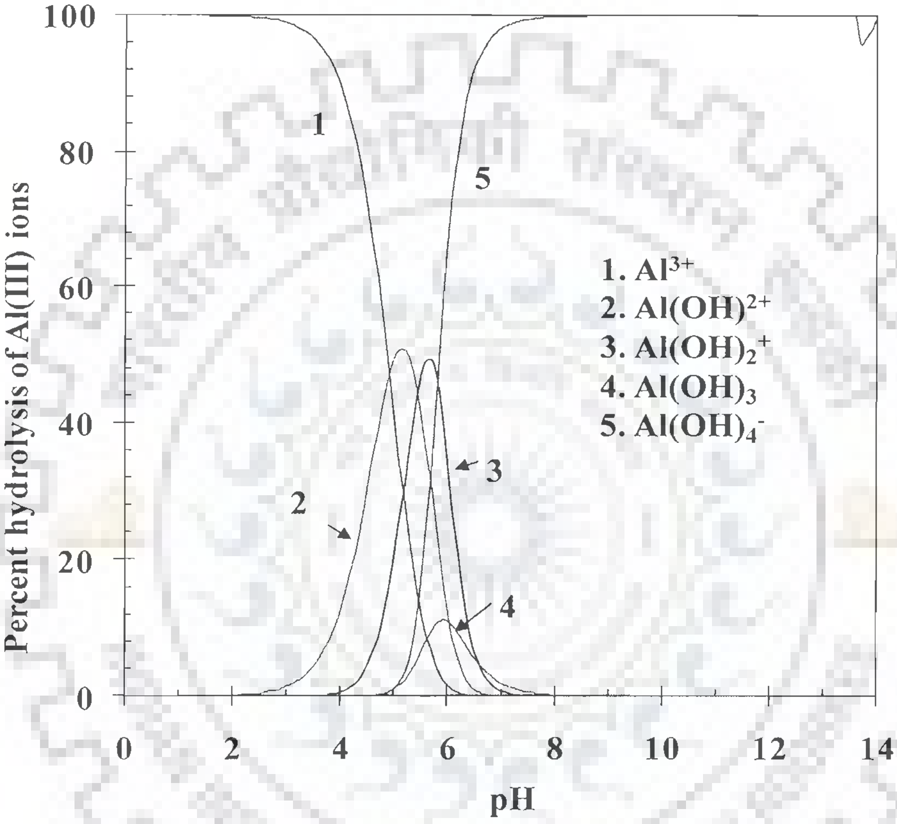


Fig. 3.1.2. Speciation diagram of Al(III).

Wang et al. (2004) reported the speciation of monomeric, fast-reacting polymeric and slow-reacting colloidal species of hydrolysed aluminum derived from PAC solution containing different ratio of OH/Al (Table 3.1.1).

Table: 3.1.1. Speciation distribution of PAC.

No.	OH/Al		pH	Monomeric Al (%)	Fast-reacting polymeric (%)	Slow-reacting colloidal species (%)
$PACl_0$	0.0	Al_2Cl_4	3.03	91.9	8.1	0.0
$PACl_{10}$	1.0	$Al_2(OH)_2Cl_4$	3.66	60.7	21.2	18.1
$PACl_{20}$	2.0	$Al_2(OH)_4Cl_2$	3.94	23.6	34.5	41.9
$PACl_{25}$	2.5	$Al_2(OH)_5Cl$	5.32	7.3	40.1	52.6

Adsorption of the metal hydrolysed products on the colloid surface causes charge neutralization, which brings about van der Walls forces become dominant (O'Melia et al., 1972). Charge neutralization alone will not necessarily produce macro-flocs (flocs that can be seen with the naked eye). Micro-flocs (which are too small to be seen) may form but will not aggregate quickly into visible flocs.

The polymeric hydrolyzed species possess high positive charges, and adsorbed to the surface of the negative colloids. This results in a reduction of the zeta potential to a level where the colloids are destabilized. The destabilized particles, along with their adsorbed hydro-metallic hydroxometallic complexes, aggregate by interparticle van der Waals forces. These forces are aided by the gentle mixing in water (Reynolds, 1982). When a coagulant forms threads or fibers which attach to several colloids, capturing and binding them together, this phenomenon is known as bridging. Some synthetic polymers and organic polyelectrolytes, instead of metallic salts, are used to assist interparticle bridging (O'Melia et al., 1972).

Adsorption sites on the colloidal particles can adsorb a polymer molecule. A bridge is formed when one or more particles become adsorbed along the length of the polymer. Bridge particles intertwined with other bridged particles during the process.

3.1.1.3. Sweep coagulation: Addition of relatively large doses of coagulants, usually aluminum or iron salts, results in precipitation as hydrous metal oxides. Most of the colloids and some of dissolved solids are literally swept from the bulk of the water by becoming enmeshed in the settling hydrous oxide floc. This mechanism is often called sweep flocculation. Sweep floc is achieved by adding so much coagulant to the water that the water becomes saturated and the coagulant precipitates out. Then the particles get trapped in the precipitant as it settles down (Duan et al., 2004).

3.2. ELECTROCHEMICAL TREATMENT (ECT)

ECT process can be another alternative process for treating dairy wastewaters. The major screened-off area in the ECT is electro-coagulation (EC), electro-flotation (EF) and electro-oxidation (EO). An ECT unit consists of anodes and cathodes in parallel mode. When electric power is applied from a power source, the anode material gets oxidized and the cathode is subjected to reduction of elemental metals and due to further reactions depending on conditions applied, removal of various pollutants takes place by EC and/or EF and/or EO mechanisms.

3.2.1. Electro-flotation (EF)

EF is a simple process in which buoyant gases bubbles generated during electrolysis take along with them the pollutant materials to the surface of liquid body. The bubbles of hydrogen and oxygen which are generated from water electrolysis move upwards in the liquid phase. A layer of foam, containing gas bubbles and floated particles is formed at the surface of water. The rate of flotation depends on several parameters such as surface tension between the water particles and gas bubbles; the bubble size distribution and bubble density; size distribution of the particles; the residence time of the solution/liquid in the EC cell and the flotation tank; the particle and gas bubble zeta potentials; and the temperature, pH of the solution (Koren and Syversen, 1995).

3.2.2. Electro-oxidation (EO)

Decomposition of organic materials through EO treatment means the oxidation of organics present in wastewater to carbon dioxide and water or other oxides. The electrochemical oxidation of wastewater is achieved in two ways. First, by direct anodic oxidation, in which organics are adsorbed at the electrode and oxidized at the surface of the electrode and second, by indirect oxidation in which some oxidizing agents are generated electrochemically which are responsible for oxidation of organics present in the solution.

The schemes of these two processes are illustrated in Fig. 3.2.1

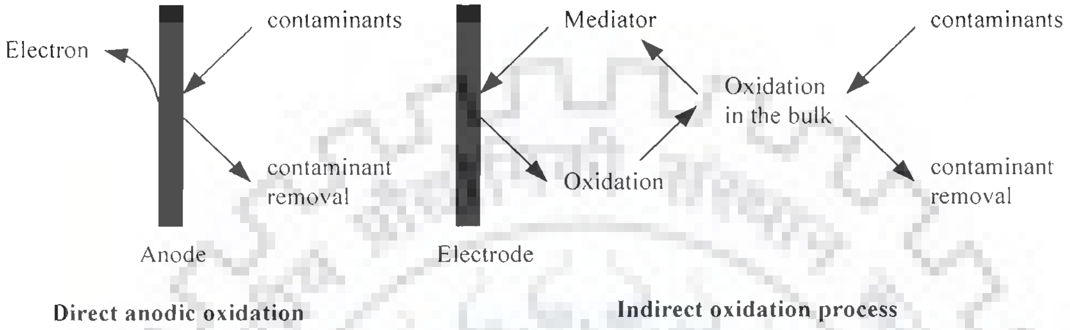


Fig. 3.2.1. Direct and indirect oxidation processes in ECT (Juttner et al., 2000).

Organic pollutants are adsorbed on the anode surface in direct anodic oxidation process, where active oxygen (adsorbed hydroxyl radicals) or chemisorbed "active oxygen" is accountable for the oxidation of adsorbed Organics pollutants. The mechanism of oxidation of organic matter on oxide anode (MO_X) was suggested by Comninellis (1994). The reactions involve are as follows:

$$H_2O + MO_X \longrightarrow MO_X[OH] + H^+ + e^- \qquad (3.2.1)$$

The adsorbed hydroxyl radicals may form chemisorbed active oxygen

$$MO_X[OH] \longrightarrow MO_{X+1} + H^+ + e^- \qquad (3.2.2)$$

The liberated chemisorbed active oxygen is responsible for the oxidation.

During the EO treatment process, two types, of oxidation is possible. In one way, toxic and non-biocompatible pollutants are converted into bio-degradable organics, so that further biological treatment can be initiated. In contrast, in other way, pollutants are oxidized to water and CO_2 and no further purification is necessary.

In an indirect oxidation process, strong oxidant such as hypochlorite/chlorine, ozone, and hydrogen peroxide (Farmer et al., 1992) are regenerated during electrolysis. Following reaction shows the formation of hypochlorite:

$$H_2O + Cl^- \longrightarrow HOCl + H^+ + 2e^- \qquad (3.2.3)$$

High voltage can led to formation of hydrogen peroxide and other molecules as follows:

$$H_2O \longrightarrow OH, O, H^+, H_2O_2 \quad (3.2.4)$$

These oxidants oxidize many inorganic and organic pollutants in the bulk solution (Abuzaid et al., 1999; Naumczyk et al., 1996; Vlyssides and Israilides, 1997; Lin and Wu, 1997).

3.2.3. Electro-coagulation (EC)

EC, like coagulation, is the process of destabilization of colloidal particles present in wastewater and can be achieved by two mechanisms: one in which an increase in ionic concentration, reduce the zeta potential, and adsorption of counter-ions on colloidal particles neutralises the particle charge; and other by well known mechanism of sweep flocculation (Duan et al., 2004).

Various reactions take place in the EC reactor during its operation. As the current is applied, the anode material undergoes oxidation and cathode gets reducted. If iron or Al electrodes are used, Fe^{2+} and Al^{3+} ion generation takes place at anode by the following reaction (Thella et al., 2008; Kumar et al., 2009)

$$Fe\,(S) \rightarrow Fe^{2+}\,(aq) + 2e^- \quad (3.2.5)$$

$$Al\,(S) \rightarrow Al^{3+}\,(aq) + 3e^- \quad (3.2.6)$$

In addition, oxygen evolution can compete with iron or aluminum dissolution at the anode via the following reaction:

$$2H_2O\,(l) \rightarrow O_2\,(g) + 4H^+\,(aq) + 4e^- \quad (3.2.7)$$

At the cathode, hydrogen evolution takes place via the following reaction:

$$3H_2O\,(l) + 3e^- \rightarrow 3/2H_2\,(g) + 3OH^-\,(aq) \quad (3.2.8)$$

Liberated Fe^{2+}/Al^{3+} and OH^- ions react to form various monomeric and polymeric hydrolyzed species. The concentration of the hydrolyzed metal species depends on the metal concentration, and the solution *pH*. These metal hydrolysed products are responsible for the coagulation of pollutants from solution, as previously discussed in section 3.1.1.2.

3.2.4. Factors affecting ECT Process

3.2.4.1. Current density (*J*), electrolysis time (*t*) and anodic dissolution: Faraday's law describes the relationship between current density (*J*) and the amount of anode material that dissolves in the solution. It is given as:

$$w = \frac{MJt}{ZF} \tag{3.2.9}$$

Where, w is the theoretical amount of ion produced per unit surface area by current density J passed for duration of time, t. Z is the number of electrons involved in the oxidation/reduction reaction, M is the atomic weight of anode material and F is the Faraday's constant (96486 C/mol).

The pollutants removal efficiency depends directly on the concentration of aluminum ions produced by the metal electrodes, which in turn as per Faradays law depends upon the t and J. When the value of t and J increases, an increase occurs in the concentration of metal ions and their hydroxide flocs. Consequently, an increase in t and J increases the removal efficiency.

Theoretically, according to the Faraday's law when 1 F of charge passes through the circuit, 28 g of iron is dissolved at each electrode individually connected to the positive node of the power supply unit. During the coagulation process with iron electrodes, the valency of the coagulant increases, with Fe^{3+} being much more effective than the Fe^{2+}.

3.2.4.2. pH: The initial *pH* (*pH$_i$*) of the wastewater will have a significant impact on the efficiency of the ECT. The effects of pH_i on the ECT of wastewater can be reflected by the solubility of metal hydroxides as shown in Fig 3.1.1 and 3.1.2. The effluent pH after ECT would increase. The incremental increase in pH with an incremental increase in the amount of current applied tends to decrease at higher current (Nielson and Smith, 2005, Mahesh et al., 2006 a). The general cause of the pH increase can be explained from the following equation:

$$2\,H_2O + 2e^- \longrightarrow H_{2(g)} + 2OH^- \text{ (cathode)} \tag{3.2.9}$$

At the cathode, generated hydrogen gas (which attaches to the flocculated agglomerates, resulting in flocs floation to the surface of the water) and this causes the pH to increase as the hydroxide-ion concentration in the water increases. This reaction is one of the dominant reactions that occur in the electro-flocculation system (Donini et al., 1994; Koren and Syversen, 1995).

Also, due to the following reaction, pH is affected:

$$2\,H_2O \longrightarrow O_2\,(g) + 4H^+ + 4\,e^- \tag{3.2.10}$$

These two reactions tend to neutralize pH. This is the reason, which, however, prevents larger pH increases due to larger hydroxides formations at higher current densities.

3.2.4.3. Conductivity and the effect of salts: Feed conductivity is an important parameter in ECT, since it directly affects the energy consumed per unit mass of pollutants removed. If conductivity is low, higher amount of energy is consumed per unit of mass of pollutants removed and vice versa. Due to this, some salts (commonly NaCl) are added to increase the conductivity of feed. When, salt is added to the solution, it reduces the solution resistance and hence, voltage distribution between the electrodes reduces. However, a too high conductivity may lead to secondary parasite reactions, diminishing the main reaction of the electrolytic decomposition. Additionally, the presence of chlorides can enhance the degradation of organic pollutants in the wastewaters due to the formation of various species (Cl_2, HOCl and ClO^-) formed as function of the pH (Deborde et al., 2008). ClO^-, which is dominating at higher pH, has been reported as better oxidant among all chlorine species (Deborde et al., 2008). Moreover, the type and concentration of salt also influences the effectiveness of the treatment. Salts of bi- and tri-valent metals are more effective than monovalent salts because of their high ionic strengths. Cl_2 and OH^- ions are generated on the surface of the anode and the cathode, respectively, when NaCl is used as an electrolyte in ECT. The organics are destroyed in the bulk solution by oxidation reaction of the regenerated oxidant. In an ECT cell, Cl_2/hypochlorite formation may take place because chloride is widely presented in many wastewaters.

3.3. ADSORPTION PROCESS

Adsorbent surfaces contain unsaturated bonds and this bond is responsible for the reactant molecules to get attached to the surface. The degree of interaction depends on the nature of adsorbate and the adsorbent. The transport of components from the solution phase into the pores of the adsorbent particles may be controlled either by one or more of the following steps: film or external diffusion, pore diffusion, surface diffusion and adsorption on the pore surface. It is necessary to calculate the slowest step involved among these steps to identify the controlling step during the adsorption process (Srivastav and Srivastava, 2009). The external mass transfer controls the adsorption process for the systems that have poor mixing, dilute concentration of adsorbate, small particle sizes of adsorbent and higher affinity of adsorbate for adsorbent. Whereas, the intraparticle diffusion controls the adsorption process for a system with good mixing, large particle sizes of adsorbent, high concentration of adsorbate and low affinity of adsorbate for adsorbent (Aravindhan et al., 2007). The parameters that affect the adsorption process are initial pH (pH_i), adsorbent dose (m_{ad}), contact time (t), initial COD concentration (C_o) and temperature (T).

3.3.1. Intra-particle Diffusion

The possibility of intra-particle diffusion was explored by using the intra-particle diffusion model (Weber and Morris, 1063).

$$q_t = k_{id} t^{1/2} + I \tag{3.3.1}$$

Where, q_t is the amount of the adsorbate adsorbed on the adsorbent (mg/g) at any t and k_{id} is the intra-particle diffusion rate constant, and values of I give an idea about the thickness of the boundary layer.

In order to check whether surface diffusion controls the adsorption process, the kinetic data were further analyzed using Boyd kinetic expression which is given by (Boyd et al., 1947):

$$F = 1 - \frac{6}{\pi^2}\exp(-B_t) \text{ or } B_t = -0.4977 - \ln(1-F) \tag{3.3.2}$$

Where, $F(t) = q_t/q_e$ is the fractional attainment of equilibrium at time t, and B_t is a mathematical function of F.

However, if the data exhibit multi-linear plots, then two or more steps influence the overall adsorption process. In general, external mass transfer is characterized by the initial solute uptake and can be calculated from the slope of plot between C/C_o versus time. The slope of these plots can be calculated either by assuming polynomial relation between C/C_o and time or it can be calculated based on the assumption that the relationship was linear for the first initial rapid phase.

3.3.2. Adsorption Kinetic

3.3.2.1. Pseudo-first-order and pseudo-second-order model: The adsorption of adsorbate from solution to adsorbent can be considered as a reversible process with equilibrium being established between the solution and the adsorbate. Assuming a non-dissociating molecular adsorption of adsorbate molecules on adsorbent, the sorption phenomenon can be described as the diffusion controlled process.

Using first order kinetics it can be shown that with no adsorbate initially present on the adsorbent, the uptake of the adsorbate by the adsorbent at any instant t is given as (Srivastava et al., 2006)

$$q_t = q_e\left[1-\exp\left(-k_f t\right)\right] \tag{3.3.3}$$

where, q_e is the amount of the adsorbate adsorbed on the adsorbent under equilibrium condition, k_f is the pseudo-first order rate constant.

The pseudo-second-order model is represented as (Blanchard et al., 1984; Ho and McKay, 1999):

$$q_t = \frac{tk_S q_e^2}{1+tk_S q_e} \tag{3.3.4}$$

The initial sorption rate, h (mg/g min), at t –> 0 is defined as

$$h = k_S q_e^2 \tag{3.3.5}$$

3.3.3. Adsorption Isotherm

Equilibrium adsorption equations are required in the design of an adsorption system and their subsequent optimization (Sharma et al., 2010). Therefore it is important to establish the most appropriate correlation for the equilibrium isotherm curves.

Srivastava et al. (2007) have discussed the theory associated with the most commonly used isotherm models. Various isotherms namely Freundlich, Langmuir, Redlich-Peterson (R-P) and Tempkin are widely used to fit the experimental data (Table 3.3.1).

The Freundlich isotherm is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface, whereas in the Langmuir theory the basic assumption is that the sorption takes place at specific homogeneous sites within the adsorbent. The R-P isotherm incorporates three parameters and can be applied either in homogenous or heterogeneous systems. Tempkin isotherm assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and the adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy.

Table 3.3.1. Various isotherm equations for the adsorption process

Isotherm	**Equation**	**Reference**	**Equation no.**
Freundlich	$q_e = K_F C_e^{1/n}$	(Freundlich, 1906)	**3.3.6**
Langmuir	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	(Langmuir, 1918)	**3.3.7**
R-P	$q_e = \frac{K_R C_e}{1 + a_R C_e^{\beta}}$	(Redlich and Peterson, 1959)	**3.3.8**
Tempkin	$q_e = B_T \ln(K_T C_e)$		**3.3.9**

K_R: R–P isotherm constant (l/g), a_R: R–P isotherm constant (l/mg), β: Exponent which lies between 0 and 1, C_e: Equilibrium liquid phase concentration (mg/l), K_F: Freundlich constant (l/mg), 1/n: Heterogeneity factor, K_L: Langmuir adsorption constant (l/mg), q_m: adsorption capacity (mg/g), K_T: Equilibrium binding constant (l/mol), B_T: Heat of adsorption.

3.4. SEQUENTIAL BATCH REACTOR (SBR)

It is a fill and draw type activated sludge system. In this system, wastewater is added to a single batch reactor, treated to remove undesirable components, and then discharged. The conventional activated sludge systems and SBR processes are the same but the difference between the two technologies is that the SBR performs equalization, biological treatment, and secondary clarification in a single tank using a time controlled sequence. Equalization, aeration, and clarification can all be achieved using a single batch reactor. Fig. 3.4.1 shows cycle of sequential batch reactor.

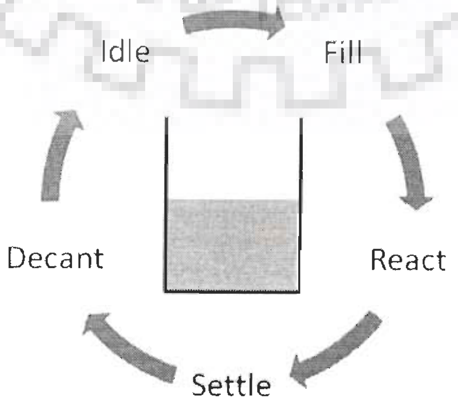


Fig. 3.4.1. Cycle of sequential batch reactor

All the SBR systems have five steps in common, which are carried out in sequence as follows:

Fill: Wastewater flows in to the reactor and mixes with the biomass already present in the reactor. Filling of influent can be varied to create the following three different conditions:

- **Static Fill:** Under a static-fill condition, influent wastewater enters into the reactor with no mixing and/or aeration. Static fill is used when there is no need to nitrification or denitrification.
- **Mixed Fill**: Under the condition of mixed-fill, influent is mixed with biomass present in the reactor but the aeration remains off. As there is no aeration, an anoxic condition appears. Anaerobic conditions can also be achieved during the mixed-fill phase. Denitrification may occur under these anoxic conditions. Denitrification is the biological conversion of nitrate-nitrogen to nitrogen gas.
- **Aerated Fill**: In condition of aerated-fill, both the aeration and the stirrer are switched on. Aerobic and anoxic environment are created inside the reactor by keeping on/off oxygen supply to the reactor. During the aerobic condition nitrification takes place. Aerated Fill can reduce the aeration time required in the react step.

React: Depending on the conditions applied: anaerobic, anoxic or aerobic reactions, substrate present in the waste water are consumed by the biomass.

Settle: After sufficient time of reaction, aeration and mixing is stopped and biomass is allowed to settle from the liquid resulting in clear supernatant.

Decant: Clear supernatant (treated waste water) is removed from the reactor.

Idle: This is the time between cycles which is used to prepare the SBR for next cycle. It is also used to adjust the cycle time between the SBR reactors. Sludge wasting is also performed during this phase.

3.4.1. Operating Parameters in SBR Process

The treatment efficiency of SBR depends on the operating parameters such as phase duration, hydraulic retention time (HRT) and organic loading, Sludge retention time (SRT), temperature, mixed liquor suspended solids (MLSS), mixed liquor volatile suspended solids (MLVSS), dissolved oxygen (DO) concentration and the strength of wastewater.

3.4.1.1. Cycle time: A cycle in SBR comprises of fill, react, settle, decant and idle phase. The total cycle time (t_C) is the sum of all these phases.

$$t_C = t_F + t_R + t_S + t_D + t_I \tag{3.4.1}$$

Where, t_F is the fill time (h), t_R is the react time (h), t_S is the settle time (h), t_D is the decant time (h), and t_I is the idle time (h).

Moreover during the react phase, organic matters, nitrogen or phosphorus removal may be achieved by arresting aerobic, anoxic or anaerobic condition, respectively. Therefore, aerobic, anoxic or anaerobic time can be found in react time (t_R). Hence

$$t_R = t_{AE} + t_{AX} + t_{AN} \tag{3.4.2}$$

Where, t_{AE} is the aerobic react time (h), t_{AX} is the anoxic react time (h), and t_{AN} is the anaerobic react time (h).

3.4.1.2. Volume exchange ratio (VER) and hydraulic retention time (HRT): Due to filling and decanting phase during a cycle, SBR operate with varying volume. Volume exchange ratio (VER) for a cycle is defined as V_F/V_T, Where, V_F is the filled volume of wastewater and decanted effluent for a cycle and V_T is the total working volume of the reactor.

HRT for the continuous system is defined as

$$\text{HRT} = \frac{(V_T)}{Q} \tag{3.4.3}$$

Where, Q is the daily waste water flow rate.

For SBR systems;

$$\text{Q} = V_F N_C \tag{3.4.4}$$

Where, N_C is the number of cycles per day and defined as:

$$\text{N}_\text{C} = \frac{24}{t_C} \tag{3.4.5}$$

Therefore, HRT for the SBR systems may be given as:

$$\text{HRT} = \frac{(t_C)}{V_F/V_T}\frac{1}{24} \tag{3.4.6}$$

3.4.1.3. Solid Retention Time (SRT): In biological treatment of wastewater, excess sludge is withdrawn from the reactor to control the sludge age (SRT). SRT determines the time (d) for which the biomass is retained in the reactor.

$$\mathrm{SRT} = \frac{V_T X t_C}{V_W X_W 24} \tag{3.4.7}$$

Where, X is the MLSS in the reactor with full filled (mg/l), X_W is the MLSS in waste stream (mg/l), and V_W is the waste sludge volume (l).

3.4.2. Nitrification and Denitrification

Nitrogen is the main source of eutrophication. In this regard, the complete oxidation of nitrogen during the treatment is favorable. Biological nitrogen is removed in two stages: aerobic nitrification and anoxic denitrification. In the nitrification process, ammonia ($N\text{-}NH_4^+$) is oxidized to nitrite ($N\text{-}NO_2^-$) (equation 3.4.8) by autotrophic bacteria called Nitroso-bacteria and generated nitrite is oxidized to nitrate ($N\text{-}NO_3^-$) (equation 3.4.9) by another group of autotrophic bacteria called Nitro-bacteria under aerobic conditions and using oxygen as the electron acceptor.

$$2NH_4^+ + 3\,O_2 \longrightarrow 2\,NO_2^- + 2H_2O + 4\,H^+ \tag{3.4.8}$$

$$2\,NO_2^- + O_2 \longrightarrow 2NO_3^- \tag{3.4.9}$$

The autotrophic bacteria produce energy for their multiplication from the oxidation of inorganic nitrogen compounds, using inorganic carbon as their source of cellular carbon. During the nitrification, alkalinity of wastewater is used which reduces the pH of influent wastewater and required amount of alkalinity to carry out the reaction (equation 3.4.8, 3.4.9) in the $CaCO_3$ form, can be calculated by the following equation;

$$NH_4^+ + 2HCO_3^- + 2\,O_2 \longrightarrow NO_3^- + 3H_2O + 2CO_2 \tag{3.4.10}$$

Biological denitrification involves the biological oxidation of many organic substrates in wastewater treatment using nitrate or nitrite as the electron acceptor under the anoxic condition or limited dissolved oxygen (DO) concentrations and nitrate is degraded to nitric oxide, nitrous oxide, and nitrogen gas (Moriyama et al., 1990; Masude et al., 1991; Von Munch et al., 1995) by following any of the two different routes. One of these routes predominates depending on the dissolved oxygen concentration (O'Neill et al., 1995).

$$NH_4^+ \longrightarrow NO_2^- \longrightarrow NO_3^- \longrightarrow NO_2^- \longrightarrow NO \longrightarrow N_2O \longrightarrow N_2$$

or

$$NH_4^+ \longrightarrow NO_2^- \longrightarrow NO \longrightarrow N_2O \longrightarrow N_2$$

During the denitrification process, pH of influent wastewater increases because of increase of alkalinity. Both heterotrophic and autotrophic bacteria are capable of denitrification. Most of these heterotrophic bacteria are facultative aerobic organisms with the ability to use oxygen as well as nitrate or nitrite, and some can also carry out fermentation in the absence of nitrate or oxygen (Metcalf and Eddy, 2003).

3.4.3. Advantages and Disadvantages of SBR

Advantages

- Equalization, primary clarification (in most cases), biological treatment, and secondary clarification can be achieved in a single reactor vessel.
- Operating flexibility and control.
- Potential capital cost savings by eliminating clarifiers and other equipments.

Disadvantages

- A higher level of sophistication, (compared to conventional systems), especially for larger systems, of timing units and controls is required.
- Higher level of maintenance (compared to conventional systems) associated with more sophisticated controls, automated switches and automated valves.
- Potential of discharging floating or settled sludge during the draw or decant phases with some SBR configurations.
- Potential plugging of aeration devices during selected operating cycles, depending on the aeration system used by the manufacturer.

Chapter – 4

COAGULATION

4.0. GENERAL

This chapter deals with the description of the materials and experimental methods adopted; results obtained and detailed discussion during the treatment of simulated dairy wastewater (SDW) using coagulation. Inorganic coagulants like poly aluminum chloride (PAC), ferrous sulphate ($FeSO_4$) and potash alum ($KAl(SO_4)_2.12H_2O$); and natural organic coagulants such as guar gum, sodium salt of carboxy methyl cellulose (Na-CMC) and sodium alginate (Na-alginate) were used.

4.1. MATERIALS AND METHODS

4.1.1. Wastewater

Dairy wastewater being rich in nutrients and carbon sources provides favourable conditions for microbial growth. Due to this, the COD and nutrients concentration of dairy wastewater alters during storage. To avoid this change in COD and nutrients during storage, SDW was used in the study. SDW was generated in the laboratory by dissolving 4 g of milk powder (Amulya brand, manufactured by Banaskantha District Cooperative Milk producer's Union Ltd., Palanpur, Uttarakhand, India) per litre of distilled water in order to make constant wastewater composition throughout the experiments. Several investigators used same method for making SDW (Ramasamy et al., 2004; Balannec et al., 2005; Leal et al., 2006, Kushwaha et al., 2010). The characteristics of the SDW used in the present study are presented in Table 4.1.1. The SDW was prepared freshly whenever required and concentration was maintained uniform throughout the study.

4.1.2. Chemicals and Coagulants

All the chemicals used in the study were of analytical reagent (AR) grade. Mercuric sulphate (Hg_2SO_4) and silver sulphate (Ag_2SO_4) were obtained from Himedia Laboratories, Mumbai (India). Potassium dichromate ($K_2Cr_2O_7$), sulfuric acid (H_2SO_4), hydrochloric acid (HCl) and sodium hydroxide (NaOH) were obtained from Ranbaxy Chemicals Ltd., New Delhi, India.

PAC was obtained from Grasim Industries Ltd., Nagda, Madhya Pradesh, India; $FeSO_4$ was procured from Ranbaxy India Ltd. SAS Nagar, Punjab, India; and $KAl(SO_4)_2.12H_2O$ was obtained from Sarabhai M chemicals, Baroda, India. Guar gum, Na-CMC and Na-alginate were supplied by HIMEDIA Laboratories Pvt. Ltd., Mumbai, India.

Table 4.1.1. Characteristics of simulated dairy wastewater.

Parameters	Average Value
pH	6.5
COD (mg/l)	3900
BOD (mg/l)	2300
COD/BOD	1.7
Total solids (mg/l)	3090
Turbidity	1740
Conductivity (µs/cm)	220
Chloride (mg/l)	31
Total Kjeldahl Nitrogen (mg/l)	113

4.1.3. Analytical Methods

COD was measured using digestion unit (DRB 200, HACH, USA) and double beam UV visible spectrophotometer (HACH, DR 5000, USA). Turbidity meter supplied by Aqualytic, Germany, was used to measure turbidity. The chloride content was determined by standard titrimetric Volhard method. Total kjeldahl nitrogen (TKN) was determined using standard Kjeldahl method. Scanning electron microscope (SEM, QUANTA, Model 200 FEG, USA) was employed to understand the morphologies of the generated sludge by the coagulation of SDW and to study the distribution of the elements in the sludge energy dispersive X-ray (EDX) was conducted. For the SEM/EDX, the samples were first ground to make the samples homogeneous and then spread on sample holders in such a manner to produce flat surfaces. After this the samples were gold coated using sputter coater (Edwards S150) to provide conductivity to the samples, and then the SEM and EDX spectra were taken. Thermo-gravimetric analysis (TGA) and differential thermal analysis (DTA) of the residues was carried out using Perkin Elemer (Pyris Diamond) thermo-gravimetric (TG) analyzer. TGA/DTA scans were recorded from 20 °C to 1000°C using a heating rate of 10 °C/min in air atmosphere.

4.1.4. Experimental Setup and Methods of Operation

Coagulation studies were performed by the jar test apparatus. Each experiment was performed by introducing a known amount of the coagulant into a beaker containing one litre of SDW of known initial *pH* (pH_i) and known initial COD concentration (C_o) of 3900 mg/l. The mixture was then agitated at 200 rpm for 5 min and then speed was reduced to 20 rpm and the system was kept at this condition for 120 min. Thereafter, the solution was kept for settling for 15 min and the supernatant was filtered through Whatman filter paper grade No. 1 and analysed for COD. The percentage removal of COD was calculated using the following relationship:

$$\text{Percent COD removal}=\frac{(C_0-C_f)100}{C_0} \qquad (4.1.1)$$

where, C_f is the final COD concentration (mg/l).

For optimization of initial *pH* ($pH_{i\text{-}in}$) for the coagulation of SDW by the inorganic coagulants, $pH_{i\text{-}in}$ was varied in the range of 5–10 at the inorganic coagulant dosage (m_{in}) of 300 mg/l for PAC and 1000 mg/l for $FeSO_4$ and $KAl(SO_4)_2.12H_2O$ at C_o = 3900 mg/l. To optimize m_{in}, coagulation experiments by inorganic coagulants were carried out by varying m_{in} values in the range of 100-5000 mg/l at the optimum initial *pH* ($pH_{i\text{-}in,op}$) and C_o = 3900 mg/l. Final *pH* ($pH_{f\text{-}in}$) and residual COD (COD_t) were monitored with time at $pH_{i\text{-}in,op}$ and optimum m_{in} ($m_{in\text{-}op}$).

But, to optimize natural organic coagulant dosage (m_{na}), coagulation experiments were carried out by varying the dosages in the range of 10-200 mg/l for all the three coagulants (guar gum, Na-CMC and Na-alginate) at the initial *pH* ($pH_{i\text{-}na}$) = 4 and C_o = 3900 mg/l. To optimize the $pH_{i\text{-}na}$ for the coagulation of SDW by natural coagulants, $pH_{i\text{-}na}$

was varied in the range of 3–10 at the optimum m_{na} ($m_{na\text{-}op}$) of 100 mg/l. The pH_i of the SDW was adjusted using 1 N aqueous solution of either H_2SO_4 or NaOH.

. The slurry from the coagulation process was used to study the settleability of the sludge. The well mixed slurry was poured in 0.5 litre graduated glass cylinder and sludge sedimentation tests were performed. No stirring was done during the tests.

4.2. RESULTS AND DISCUSSION

4.2.1. Inorganic Coagulants (Kushwaha et al., 2010b)

4.2.1.1. Effect of $pH_{i\text{-}in}$: Fig. 4.2.1(a) represents the effect of $pH_{i\text{-}in}$ on the COD removal. It is observed that as the $pH_{i\text{-}in}$ of SDW was increased, the COD removal increased up to $pH_{i\text{-}in}$ = 8.0 giving maximum COD removal efficiency of 69.2, 65.3 and 57.3% for PAC, $FeSO_4$ and $KAl(SO_4)_2.12H_2O$, respectively, and beyond $pH_{i\text{-}in}$ = 8.0, COD removal decreased. For $pH_{i\text{-}in} > 8.0$, the decrease in removal efficiency is higher for PAC and $KAl(SO_4)_2.12H_2O$ as compared to that for $FeSO_4$. For $pH > 8$, speciation of Al(III) (Fig. 3.1.2) shows that the aluminium present in the water is in the form of $Al(OH)_4^-$ ions. This ions reduces the COD removal by PAC and $KAl(SO_4)_2.12H_2O$ due to electrostatic repulsion between negatively charged colloidal particles present in the dairy wastewater and $Al(OH)_4^-$ ions. However, for $FeSO_4$, speciation of Fe(II) (Fig. 3.1.1) shows formation of Fe^{2+} and various hydrolysis species like $Fe(OH)^+$ and $Fe(OH)_2$ at $pH > 8$. $Fe(OH)_3^-$ ions formation takes place at $pH > 10.5$. Hence, the small decrease in COD removal efficiency by $FeSO_4$ for $8 < pH \leq 10$ is due to the decrease in charge neutralization efficiency by the added $FeSO_4$ due to formation of less positively charged and neutral colloid like $Fe(OH)^+$ and $Fe(OH)_2$.

Fig. 4.2.1(b) shows the parity plot between $pH_{i\text{-}in}$ and $pH_{f\text{-}in}$ for the treatment of SDW at various $pH_{i\text{-}in}$. It may be seen that $pH_{f\text{-}in} < pH_{i\text{-}in}$ in full studied range. It is well known that addition of coagulants (PAC, $FeSO_4$ and $KAl(SO_4)_2.12H_2O$) leads to release of H^+ ions which decrease the pH of the solution (Benjamin, 2002; Duan and Gregory, 2003; Wang et al., 2004). Also removal of milk proteins and other components from SDW decreases the pH (Webb et al., 1965).

Hence, $pH_{i\text{-}in}$ = 8.0 was taken as $pH_{i\text{-}in,op}$ for all three coagulants and further experiments were conducted at $pH_{i\text{-}in,op}$ = 8.0 in order to find $m_{in\text{-}op}$.

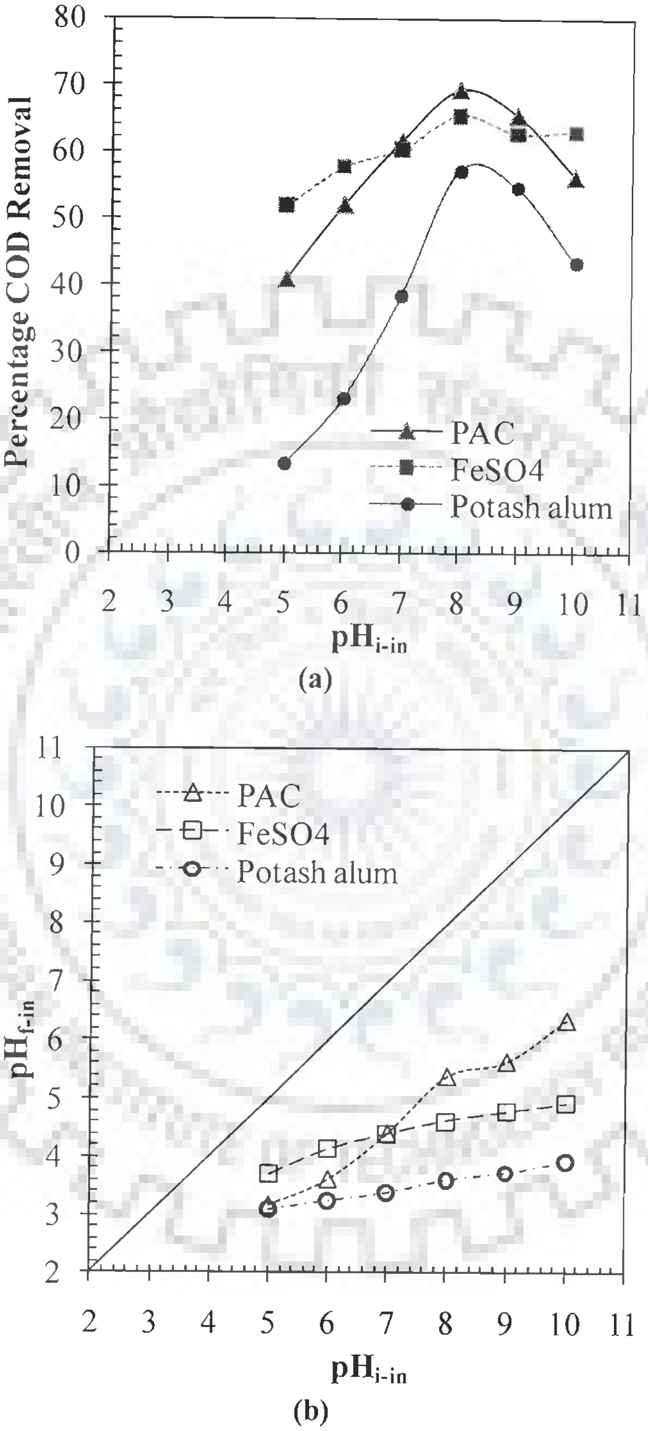


Fig. 4.2.1. Effect of $pH_{i\text{-}in}$ on (a) COD removal (b) $pH_{f\text{-}in}$ of SDW by various coagulants. m_{in} = 300 mg/l for PAC and m_{in} = 1000 mg/l for $FeSO_4$ and $KAl(SO_4)_2.12H_2O$.

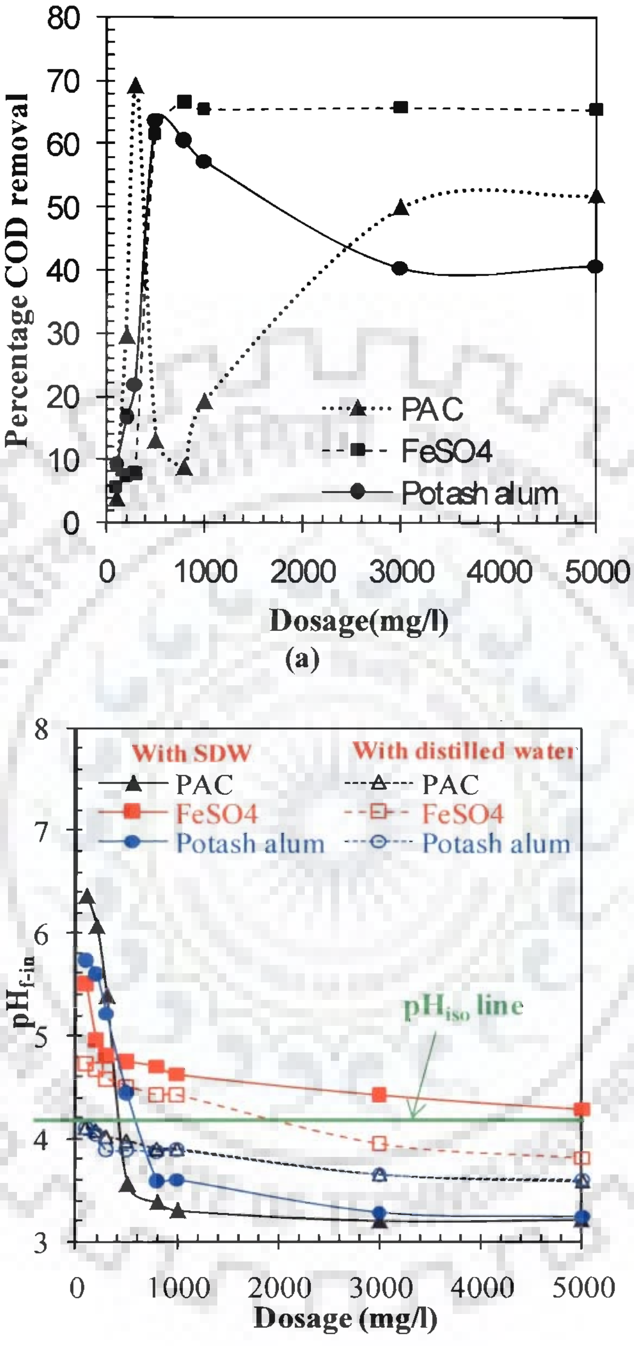
4.2.1.2. Effect of m_{in}: Fig. 4.2.2a.b represent the effect of m_{in} on COD removal efficiency and pH_{f-in} for the coagulation of SDW at $pH_{i-in,op} = 8.0$. It is clear from Fig. 4.2.2(a) that COD removal behavior on increasing m_{in} values is different for each of the coagulant. For PAC, COD removal efficiency first increased then decreased and again increased and finally became constant on increasing m_{in} value. Whereas, for $FeSO_4$, it increased till it became constant on increasing m_{in} value. For $KAl(SO_4)_2.12H_2O$, COD removal efficiency first increased then decreased till it became constant on increasing m_{in} value.

Fig. 4.2.2(b) shows the effect of m_{in} values on pH_{f-in} of SDW and distilled water (DW) at $pH_{i-in,op} = 8.0$. It can be seen that addition of coagulants to DW alone, decreased the pH_{f-in} of DW. For PAC, $FeSO_4$ and $KAl(SO_4)_2.12H_2O$, pH_{f-in} of DW varied in the range of 4.11-3.58, 4.73-3.81 and 4.1-3.6, respectively, when m_{in} was varied between 100-5000 mg/l. Thus, the pH_{f-in} values in DW are higher for $FeSO_4$ as compared to that of PAC and $KAl(SO_4)_2.12H_2O$.

For PAC, COD removal efficiency first increased with an increase in m_{in} value from 100 to 300 mg/l giving maximum COD removal efficiency of 69.2% at $m_{in-op} = 300$ mg/l. pH_{f-in} of SDW decreased sharply from 6.37 to 5.4 on increasing m_{in} value from 100 to 300 mg/l. The colloidal nature of dairy wastewater is mainly due to the casein (milk protein) (Herrington, 1948). Dairy wastewater has the isoelectric point (pH_{iso}) around 4.2 (Selmer-olsen et al., 1996). The milk proteins contained in the SDW are negatively charged at $pH > pH_{iso}$ and get removed by positively charged aqua-aluminum cations formed from PAC. The increase in COD removal efficiency is due to an increase in concentration of various hydrolysis species which destabilize the colloidal particles. On further increasing the m_{in} value up to 800 mg/l, pH_{f-in} decreased to 3.4 ($< pH_{iso}$) and COD removal efficiency decreased to minimum value of 8.85% at $m_{in} = 800$ mg/l. Since at $m_{in} =$ 800 mg/l, $pH_{f-in} < pH_{iso}$, therefore, charge reversal of milk proteins caused decrease in COD removal. With an increase in m_{in} from 1000 to 5000 mg/l, pH_{f-in} decreased to 3.2, however, COD removal efficiency again increased and became nearly constant giving 50% COD removal at $m_{in} = 3000$ mg/l. Formation of large amount of hydroxide flocs is responsible for COD removal by sweep coagulation at these higher dosages. It is known that the presence of milk proteins and other components in SDW keep the pH constant, whereas, removal of these components decreases the pH (Webb et al., 1965). It can be interpreted that the decrease in pH_{f-in} for PAC is faster till $m_{in} = m_{in-op}$, the point where COD removal efficiency is highest. However, the pH_{f-in} in SDW at $m_{in} > m_{in-op}$ is still lower than that of in DW because of the charge reversal of colloids present in SDW at $pH_{f-in} < pH_{iso}$ due to presence of high amount of PAC.

For $FeSO_4$, an increase in m_{in} value increased the COD removal efficiency due to an increase in concentration of Fe^{2+} ions which destabilized the colloidal particles giving maximum COD removal efficiency of 66.5% at m_{in-op} = 800 mg/l. This increase in COD removal efficiency caused decrease in pH_{f-in} sharply from 5.50 to 4.7. For $m_{in} > m_{in-op}$, COD removal efficiency became nearly constant at $pH_{f-in} \approx 4.3$. Because the $pH_{f-in} > pH_{iso}$ of SDW for all value of m_{in} (Fig. 4.2.2b), the colloids present in SDW are always negatively charged. Since the metal based coagulants can remove a certain portion of dissolved organics only, hence, charge neutralisation of negatively charged colloids by Fe^{2+} ions maintained constant COD removal efficiency at $m_{in} > m_{in-op}$.

For $KAl(SO_4)_2.12H_2O$, COD removal efficiency increased with an increase in m_{in} value from 100 to 500 mg/l giving maximum value of 63.8% at m_{in-op} = 500 mg/l. This was due to charge neutralization by various hydrolysis species. pH_{f-in} decreased sharply from 5.7 to 4.5 on increasing m_{in} value from 100 to 500 mg/l. COD removal efficiency decreased to 40.38% on increasing m_{in} value to 3000 mg/l, and thereafter COD removal efficiency became nearly constant. For $500 < m_{in} \leq 3000$ mg/l, $pH_{f-in} < pH_{iso}$ and therefore, the decrease in the COD removal efficiency is mainly due to charge reversal of colloids. However at $m_{in} \geq 3000$ mg/l, pH_{f-in} is still less than pH_{iso}, however, generation of large amount of hydroxide flocs help in maintaining constant COD removal by sweep coagulation.



(b)

Fig. 4.2.2. Effect of coagulant dosage (a) on COD removal at $pH_{i\text{-}in,op}$ = 8, (b) on variation of $pH_{f\text{-}in}$ of SDW and distilled water at $pH_{i\text{-}in,op}$ = 8. Filled markers are for SDW and unfilled markers are for distilled water. *pH* at isoelectric point (pH_{iso} = 4.2) of SDW is shown by solid line.

4.2.1.2.1. Effect of time: The experiments were also conducted to study the effect of time on COD removal efficiency and $pH_{f\text{-}in}$ of SDW at $m_{in\text{-}op}$ of various coagulants and $pH_{i\text{-}in,op}$ = 8.0 for C_o = 3900 mg/l (Fig. 4.2.3a, b). In these experiments, the time was measured from the moment of introduction of coagulants into SDW. From Fig. 4.2.3b, it is clear that the $pH_{f\text{-}in}$ of SDW decreased to 5.5, 5.3 and 4.5 for the PAC, $FeSO_4$ and $KAl(SO_4)_2.12H_2O$, respectively, in 5 min only (just after mixing of coagulants with SDW) and the reduction in *pH* continued up to 30 min and stabilized to 5.4, 4.7 and 4.5 for the PAC, $FeSO_4$ and $KAl(SO_4)_2.12H_2O$, respectively. Maximum COD removal efficiency of 69.2, 66.5 and 63.8%, respectively, were achieved in 30 min by PAC, $FeSO_4$ and $KAl(SO_4)_2.12H_2O$ at their respective $m_{in\text{-}op}$ and $pH_{i\text{-}in,op}$ = 8.0. Beyond 30 min, COD removal efficiency became constant. Therefore, the $pH_{f\text{-}in}$ after 30 min treatment can be considered as effective *pH* ($pH_{in\text{-}effective}$) for the coagulation process.

Other parameters such as total nitrogen (TKN), turbidity, conductivity, chloride and total solids (TS) were also calculated for the treated effluent at $m_{in\text{-}op}$ and $pH_{i\text{-}in,op}$, and the respective values are given in Table 4.2.1.

Table 4.2.1. Characteristics of SDW and effluents treated by various coagulants.

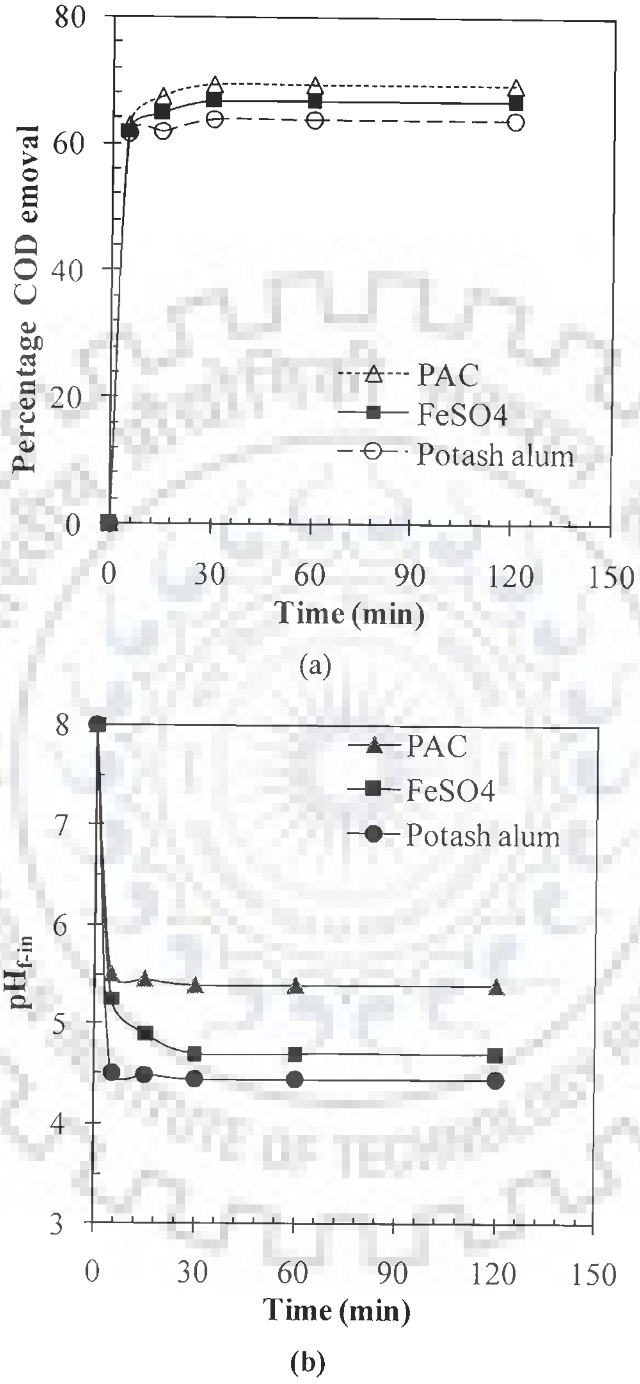
Parameters	Average Values			
		Treated SDW		
	SDW	**PAC**	**$FeSO_4$**	**$KAl(SO_4)_2.12H_2O$**
pH	6.5	5.4	4.7	4.5
COD (mg/L)	3900	1200	1305	1410
Total solids (mg/L)	3090	1930	2160	1970
Turbidity (NTU)	1740	1.6	0.8	1.0
Conductivity (µs/cm)	220	500	749	525
Chloride (mg/L)	31	46.94	19.9	22.96
Total Kjeldahl Nitrogen (mg/l) (mg/L)	113	8.7	8.27	9.29

4.2.1.3. Mechanism of coagulation by inorganic coagulants: Coagulation is the process of destabilization of colloidal particles and can be achieved by two mechanisms: one in which an increase in ionic concentration causes reduction in the zeta potential and adsorption of counter-ions to neutralize the particle charge; and other by sweep flocculation. Colloidal particle destabilization by adsorption of counter-ions is more promising than increasing ionic concentration to reduce zeta potential because of requirement of small quantity of coagulants in the adsorption process (Duan and Gregory, 2003). The $pH_{in\text{-}effective}$ of PAC was found to be 5.4. As per the speciation of PAC given by Wang et al. (2004), aluminum species are 7.3% monomeric, 40.1% fast-reacting polymeric and 52.6% slow-reacting colloidal species at $pH = 5.32$ (Table 3.1.1). Also at $pH_{in\text{-}effective} = 5.4$, aluminum present in the water (as calculated from speciation diagram of Al(III)), Fig. 3.1.2) is in the form of 6% Al^{3+}, 42% $Al(OH)^{2+}$, 42% $Al(OH)_2^+$, 4% $Al(OH)_3$ and 6% $Al(OH)_4^-$. Therefore, mechanism of coagulation by PAC is partly due to charge neutralization of negatively charged colloidal particles present in SDW by monomeric, fast-reacting polymeric colloidal species, and partly by adsorption of slow-reacting colloidal species on the adsorption sites of colloids, and minutely by sweep coagulation.

At $pH_{in\text{-}effective} = 4.5$ for $KAl(SO_4)_2.12H_2O$, speciation of Al(III) shows the presence of 72% Al^{3+}, 24% $Al(OH)^{2+}$ and 4% $Al(OH)_2^+$ in the water. Therefore, coagulation mechanism of SDW by $KAl(SO_4)_2.12H_2O$ is because of charge neutralisation by Al^{3+} and also by adsorption of $Al(OH)^{2+}$ and $Al(OH)_2^+$ onto negatively charged colloidal particles present in SDW. Speciation of Fe(II) ions at $pH_{in\text{-}effective} = 4.7$ for $FeSO_4$ shows that Fe^{2+} ions are dominating. Therefore, the mechanism of charge neutralisation is playing pivotal role in COD removal by $FeSO_4$.

4.2.1.4. Slurry settling characteristic

Fig. 4.2.4 shows the settling of slurry produced by the coagulants in terms of the sludge-supernatant interface as a function of settling time. At the start of time course, a fast and steady decrease in the height of the sludge-supernatant interface (shown by nearly constant slope) was observed which exhibits the regime of zone settling. Thereafter in the transition settling period, the slope changed continuously with time. Finally, compression settling took place with much smaller but steady rate of decrease in the height of the sludge-supernatant interface.



(a)

(b)

Fig. 4.2.3. Effect of time on (a) COD removal (b) $pH_{f\text{-}in}$ of SDW by various coagulants. $m_{in\text{-}op}$ = 300 mg/l for PAC, 800 mg/l for $FeSO_4$ and 500 mg/l for $KAl(SO_4)_2.12H_2O$ and $pH_{i\text{-}in,op} = 8$.

Table 4.2.2 shows the settling characteristics of sludge produced by the coagulants PAC, FeSO4 and $KAl(SO_4)_2.12H_2O$. The concentration of sludge (C) at a time *t* was determined by using the following expression

$$C = C_{o-s}\frac{H_o}{H} \qquad (4.2.1)$$

where, C_{o-s} is initial sludge concentration at $t = 0$, H_o is the initial height and H is the interface height. The sludge instantaneous settling velocity was calculated as the slope of the sludge settling curve within the zone settling regime (Fig. 4.2.4).

The most common parameter, sludge volume index (SVI), was also used to quantify the settling characteristics of the sludge generated by the various coagulants. SVI is defined as the volume (ml) occupied by 1 g of the sludge after 30 min of the settling. The SVI was calculated from the following relation.

$$SVI = \frac{1000\ V}{SS} \qquad (4.2.2)$$

Where, V is the settled sludge volume (ml/l) and SS is the suspended solids concentration (mg/l).

SVI of the slurry produced by PAC, FeSO4 and $KAl(SO_4)_2.12H_2O$ was found to be 86, 140 and 66 ml/g, respectively. Thus, slurries produced by PAC and $KAl(SO_4)_2.12H_2O$ have SVI < 100 indicating very good settleability.

Table 4.2.2. Settling characteristics of the sludge generated by various coagulants.

Time (t) (min)	U (cm/min)			Cx1000 (g/cm^3)			Flux (g/cm^2 min)		
	PAC	$FeSO_4$	Potash Alum	PAC	$FeSO_4$	Potash Alum	PAC	$FeSO_4$	Potash Alum
0	1.86	2.50	2.80	1.86	1.16	2.22	3.46E-03	2.90E-03	6.21E-03
2	1.49	1.81	1.98	1.86	1.23	2.34	2.77E-03	2.22E-03	4.64E-03
4	1.16	1.23	1.31	2.03	1.36	2.77	2.35E-03	1.67E-03	3.63E-03
6	0.87	0.77	0.77	2.32	1.72	3.50	2.02E-03	1.33E-03	2.71E-03
8	0.63	0.43	0.38	2.61	2.20	4.85	1.63E-03	9.55E-04	1.86E-03
10	0.42	0.21	0.14	3.21	2.94	7.51	1.36E-03	6.28E-04	1.02E-03
15	0.10	0.18	0.14	5.84	2.99	6.86	5.68E-04	5.50E-04	9.31E-04

U = Settling velocity

4.2.1.5. Physical and elemental analysis of sludge: SEM and EDX analysis were conducted to study the morphological and elemental features of generated sludge. SEM images of sludge generated of SDW by inorganic coagulants (PAC, $FeSO_4$ and $KAl(SO_4)_2.12H_2O$) are shown in Fig. 4.2.5. These figures indicate surface properties and microstructure of the sludge generated by these coagulants. The texture of the sludge generated by PAC and $FeSO_4$ are not hard but have somewhat puffy type texture (Fig. 4.2.5a,b). It can also be seen that the sludge generated by PAC and $FeSO_4$ have fibrous and porous structure. Whereas, sludge generated by $KAl(SO_4)_2.12H_2O$ is very hard and there are no pores on the surface (Fig. 4.2.5 c).

EDX of sludge generated with coagulants PAC, $FeSO_4$ and $KAl(SO_4)_2.12H_2O$ showed presence of 81.2, 78.3 and 78.9% carbon; 0.25, 0.19 and 0.18% magnesium; 2.54, 0.23 and 4.38% aluminum; 3.68, 2.15 and 0.46% silica; 0.42, 01.09 and 0.36% calcium; and 0.04, 5.21 and 0.14% iron by mass, respectively (Fig. 4.2.6). The presence of carbon is highest (81.2%) in the PAC sludge. This may be due to the highest COD removal by the PAC. Also, it may be seen that PAC and $KAl(SO_4)_2.12H_2O$ sludge contain 2.5% and 4.4% aluminum. Higher amount of aluminum in $KAl(SO_4)_2.12H_2O$ may be due to its higher coagulant dosage (500 mg/l) as compared to that of PAC (300 mg/l). Sludge generated with $FeSO_4$ was found to contain 5.2% iron. Since the sludge generated contain significant amount of metals, they need to be properly disposed.

4.2.1.6. Disposal of sludge generated: The sludge generated by the coagulants were dried at ~105°C and studied for the thermal degradation characteristics to investigate the oxidation behaviour for the possible use as fuel. TGA/DTA curves of the generated sludge for the heating rate of 10 °C/min in air environment are shown in Fig. 4.2.7. The degradation characteristics obtained from these figures like weight loss with temperature, enthalpy change, peak temperature, etc. are shown in Tables 4.2.2-4.2.4.

The TGA patterns shows ~7.0% loss of bound moisture and some volatile matter evolution from ~30 to 200 °C (Fig. 4.2.7a). The inflection temperature for the sludge produced by PAC and $KAl(SO_4)_2.12H_2O$ was found to be 200 °C, whereas, for $FeSO_4$ generated sludge it was 175 °C.

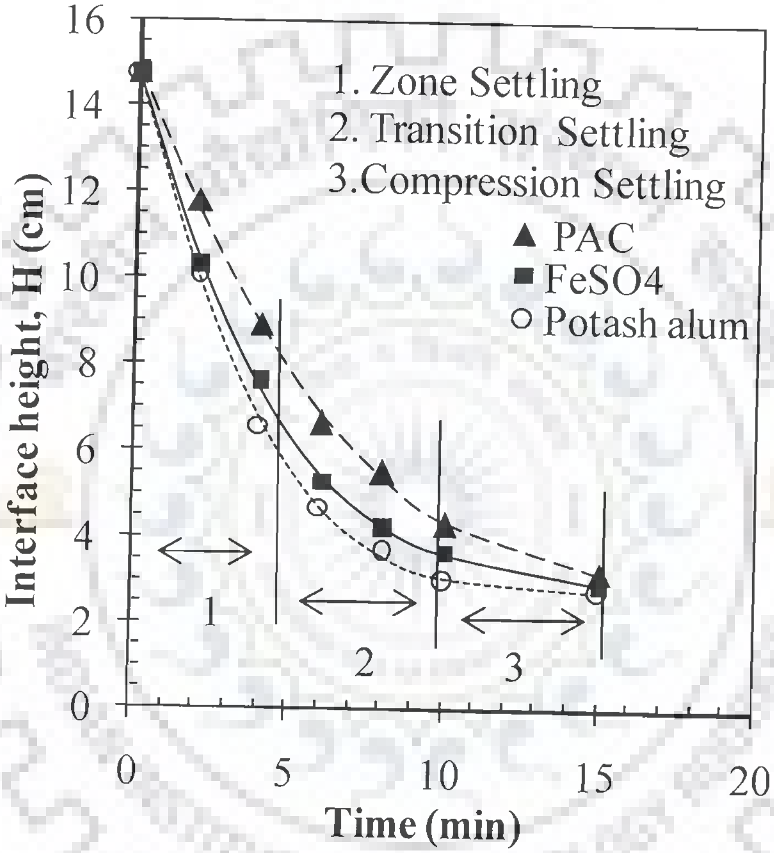
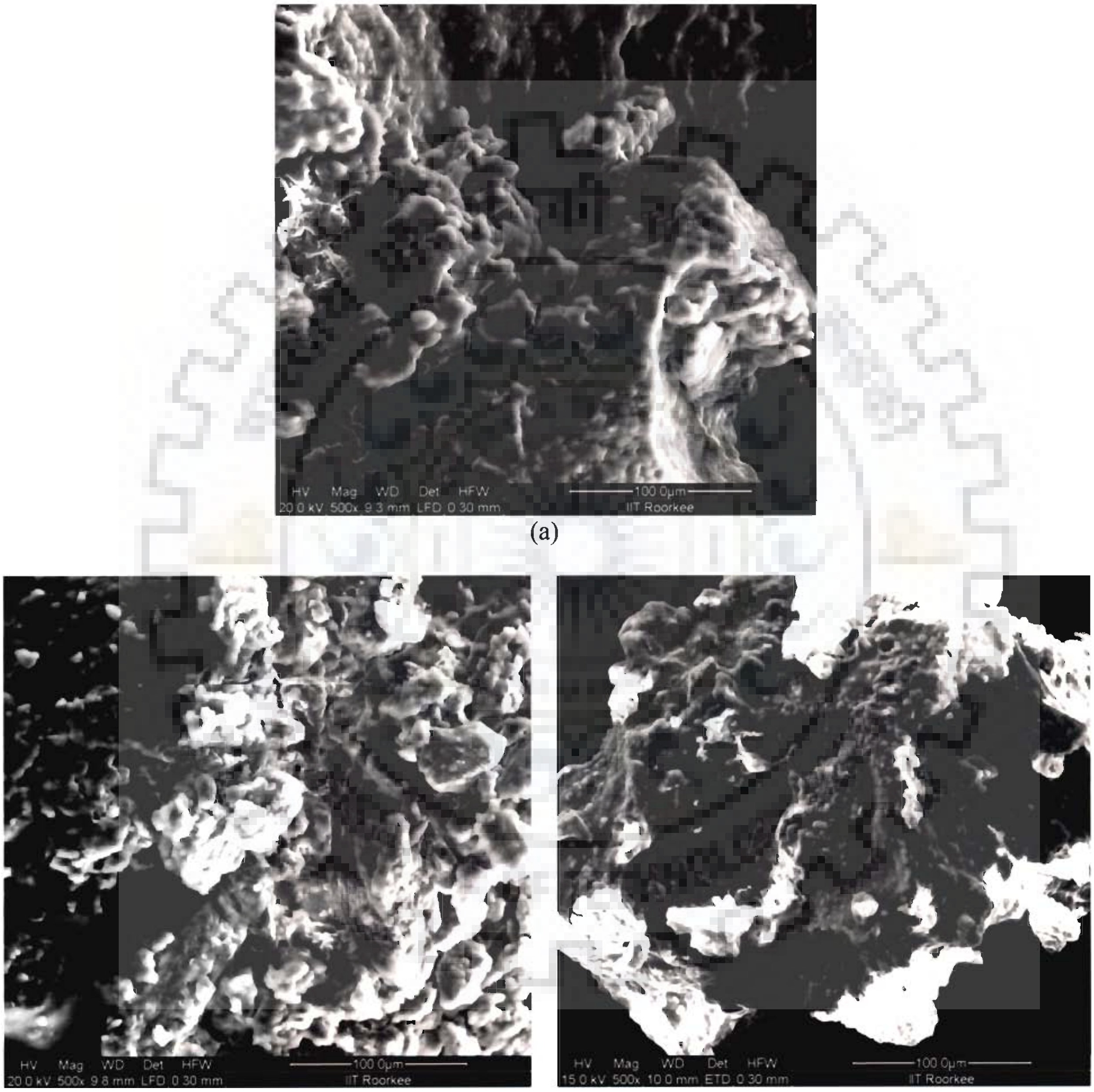


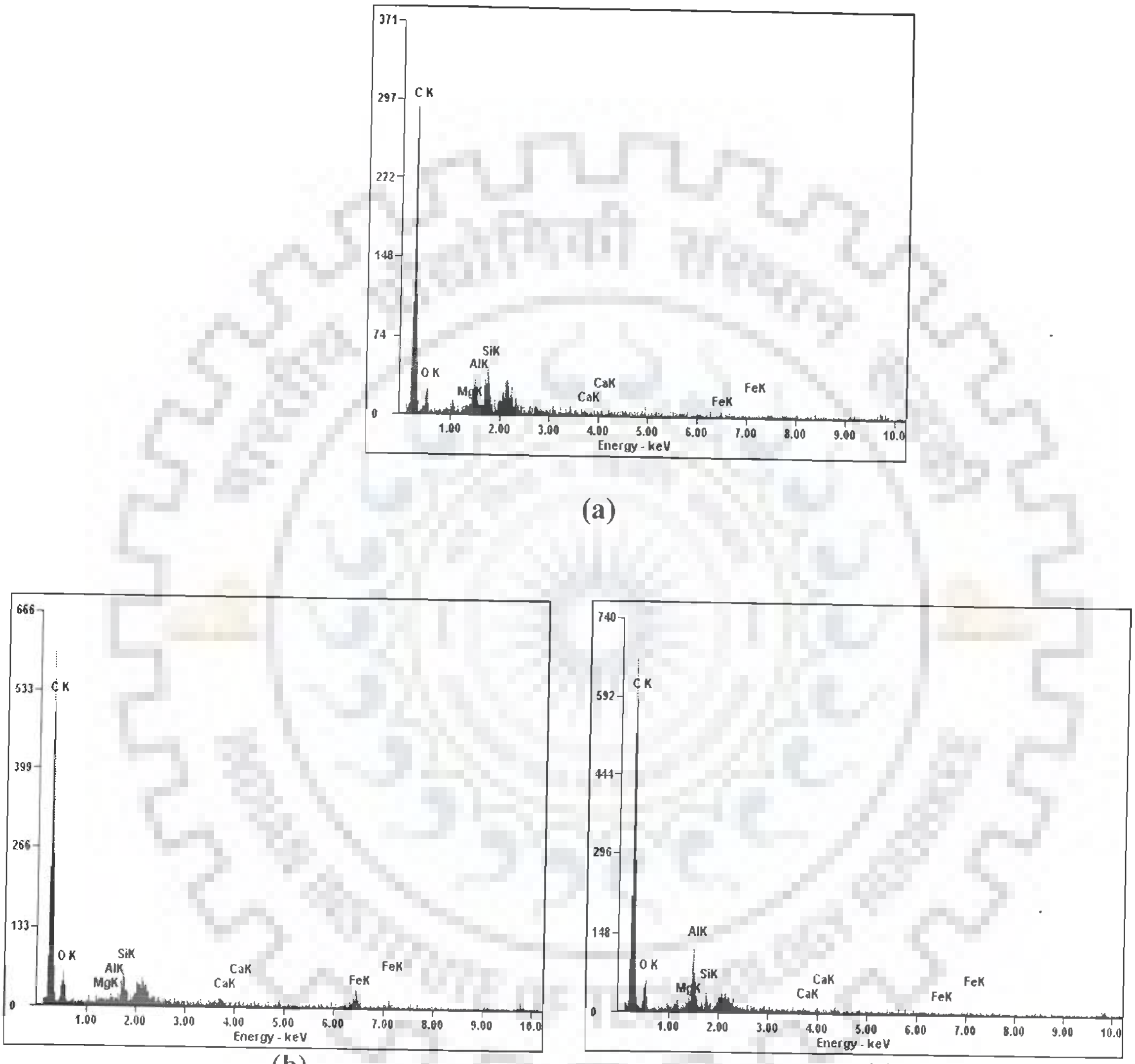
Fig. 4.2.4. Settling curves of slurry from the coagulation of SDW by various coagulants.



(a)

(b) (c)

Fig. 4.2.5. SEM images of generated sludge during the coagulation of SDW by coagulants (a) PAC (b) $FeSO_4$ (c) $KAl(SO_4)_2.12H_2O$.



(a)

(b)

(c)

Fig. 4.2.6. EDX spectra of generated sludge during the coagulation of SDW by coagulants (a) PAC (b) $FeSO_4$ (c) $KAl(SO_4)_2.12H_2O$.

The degradation temperature range for very rapid mass loss were found to be 200-650, 175-500 and 200-695 °C; and the degradation percentage of mass within these temperature ranges were 77.2, 76 and 80.6% for sludge produced by coagulants PAC, $FeSO_4$ and $KAl(SO_4)_2.12H_2O$, respectively (Table 4.2.3). The temperature (T_{max}) at which maximum rate of weight loss occurred were found to be 347, 482 and 348 °C; and the corresponding maximum rate of weight loss were found to be 0.905, 0.753 and 0.699 mg/min for PAC, $FeSO_4$ and $KAl(SO_4)_2.12H_2O$, respectively (Table 4.2.3). On increasing the temperature up to 1000 °C (beyond the upper limit of maximum degradation temperature range), negligible weight loss of ~1-3% was observed. Overall, sludge generated by PAC, $FeSO_4$ and $KAl(SO_4)_2.12H_2O$ showed total weight loss of 85.6, 86.6 and 87.9%, respectively.

The properties of DTA patterns of the sludge are presented in Table 4.2.4. The oxidation of the sludges generated by various coagulants show exothermicity in different temperature range (Fig. 4.2.7b). Table 4.2.4 shows the temperature span of this exothermicity. Three exothermic peaks could be observed on DTA curves of sludge generated by various coagulants (Fig. 4.2.7b and Table 4.2.4). The first exothermic peak around 200 °C can be related to the non-enzymatic browning (NEB). NEB is the complex reaction which takes place between carbohydrates and caseinate at ≈200 °C to form brown color products. This reaction is also known as advanced malliard reaction and is exothermic in nature (Vuataz et al., 2009). The second exothermic peak ≈350 °C corresponds to decomposition of proteins, carbohydrates and fats (Francioso et al., 2007). The third peak at ≈500 °C involves the oxidation of remaining carbonaceous materials.

Generally, average amount of heat evolution due to oxidation of carbohydrates, proteins and fats are 17.2, 23.9 and 39.7 MJ/kg, respectively (Potter and Hotchkiss, 2005). Heating value of the sludge generated by PAC, $FeSO_4$ and $KAl(SO_4)_2.12H_2O$ were found to be 20.7, 29.6 and 17.3 MJ/kg, respectively. Thus, the sludge generated can be dried and used as a fuel in the boilers/incinerators or can be used for the production of fuel-briquettes. The bottom ash may be blended with clay and or cementious mixtures to make fire bricks or for other construction purposes.

Table 4.2.3. Thermal degradation characteristics of the sludge generated by different coagulants.

Parameters	PAC	$FeSO_4$	$KAl(SO_4)_2.12H_2O$
Drying Range (°C)	27-200	37-180	24-200
Moisture %	7.1	6.1	7.0
Degradation Range (°C)	200-650	175-500	200-695
T_{max} (°C)	347	482	348
Max. Rate of Weight Loss (mg/min)	0.905	0.753	0.699

T_{max} (°C) refers to the temperature at which maximum rate of weight loss occurred.

Table 4.2.4. DTA of the sludge generated by different coagulants.

Coagulants		ΔH	T_{1i} (°C)	T_{1f} (°C)
PAC	I exothermic peak	-0.287×10^{-6}	220	265
	II exothermic peak	-0.924×10^{-6}	325	410
	III exothermic peak	-1610	455	600
$FeSO_4$	I exothermic peak	-0.152×10^{-6}	175	225
	II exothermic peak	-0.169×10^{-6}	330	375
	III exothermic peak	-3100	420	510
$KAl(SO_4)_2.12H_2O$	I exothermic peak	-0.228×10^{-6}	220	270
	II exothermic peak	-0.464×10^{-6}	330	390
	III exothermic peak	-2450	460	660

T_{1i} refers to the onset temperature of the exothermic reaction; T_{1f} refers to the final temperature of exothermicity.

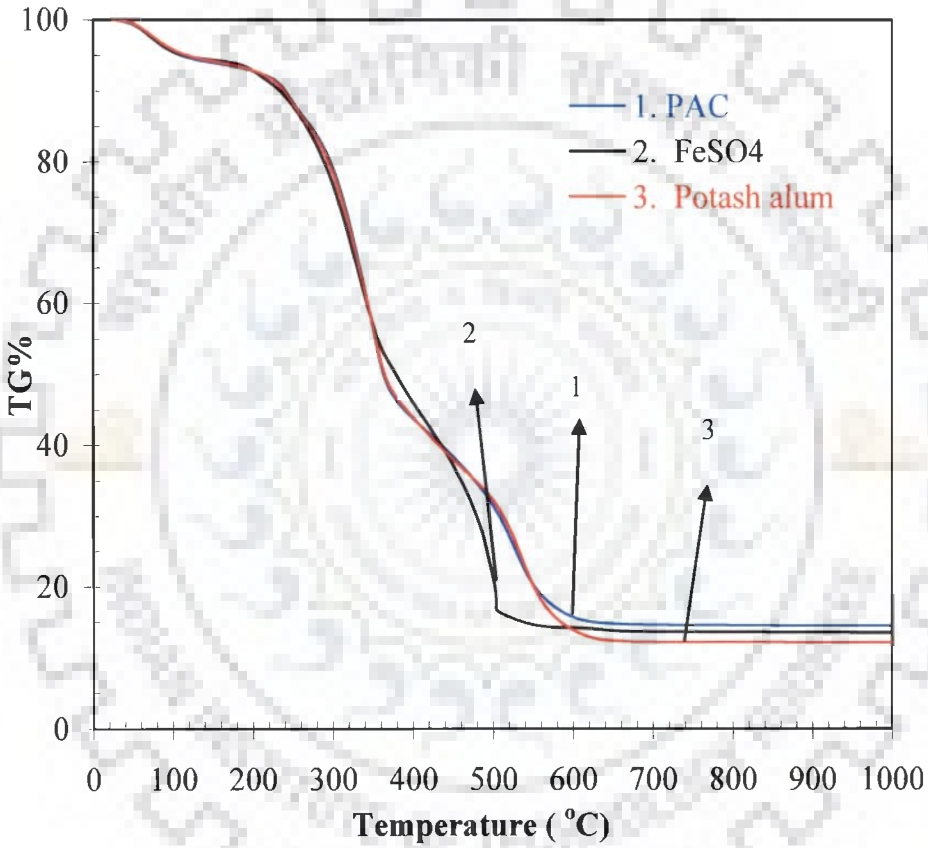
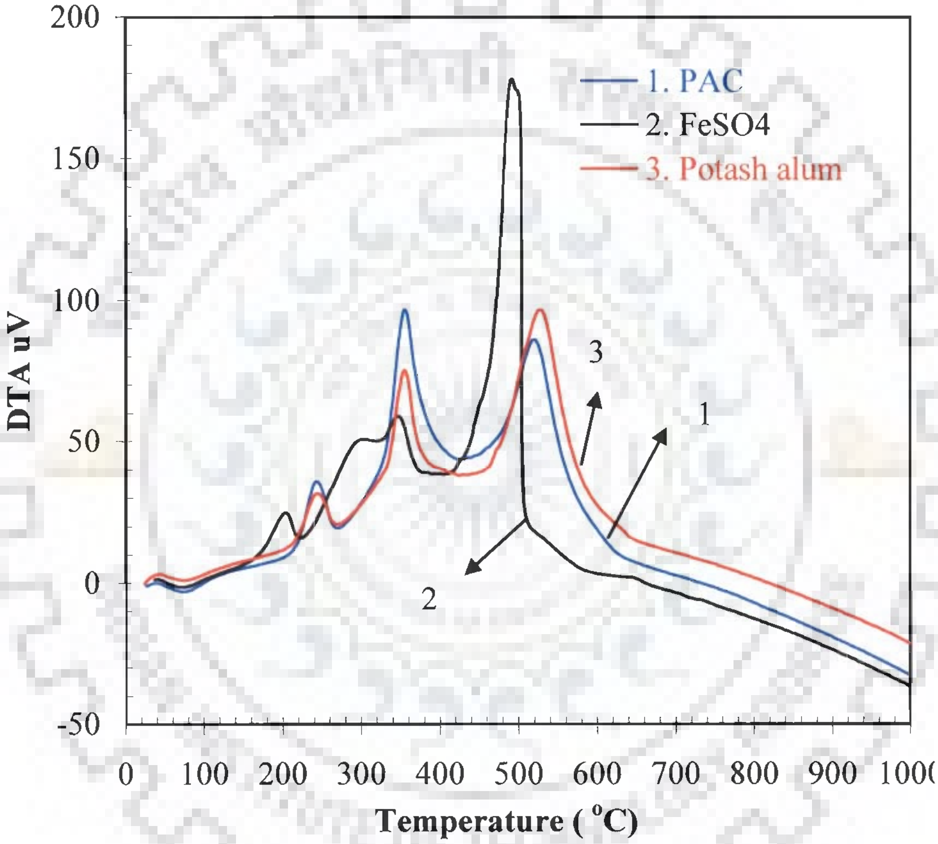


Fig. 4.2.7a. TGA graphs of sludge generated by coagulation of SDW by various coagulants.



(b)

Fig. 4.2.7b. DTA graphs of sludge generated by coagulation of SDW by various coagulants.

4.2.2. Organic Coagulants

4.2.2.1. Effect of m_{na}: The effect of m_{na} on the coagulation of SDW by guar gum, Na-CMC and Na-Alginate was studied at C_o = 3900 mg/l and pH_{i-na} = 4.0. For guar gum and Na-Alginate, an increase in m_{na} resulted in increased COD removal up to 66.7% for guar gum and 74.23% for Na-Alginate, respectively at m_{na} = 100 mg/l; and thereafter the removal efficiency decreased sharply and became almost constant at 58.1% for guar gum and 61.5% for Na-Alginate at m_{na} = 400 mg/l. However with Na-CMC, removal increased with an increase in m_{na} up to 66.92% at m_{na} = 100 mg/l and then became almost constant at 66.03% at m_{na} = 400 mg/l (Fig. 4.2.8). Dairy wastewater has the isoelectric point (pH_{iso}) around 4.2. SDW is mainly composed of milk proteins which are positively charged at $pH_{i-na} < pH_{iso}$ (Selmer-olsen et al, 1996). Therefore, the milk proteins destabilization may be explained by the adsorption and charge neutralization of negatively charged anionic coagulants on the positively charged protein particles, and thus they aggregate together resulting in bigger size flocs and ultimately get removed by settling. On increasing m_{na}, COD removal efficiency increases due to destabilization of more and more milk proteins. But the lower COD removal efficiency at higher dosage for the coagulants, guar gum and Na-Alginate, is due to the surface charge reversal of the protein particles due to the continuous adsorption of anionic coagulants (guar gum and Na-Alginate) on protein particles and hence, restabilization of protein particles. The optimum m_{na} was found to be 100 mg/l for all the coagulants.

4.2.2.2. Effect of initial pH (pH_{i-na}): In the process of coagulation, pH of the aqueous solution is an important controlling parameter because colloidal stability depends on pH. Fig. 4.2.9 represents the effect of pH_{i-na} on the COD removal and final pH (pH_{f-na}) of SDW by guar gum, Na-CMC and Na-alginate. It can be seen from the Fig. 4.2.9 that as the pH_{i-na} of the SDW is increased, the removal first increased up to pH_{i-na} = 4 and after removal efficiency decreased very sharply up to the pH_{i-na} = 6 for all the coagulants. On increasing the pH beyond pH_{i-na} = 6, the removal became almost constant. The highest removal efficiency of 66.7%, 66.9% and 74.2% for guar gum, Na-CMC and Na-alginate, respectively, was obtained at pH_{i-na} = 4.0.

As explained earlier, dairy wastewater has the isoelectric point (pH_{iso}) around 4.2 (Selmer-olsen et al, 1996). Hence, the destabilization of colloids occur by lowering the pH to pH_{i-na} = 4.2 without addition of any coagulants. From the Fig. 4.2.9, it is clear that the

COD removal is 63.8% at $pH_{i\text{-}na}$ = 4 without addition of coagulants. But the addition of organic coagulants at $pH_{i\text{-}na}$ = 4.0 enhanced the COD removal efficiency up to 66.7%, 66.9% and 74.2% for guar gum, Na-CMC and Na-alginate, respectively. Hence, it may be concluded that the anionic coagulants such as guar gum, Na-CMC and Na-alginate function as flocculation-aids. This is due to the fact that milk proteins of SDW are positively charged at $pH_{i\text{-}na} < pH_{iso}$. Milk proteins get destabilized by negatively charged anionic coagulants. However, for $pH_{i\text{-}na} > pH_{iso}$, the proteins are negatively charged and do not get destabilized by anionic coagulants, and thus removal efficiency was lower at $pH_{i\text{-}na}$ > 4.2. This explains the results shown in Fig. 4.2.9a. Fig. 4.2.9b explains the effect of organic coagulants guar gum, Na-CMC and Na-alginate on $pH_{f\text{-}na}$ of SDW. It can be seen that $pH_{f\text{-}na}$ is nearly same as $pH_{i\text{-}na}$. Hence, it can be concluded that natural organic coagulants do not affect the $pH_{i\text{-}na}$.

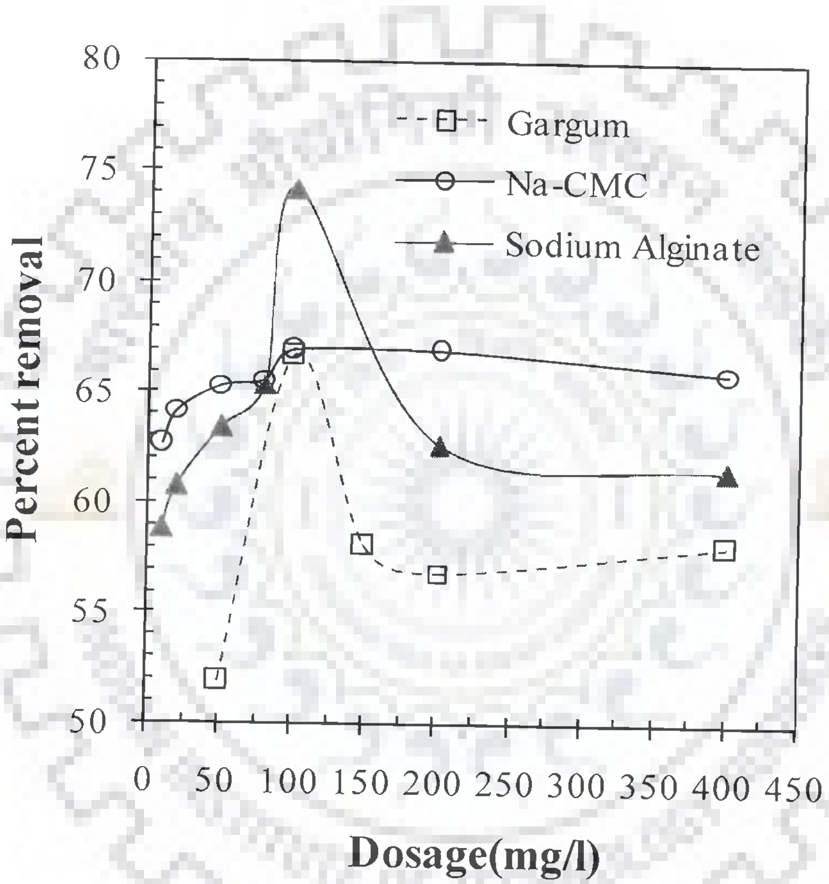
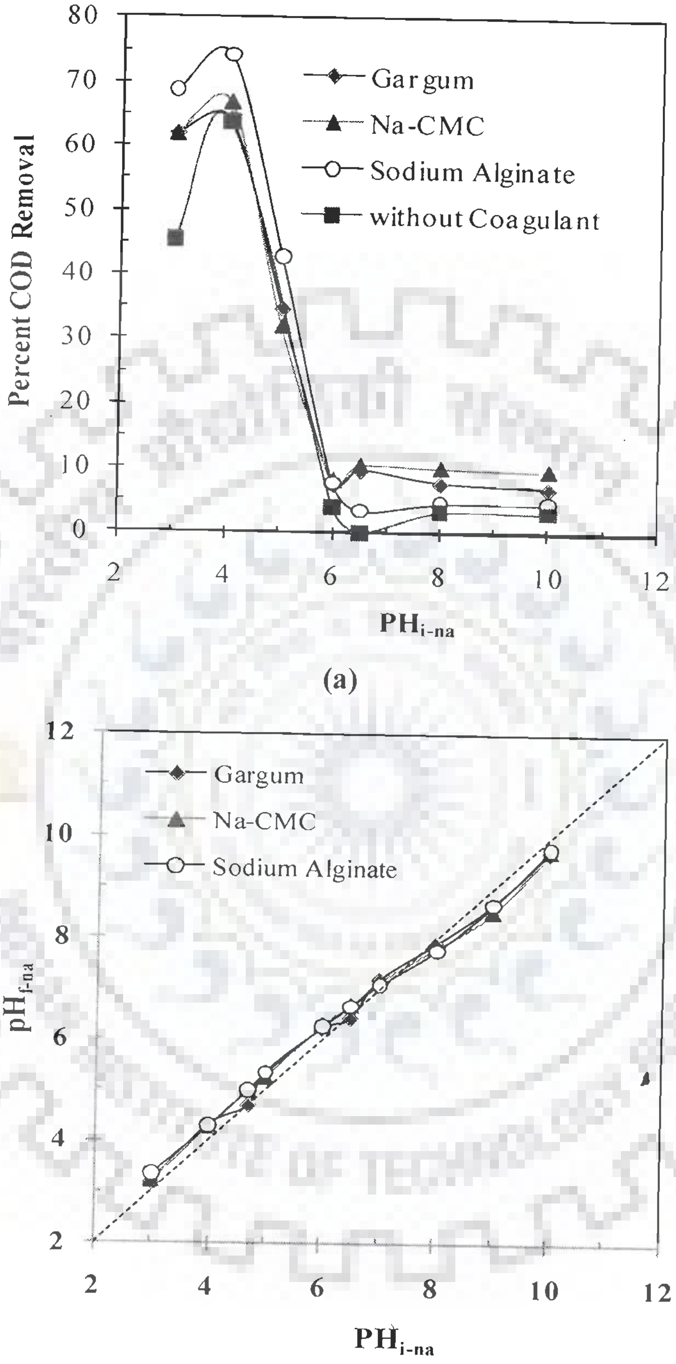


Fig. 4.2.8. Effect of dosage on the COD removal of SDW by natural organic coagulants, C_0 = 3900 mg/l, $pH_{i\text{-}na}$ = 4.0 for all the coagulants.



(b)

Fig. 4.2.9. Effect of $pH_{i\text{-}na}$ on (a) COD removal of SDW (b) $pH_{f\text{-}na}$ by natural organic coagulants, C_0 = 3900 mg/l, m_{na} = 100 mg/l for all the coagulants.

Chapter – 5

ELECTRO-CHEMICAL TREATMENT

5.0. GENERAL

This chapter reports electrochemical treatment (ECT) of SDW. Experimental set-up, chemicals and electrodes used and various studies performed during the SDW treatment by ECT have been explained in detail. Results obtained during the treatment of SDW and their interpretations have been discussed in detail.

5.1. MATERIALS AND METHODS

5.1.1. Wastewater

Wastewater used in this study was the same as described in section 4.1.1.

5.1.2. Chemicals and Electrodes

Chemicals used in this study were the same as described in section 4.1.2. The aluminum (Al) and iron (Fe) were used as electrode material. These metals were procured from the local suppliers in the form of sheets having thickness of 1 mm and 1.5 mm for Al and Fe, respectively. Then, the Al and Fe sheets were cut to dimensions of 10 cm×8.5 cm. For the cleaning of Fe electrodes, they were first degreased and then treated with 15% HCl followed by washing with distilled water. Washed Fe electrodes were oven dried prior to their use in the ECT experiments.

5.1.3. Analytical Methods

Various analytical methods used have been described in section 4.1.3.

5.1.4. Experimental Setup and Methods of Operation

5.1.4.1. Reactor: Cuboid shape batch reactor of dimension 108 mm×108 mm×130 mm having working volume 1.5 litre was fabricated of Perspex sheet to conduct the ECT experiments of SDW. Schematic diagram of experimental setup is shown in Fig. 5.1.1. Magnetic stirrer was used to agitate the SDW. Two pairs of Al or Fe electrodes of thickness 1 mm and 1.5 mm, respectively, each having dimensions of 10 cm × 8.5 cm with inter-electrode spacing of 1 cm were connected in parallel mode. Total submerged area of electrodes into the SDW was 9.50 cm×8.5 cm. Current was maintained constant by means of a precision direct current power supply (0–20 V, 0–5 A) fitted with an ammeter and voltmeter.

5.1.4.2. Experimental design and Experimental procedure: In this study, four factors and five level full factorial central composite (CC) design, based on response surface methodology (RSM) were used and data obtained were analyzed by Design-Expert trial version. RSM is an effective statistical tool for collection of mathematical and statistical information useful for developing, improving and optimizing processes and can be used to evaluate the relative significance of several affecting parameters even in the presence of complex interactions. The main advantage of RSM is the reduced number of experiments needed to provide sufficient information to optimise the process.

Four operational parameters, namely J: 61.73–308.64 A/m^2; m (weight of NaCl): 0-2 g/l; t: 10–90 min and pH_i: 5–11, have been taken as input parameters and percentage COD removal (Y_1) and specific energy consumed (KWh per kg of COD removed) (Y_2) have been taken as a responses of the system. Working range of operational parameters were decided by conducting preliminary experiments with varying operational parameters for COD removal (not shown here). Table 5.1.1 represents the variables and their levels whereas actual experimental design matrix is given in Table 5.1.2 and 5.1.3, for each of electrode, Al and Fe, respectively. For statistical calculations, the levels for the four parameters X_i (X_1 (J), X_2 (m), X_3 (t), X_4 (pH_i)) were coded as x_i according to the following relationship:

$$x_i = \frac{(X_i - X_0)}{\delta X} \qquad (5.1.1)$$

Where x_i is coded (dimensionless) value of parameter X_i, X_0 is value of the parameter X_i at the centre point and δX represents the step change. Based on this the levels were designated as −2, −1, 0, +1, and +2.

A total of 30 experiments, designed by RSM (Table 5.1.2 and 5.1.3), were conducted to study the effects of the four independent parameters on Y_1 and Y_2 for each of Al and Fe electrodes. The pH of the SDW was adjusted to desired level by adding 0.1 N NaOH or 0.1 N H_2SO_4 solutions. In the beginning of experiment, the SDW with initial COD concentration (C_o = 3900 mg/l) and requisite m value was adjusted to desired pH, as per that particular run. Time, t, was measured when power supply was switched on. J was maintained constant during the run. After the desired t, samples were taken from the reactor and its final COD was measured. The percentage COD removal was calculated using the following relationship:

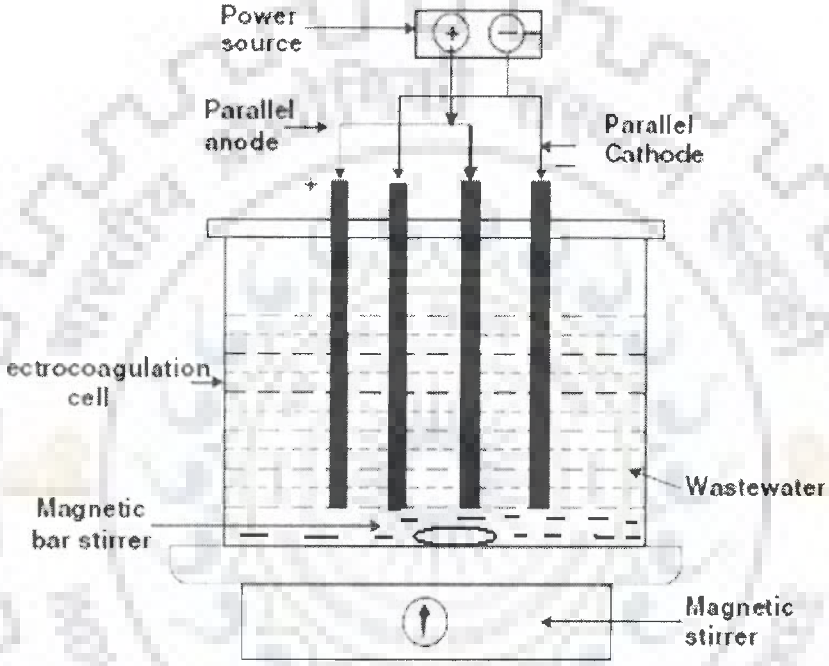


Fig. 5.1.1. Schematic diagram of experimental setup used for the ECT of SDW.

$$\text{Percent COD removal}(Y) = \frac{(C_0 - C_f)100}{C_0} \tag{5.1.2}$$

where, C_f is the final COD concentration (mg/l) after t (min). The data obtained from the experiments was analyzed using Design-Expert trial version. Three analytical steps: adequacy of various models test (sequential model sum of squares and model summary statistics), analysis of variance (ANOVA) and the response surface plotting were performed to establish an optimum condition for the responses Y_1 and Y_2.

The data obtained by the experiments set suggested were fitted to a second-order polynomial model equation:

$$Y = b_o + \sum_{i=1}^{4} b_i X_i + \sum_{i=1}^{4} b_{ii} X_i^2 + \sum_{i=j}^{3} \sum_{i=j+1}^{4} b_{ij} X_{ij} \tag{5.1.3}$$

Where, Y is Response; b_o, b_i, b_{ii}, b_{ij} are constant coefficients and X_i the uncoded independent variables. The significant terms in the model were found by analysis of variance (ANOVA) for each response. Significance was judged by determining the probability level that the F-values calculated from the data is less than 5%. The model adequacies were checked by R^2, adjusted-R^2, predicted-R^2 and prediction error sum of squares (PRESS). A good model will have a large predicted R^2, and a low PRESS.

Table 5.1.1. Process parameters and their levels for ECT of SDW.

Variable, unit	**Factors**	**Level**				
	x_i	**−2**	**−1**	**0**	**1**	**2**
Current density, J (Am^{-2})	X_1	61.73	123.46	185.19	246.91	308.64
Mass of salt (NaCl), m (g/l)	X_2	0	0.5	1	1.5	2
Time of electrolysis, t (min)	X_3	10	30	50	70	90
Initial pH, pH_i	X_4	5	6.5	8.0	9.5	11

Table 5.1.2. Full factorial design used and responses for the ECT of SDW by Al electrodes.

Standard order	*J* (X_1)	*m* (X_2)	*t* (X_3)	pH_i (X_4)	Y_1		Y_2	
					$Y_{1\,exp}$ (%)	$Y_{1\,pre}$ (%)	$Y_{2\,exp}$	$Y_{2\,pre}$
1	123.46	0.5	30	6.5	23.3	28.4	1.10	1.02
2	246.91	0.5	30	6.5	65.4	61.6	1.31	1.90
3	123.46	1.5	30	6.5	25.0	29.8	1.03	0.80
4	246.91	1.5	30	6.5	36.7	45.2	1.40	1.77
5	123.46	0.5	70	6.5	38.9	43.7	1.54	1.58
6	246.91	0.5	70	6.5	66.9	68.4	2.98	3.56
7	123.46	1.5	70	6.5	63.8	58.1	0.94	0.91
8	246.91	1.5	70	6.5	61.5	65.1	1.94	2.98
9	123.46	0.5	30	9.5	15.4	16.4	1.67	1.95
10	246.91	0.5	30	9.5	42.3	48.2	1.92	2.31
11	123.46	1.5	30	9.5	19.2	18.0	1.33	1.11
12	246.91	1.5	30	9.5	32.3	32.1	1.59	1.57
13	123.46	0.5	70	9.5	50.8	42.5	1.18	1.93
14	246.91	0.5	70	9.5	66.2	65.9	2.86	3.39
15	123.46	1.5	70	9.5	48.8	57.1	1.23	0.65
16	246.91	1.5	70	9.5	67.7	62.8	1.77	2.20
17	61.73	1	50	8	26.9	24.9	0.66	0.80
18	308.64	1	50	8	66.5	63.8	2.68	3.23
19	185.19	0	50	8	59.6	59.1	6.09	3.37
20	185.19	2	50	8	61.5	57.4	1.04	1.96
21	185.19	1	10	8	30.3	22.7	0.56	0.67
22	185.19	1	90	8	65.8	68.7	2.34	1.86
23	185.19	1	50	5	51.5	44.7	1.24	1.40
24	185.19	1	50	11	28.2	30.4	2.08	1.55
25	185.19	1	50	8	57.7	55.1	1.48	1.55
26	185.19	1	50	8	55.8	55.1	1.53	1.55
27	185.19	1	50	8	54.2	55.1	1.58	1.55
28	185.19	1	50	8	53.5	55.1	1.60	1.55
29	185.19	1	50	8	52.3	55.1	1.63	1.55
30	185.19	1	50	8	56.9	55.1	1.50	1.55

Table 5.1.3. Full factorial design used and responses for the ECT of SDW by Fe electrodes.

Standard order	$J\ (X_1)$	$m\ (X_2)$	$t\ (X_3)$	$pH_i\ (X_4)$	Y_1		Y_2	
					$Y_{1\ exp}$ (%)	$Y_{1\ pre}$ (%)	$Y_{2\ exp}$	$Y_{2\ pre}$
1	123.46	0.5	30	6.5	25.62	30.61	0.67	0.75
2	246.91	0.5	30	6.5	60.23	49.47	1.14	1.22
3	123.46	1.5	30	6.5	9.62	7.08	1.33	1.80
4	246.91	1.5	30	6.5	23.69	29.23	2.53	2.11
5	123.46	0.5	70	6.5	64.23	55.00	0.62	0.57
6	246.91	0.5	70	6.5	64.23	63.58	2.48	3.17
7	123.46	1.5	70	6.5	32.31	37.64	0.93	0.37
8	246.91	1.5	70	6.5	60.23	49.51	2.32	2.81
9	123.46	0.5	30	9.5	10.38	17.31	3.70	2.73
10	246.91	0.5	30	9.5	25.00	24.81	2.74	2.92
11	123.46	1.5	30	9.5	6.15	11.95	3.82	2.75
12	246.91	1.5	30	9.5	17.31	22.74	3.21	2.78
13	123.46	0.5	70	9.5	25.00	24.61	3.59	3.63
14	246.91	0.5	70	9.5	23.08	21.82	6.91	5.95
15	123.46	1.5	70	9.5	18.46	25.42	2.97	2.40
16	246.91	1.5	70	9.5	25.77	25.93	5.03	4.57
17	61.73	1	50	8	23.08	14.83	0.37	1.26
18	308.64	1	50	8	27.31	34.20	3.91	3.89
19	185.19	0	50	8	43.46	49.42	3.44	3.47
20	185.19	2	50	8	37.31	30.00	2.29	3.13
21	185.19	1	10	8	15.69	8.77	0.54	1.15
22	185.19	1	90	8	30.77	36.34	2.50	2.75
23	185.19	1	50	5	46.15	55.84	1.27	0.45
24	185.19	1	50	11	30.00	18.96	2.49	4.18
25	185.19	1	50	8	46.92	44.68	0.91	0.96
26	185.19	1	50	8	44.23	44.68	0.97	0.96
27	185.19	1	50	8	46.54	44.68	0.92	0.96
28	185.19	1	50	8	42.69	44.68	1.00	0.96
29	185.19	1	50	8	42.31	44.68	1.01	0.96
30	185.19	1	50	8	45.38	44.68	0.94	0.96

5.1.4.3. Multi-response optimization: Since in this study, there are two responses, therefore, multi-response processes optimization by desirability function approach used to optimize the electrochemical treatment. Simultaneous optimization combines all the different response requirements into one composite requirement.

One-sided desirability d_i is given by:

$$d_i = \begin{cases} 0 & \text{if } \; Y_i \leq Y_{i-\min} \\ [\dfrac{Y_i - Y_{i-\min}}{Y_{i-\max} - Y_{i-\min}}]^r & \text{if } \; Y_{i-\min} < Y_i < Y_{i-\max} \\ 1 & \text{if } \; Y_i \geq Y_{i-\max} \end{cases} \tag{5.1.4}$$

Where, Y_i is response values, Y_{i-min} and Y_{i-max} is minimum and maximum acceptable values of response *i*, and *r* is a weight and a positive constant, used to determine scale of desirability.

Among the multi-response optimization techniques, desirability function approach is one of the most frequently used in practice (Derringer et al., 1980). The desirability lies between 0 and 1 representing the closeness of a response to its ideal value. If a response falls within the unacceptable intervals, the desirability is 0, and if a response falls within the ideal intervals or the response reaches its ideal value, the desirability is 1. Meanwhile, when a response falls within the tolerance intervals but not the ideal interval, or when it fails to reach its ideal value, the desirability lies between 0 and 1. The more closely the response approaches the ideal intervals or ideal values, the closer the desirability is to 1.

In the multi-response processes optimization, desirability function transforms each response to a corresponding desirability value between 0 and 1. All the desirability is combined to form a composite desirability function which converts a multi-response into a one single response. The individual desirability functions are combined in order to obtain the overall desirability D, as follows:

$$D = (d_1 \times d_2 \times d_3 ....)^{\frac{1}{k}} \tag{5.1.5}$$

Where, $0 \leq D \leq 1$ and k is the number of responses.

If all of the quality characteristics reach their ideal values, the desirability d_i is 1 for all *i*. Consequently, the total desirability is also 1. If any one of the responses does not reach its ideal value, the desirability d_i is below 1 for that response and the total desirability is below 1. If any one of the responses cannot meet the quality requirements, the desirability d_i is 0 for that response. Total desirability will then be 0.

5.2. RESULTS AND DISCUSSION (Kushwaha et al., 2010c and d)

5.2.1. Statistical Analysis and Fitting of Second-Order Polynomial Equation

The responses (Y_1 and Y_2) by ECT of SDW by the Al and Fe electrodes were measured according to the conditions of various operational parameters as given in design matrix and the results are shown in Table 5.1.2 and Table 5.1.3. Linear, interactive, quadratic and cubic models were fitted to the experimental data to obtain the regression equations. In order to decide about the adequacy of various models, sequential model sum of squares and model summary statistics were tested and results are given in Table 5.2.1 and Table 5.2.2 for Al and Fe electrodes, respectively. Sequential model sum of squares showed that quadratic model best fits the experimental data for responses Y_1 and Y_2 for both Al and Fe electrodes.

For Al electrode, analysis of variance (ANOVA) result showed F-value of 13.48 and 3.32 for Y_1 and Y_2, respectively, implying that the quadratic model is significant (Table 5.2.3 and Table 5.2.4). Values of "Prob > F" less than 0.05 indicate that model terms are significant and "Prob > F" lower than 0.0001 for the second-order polynomial fitting indicates that the model is statistically highly significant, and that the model terms are significant at 95% probability level. For the response Y_1, ANOVA table obtained from the response surface quadratic model shows that J and t are highly significant, whereas, pH_i, J^2, pH_i^2 and $J \times m$ are significant terms. The final quadratic equation in terms of coded factors for Y_1 by Al electrode is given below:

$$Y_1 = 55.06 + 9.71X_1 + 11.5X_3 - 3.57X_4 - 2.67X_1^2 - 4.38X_4^2 - 4.43X_1X_2 \qquad (5.2.1)$$

However, for response Y_2, model terms J, m, t and m^2 are significant. The quadratic equation in terms of coded factors for Y_2 by Al electrode is given below:

$$Y_2 = 1.55 + 0.61X_1 - 0.35X_2 + 0.3X_3 - 0.28X_2^2 \qquad (5.2.2)$$

Table 5.2.1. Adequacy of the models tested for Y_1 and Y_2 for Al electrodes.

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	Remark	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	PRESS	Remarks
					COD removal (Y_1)							
Mean	69621.21	1	69621.21									
Linear	5745.51	4	1436.38	17.50	< 0.0001		9.06	0.74	0.69	0.61	3054.77	
2FI	675.47	6	112.58	1.55	0.2146		8.51	0.82	0.73	0.48	4055.09	
Quadratic	802.18	4	200.55	5.24	0.0076		6.19	0.93	0.86	0.59	3212.45	
Cubic	466.84	8	58.35	3.81	0.0473	AL	3.91	0.99	0.94	-0.58	12336.29	AL
Residual	107.17	7	15.31									
Total	77418.39	30	2580.61									
					Energy consumption (Y_2)							
Mean	96.41	1	96.41									
Linear	14.01	4	3.50	7.72	0.0003		0.67	0.55	0.48	0.31	17.54	
2FI	2.38	6	0.40	0.84	0.5523		0.69	0.65	0.46	0.03	24.49	
Quadratic	2.77	4	0.69	1.68	0.2061		0.64	0.76	0.53	-0.40	35.52	
Cubic	5.67	8	0.701	8.72	0.0049	AL	0.28	0.98	0.91	-2.10	78.63	AL
Residual	0.56	7	0.08									
Total	121.76	30	4.06									

DF denotes the degree of freedom and AL denotes aliased.

Table 5.2.2. Adequacy of the models tested for Y_1 and Y_2 for Fe electrodes.

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	Rem-ark	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	PRESS	Rem-arks
						COD removal (Y_1)						
Mean	34215.3	1	34215.3									
Linear	4310.09	4	1077.52	8.05	0.0003		11.57	0.56	0.49	0.36	4866.25	
2FI	906.49	6	151.08	1.18	0.3594		11.33	0.68	0.51	0.18	6297.40	
Quadratic	1352.48	4	338.12	4.67	0.0120		8.51	0.86	0.73	0.19	6175.79	
Cubic	982.05	8	122.76	8.25	0.0058	AL	3.86	0.99	0.94	-0.61	12331.53	AL
Residual	104.19	7	14.88									
Total	41870.6	30	1395.69									
						Energy consumption (Y_2)						
Mean	147.65	1	147.65									
Linear	35.33	4	8.83	6.7	0.0008		1.15	0.52	0.44	0.31	46.83	
2FI	8.45	6	1.41	1.09	0.4032		1.14	0.64	0.45	-0.01	69.30	
Quadratic	13.85	4	3.46	4.87	0.0102		0.84	0.84	0.70	0.10	61.45	
Cubic	8.41	8	1.05	3.26	0.0688	AL	0.57	0.97	0.86	-3.75	324.39	AL
Residual	2.26	7	0.32									
Total	215.95	30	7.2									

AL = Aliased.

Table 5.2.3. ANOVA for response surface quadratic model Y_1 by Al electrode.

Source	**Coefficient estimate**	**Sum of Squares**	**DF[#]**	**Mean Square**	**F Value**	**Prob > F**	
Model		7223.16	14	515.94	13.48	< 0.0001	Significant
Intercept	55.06						
X_1	9.71	2264.19	1	2264.19	59.17	< 0.0001	Highly significant
X_2	-0.42	4.35	1	4.35	0.11	0.7408	
X_3	11.5	3171.24	1	3171.24	82.87	< 0.0001	Highly significant
X_4	-3.57	305.74	1	305.74	7.99	0.0128	Significant
X_1^2	-2.67	195.9	1	195.9	5.12	0.0389	Significant
X_2^2	0.79	17.08	1	17.08	0.45	0.5142	
X_3^2	-2.35	150.9	1	150.9	3.94	0.0657	
X_4^2	-4.38	527.18	1	527.18	13.78	0.0021	Significant
X_1X_2	-4.43	314.68	1	314.68	8.22	0.0117	Significant
X_1X_3	-2.11	71.35	1	71.35	1.86	0.1922	
X_1X_4	-0.32	1.67	1	1.67	0.04	0.8372	
X_2X_3	3.26	169.78	1	169.78	4.44	0.0524	
X_2X_4	0.046	0.03	1	0.03	0.000883	0.9767	
X_3X_4	2.72	117.96	1	117.96	3.08	0.0995	
Residual		574.00	15	38.27			
Lack of Fit		552.29	10	55.23	12.71	0.0059	
Pure Error		21.72	5	4.34			
Cor Total		7797.17	29				

Degree of freedom

Table 5.2.4. ANOVA for response surface quadratic model for Y_2 by Al electrode.

Source	Coefficient estimate	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model		19.17	14	1.37	3.32	0.0137	Significant
Intercept	1.55						
X_1	0.61	8.88	1	8.87	21.54	0.0003	Significant
X_2	-0.35	2.98	1	2.98	7.24	0.0168	Significant
X_3	0.3	2.12	1	2.12	5.15	0.0385	Significant
X_4	0.04	0.03	1	0.032	0.08	0.7829	
X_1^2	0.11	0.36	1	0.36	0.88	0.3629	
X_2^2	0.28	2.10	1	2.10	5.01	0.0393	Significant
X_3^2	-0.07	0.15	1	0.15	0.36	0.5598	
X_4^2	-0.02	0.01	1	0.01	0.028	0.8704	
X_1X_2	0.02	0.009	1	0.01	0.02	0.8845	
X_1X_3	0.27	1.20	1	1.20	2.92	0.1078	
X_1X_4	-0.13	0.27	1	0.27	0.66	0.4284	
X_2X_3	-0.11	0.20	1	0.20	0.48	0.4970	
X_2X_4	-0.15	0.37	1	0.37	0.90	0.3572	
X_3X_4	-0.14	0.33	1	0.33	0.79	0.3875	
Residual		6.18	15	0.41			
Lack of Fit		6.16	10	0.62	177.4926	< 0.0001	
Pure Error		0.02	5	0.003			
Cor Total		25.351	29				

Table 5.2.5. ANOVA for response surface quadratic model for Y_1 by Fe electrode.

Source	Coefficient estimate	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model		6569.05	14	469.28	6.48	0.0004	Significant
Intercept	44.68						
X_1	4.84	562.9	1	562.90	7.77	0.0138	Significant
X_2	-4.86	565.88	1	565.89	7.81	0.0136	Significant
X_3	6.89	1140.73	1	1140.73	15.75	0.0012	Significant
X_4	-9.22	2040.57	1	2040.57	28.18	< 0.0001	Highly significant
X_1^2	-5.04	696.87	1	696.87	9.62	0.0073	Significant
X_2^2	-1.24	42.34	1	42.34	0.58	0.4564	
X_3^2	-5.53	839.06	1	839.06	11.59	0.0039	Significant
X_4^2	-1.82	90.84	1	90.84	1.25	0.2803	
X_1X_2	0.82	10.82	1	10.81	0.15	0.7046	
X_1X_3	-2.57	105.85	1	105.85	1.46	0.2454	
X_1X_4	-2.84	129.17	1	129.17	1.78	0.2016	
X_2X_3	1.54	38.10	1	38.11	0.53	0.4794	
X_2X_4	4.54	330.26	1	330.26	4.56	0.0496	Significant
X_3X_4	-4.27	292.28	1	292.28	4.04	0.0629	
Residual		1086.25	15	72.42			
Lack of Fit		1067.5	10	106.75	28.47	0.0009	
Pure Error		18.75	5	3.75			
Cor Total		7655.3	29				

Table 5.2.6. ANOVA for Response Surface Quadratic Model for Y_2 for Fe electrode.

Source	**Coefficient estimate**	**Sum of Squares**	**DF**	**Mean Square**	**F Value**	**Prob > F**	
Model		57.63	14	4.12	5.78	0.0008	Significant
Intercept	0.96						
X_1	0.66	10.41	1	10.41	14.63	0.0017	Significant
X_2	-0.08	0.17	1	0.17	0.24	0.6331	
X_3	0.40	3.86	1	3.86	5.43	0.0342	Significant
X_4	0.93	20.89	1	20.89	29.36	< 0.0001	Highly significant
X_1^2	0.40	4.46	1	4.47	6.27	0.0243	Significant
X_2^2	0.58	9.38	1	9.38	13.18	0.0025	Significant
X_3^2	0.25	1.69	1	1.69	2.38	0.1438	
X_4^2	0.34	3.14	1	3.14	4.42	0.0529	
X_1X_2	-0.04	0.03	1	0.03	0.037	0.8507	
X_1X_3	0.53	4.55	1	4.55	6.4	0.0231	Significant
X_1X_4	-0.07	0.08	1	0.08	0.11	0.7459	
X_2X_3	-0.31	1.55	1	1.55	2.18	0.1602	
X_2X_4	-0.26	1.06	1	1.06	1.49	0.2416	
X_3X_4	0.27	1.18	1	1.18	1.66	0.2173	
Residual		10.67	15	0.71			
Lack of Fit		10.67	10	1.07	614.18	< 0.0001	Significant
Pure Error		0.009	5	0.002			
Cor Total		68.31	29				

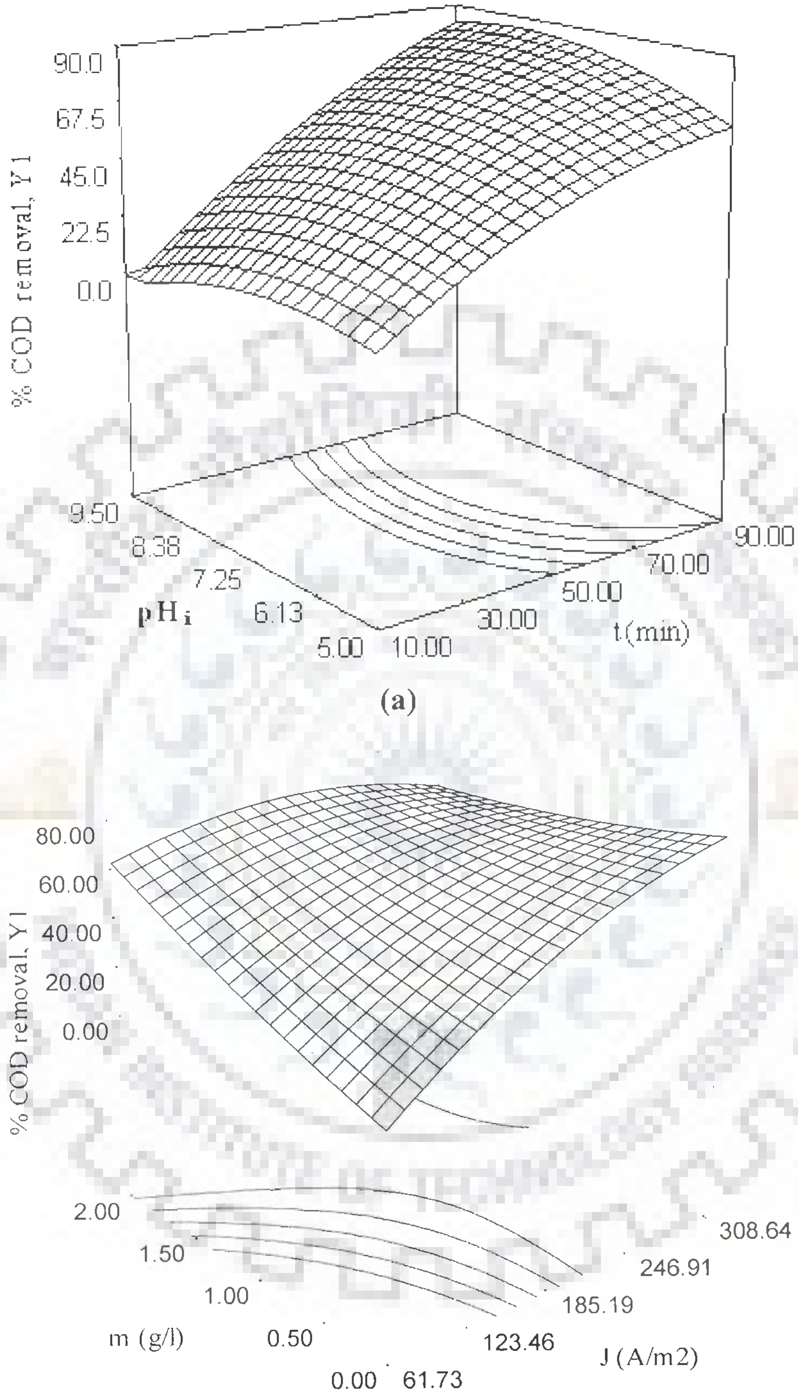
For Fe electrode, ANOVA result showed F-value of 6.48 and 5.78 for Y_1 and Y_2, respectively, implying that the quadratic model is significant (Table 5.2.5 and Table 5.2.6). ANOVA results showed that that *pH* is highly significant term, whereas, *J*, *m*, *t*, J^2, t^2, and $m\times pH$ are significant terms for response Y_1, whereas, for response Y_2, *J*, *t*, *pH*, J^2, m^2, and $J\times t$ are significant terms. The final quadratic equations in terms of coded factors for responses Y_1 and Y_2 by Fe electrode are given below:

$$Y_1 = 44.68 + 4.84X_1 - 4.86X_2 + 6.89X_3 - 9.22X_4 - 5.04X_1^2 - 5.53X_3^2 + 4.54X_2X_4 \tag{5.2.3}$$

$$Y_2 = 0.96 + 0.66X_1 + 0.40X_3 - 0.93X_4 - 0.40X_1^2 + 0.58X_2^2 + 0.53X_1X_3 \tag{5.2.4}$$

5.2.2. Effects of J, m, t and pH$_i$ on Y_1

5.2.2.1. ECT of SDW by Al electrode: Three-dimensional response surface graphs for response Y_1 by various operational parameters *J, m, t* and pH_i are shown in Fig. 5.2.1 by Al electrode. In the present study, the COD removal efficiency was found to increase with an increase in pH_i up to $pH_i \approx 6.50$ and beyond that COD removal started to decrease (Fig. 5.2.1 a). This trend of COD removal was found to follow at every *t* (Fig. 5.2.1a). Dairy wastewater has the isoelectric point (pH_{iso}) around 4.2 (Selmer-Olsen et al., 1996). Thus, the milk proteins contained in the SDW are negatively charged at $pH > pH_{iso}$. These milk proteins get destabilized by positively charged hydrolysed aluminum species like Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$, etc. Thus, the colloidal particles present in the SDW aggregate together to form bigger size flocs and ultimately get removed by settling. Also, the speciation of Al (III) shows that the $Al(OH)_3$ species are formed in the *pH* range of 5-7, which help in the removal of colloids by sweep coagulation. Since the optimum pH_i was found to be ≈6.5, it seems that both charge neutralization of anionic colloids by monomeric cationic aluminum species and sweep coagulation with amorphous aluminum hydroxide help in maximum COD removal at $pH_i \approx 6.5$. However, for $pH_i > 6.5$, formation of negatively charged $Al(OH)_4^-$ causes the reduction in COD removal.



(a)

(b)

Fig. 5.2.1. Three-dimensional response surface graphs for the EC treatment of SDW by Al electrode (a) %COD removal, Y_1 versus *t* and pH_i at *m* = 2.0 g/l, *J* = 123.46 A/m^2; (b)%COD removal, Y_1 versus *J* and *m* at *t* = 74 min, pH_i = 6.5.

Faraday's law (equation 3.4.8) describes the relationship between *J* and the amount of anode material that dissolves in the solution. The COD removal efficiency depends directly on the concentration of Al^{3+} ions produced by the aluminum electrodes, which in turn as per Faradays law depends upon the *t*. When the value of *t* increases, an increase occurs in the concentration of aluminum ions and their hydroxide flocs. Consequently, an increase in *t* increases the COD removal efficiency. It may be seen in Fig. 5.2.1a, that the COD removal efficiency with *t* was found to be maximum at near about 70 min and then it remained constant with an increase in *t*. Fig. 5.2.1b reveals the variation of the COD removal efficiency with *J* and *m*. It may be seen in Fig. 5.2.1b that the COD removal efficiency increased with an increase in *J* upto 270 A/m^2 after which *J* had very marginal effect on the COD removal efficiency. Similar to *t*, an increase in *J* increase the amount of aluminum dissolved from the electrode for any constant *t* value. Consequently, higher amount of aluminum ions or hydroxides produced at higher *J* value resulted in higher COD removal efficiency.

It is observed that for $t > 70$ min and $J > 270$ A/m^2, an increase in *t* or *J* value did not improve the COD removal efficiency further. It is due to the fact that all the COD present in the SDW in the colloidal form gets removed at $t \approx 70$ min and $J \approx 270$ A/m^2, the remaining COD which is due to the dissolved organics does not gets removed despite an increase in *t* or *J* value. This may be inferred to the fact that electrochemical phenomena are limited by external mass transfer on the electrodes. Aluminum ion hydroxide species formed during electro-coagulation process stick with the electrode surface and grow like a film with the time. Therefore, performance of the EC process is affected due to extra resistance imposed by this film, and hence, COD removal is limited (Ghosh et al., 2008). Additionally, if the adsorption of organics on various hydroxide species prevails, which is greatly affected by the mixing, this may also be sensitive to external mass transfer and limit the COD removal efficiency. Various investigators have suggested that there is probably a transition between a domain of current in which the kinetics of electrolysis is the limiting step and another domain in which removal is limited by physical mechanisms such as mixing (Panizza et al., 2001; Essadki et al., 2009). At higher current, mass transfer could be hindered by the increased gas production also. Fig. 5.2.1b also shows the effect of *m* on the COD removal efficiency from SDW. During ECT with NaCl, chlorine gas gets generated at anode. Depending on the pH, chlorine forms various chlorine species (Cl_2, HOCl and ClO^-) in the reactor. These species can indirectly oxidise the organic material present in the SDW. Fig. 5.2.2 shows the distribution of various species (Cl_2, HOCl and ClO^-) formed as function of the pH (Deborde et al., 2008). ClO^-, which is dominating at higher pH, has been reported as better oxidant among all chlorine species (Deborde et al., 2008). The COD removal efficiency increased with an increase in m for lower J values ($J \leq 180$ A/m^2). However, for $J > 180$ A/m^2, increase in m value decreases COD removal efficiency (Fig. 5.2.1b). The increase in COD removal efficiency with an increase in m at lower J value may be due to an increase in conductivity of the solution which increases the aluminum dissolution rate and hypochlorite concentration in the reactor which indirectly oxidise the COD. However, at higher J values, there is higher aluminum dissolution, and at this condition, increased m value helps in generation of large amount of aluminum ions. Excess aluminum ions cause charge reversal of the negatively charged colloidal particles present in the SDW (Canizares et al., 2005), which causes decrease in COD removal efficiency.

5.2.2.2. ECT of SDW by Fe electrode: Fig. 5.2.3a shows the effect of m and pH on percent COD removal. At higher pH, COD removal efficiency increases with an increase in m value, however at lower pH ($5 \leq pH \leq 7$), COD removal decreases with an increase in m value. The increase in COD removal efficiency at higher pH may be due to the increase in concentration of ClO^- which is considered to be a good oxidant as discussed in section 5.2.2.1 (Fig. 5.2.2). At lower pH ($5 \leq pH \leq 7$), increased amount of Cl^- formed at increased m reacts with Fe^{2+}. Thus at higher m, amount of Fe^{2+} available for neutralization of negatively charged colloids in SDW decreases which consequently decreases the COD removal efficiency.

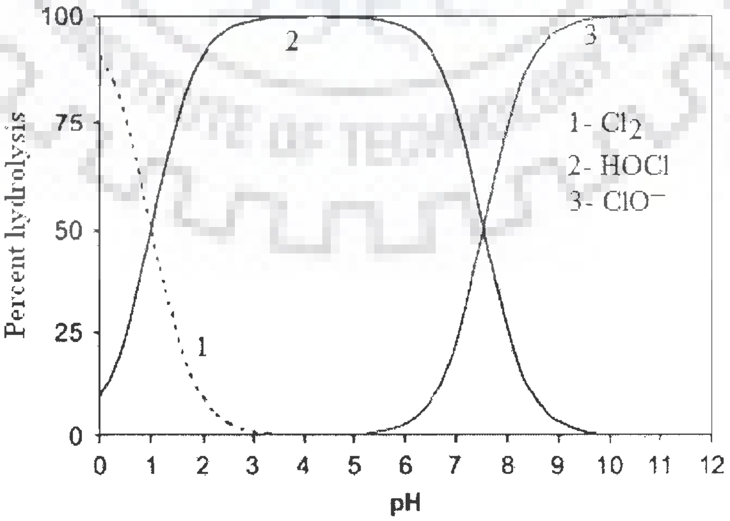
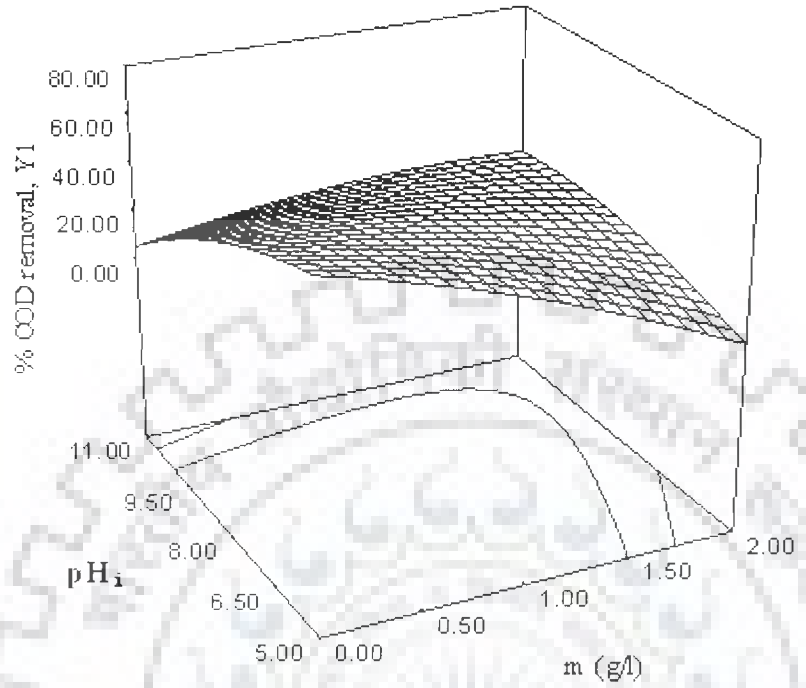
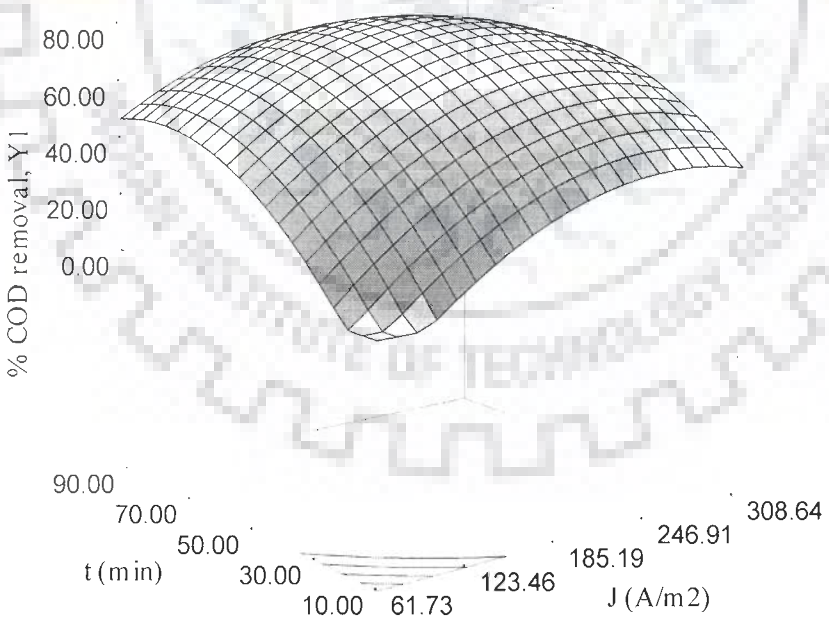


Fig. 5.2.2. Speciation diagram of Chlorine species.



(a)



(b)

Fig. 5.2.3. Three-dimensional response surface graphs for the ECT of SDW by Fe electrodes (a) %COD removal, Y_1 versus *m and pH_i at J = 270* A/m^2, *t* = 50 min (b)%COD removal, Y_1 versus *J* and *t* at *m* = 0.0 g/l, *pH* = 7.0

Also, for all values of *m* < 1 g/l, COD removal efficiency increases with an increase in *pH* up to *pH* ≈7.0 beyond that COD removal started decreasing. However, for all *m* > 1 g/l, the effect of *pH* on COD removal efficiency was marginal. Milk proteins contained in the SDW are negatively charged at $pH > pH_{iso}$ (= 4.2) and get destabilized by positively charged iron species like Fe^{2+}, $Fe(OH)^{+}$, etc (Fig. 3.2.1). Thus, the colloidal particles present in the SDW aggregate together to form bigger size flocs and ultimately get removed by settling. Also, the $Fe(OH)_2$ species formed at higher *pH* help in the removal of colloids by sweep coagulation. Since the optimum *pH* was found to be ≈7.0, charge neutralization of anionic colloids by Fe^{2+} help in maximum COD removal at *pH*≈7.0. However, for the higher *pH* range, a decrease in concentration of Fe^{2+} ions and formation of negatively charged $Fe(OH)_3^-$ at higher *pH* causes reduction in COD removal (Fig. 3.2.1).

Fig. 5.2.3b shows the dependence of the COD removal efficiency on *J* and *t*. Fig. 5.2.3b reveals that there is no COD removal for $J <$ 123.46 A/m^2 and $t <$ 30 min. Beyond these points, COD removal efficiency increases with an increase in *J* and t up to 270 A/m^2 and 50 min, respectively. The COD removal efficiency depends directly on the concentration of Fe^{2+} ions produced by the electrodes, which in turn as per Faradays law (equation 3.4.8) depends upon the *J* and t. For $J <$ 123.46 A/m^2 and $t <$ 30 min, Fe^{2+} ions generation was not enough to cause any COD removal. However, at higher *J* and *t*, higher COD removal efficiency is found due to generation of higher amount of Fe^{2+} ions. This trend of COD removal was followed for any value of *J* and constant *t*, and vice versa. However, for $J >$ 270 A/m^2 and $t >$ 50 min, an increase in *J* or *t* value did not improve the COD removal efficiency further due to the mass transfer limitations as discussed in section 5.2.2.1.

5.2.3. Effects of J, m, t and pH_i on Y_2

5.2.3.1. ECT of SDW by Al electrode: Fig. 5.2.4 shows the effect of *J*, *m*, *t* and pH_i on energy consumed (kWh) and specific energy consumed (Y_2). It may be seen in Fig. 5.2.4a that energy consumed always increased with *t* for all pH_i, however, Fig. 5.2.4b shows that at higher pH_i (> 6), specific energy consumed decreased with an increase in *t*. This is due to the fact that COD removal was higher at $pH_i > 6$ and $t > 30$ min. Fig. 5.2.4a also shows that energy consumed (kWh) first increased with an increase in pH_i and then decreased for $pH_i > 7$. It is known that hydroxides of aluminum get formed at $pH \approx 7$. These hydroxide species stick on the electrode surface and grow like a film. Increase in resistance due to formation of this film increases the energy consumption at $pH \approx 7$ (Ghosh et al., 2008). It may be seen in the Fig. 5.2.4c,d that an increase in J for any m increased the energy consumed (kWh) and specific energy consumed. Fig. 5.2.4c,d also show that energy consumed and specific energy consumed first decreased with an increase in m value giving minimum values at $m \approx 1$ g/l, and thereafter, both increased with an increase m. This trend was followed at every J. At a constant J, an increase in m value reduces the voltage between the electrodes, and hence energy consumed gets reduced for a given amount of COD removal. However, at high m (> 1 g/l), chlorine species get formed during EC treatment, thus, consuming a high percentage of the applied current and increasing the energy consumed (Díaz et al., 2010).

5.2.3.2. ECT of SDW by Fe electrode: It may be seen in Fig. 5.2.5a that specific energy consumed (Y_2) always increased with t for all pH_i. For $pH_i < 7$, increase in specific energy consumed is marginal, but for $pH_i > 7$, specific energy consumed is sharp. It has been explained earlier in section 5.2.2.2 that maximum COD removal was found at $pH_i \approx 7$ and beyond that COD removal started decreasing. Due to this specific energy consumed is marginal for $pH_i < 7$, and increases sharply for $pH_i > 7$. The effect of m and J on energy consumption is shown in Fig. 5.2.5b. It may be seen that at any J, an increase in m value from 0 to 1 g/l lead to decrease in specific energy consumed. This may be due to the fact that addition of NaCl to the solution increases the conductivity and reduces the voltage required between the electrodes to produce a constant J, and hence energy consumed gets reduced for a given amount of COD removal. However, further increase in m from 1 to 2 g/l lead to an increase in energy consumed. This may be due to the fact that at higher sodium chloride concentration, chlorine species get formed during the EC process, thus, consuming a high percentage of the applied current and increasing the energy consumed (Díaz et al., 2010).

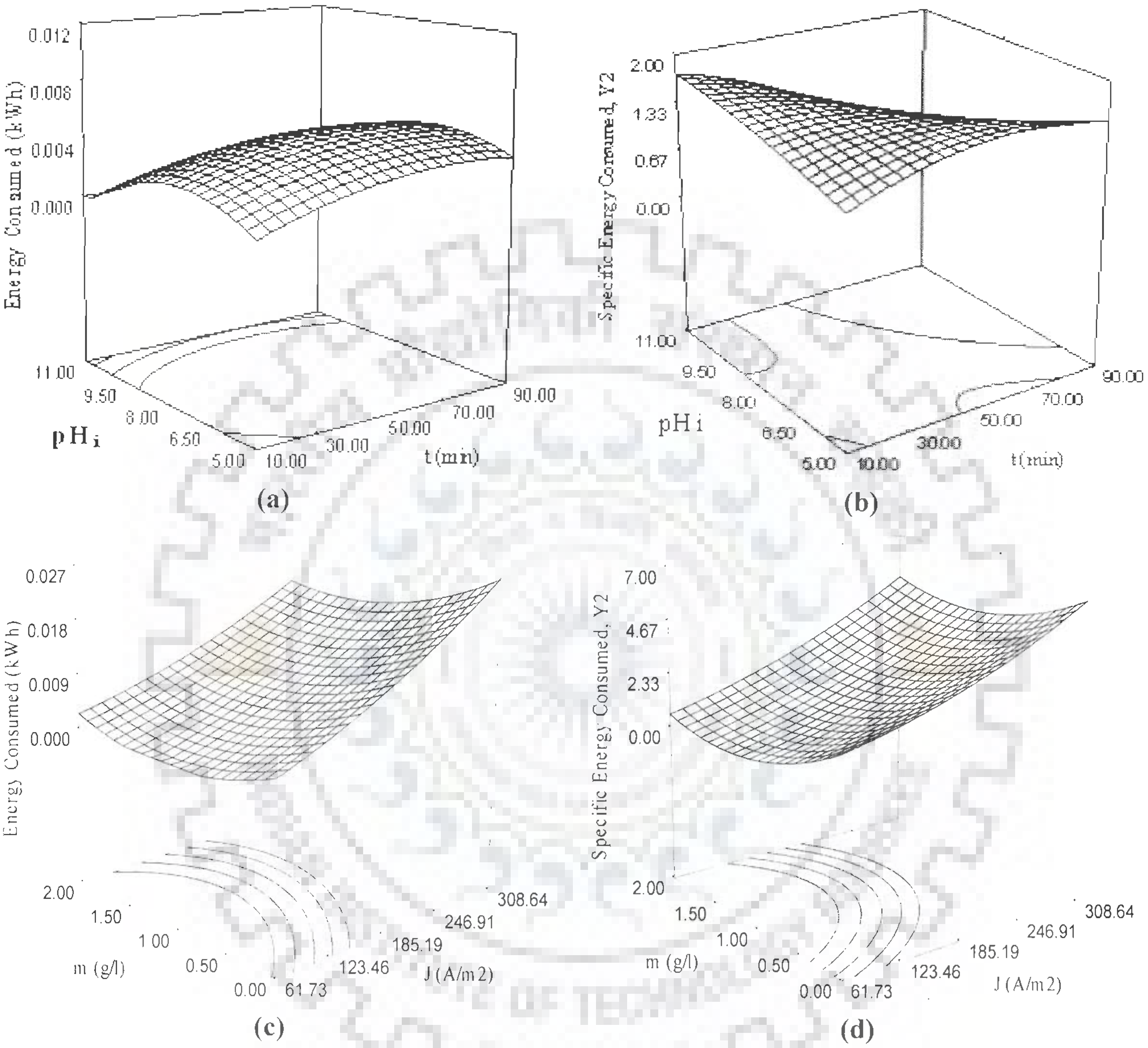


Fig. 5.2.4. Three-dimensional response surface graphs for the EC treatment of SDW by Al electrode (a) Energy consumed (kWh) versus *t* and *pH_i* at *m* = 2.0 g/l, *J* = 123.46 A/m^2; (b) Specific energy consumed, Y_2 versus *t* and *pH_i* at *m* = 2.0 g/l, *J* = 123.46 A/m^2; (c) Energy (kWh) consumed versus *J* and *m* at *t* = 74 min, pHi **= 6.5; and (d) Specific energy consumed, Y_2 versus *J* and *m* at *t* = 74 min, *pH_i* = 6.5.**

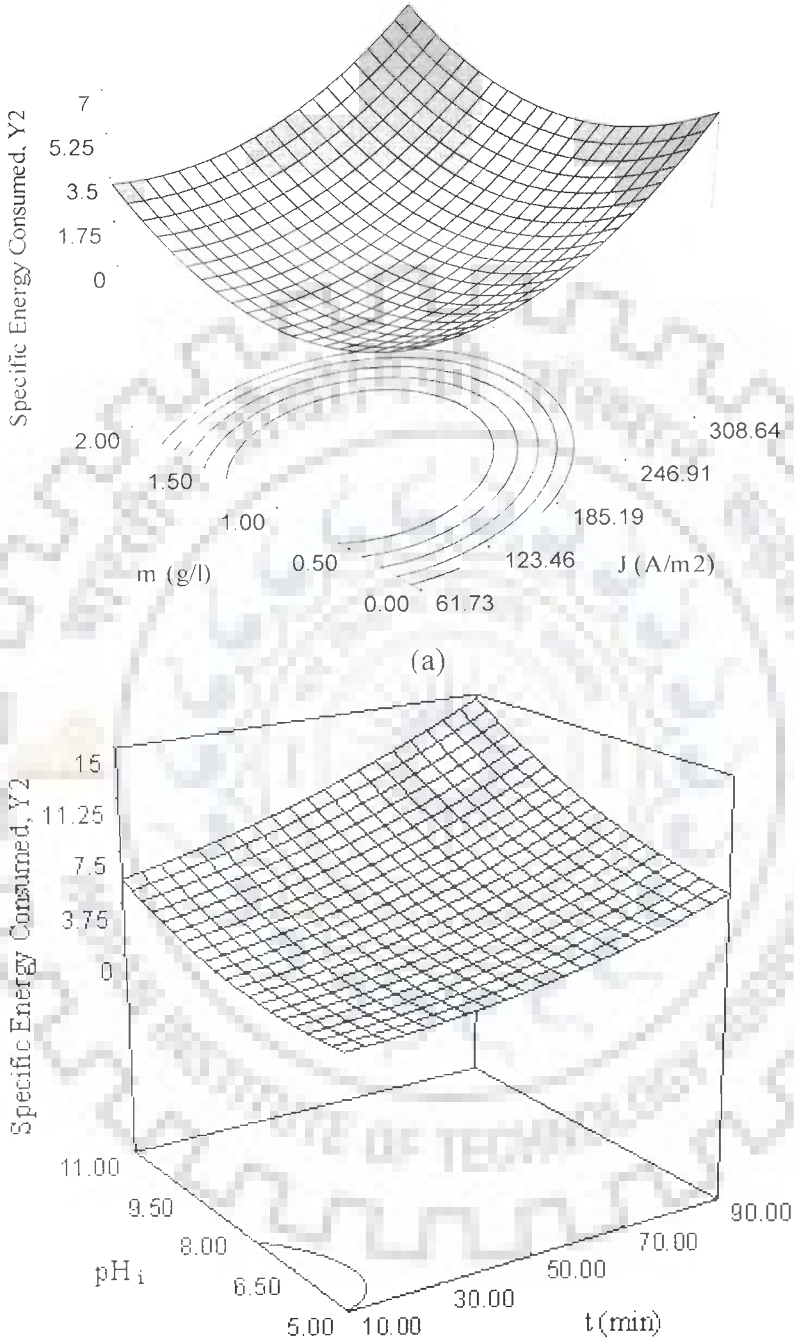


Fig. 5.2.5. Three-dimensional response surface graphs for the ECT of SDW by Fe electrodes (a) Specific energy consumed, Y_2 versus *J* and *m* at *t* = 50 min, *pH* = 7.0 (b) Specific energy consumed, Y_2 versus *t* and pH_i at *m* = 0.0 g/l, *J* = 270 A/m^2.

5.2.4. Optimization Analysis

For ECT treatment of SDW, response Y_1 is to be maximized while Y_2 is to be minimized. Since the optimum conditions for responses Y_1 and Y_2 are not same, the desirability function approach could be utilized to get the maximum Y_1 and minimum Y_2 simultaneously. The constraints applied for the optimization of various operational parameters is given in Table 5.2.7.

5.2.4.1. ECT of SDW by Al electrode: For Y_1 and Y_2 the minimum acceptable values considered are 55% and 1.55 kWh/kg COD removed (minimum experimental value which does not depend on any factors and interaction of factors) and maximum values are 100% and 5.0 kWh/kg COD removed (the maximum value that may reach), respectively. Thus, one-sided desirability of Y_1 (d_1) is achieved as follow:

$$d_1 = \begin{cases} 0 & \text{if} \quad Y_1 \le 55 \\ [\frac{Y_1 - 55}{100 - 55}] & \text{if } 55 < Y_1 < 100 \\ 1 & \text{if } Y_1 \ge 100 \end{cases} \tag{5.2.5}$$

In a same way, one-sided desirability of Y_2 (d_2)

$$d_2 = \begin{cases} 1 & \text{if} \quad Y_2 < 0.56 \\ [\frac{5 - Y_2}{5 - 0.56}] & \text{if } 0.56 \le Y_2 \le 5 \\ 0 & \text{if } Y_2 > 5 \end{cases} \tag{5.2.6}$$

In the above both equations $r = 1$. The overall desirability D is calculated by the following equation:

$$D = \sqrt{d_1 d_2} \tag{5.27}$$

By using D as a new desirability, the optimum values of operational parameters were found to be $J = 123.46$ A/m^2, $m = 2.0$ g, $t = 74$ min and $pH_i = 6.5$ which produced overall $D = 0.515$. The responses Y_1 and Y_2 were 70.91% and 1.32 kWh/kg COD removed (Table 5.2.8 and 5.2.9).

To verify the optimization result three verification run were conducted with the optimized set of operational parameters. The average value of responses Y_1 and Y_2 were found to be 68% and 1.2 kWh/kg COD removed, respectively, which are very close to predicted values (Table 5.2.9). Other parameters like TS, TKN and turbidity removal efficiencies were also evaluated at the optimum condition and were found to be 54.3%, 90.9% and 99.8%, respectively (Table 5.2.10).

At optimized set of operational parameters, dissolved amount of aluminum electrodes after EC treatment was calculated and found to be 0.343 g. Dissolved mass of aluminum corresponded to 84% of the theoretical amount expected. The lower value of anode performance was probably due to the competition between Al^{3+} ions dissolution and O_2 and Cl_2 evolution at the anode (Gao et al., 2010). Also, the formation of hydroxide film at the anode surface lowers the anode performance (Ghosh et al., 2008).

pH of the ECT system changes with time. Fig. 5.2.6 shows the final pH_f with time (t) for the run carried out under optimum condition. It is clear from Fig. 5.2.6 that pH_f increased from 6.5 to 7.85 within 5 min and after 30 min pH_f stabilizes to ≈8.5. This equilibrium pH_f is due to a dynamic balance between the complex chemical reactions involving a H^+ or OH^- donor and acceptor during ECT. This stable alkaline pH_f can be attributed to the cathodic water reduction, equation 3.2.8, being predominant over the anodic water oxidation, equation 3.2.7 and aluminum hydroxylation reactions equations (3.1.4-3.1.7) (Ahlawat et al., 2008).

From the speciation of Al (III) (Fig. 3.1.2), $Al(OH)_4^-$ fully dominates after $pH \approx 7.5$, which is not efficient to remove COD. Therefore, there should be no COD removal for $pH \geq 7.5$, but, experimentally, it was seen that still there is COD removal. COD removal for $pH \geq 7.5$ is due to the hypochlorite formation in the reactor (formed by successive reaction from chlorine) which indirectly oxidise the COD. For $6.5 \leq pH < 7.5$, various positively charged hydrolyzed aluminum species are responsible for the COD removal (explained in section 3.1).

Therefore, both electro-coagulation and electro-oxidation mechanisms are responsible for the SDW treatment, and hence, ECT is the real mechanism of SDW treatment.

Table 5.2.7. Constraints applied for the optimization of ECT of SDW by Al and Fe electrode.

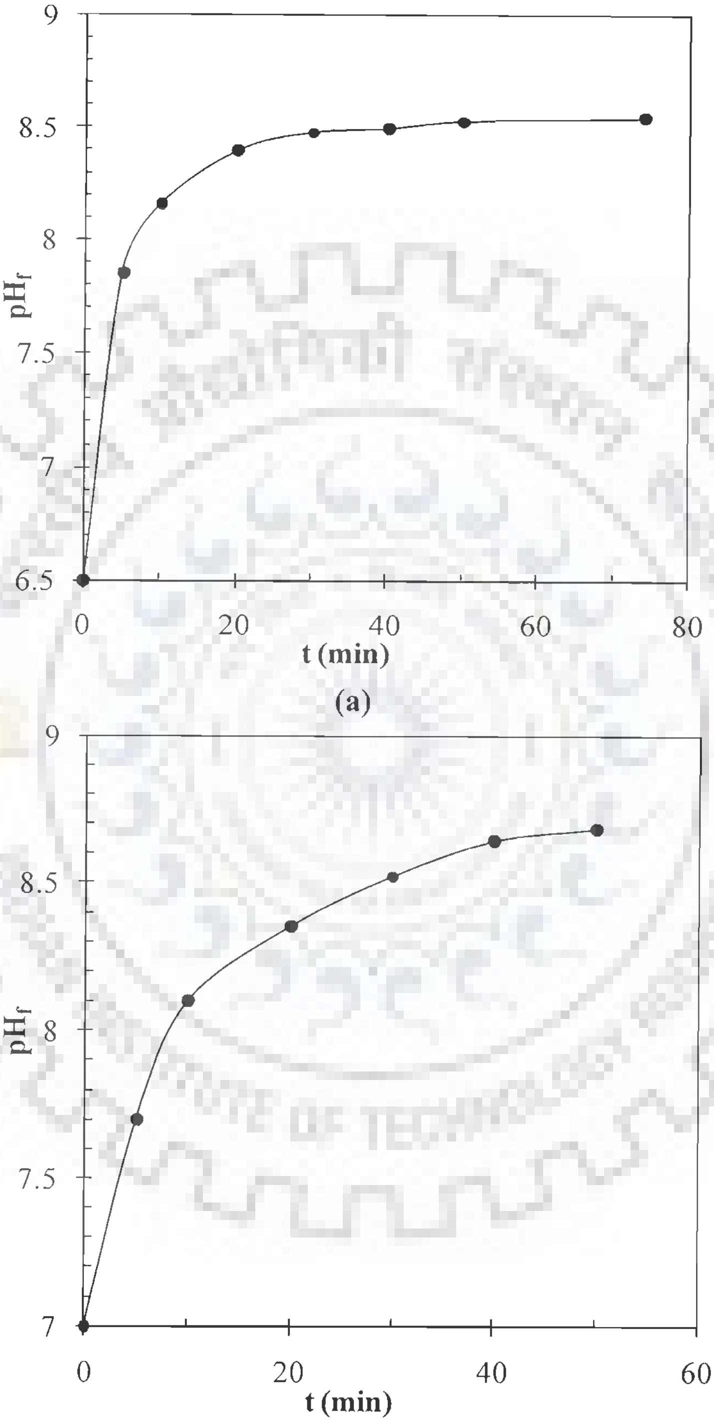
Variables	Objective	Lower Limit	Upper Limit
Al electrode			
J (Am^{-2})	minimize	123.46	308.64
m (g/l)	is in range	0	2
t (min)	minimize	10	90
pH_i	is in range	5	7
Fe electrode			
J (Am^{-2})	minimize	200	308.64
m (g/l)	is in range	0	2
t (min)	minimize	10	90
pH_i	is in range	5	7

Table 5.2.8. Optimum condition for ECT of SDW by Al and Fe electrode.

Variables	Optimum values	
	Al electrode	Fe electrode
J (Am^{-2})	123.46	270
m (g/l)	2.0	0.0
t (min)	74	50
pH_i	6.5	7.0

Table 5.2.9. Experimental and predicted values of Y_1 and Y_2 at optimum condition.

Parameters		ECT by Al electrode	ECT by Fe electrode
D		0.515	0.664
Y_1	**Pre**	70.21%	72.5%
	Exp	68.08%	70%
Y_2	**Pre**	1.32	2.61
	Exp	1.22	2.76



(a)

(b)

Fig. 5.2.6. Graph of *t* versus pH_f for the ECT of SDW at optimum condition by (a) Al electrode (b) Fe electrode.

5.2.4.2. ECT of SDW by Fe electrode: For Y_1 and Y_2, the minimum acceptable values considered that does not depend on any factors and interaction of factors are 45% and 0.96 kWh/kg COD removed and maximum values are 100% and 15.0 kWh/kg COD removed (the maximum value that may reach), respectively. Thus, one-sided desirability of Y_1 (d_1) is achieved as follow:

$$d_1 = \begin{cases} 0 & if \quad Y_1 \le 45 \\ [\dfrac{Y_1 - 45}{100 - 45}] & If \; 45 < Y_1 < 100 \\ 1 & if \; Y_1 \ge 100 \end{cases} \tag{5.2.8}$$

In a same way, one-sided desirability of Y_2 (d_2)

$$d_2 = \begin{cases} 1 & if \quad Y_2 < 0.37 \\ [\dfrac{15 - Y_2}{15 - 0.37}] & If \; 0.56 \le Y_2 \le 15 \\ 0 & if \; Y_2 > 15 \end{cases} \tag{5.2.9}$$

By using $D = \sqrt{d_1 . d_2} = 0.664$ as a new desirability, optimum value of J, t and pH were found to be 270 A/m^2, 50 min, and 7.0, respectively, while m was found to be zero (Table 5.2.8 and 5.2.9). The responses Y_1 and Y_2 were 72.5% and 2.61 kWh/kg COD removed. By conducting three verification runs at the optimized set of operational parameters, average value of responses Y_1 and Y_2 were found to be 70% and 2.76 kWh/kg COD removed, respectively, which are very close to predicted values (Table 5.2.9). Other parameters like TS, TKN and turbidity removal efficiencies were also evaluated at the optimum condition and were found to be 48.2%, 92.75% and 99.8%, respectively (Table 5.2.10).

Fig. 5.2.6 shows the final pH_f with time (t) for optimum condition run. pH_f increased from 7.0 to 8.3 within 20 minutes and after that up to 50 min pH_f increased to 8.6 which is nearly constant. This equilibrium pH_f is due to a dynamic balance between the complex chemical reactions involving a H^+ or OH^-donor and acceptor during ECT.

Table 5.2.10. Characteristics of SDW and treated SDW by ECT at optimum condition.

Parameters	**Average Value**		
	Before EC treatment	**After EC treatment by Al electrode**	**After EC treatment by Fe electrode**
pH	6.5	8.6	8.6
COD (mg/l)	3900	1245	1170
Total solids (mg/l)	3090	1410	1485.5
Turbidity (NTU)	1740	2.0	3.49
Chloride (mg/l)	31	24.2	22.63
Total Kjeldahl Nitrogen (TKN) (mg/l)	113	10.3	8.2

5.2.5. Operating Cost Analysis

The major contributor to operating cost, electrical energy cost (C_{energy}) and consumed electrode cost ($C_{electrode}$) required to treat one Kg of COD by ECT of SDW at optimum condition with Al and Fe electrodes were calculated (Table 5.2.11).

Dairy plant generates wastewater having COD in the range of 0.43-15.2 kg/m^3 (Passeggi et al., 2009). In the present study, 68 and 70% COD removal was observed by Al and iron electrodes, respectively, at optimum conditions. Therefore, to reduce COD of one m^3 of dairy wastewater to 0.137-4.851 kg/m^3 by Al electrode and 0.129-4.6 kg/m^3 by Fe electrode, combined C_{energy} and $C_{electrode}$ cost is in the range of ₹ 5.6–199.35 and ₹ 3.24–114.75 by Al and Fe electrode, respectively.

Table 5.2.11. Cost Analysis of SDW treatment by ECT at optimum condition.

Cost	**Aluminum**	**Iron**
Electrical energy consumed (kWh/kg of COD removed)	1.22	2.76
Electrical energy price in India (₹ per kWh)	3.10	
C_{energy} (₹ per kg of COD removed)	3.78	8.55
Electrode consumed (g/kg of COD removed)	86.12	54.95
Electrode price in the India (₹), per kg	180.0	40.0
$C_{electrode}$ (₹ per kg of COD removed)	15.50	2.20
Total Cost **(₹ per kg of COD removed)**	**19.28**	**10.75**

1 $≈47 ₹

5.2.6. Physico-Chemical Analysis of Electrodes and Residues

5.2.6.1. ECT of SDW by Al electrode: The morphologies of electrodes and residues were examined by conducting SEM and EDX analysis. SEM images of fresh aluminum electrode, used electrode before and after cleaning are shown in Fig. 5.2.7 and dried residues are shown in Fig. 5.2.8. From the SEM of fresh aluminum electrode (Fig. 5.2.7a), it can be observed that there are fewer dents on the surface prior to its use for ECT of SDW, however, the surface is rough. Fig. 5.2.7b shows the SEM of the same electrode in one ECT experiment before its cleaning. Amorphous organics clearly can be seen deposited on the surface of the uncleaned aluminum electrode. Fig. 5.2.7c shows the SEM of cleaned electrode after its several uses in ECT experiments. Cleaned electrode surface is now found to contain a number of dents of varying sizes formed around the active sites where the electrode dissolution took place producing aluminum ions.

SEM images of dried sludge and scum obtained during the ECT of SDW is shown in Fig. 5.2.8. This figure reveals surface texture and porosity of the sludge and scum. Fig. 5.2.8a shows that the sludge is having harder texture as compared to scum. Scum (Fig. 5.2.8b) has puffy texture with pores of varying sizes on the surface. The puffy texture of scum is due to the evolution of hydrogen gas from cathode of ECT system.

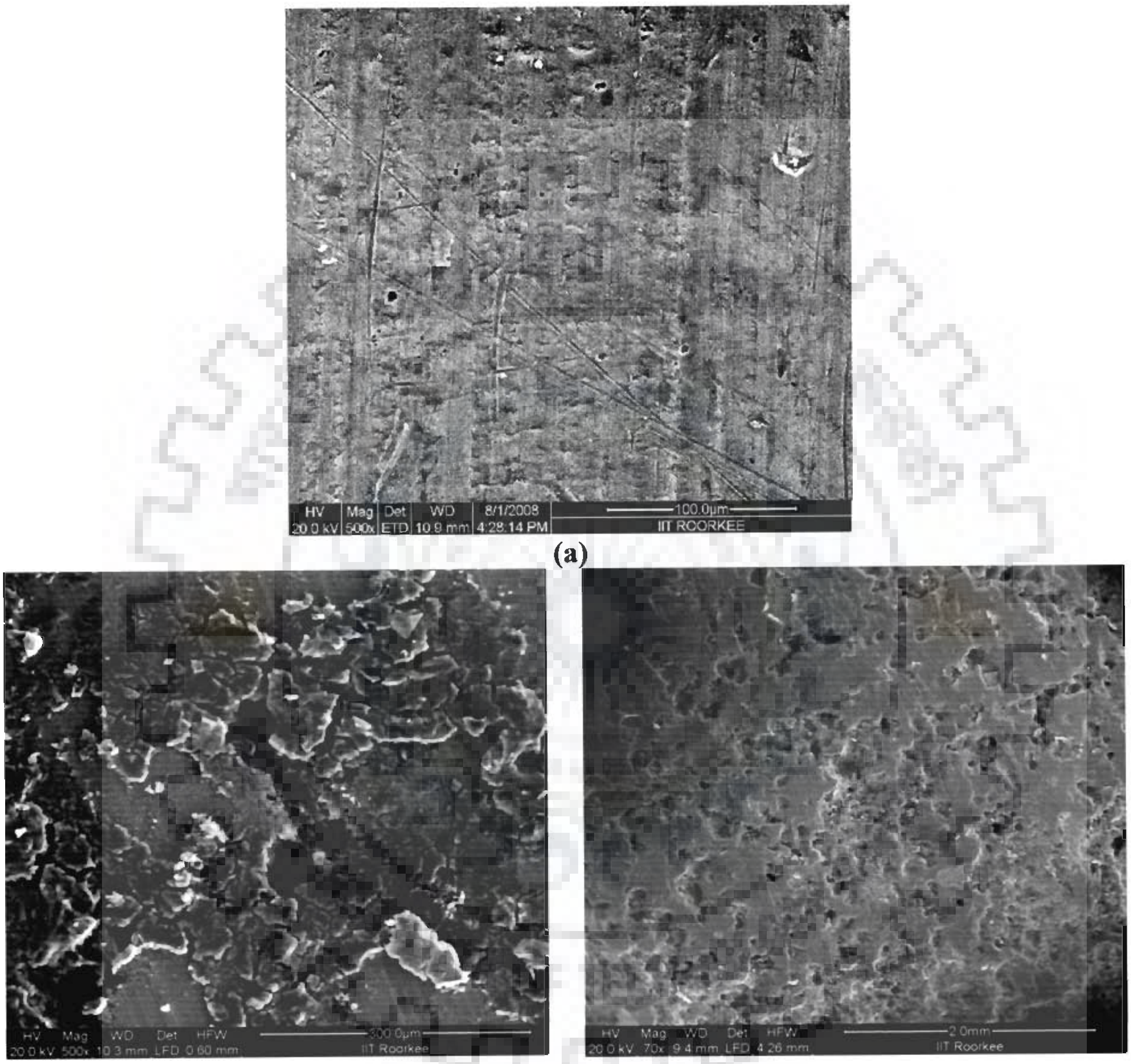
EDX was conducted to study the distribution of the elements in sludge and scum generated at optimum condition by ECT of SDW. EDX analysis showed the presence of 64.3% and 69.9% carbon, 23.8% and 19.31% oxygen, 9.10% and 8.34% aluminum, 0.34% and 0.77% sulphur, 0.12% and 0.52% potassium, 2.30% and 0.90% calcium; and 0.39% and 0.28% iron in sludge and scum, respectively. Thus, scum is found to contain higher amount of carbon as compared to sludge. Considering this fact, it seems that electro-flotation is much more effective than electro-coagulation in COD removal.

Aluminum mass balance was also performed for sludge and scum generated at optimum condition and calculation is shown in Table 5.2.12. Out of the total aluminum dissolved from the electrodes into the reactor, 27-29.21% goes to the scum, 71.1-73.33% goes into the sludge and rest goes to the treated SDW.

Treated SDW contained 9.54 mg/l of aluminum. No limit has been set by Government of India for discharge of aluminum containing effluents. EPA has also not given any maximum concentration limit on aluminum in its national primary drinking water regulations. However, it has prescribed a limit of 0.2 mg/l in national secondary drinking water regulations which are not mandatory (EPA). Obviously, the treated effluent will require further treatment by other physico-chemical and biological method to remove the remaining COD, aluminum, etc.

Table 5.2.12. Al mass balance calculation at optimum condition (Basis: 1.5 litre of SDW).

Total aluminum introduced	
Aluminum in SDW (mg/l)	0.09
Total aluminum in SDW (g)	0.0001
Aluminum eroded by electrolysis (g) (Experimentally determined)	0.343
Total aluminum going in to the system (SDW feed + eroded) (g)	0.3431
Total aluminum in residues and treated SDW	
Sludge generated (g)	2.68
Total aluminum in sludge (g)	0.2439
Scum generated (g)	1.11
Total aluminum in scum (g)	0.0926
Al in treated SDW (mg/l)	9.54
Total aluminum in treated SDW (g)	0.0143
Total aluminum (residues + treated SDW) (g)	0.3508
% Error	**-2.22**

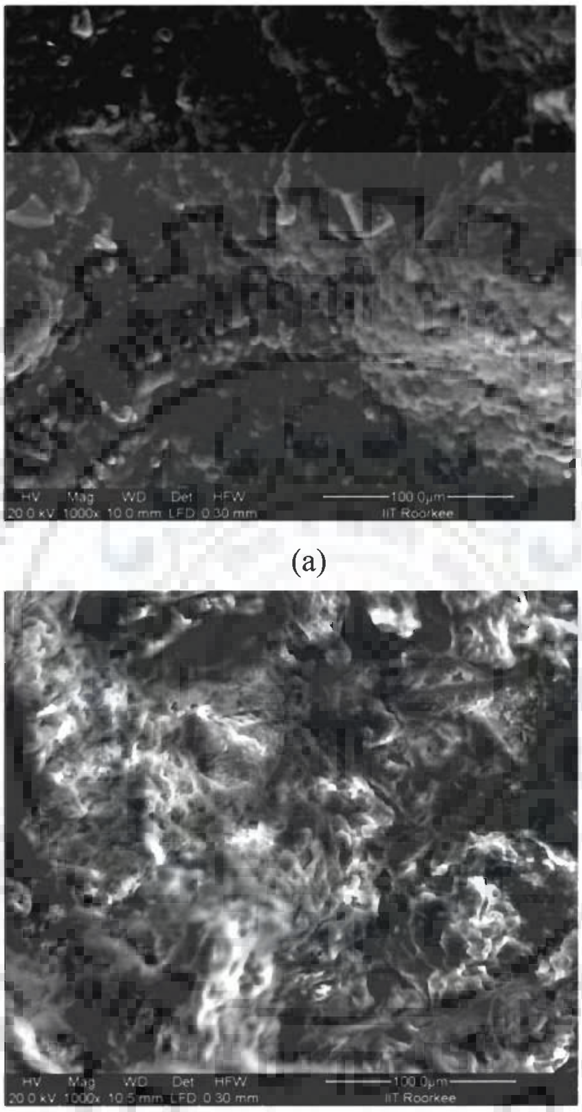


(a)

(b)

(c)

Fig. 5.2.7. SEM images of aluminum electrode (a) un-used (b) un-cleaned (c) cleaned after its use in ECT of SDW.



(a)

(b)

Fig. 5.2.8. **SEM images of generated (a) sludge (b) scum by ECT of SDW with Al electrode.**

5.2.6.2. ECT of SDW by Fe electrode: To study the morphologies of electrodes and residues, SEM and EDX analysis were conducted. SEM images of fresh iron electrode used electrode before and after cleaning and of dried sludge and scum obtained during the ECT of SDW are shown in Fig. 5.2.9. The SEM of fresh iron electrode (Fig. 5.2.9a) revels fewer dents and rough surface prior to its use in ECT of SDW, however, the. Fig 5.2.9b shows the SEM of the same electrode in one ECT experiment before its cleaning. Organics from the SDW clearly can be seen deposited on the uncleaned iron electrode surface. While, a number of dents of varying sizes formed around the active sites where the electrode dissolution took place, were found on cleaned electrode surface after its several uses in EC experiments (Fig. 5.2.9c). SEM images of dried sludge and scum obtained during the ECT of SDW are shown in Fig. 5.2.10. Fig. 5.2.10 shows hard surface texture of the sludge and scum. There are no pores on the surface of sludge (Fig. 5.2.10a), however, pores of varying sizes can be seen on the surface of scum (Fig. 5.2.10b). The porous characteristic of scum is due to hydrogen evolution through scum.

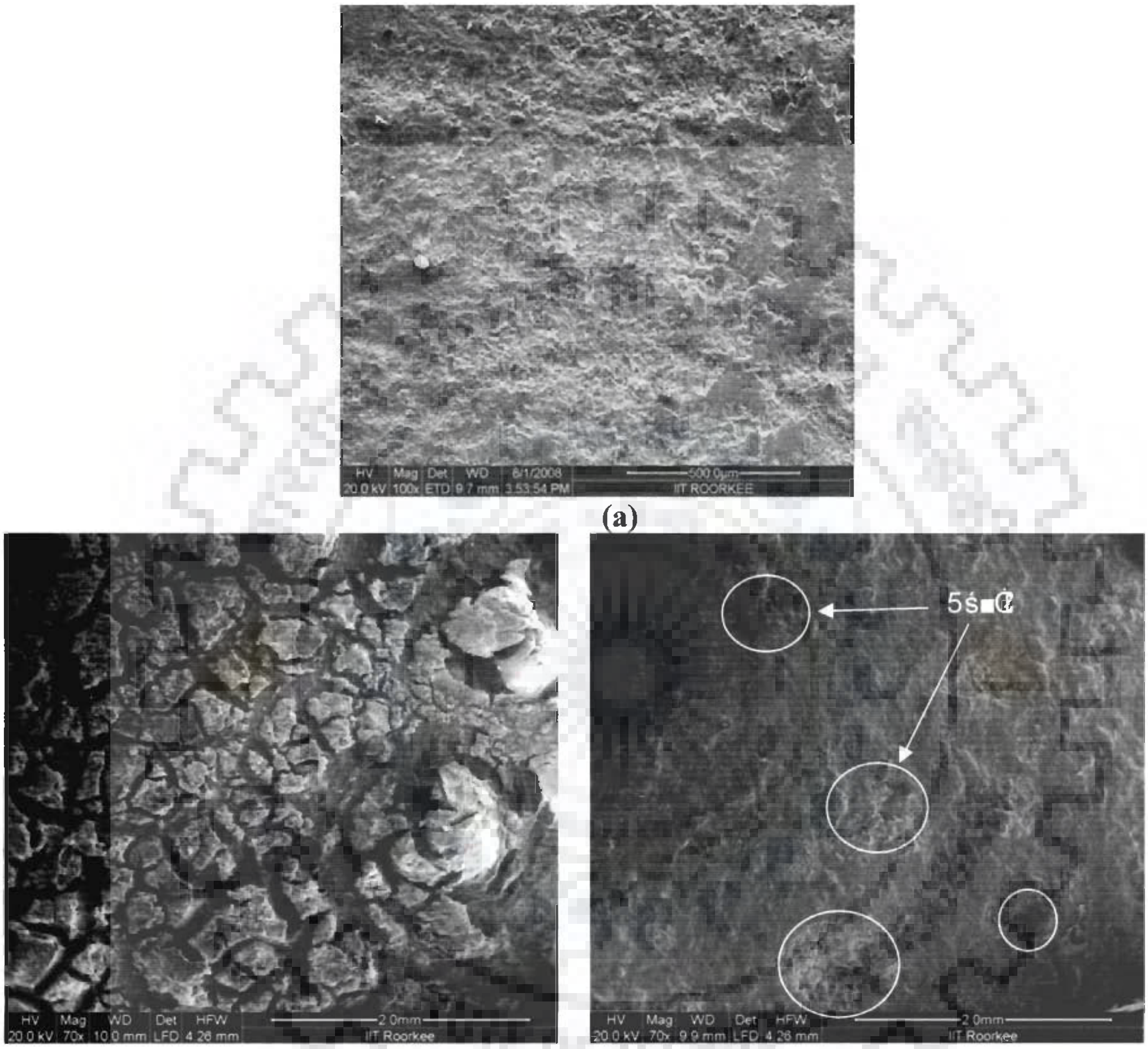
EDX was conducted to study the distribution of the elements in generated sludge and scum by EC of SDW. EDX analysis showed the presence of 60.5% and 82.7% carbon, 26.5% and 10.4% oxygen, 0.72% and 0.85% aluminum, 0.21% and 0.50% sulphur, 0.32% and 0. 20% potassium, 0.89% and 0.91% calcium; and 10.86% and 4.45% iron in sludge and scum, respectively. Thus, scum is found to contain higher amount of carbon as compared to sludge whereas sludge is found to contain higher amount of iron. The mechanism of COD removal by ECT seems to be a combination of electro-coagulation, electro-floatation and electro-oxidation. But considering the fact that scum is found to contain higher amount of carbon as compared to sludge, it seems that electro-flotation is much more effective than electro-coagulation in COD removal.

Fe mass balance was also performed for sludge and scum generated at optimum condition and calculation is shown in Table 5.2.13. Out of the total Fe dissolved from the electrodes into the reactor, 4-7.4% goes to the scum, 81.5-85% goes into the sludge and rest goes to the treated SDW.

Treated SDW contained 6.74 mg/l of Fe. Central Pollution Control Board (CPCB), Government of India has prescribed maximum concentration limit of 3 mg/l of Fe in general standards for discharge of environmental pollutants (part-A: effluents). Obviously, the treated effluent will require further treatment by other physico-chemical and biological method to remove the remaining COD, Fe, etc.

Table 5.2.13. Fe mass balance calculation at optimum condition (Basis: 1.5 litre of SDW).

Total Fe introduced	
Fe in SDW (mg/l)	0.5
Total Fe in SDW (g)	0.0008
Fe eroded by electrolysis (g) (Experimentally determined)	0.23
Total Fe going in to the system (SDW feed + eroded) (g)	0.23
Total Fe in residue and treated SDW	
Sludge generated (g)	1.76
Total Fe in sludge (g)	0.19
Scum generated (g)	0.37
Total Fe in scum (g)	0.02
Fe in treated SDW (mg/l)	6.74
Total Fe in treated SDW (g)	0.01
Total Fe (residues + treated SDW) (g)	0.22
% Error	**3.54**

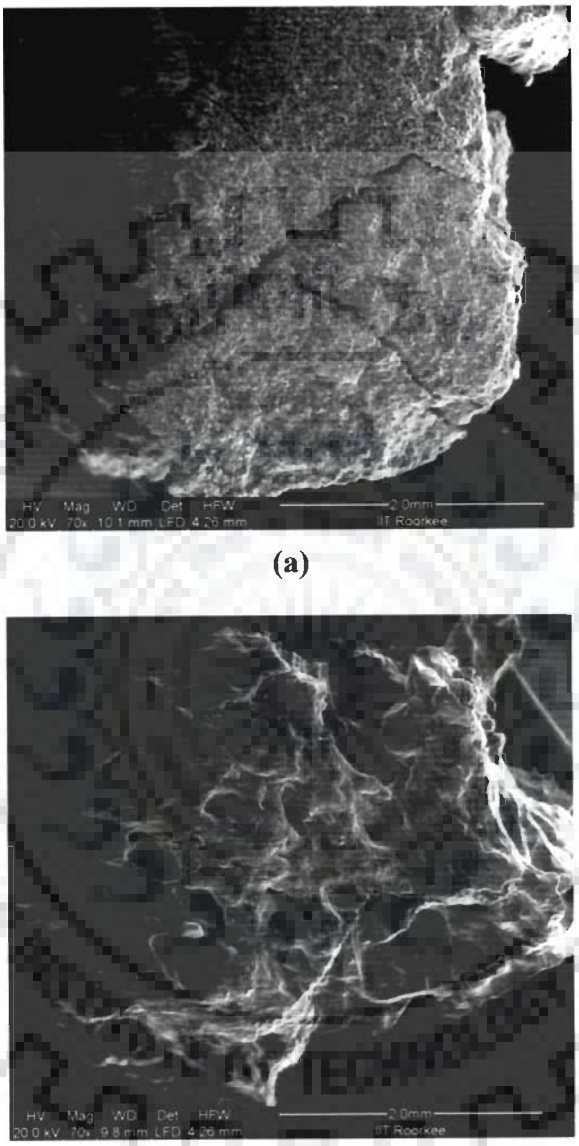


(a)

(b)

(c)

Fig. 5.2.9. SEM images of fe electrode **(a)** un-used **(b)** un-cleaned **(c)** cleaned after its use in ECT of SDW by Fe electrode



(a)

(b)

Fig. 5.2.10. SEM images of generated (a) sludge (b) scum by ECT of SDW with Fe electrode.

5.2.7. Thermal Analysis of Residues

To check whether the generated sludge and scum could be oxidized as fuel in high temperature conditions such as those encountered in boilers and furnaces, thermal degradation characteristics of the sludge and scum were studied by thermogravimetric (TG) instrument.

5.2.7.1. ECT of SDW by Al electrode: The thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) curves of the sludge and scum for the heating rate of 10 °C /min in the environment of air are shown in Fig. 5.2.11. The TG traces can be divided in three oxidation zones. First oxidation zone (23-200 °C for sludge and 20-250 °C for scum) describes loss of moisture and some volatile matter evolution. In this zone, there is loss of 9.4% and 11.7% mass of sludge and scum, respectively. Drying at higher temperature (> 100 °C) occurs due to loss of the bound moisture of the particles. The lack of endothermic peak in the first oxidation zone indicates the lack of any phase change during the heating process. The second oxidation zone lies between 200 to 550 °C and 250 to 600 °C for the sludge and scum, respectively. In this zone, the weight loss ~57.2% and ~68.3% was observed for sludge and scum, respectively. The strong exothermic peak for sludge and scum centred between 250 to 400 °C shows the degradation by oxidation. It can also be seen that scum has higher exothermicity than sludge (Fig. 5.2.11). This is due to higher carbon content of scum which was confirmed by EDX analysis. The weight loss in this zone is mainly due to the carbon oxidation and evolution of CO_2 and CO. A third oxidation zone with weight loss ~1% can be envisaged at higher temperatures up to 1000 °C. Overall, generated sludge and scum by EC treatment of SDW showed total weight loss of 68% and 80.8%, respectively. The higher oxidation of scum may be due to its higher carbon content. The strong exothermic peak associated with oxidation of sludge and scum confirms the high energy evolution.

5.2.7.2. ECT of SDW by Fe electrode: Thermographs of the sludge and scum are shown in Fig. 5.2.12. Thermographs show three thermal breakdown regions of the organic matters present in the residues. There is loss of moisture and low boiling point organic matters up to 200 °C for sludge and scum, and due to this weight loss of 7.7% and 6.8% were observed for sludge and scum, respectively. A sharp decrease in weight loss can be seen from 200 °C for both sludge and scum indicating ignition temperature of both sludge and scum being 200 °C. Highest weight loss of ~50% and ~78.4% within the entire temperature range of study were established in temperature zone 200-450 °C and 200-510 °C for the sludge and scum, respectively. The maximum rate of weight loss of 0.704 mg/min and 0.656 mg/min were obtained at 280 °C and 496 °C for sludge and scum, respectively. Peak temperature is the measure of the combustibility. Lower the peak temperature, easier is the ignition of the fuel. Therefore, sludge is easier to ignite than scum. It can also be seen that scum has higher exothermicity than sludge. Weight loss of ~0.6% and ~1.4% for sludge and scum, respectively, can be envisaged at higher temperature oxidation up to 1000 °C. Overall, generated sludge and scum by EC treatment of SDW showed total weight loss of 58.3% and 86.7%, respectively. The higher oxidation of scum may be due to higher carbon content which was shown in elemental analysis.

5.2.8. Disposal of residues

Heating value of the sludge and scum generated by ECT of SDW by Al electrode were found to be 16.51 MJ/kg and 19.23 MJ/kg, respectively, and by Fe electrode 17.72 MJ/kg and 18.73 MJ/kg, respectively. Thus, the generated sludge and scum by EC treatment of SDW can be dried and used as a fuel in the boilers/incinerators, or can be used for the production of fuel-briquettes. The bottom ash may be blended with clay to make fire bricks, thus, disposing of generated sludge and scum by EC treatment of SDW through chemical and physical fixation (Thakur et al., 2009). Fire clays vary considerably in chemical composition and contain alumina, silica, iron oxides, magnesia, lime, soda, potash, etc. The percentage of alumina and silica (taken together) is high (50-90%), and the percentage of other components is low (Carter et al., 1982; Al-Amaireh, 2009). The bottom ash obtained after incineration of scum and sludge obtained after treatment with Fe electrode contained 67.1% and 60.7% iron, 15.08% and 19.56% oxygen, 0.43% and 8.69% silicon, 5.66% and 3.54% calcium, 3.24% and 3.48% carbon, 4.15% and 2.24% phosphorus, 2.21% and 1.52% nitrogen; and 0.6% and 0.3% aluminum. These bottom ashes may be blended with clay with higher ratio of clay to make fire bricks. Few studies have shown that addition of finely divided materials, such as silica, fly ash, etc. to clays and Portland cement not only increases heat resistance of these materials but also improves the microstructure and compressive strength of cement pastes (Heikal, 2000). Thus, sludge and scum generated by EC treatment of SDW can be disposed off through chemical and physical fixation (Thakur et al., 2009).

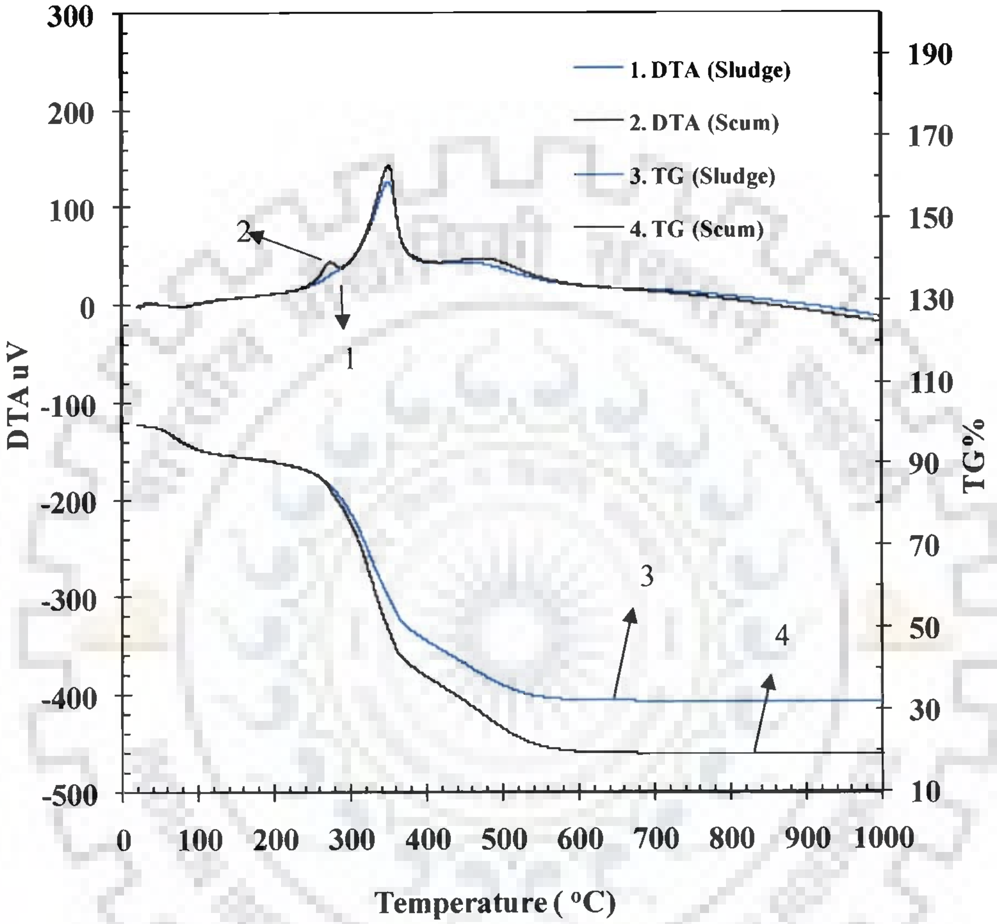


Fig. 5.2.11. TG/DTA of sludge and scum generated by the ECT of SDW with aluminum electrodes at optimum conditions.

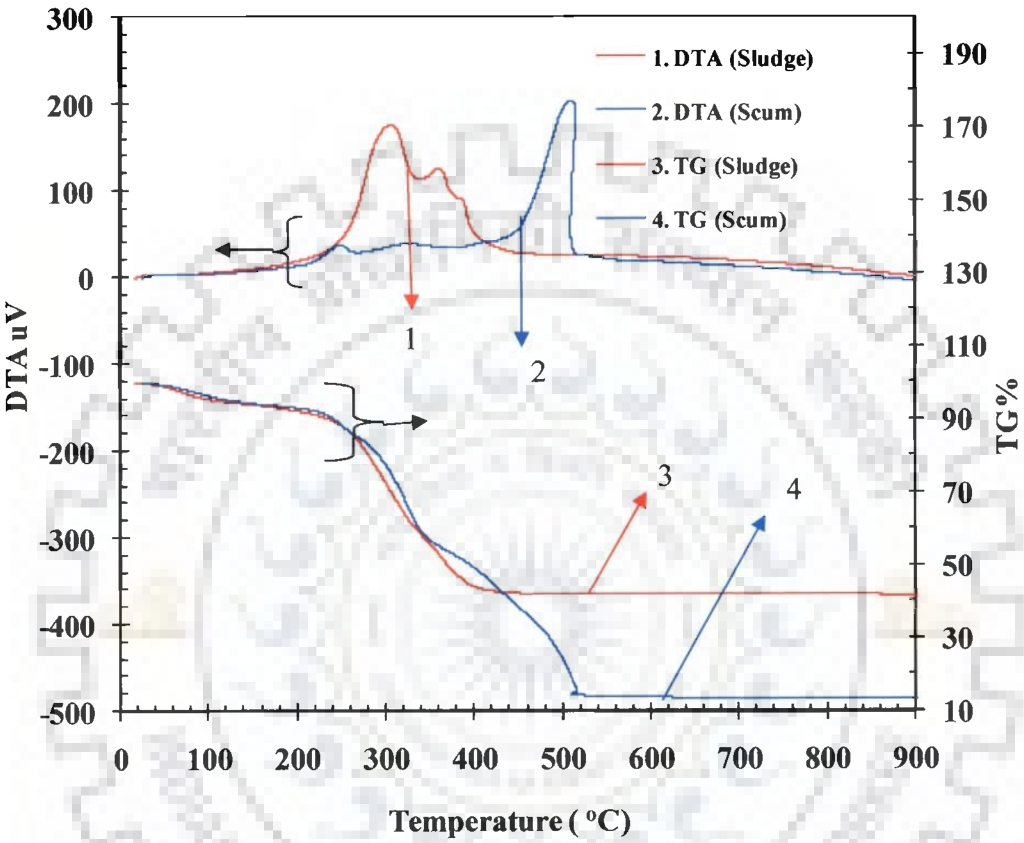


Fig. 5.2.12. TG/DTA of sludge and scum generated by the ECT of SDW with Fe electrodes at optimum conditions.

Chapter – 6

ADSORPTION

6.0. GENERAL

This chapter describes the materials, methods, results and their discussion for the adsorptive treatment of SDW by adsorbents such as activated carbon commercial-grade (ACC) and bagasse fly ash (BFA).

6.1. MATERIALS AND METHODS

6.1.1. Wastewater

SDW used in this study was the same as used for coagulation and ECT. Its method of preparation and characteristics are described in section 4.1.1.

6.1.2. Adsorbents and their Characterisation

All the chemicals used have been described in section 4.1.2. Coconut-based ACC was supplied by Zeo-Tech Adsorbents Pvt. Ltd., New Delhi, India. It was used as procured, except for the removal of very fine particles by sieving. BFA was collected from the particulate collection device attached to the flue gas line of a bagasse-fired boiler stack from a nearby sugar mill (Deoband sugar mill, U.P., India). It was used as an adsorbent without any pretreatment. Important characteristics of ACC and BFA are as follows:

The average particle size of ACC and BFA were 1.67 mm and 0.177 mm, respectively. Bulk density and heating value of ACC were determined as 599.3 kg/m^3 and 18.8 MJ/kg, respectively. For BFA, respective values were 185.5 kg/m^3 and 19.2 MJ/kg, respectively. The d-spacing values provided by the XRD spectra of ACC reflected the presence of Moganite (SiO_2), Akdalaite ($(Al_2O_3)_4.H_2O$), Tamarugite ($NaAl(SO_4)_2.6H_2O$) Fersilicate (FeSi) and Majorite ($Mg_3(Fe,Al,Si)_2(SiO_4)_3$) whereas Silica ($SiO_2$), Wollastonite ($CaSiO_3$), Aragonite ($CaCO_3$) and Akdalaite ($(Al_2O_3)_4.H_2O$) were the major components identified in BFA.

The BET surface area of ACC and BFA were 336.6 and 168.4 m^2/g, respectively. The analysis of the BJH adsorption pore distribution for ACC showed that the micro-pores ($d < 20$ Å) had a total pore area of about 24%, meso-pores accounted for about 76% of the total pore area. The analysis of BFA showed that the meso-pores ($20 \text{ Å} < d < 500 \text{ Å}$) had a total pore area of about 99% and that the macro-pores accounted for about 1% of the total pore area. The BET average pore diameter of ACC and BFA were found to be 31.03 and 25.54 Å, respectively. Thus, BFA exhibits higher meso-porous nature among the two adsorbents.

6.1.3. Analytical Methods

Various analytical methods used have been described in section 4.1.3.

6.1.4. Experimental Programme

For each experiment, a known amount of the adsorbent was introduced into 100 ml stoppered conical flasks in which 100 ml of the SDW of known COD and pH_i was already present. This mixture was kept in a temperature-controlled shaker at a constant speed of 150 rpm at a pre-decided constant temperature for 8 h to attain the equilibrium. The adsorbent was separated from the wastewater after 8 h and analysed for COD. The percentage removal of COD was calculated using the following relationship:

$$\text{Percent COD removal} = \frac{(C_0 - C_e)100}{C_0} \qquad (6.1.1)$$

Where, C_e is the equilibrium COD concentration (mg/l).

Dosage study was carried out by varying the dosages (m_{ad}) in the range of 0.5-25 g/l for both the adsorbents at the optimum pH_i ($pH_{i\text{-}opt}$) and 303 K. The adsorption of SDW by the adsorbents was studied over a pH_i range of 3–10 at 303 K. The pH_i of the adsorbate solutions was adjusted using 1 N aqueous solution of either H_2SO_4 or NaOH. The m_{ad} value was kept constant at 20 g/l for ACC and 10 g/l for BFA.

6.1.4.1. Kinetics of adsorption: Kinetic parameters were evaluated using pseudo-first-order and pseudo-second-order model (equation 3.3.3and 3.3.4) at various C_0 values (390-3900 mg/l) at optimum m_{ad} ($m_{ad\text{-}opt}$) of ACC and BFA at ($pH_{i\text{-}opt}$). The amount of adsorbate adsorbed, q_t (mg/g), at any time t was calculated as:

$$q_t = \frac{(C_0 - C_t)}{m_{ad}} V \qquad (6.1.2)$$

Where, C_t is the COD concentration (mg/l) at time t, V is the volume of the solution (l).

Marquardt's percent standard deviation (MPSD) error function (Marquardt, 1963) was employed to find out the most suitable kinetic model to represent the experimental data. This error functions is given as:

$$MPSD = 100\sqrt{\frac{1}{n_m - n_p}\sum_{i=1}^{n}\left(\frac{q_{t,i,\exp} - q_{t,i,cal}}{q_{t,i,\exp}}\right)^2} \tag{6.1.3}$$

In this equation, the subscript 'exp' and 'cal' represent the experimental and calculated values, n_m is the number of measurements, and n_p is the number of parameters in the model.

6.1.4.2. Isothermal study: Equilibrium adsorption equations are required in the design of adsorption systems and their subsequent optimization. Therefore, it is important to establish the most appropriate correlation for the equilibrium isotherm curves. Isothermal experiments were performed at 283, 293 and 303 K with C_0 values of 390-3900 mg/l at $pH_{i\text{-}opt}$ and $m_{ad\text{-}opt}$ of ACC and BFA. Various isotherms such as Freundlich, Langmuir and Redlich-Peterson (R-P) (equation 3.3.6-3.3.8) were used to represent the adsorption equilibrium data.

The adsorbents were separated from the SDW after 8 h and analysed for C_e. The equilibrium adsorption uptake, q_e (mg/g), were calculated using the following relationship:

$$q_e = \frac{(C_0 - C_e)}{w}V \tag{6.1.4}$$

The Chi-square error analysis function was used to find out best fit isotherm model. It is given as:

$$CHI^2 = \sum_{i=1}^{n}\frac{(q_{e,i,\exp} - q_{e,i,cal})^2}{q_{e,i,\exp}} \tag{6.1.5}$$

Thermodynamics of adsorption process have also been studied and the change in Gibbs free energy and the enthalpy, and heat of adsorption have also been determined.

6.2. RESULTS AND DISCUSSION (Kushwaha et al., 2010e)

6.2.1. Effect of Adsorbent Dosage (m_{ad})

The effect of m_{ad} on the adsorption of SDW by ACC and BFA was studied at C_o = 3900 mg/l. An increase in ACC and BFA dosage resulted in an increase in COD removal up to a certain value and thereafter the removal efficiency remained almost constant. An increase in the removal with the increase in m_{ad} can be attributed to greater surface area and the availability of more adsorption sites. At $m_{ad} \geq 20$ g/l for ACC and at $m_{ad} \geq 10$ g/l for BFA, the incremental COD removal became very less. This is due to the fact that for $m_{ad} \geq m_{ad\text{-}opt}$, the removal efficiency depends more upon the concentration of the solution and less depends upon the m_{ad}. Thus, the $m_{ad\text{-}opt}$ for COD removal from SDW by ACC and BFA was 20 g/l and 10 g/l, respectively.

6.2.2 Effect of Initial pH (pH_i)

The pH value of the aqueous solution is an important controlling parameter in the process of adsorption. Fig. 6.2.1 represents the effect of pH_i on the COD removal of SDW by ACC and BFA. For both the adsorbents, highest removal efficiency of 68.7% for ACC and 26% for BFA was obtained at $pH_i = 4.8$. The system pH changes during the adsorption process. For the experiments with C_o = 3900 mg/l, the final pH values (pH_f) of the adsorption process are shown as a function of pH_i in Fig. 6.2.1. For ACC, the pH_f values are lower than the pH_i values for $pH_i > 5.5$. However, for some experiments ($pH_i < 5.5$) the pH_f values are greater than pH_i. However, for BFA, the pH_f values are greater than the pH_i values in full studied range except for $pH_i > 9.8$. It may be observed in the Fig. 6.2.1 that as the pH_i values increases, the COD removal efficiency decreases for both the adsorbents. Since the rise in pH is lower for ACC, its COD removal efficiency is higher. In case of BFA, pH_f increases faster as well as it shows positive change in pH. Thus its removal efficiency is lower. It may also be inferred that the COD removal efficiency is higher if $pH_f \leq 4.8$ or $pH_f \leq 5.5$. In further studies, $pH_{i\text{-}opt} = 4.8$ was taken as optimum pH_f. Therefore, $pH_i = 4.8$ for both the adsorbents.

The FTIR spectra of the blank and SDW loaded ACC and BFA are shown in Fig. 6.2.2. All spectra show sharp peaks at ~1635 and ~1385 cm^{-1}. The peak around ~1635 cm^{-1} may be due to the CO group stretching from aldehydes and ketones, and the band around ~1385 cm^{-1} in both the adsorbents may be attributed to the carboxyl-carbonate structures. These FTIR spectra also show transmittance around 1110 cm^{-1} region due to the vibration of the CO group in lactones (Davila-Jimenez et al., 2005). A broad band between 3100 and 3700 cm^{-1} in BFA is indicative of the presence of both free and hydrogen bonded OH groups on the BFA surface. This stretching is due to both the silanol groups (SiOH) and adsorbed water (peak at 3400 cm^{-1}) on the surface (Abou-Mesalam, 2003).

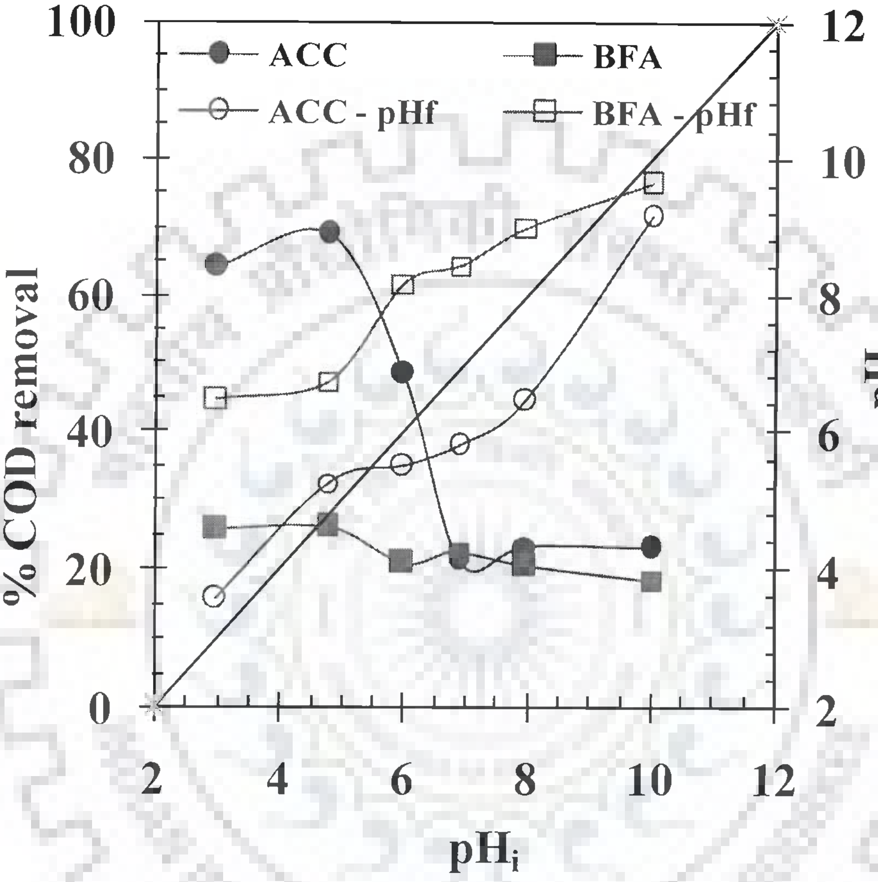


Fig. 6.2.1. Effect of pH_i on the COD removal of SDW by ACC and BFA (T = 303 K, t = 8 h, C_o = 3900 mg/l, $m_{ad\text{-}opt}$ = 20 g/l for ACC, $m_{ad\text{-}opt}$ = 10 g/l for BFA).

SDW loaded ACC and BFA show shifting of peaks from about 1635, 1385 and 1110 cm^{-1}. This means that the functional groups at these wave numbers participate in the SDW treatment. The shifting occurs both to higher and lower wave numbers. Although some inference can be drawn about the surface functional groups participating in the adsorption, the weak and broad bands do not provide any authentic information about the nature of the adsorption.

The morphologies of blank and SDW loaded ACC and BFA have been examined by SEM and EDX analysis. The SEMs of the blank and SDW loaded ACC and BFA are shown in Fig. 6.2.3. This figure reveals surface texture and porosity of the blank and SDW loaded adsorbents. SEM micrographs at lower magnification (50x) does not show much difference in the texture of the blank and SDW loaded ACC. It only shows that the ACC is crystalline in nature and with varying particle size. However, at higher magnification (5000x) some difference in the surface texture of the blank and SDW loaded ACC can be envisaged. Blank ACC shows porous structures with pores of varying sizes. Numbers of pores observed in the loaded ACC are less as compared to that in the blank ACC. SEM of BFA at 50x magnification shows its fibrous and porous structure. After the treatment, the fibres not only get reduced in size but also their pores get filled-up by SDW molecules. It can be inferred from these figures that the surface texture of the ACC and BFA changes after the SDW components loading. The change in surface texture of ACC is less as compared to that of BFA.

EDX was conducted to study the distribution of the elements in blank and SDW loaded ACC and BFA (Table 6.2.1). EDX analysis showed the presence of 72.01% and 82.7% carbon, 0.67% and 0.81% magnesium, 1.01% and 0.22% aluminum, and 2.33% and 3.30% silica in blank ACC and BFA, respectively. SDW loaded ACC and BFA were found to contain 77.3% and 86.8% carbon, 0.35% and 0.32% magnesium, 2.50% and 0.14% aluminum and 5.72% and 2.86% silica, respectively. Thus, SDW loaded ACC and BFA contain higher amount of carbon as compared to blank ACC and BFA. This may be due to the loading of SDW on to blank ACC and BFA.

6.2.3. Effect of Contact Time

SDW having C_0 = 390-3900 mg/l and $pH_{i\text{-}opt}$ = 4.8, were kept in contact with the ACC ($m_{ad\text{-}opt}$ = 20 g/l) and BFA ($m_{ad\text{-}opt}$ = 10 g/l) for 8 h. Fig. 6.2.4 shows the effect of contact time (by data points) on adsorptive COD removal of SDW by ACC and BFA.

Very rapid uptake can be seen during first 15 min for both ACC and BFA. After 3 h, COD uptake nearly reached the equilibrium value. This rapid uptake of COD and attaining of equilibrium in a short period indicates the efficacy of the adsorbents used for its use in dairy wastewater treatment. At the later stages, there is no significant COD removal due to the lesser availability of vacant surfaces on the solid surface and due to the large resistance offered to the SDW components in the bulk phase by the SDW components already adsorbed in the initial stages of adsorption. Contact time of 3 h can be assumed to be equilibrium time for the adsorption of SDW onto ACC and BFA.

6.2.4. Kinetics of Adsorption

Two kinetic models, namely, pseudo-first-order and pseudo-second-order have been used to test their validity with the kinetic experimental adsorption data. The best-fit values of parameters along with the correlation coefficients and MPSD values are given in Table 6.2.2. It may be seen that the adsorption kinetics can be satisfactorily and adequately represented by the pseudo second-order model using non-linear regression fit. The fit of pseudo second-order model is shown in Fig. 6.2.4 by solid line for COD removal of SDW by ACC and BFA.

Table 6.2.1. EDX properties of blank and SDW loaded ACC and BFA.

Element	ACC (weight %)		BFA (weight %)	
	Unloaded	Loaded	Unloaded	Loaded
C	72.01	77.32	82.79	86.85
O	18.25	11.10	08.80	07.71
Mg	00.69	00.35	00.81	00.32
Al	01.01	02.50	00.22	00.14
Si	02.33	05.72	03.30	02.86
P	01.16	00.22	00.55	00.51
S	00.58	00.28	00.54	00.30
K	00.48	00.24	01.96	00.66
Ca	01.97	00.37	00.90	00.65
Fe	01.53	01.92	00.13	00.00

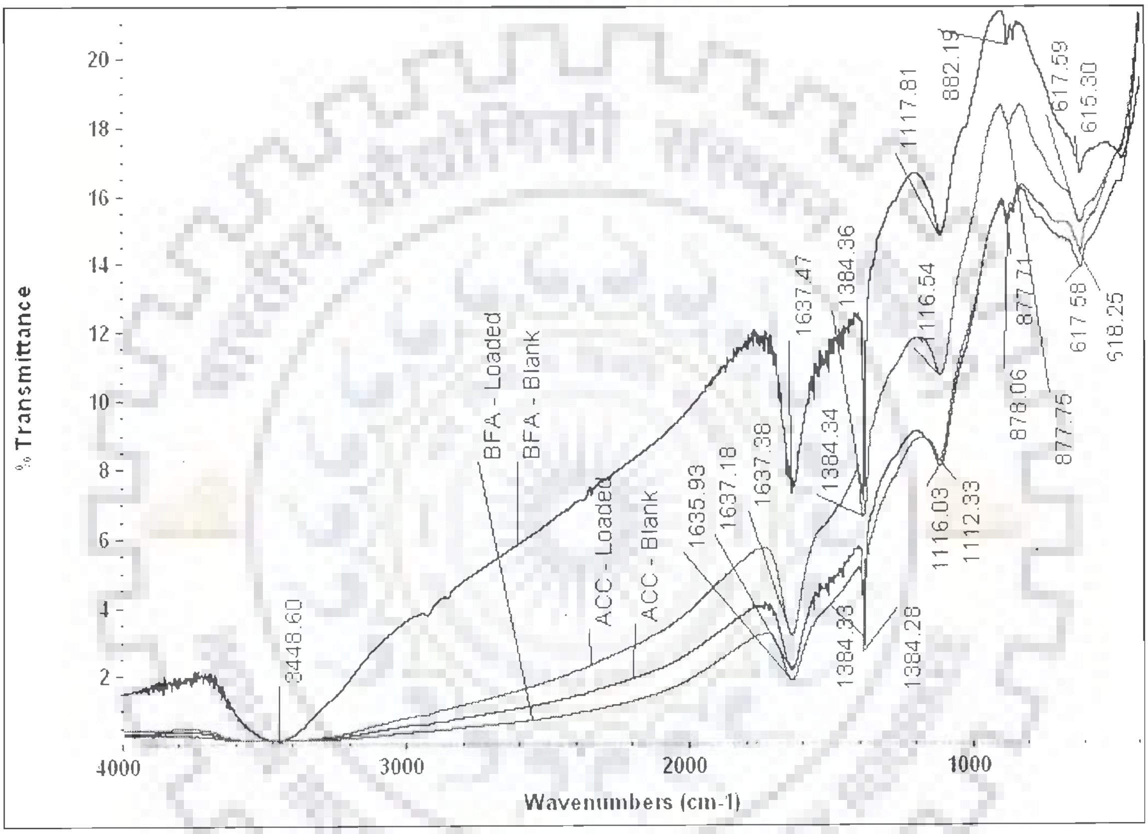
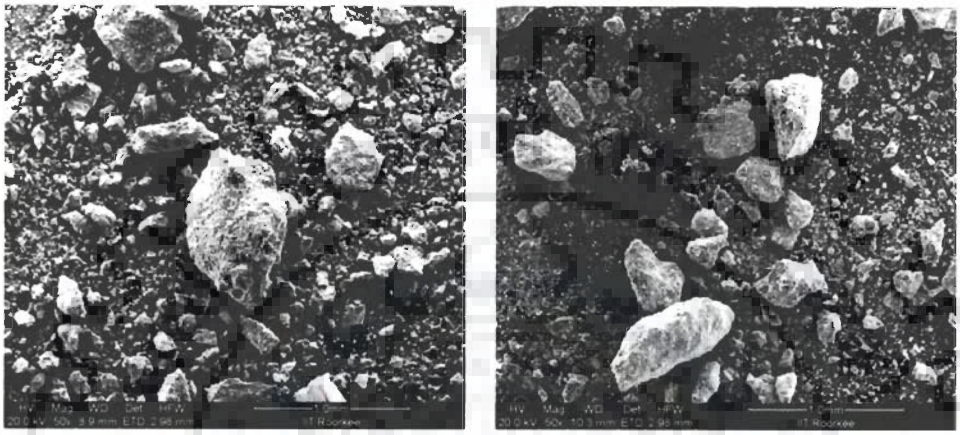
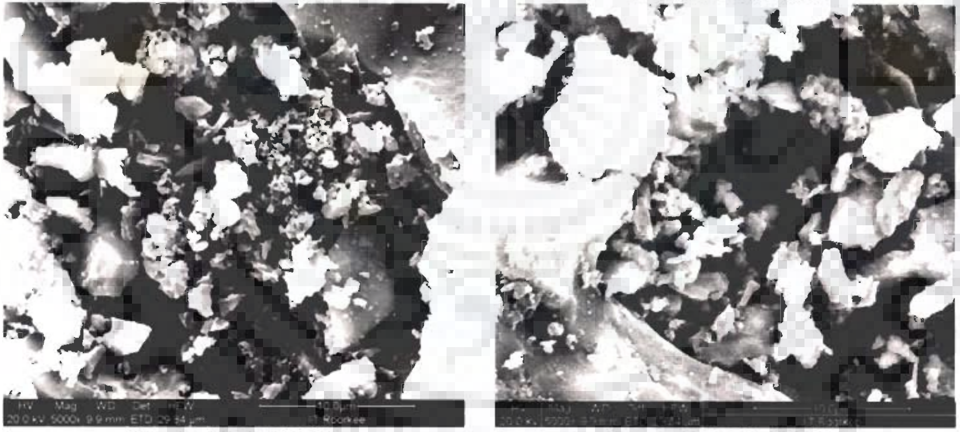


Fig. 6.2.2. FTIR of blank and SDW loaded ACC and BFA at $m_{ad\text{-}opt}$ and $pH_{i\text{-}opt}$.

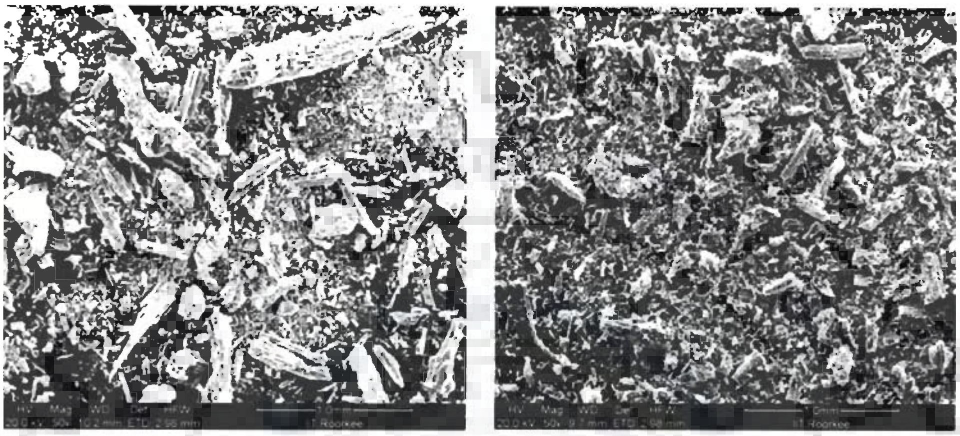


Blank-ACC 50X **Loaded-ACC 50X**



Blank-ACC 5000X **Loaded-ACC 5000X**

Fig. 6.2.3a. SEM of blank and SDW loaded ACC.



Blank-BFA 50X **Loaded-BFA50X**

Blank-BFA 3000X **Loaded-BFA 3000X**

Fig. 6.2.3b. SEM of blank and SDW loaded BFA.

From Table 6.2.2, it is observed that the h and q_e values increase with an increase in C_0, whereas, k_s decreases with an increase in C_0. The rate of uptake is limited by the C_0 and the components affinity to the adsorbent, diffusion coefficient of the adsorbate in the bulk and solid phases, the pore size distribution of the adsorbent, and the degree of mixing (Zogorski et al., 1976). They provide the necessary driving force to overcome the resistances to the mass transfer of SDW components between the aqueous and the solid phases. The increase in C_0 also enhances the interaction between SDW components and the adsorbent. The rate of adsorption also increases with the increase in C_0 due to increase in the driving force.

6.2.5. Controlling Mechanism

The transport of SDW components from the solution phase into the pores of the adsorbent particles may be controlled either by one or more of the following steps: film or external diffusion, pore diffusion, surface diffusion and adsorption on the pore surface. It is necessary to calculate the slowest step involved among these steps to identify the controlling step during the adsorption process (Srivastav and Srivastava, 2009). It is expected that the intraparticle diffusion may be the rate controlling-step during SDW components adsorption onto ACC and BFA. This is due to the fact that intraparticle diffusion controls the adsorption process for systems with good mixing, large particle sizes of adsorbent and high concentration of adsorbate (Aravindhan et al., 2007). If the Weber-Morris plot of q_t versus $t^{0.5}$ satisfies the linear relationship with the experimental data, then the adsorption process is assumed to be controlled by intra-particle diffusion only. However, if the data exhibit multi-linear plots, then two or more steps influence the overall adsorption process.

External mass transfer is characterized by the initial solute uptake. In the present study, it was assumed that the external mass transfer occurred in the first 15 min and that the relationship between C/C_0 versus time for first 15 min was linear. The initial adsorption rates (K_s) (min^{-1}) were quantified as $(C_{15\,min}/C_o)/15$. The calculated K_s values for an initial SDW concentration of 390, 975, 1950 and 3900 mg/l were found to be 0.028, 0.030, 0.027 and 0.026 min^{-1}; and 0.053, 0.049, 0.051 and 0.051 min^{-1} for ACC and BFA, respectively.

Table 6.2.2. Kinetic parameters for the COD removal of SDW by ACC and BFA (*t* = 8 h, C_0=3900-390 mg/l, *m*=20 g/l for ACC, *m*=10 g/l for BFA).

Pseudo-first-order model

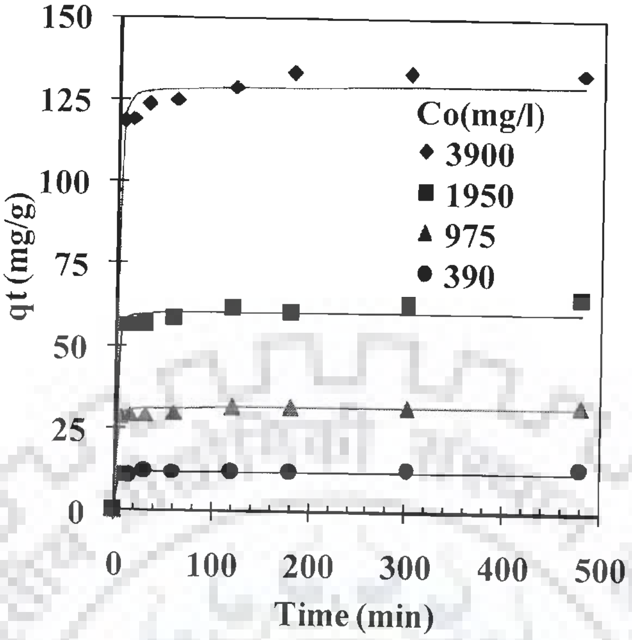
C_0 (mg/l)	$q_{e,exp}$ (mg/g)	$q_{e,calc}$ (mg/g)	k_f (min^{-1})	R^2	MPSD
ACC					
390	13.3	12.0	0.437	0.974	10.85
975	32.3	30.0	0.808	0.987	11.06
1950	65.0	60.5	0.415	0.976	13.83
3900	134.0	129.5	0.499	0.987	9.62
BFA					
390	15.0	9.0	0.219	0.737	50.22
975	36.5	32.4	0.237	0.918	25.34
1950	57.0	56.0	0.258	0.982	15.65
3900	101.5	93.1	0.226	0.989	11.29

Pseudo-second-order model

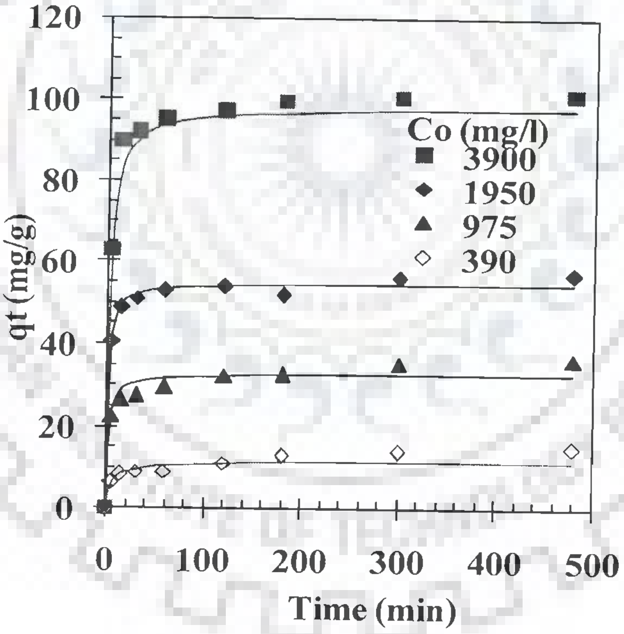
C_o (mg/l)	$q_{e,calc}$ (mg/g)	k_s (g/mg min)	*h* (mg/g min)	R^2	MPSD
ACC					
390	12.3	0.104	15.8	0.984	9.28
975	31.6	0.063	62.3	0.993	6.56
1950	60.6	0.048	175.5	0.985	9.98
3900	129.8	0.017	279.9	0.992	7.78
BFA					
390	11.6	0.013	1.7	0.889	36.14
975	32.9	0.013	14.2	0.959	17.06
1950	55.0	0.010	31.0	0.995	5.73
3900	98.4	0.004	35.0	0.996	8.33

Intra-particle diffusion

C_o (mg/l)	$k_{id,1}$ (mg/g min$^{1/2}$)	I_1 (mg/g)	R^2	$k_{id,2}$ (mg/g min$^{1/2}$)	I_2 (mg/g)	R^2
ACC						
390	0.415	9.545	0.827	0.810	11.30	0.692
975	0.225	28.19	0.922	0.650	30.64	0.7
1950	0.463	54.99	0.812	0.435	55.45	1
3900	1.317	115.5	0.979	0.054	122.8	1
BFA						
390	0.550	5.326	0.945	0.217	10.22	1
975	1.199	20.67	0.916	0.418	27.56	0.919
1950	4.887	29.67	1	0.333	49.56	0.772
3900	16.49	26.11	1	0.577	90.35	0.877



(a) ACC



(b) BFA

Fig. 6.2.4. Effect of contact time on the COD removal of SDW by ACC and BFA. Experimental data points given by the symbols and the lines predicted by the pseudo-second-order model. $T = 303$ K, $m_{ad\text{-}opt} = 20$ g/l for ACC, $m_{ad\text{-}opt} = 10$ g/l for BFA.

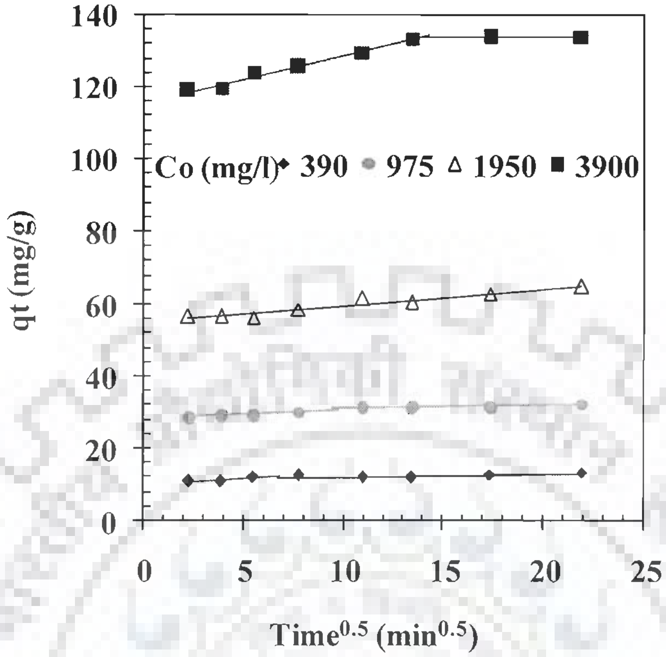
Fig. 6.2.5 shows a representative q_t versus $t^{0.5}$ plot for SDW adsorption onto ACC and BFA for C_o = 390, 975, 1950 and 3900 mg/l at 303 K and $pH_{i\text{-}opt}$ = 4.8. In Fig. 6.2.5, the plots are not linear over the whole time range, implying that the more than one process is controlling the adsorption process. The first portion (line not drawn for the clarity of picture) gives the diffusion of SDW components through the solution to the external surface of adsorbent or boundary layer diffusion. Further two linear portions depict intra-particle diffusion. The second linear portion is attributed to the gradual equilibrium stage with intra-particle diffusion dominating. The third portion is the final equilibrium stage for which the intra-particle diffusion starts to slow down due to the extremely low adsorbate concentration left in the solution. The slope of the linear portions ($k_{id,1}$ and $k_{id,2}$) defined as rate parameters and are characteristics of the rate of adsorption in the region where intra-particle diffusion is rate controlling. Extrapolation of the linear portions of the plots back to the y-axis gives the intercepts that provide the measure of the boundary layer thickness. It seems that the intra-particle diffusion of SDW components into mesopores (third portion) is the rate controlling step in the adsorption process. Slopes of second and third portions ($k_{id,1}$ and $k_{id,2}$) are higher for higher C_o, which corresponds to an enhanced diffusion of SDW components through meso- and micro-pores. This is due to the greater driving force at higher C_o. The deviation of straight lines from the origin indicates that the pore diffusion is not the sole rate-controlling step. Therefore, the adsorption proceeds via a complex mechanism consisting of both surface adsorption and intra-particle transport within the pores of ACC and BFA.

The multi-phasic nature of intraparticle diffusion plot confirms the presence of both surface and pore diffusion. In order to predict the actual slow step involved, the kinetic data were further analyzed using Boyd kinetic expression. Equation (3.3.2) was used to calculate B_t values at different time t. The linearity of the plot of B_t versus t was used to distinguish whether surface or intra-particle transport controls the adsorption rate. It was observed that the relation between B_t and t (not shown here) was non-linear (R^2 = 0.63-0.97) at all concentrations for both the adsorbents confirming that surface diffusion is the not the sole rate-limiting step. Thus, both surface and pore diffusion seem to be the rate-limiting steps in the adsorption process and the adsorption proceeds via complex mechanism.

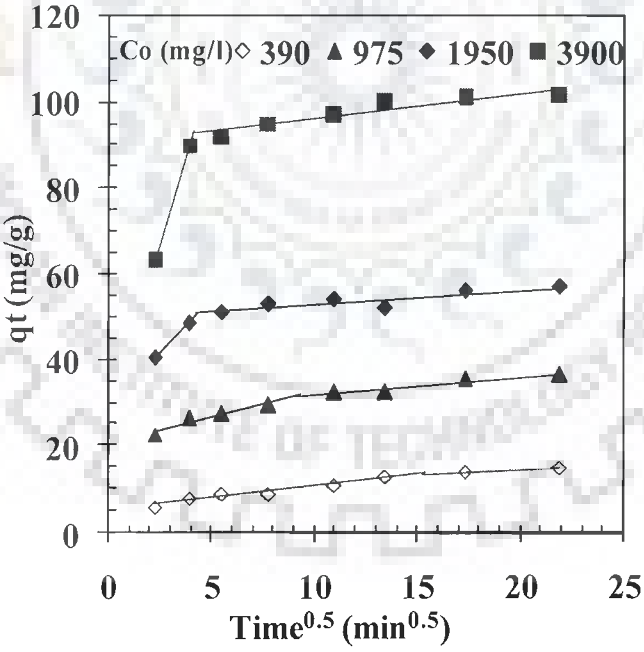
6.2.6. Adsorption Isothermal Study

6.2.6.1. Effect of temperature (*T*): *T* has a pronounced effect on the adsorption capacity of the adsorbents. Adsorption of SDW onto ACC and BFA were studied at different *T* ranging from 283-303 K. The absorptivity of the SDW components was found to increase with an increase in T. Adsorption is generally an exothermic process. However, if the adsorption process is controlled by the diffusion process (intraparticle transport-pore diffusion), the adsorption capacity will increase with an increase in temperature. This is basically due to the fact that the diffusion is an endothermic process (Srivastava et al., 2007). With an increase in temperature, the mobility of the SDW components increases and the retarding forces acting on the diffusing components decrease, thereby increasing the adsorptive capacity of adsorbent. It is known from the previous section that the diffusion of SDW components into pores of the adsorbent is not the only rate-controlling step, and the diffusion process could be ignored with adequate contact time. Therefore, the increase in adsorption capacity with an increase in temperature may be attributed to chemisorptive nature of adsorption.

6.2.6.2. Isotherm modelling: The parameters, R^2 and CHI^2 values for the Freundlich, Langmuir and R-P isotherms fitting to the experimental data are listed in Table 6.2.3. It may be concluded by comparing the CHI^2 and R^2 values, that R-P isotherm generally best-fits the equilibrium adsorption of SDW components onto both ACC and BFA at all temperatures except at 283 K for BFA where Freundlich isotherm best-fit the isotherm data. The CHI^2 values are similar for R-P and Freundlich isotherm and any of the two can be used for isotherm modeling. The fitting of various isotherms on the experimental data points is shown in Fig. 6.2.6 by solid lines. K_F and $1/n$ indicate the adsorption capacity and adsorption intensity, respectively. Higher value of $1/n$ indicates the higher affinity between the adsorbate and adsorbent, and heterogeneity of the adsorbent sites. It may be concluded from Table 6.2.3 that the ACC has greater heterogeneity for SDW components. The K_F value is considered an indicator of the adsorption capacity of ACC and BFA. The magnitude of K_F also showed the higher uptake of SDW components at higher temperature for both the adsorbents indicating endothermic nature of adsorption. The q_m value indicates the affinity of the SDW components to bind with the adsorbents. A high q_m value indicates a higher affinity. The data in Table 6.2.3 indicate that values of q_m increased with increase in temperature confirming endothermic nature of overall-sorption process for all SDW-adsorbent systems. It also shows that ACC has higher adsorption capacity as compared to BFA at all temperatures. This may be due to the higher surface area of ACC (336.6 m^2/g) as compared to that of BFA (168.39 m^2/g).

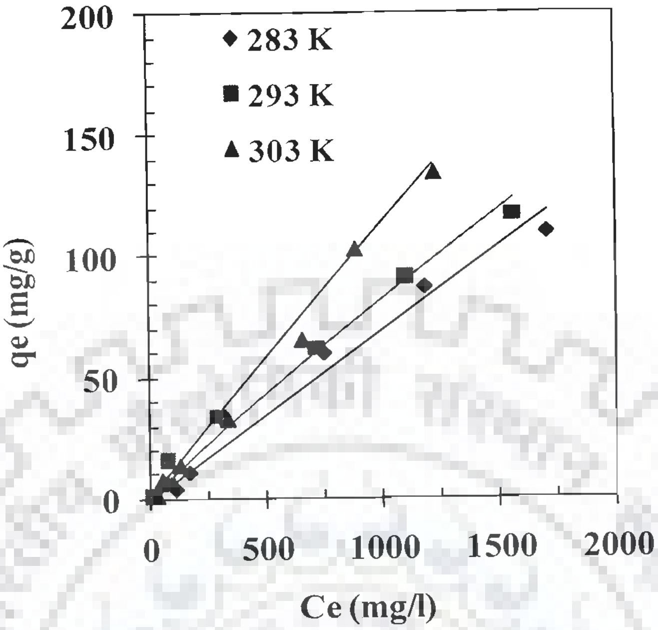


(a) ACC

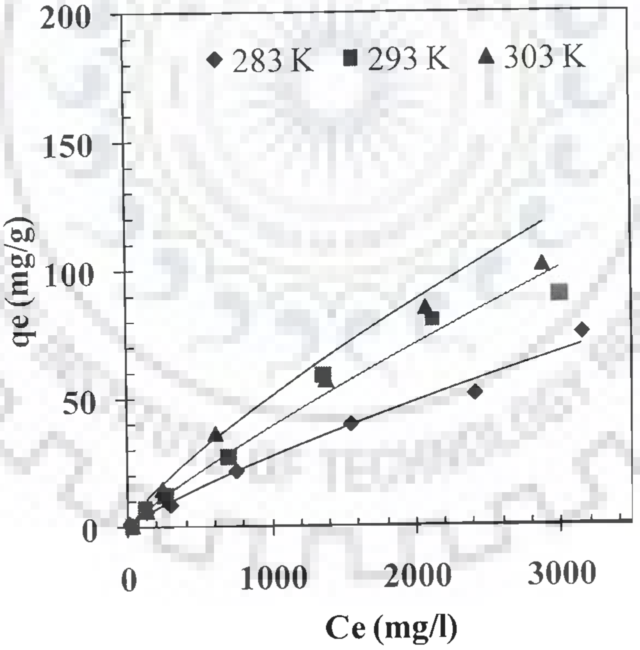


(b) BFA

Fig. 6.2.5. Weber-Morris plot for the treatment of SDW by ACC and BFA. t = 8 h, C_o = 390-3900 mg/l, $m_{ad\text{-}opt}$ = 20 g/l for ACC, $m_{ad\text{-}opt}$ = 10 g/l for BFA.

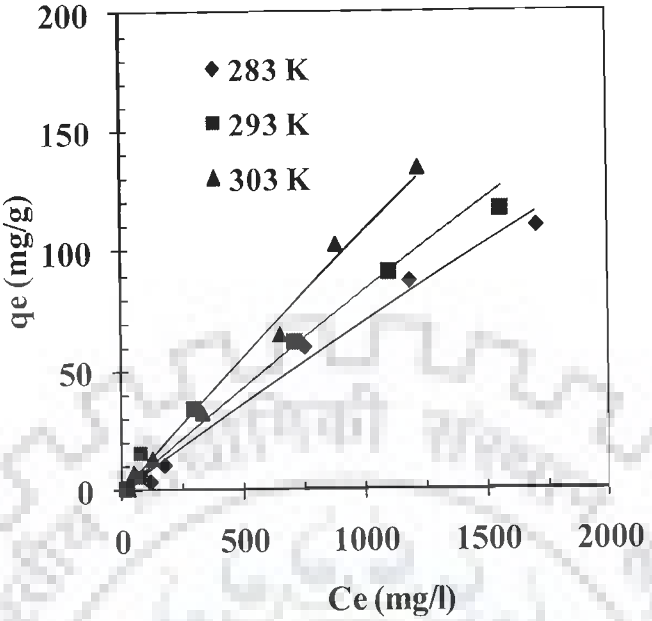


(a) ACC

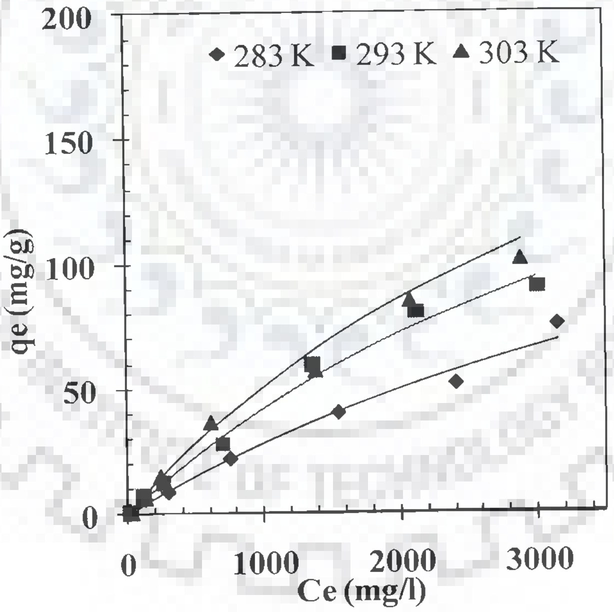


(b) BFA

Fig. 6.2.6a. Equilibrium adsorption isotherms at different temperature for the treatment of SDW by ACC and BFA. Experimental data points given by symbols and the lines predicated by Freundlich isotherm model. t = 8 h, C_o = 390-3900 mg/l, m = 20 g/l for ACC, m = 10 g/l for BFA.

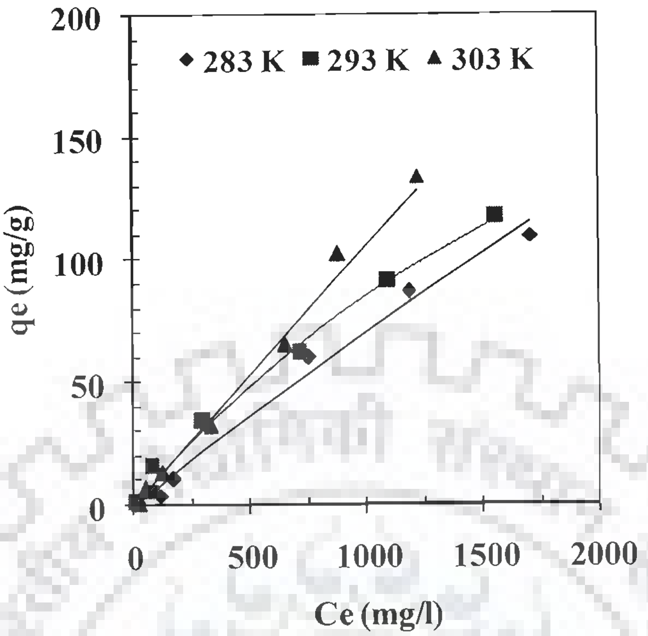


(a) ACC

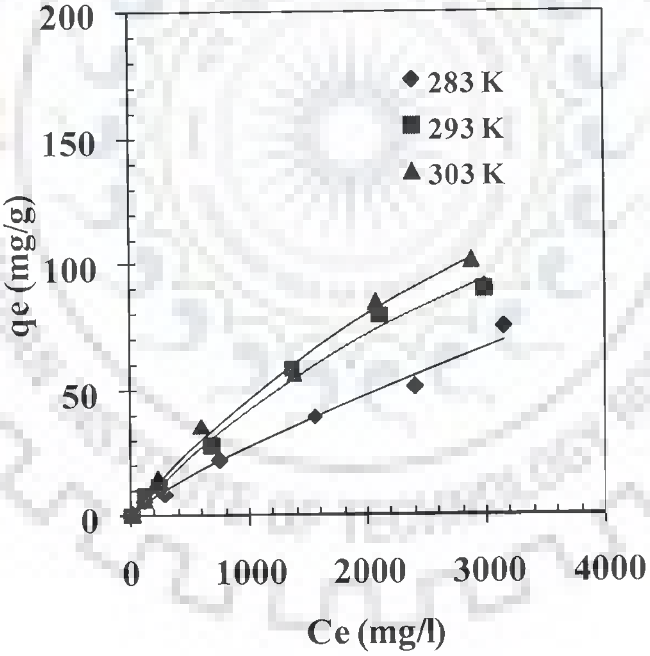


(b) BFA

Fig. 6.2.6b. Equilibrium adsorption isotherms at different temperature for the treatment of SDW by ACC and BFA. Experimental data points given by symbols and the lines predicated by Langmuir isotherm model. $t = 8$ h, $C_o = 390\text{-}3900$ mg/l, $m = 20$ g/l for ACC, $m = 10$ g/l for BFA.



(a) ACC



(b) BFA

Fig. 6.2.6C. Equilibrium adsorption isotherms at different temperature for the treatment of SDW by ACC and BFA. Experimental data points given by symbols and the lines predicated by R-P isotherm model. t = 8 h, C_o = 390-3900 mg/l, m = 20 g/l for ACC, m = 10 g/l for BFA.

Table 6.2.3. Isotherm parameters for the Treatment of SDW by ACC and BFA (t = 8 h, $pH_{i\text{-}opt}$ = 4.8, m_{ad} = 20 g/l for ACC, m_{ad} = 10 g/l for BFA).

Freundlich $q_e = K_F C_e^{1/n}$

T (K)	K_F ((mg/g)/(l/mg)$^{1/n}$)	$1/n$	R^2	CHI^2
ACC				
283 K	0.070	0.999	0.975	10.090
293 K	0.148	0.915	0.991	7.149
303 K	0.152	0.959	0.993	4.540
BFA				
283	0.102	0.811	0.9885	1.356
293	0.103	0.859	0.9752	4.139
303	0.217	0.790	0.9926	7.141

Langmuir $q_e = \dfrac{q_m K_L C_e}{1 + K_L C_e}$

T (K)	K_L (l/mg)	q_m(mg/g)	R^2	CHI^2
ACC				
283	0.00006	1327.978	0.980	9.792
293	0.00006	1408.473	0.989	8.373
303	0.00007	1596.736	0.993	11.149
BFA				
283	0.0002	208.613	0.9833	2.520
293	0.0002	248.021	0.9894	2.181
303	0.0002	278.497	0.9939	4.988

Redlich-Peterson $q_e = \dfrac{K_R C_e}{1 + a_R C_e^{\beta}}$

T (K)	K_R (l/g)	a_R (l/mg)$^{1/\beta}$	β	R^2	CHI^2
ACC					
283	0.074	0.0001	1.000	0.980	9.792
293	0.117	0.0007	0.910	0.994	5.479
303	0.106	0.0007	0.000	0.994	8.926
BFA					
283	0.032	0.0006	0.8256	0.9885	2.407
293	0.051	0.0002	0.9990	0.9893	2.182
303	0.057	0.0002	0.9990	0.9937	3.356

6.2.7. Estimation of Thermodynamic Parameters

Classical thermodynamics gives equation 6.2.1 for the calculation of the Gibbs free energy change (ΔG^0), entropy change (ΔS^0) and heat of adsorption (ΔH^0) from variation of adsorption equilibrium constant (K_D) with T.

$$\ln K_D = \frac{-\Delta G^0}{RT} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R}\frac{1}{T} \tag{6.2.1}$$

Where, R is the universal gas constant (8.314 J/mol K). K_D is found from the slope of $ln(q_e/C_e)$ versus q_e (Srivastava et al., 2007).

The adsorption of SDW components onto ACC and BFA is endothermic in nature, giving a positive value of ΔH^0 (Table 6.2.4). The positive ΔH^0 value confirms the endothermic nature of the overall-adsorption process. In physisorption, the bond between adsorbate and adsorbent is van der Walls interaction and adsorption energy is typically 5-10 kJ/mol. In the case of chemisorption, a chemical bond is formed between molecules and the surface; the adsorption energy is comparable to the energy of a chemical bond. The chemisorption energy is, generally, 30-70 kJ/mol for (Murzin and Salami, 2005).

Table 6.2.4. Thermodynamics parameters for the adsorption of SDW by ACC and BFA (t = 8 h, C_o = 3900-390 mg/l, $m_{ad\text{-}opt}$ = 20 g/l for ACC, $m_{ad\text{-}opt}$ = 10 g/l for BFA).

Temp. (K)	$K_D \times 10^{-3}$ (l/kg)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (kJ/mol K)
ACC				
283	57.94	-9.55	25.72	125.86
293	132.34	-11.90		
303	117.98	-12.02		
BFA				
283	37.67	-8.54	17.26	91.53
293	55.46	-9.79		
303	60.94	-10.35		

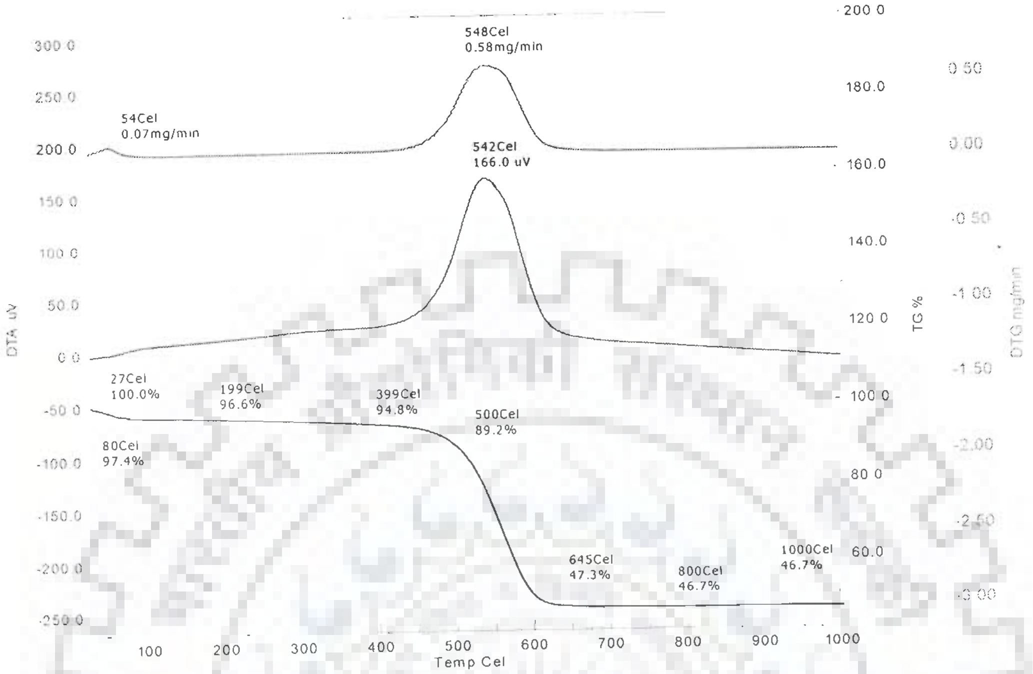
In the present study, ΔH^0 value is 25.72 kJ/mol for ACC and 17.26 kJ/mol for BFA. Therefore, it seems that the adsorption of SDW components onto ACC and BFA is neither fully physical nor fully chemical and some complex mechanism dictates the adsorption process. The positive value of ΔS^0 suggests increased randomness at the solid/solution interface with some structural changes in the adsorbate and adsorbent, and an affinity of the ACC and BFA towards SDW components. Also, positive ΔS^0 value corresponds to an increase in the degree of freedom of the adsorbed species. ΔG^0 values are negative indicating that the adsorption process led to a decrease in Gibbs free energy. Negative ΔG^0 indicates the feasibility and spontaneity of the adsorption process.

6.2.8. Disposal of ACC and BFA

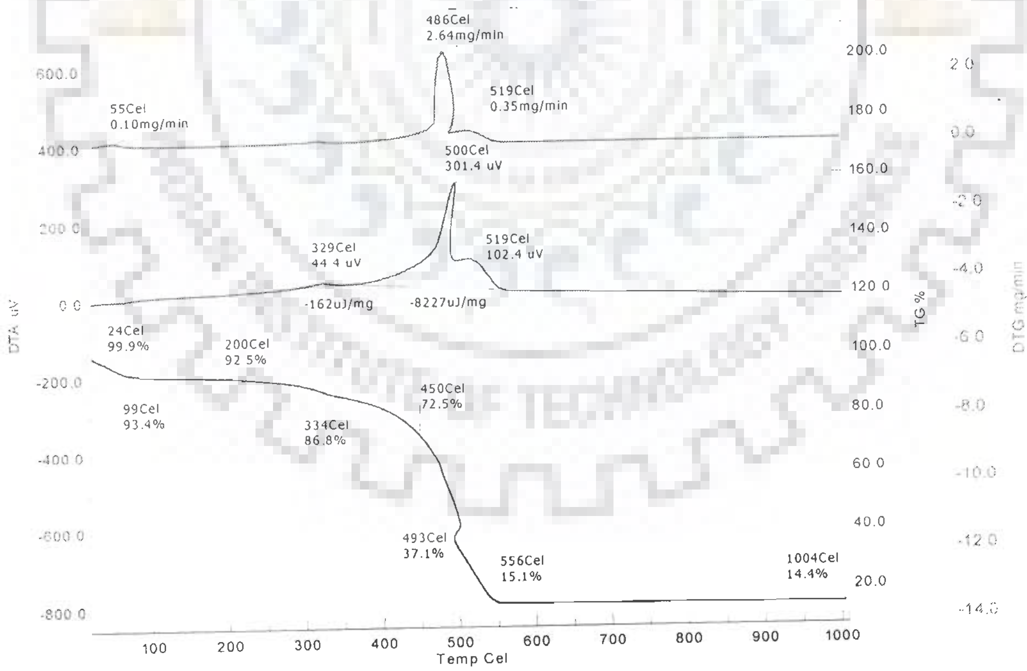
The thermo gravimetric analysis (TGA), differential thermal analysis (DTA) and differential thermal gravimetery (DTG) curves of the blank and loaded ACC and BFA for the heating rate of 10 °C /min are shown in Fig. 6.2.7. The TG traces shows 10.8% loss of moisture and some volatile matter evolution from 24 °C to 500 °C for loaded ACC; and 20% moisture and volatile matter loss from 24 °C to 350 °C in loaded BFA. Higher temperature drying (> 100 °C) occurs due to loss of the surface bound water of the particles. Adsorbents do not show any endothermic transition in the first oxidation zone indicating the lack of any phase change during the heating process (Ng et al., 2002). The weight loss ~41.9% occurred between temperature ~500 °C to ~645 °C for loaded ACC, and for loaded BFA weight loss of 71.6% occurred from ~334 °C to ~556 °C. The strong exothermic peak for loaded ACC centered between 400 °C to 700 °C and for BFA between 400 °C to 550 °C shows the degradation of sample by oxidation. Generally, when the carbonaceous compounds are heated at higher temperatures, the surface groups decompose, producing CO (200-600 °C), CO_2 (450-1000 °C), water vapor and free hydrogen (500-1000 °C) (Mall et al., 2006). Therefore, the weight loss in second oxidation zone may be due to the evolution of CO_2 and CO. A third oxidation zone with weight loss < 1% can be envisaged at higher temperatures up to 1000 °C. Overall SDW loaded ACC and BFA showed total weight loss of 53.3% and 85.6%, respectively. The higher oxidation of BFA may be due to its higher carbon content as shown by EDX analysis earlier.

Heating value of loaded ACC and BFA were determined as 19.8 MJ/kg and 15.2 MJ/kg, respectively. Thus, the loaded ACC and BFA can be dried and used as a fuel in the boilers/incinerators, or can be used for the production of fuel-briquettes. The bottom ash may be blended with clay to make fire bricks, or with cement-concrete mixture to make colored building blocks thus disposing of SDW loaded ACC and BFA through chemical and physical fixation.

The adsorption capacities of adsorbents are given in Table 6.2.3. It is observed that the adsorption capacity of ACC is higher for SDW adsorption than that of BFA. However, BFA is available in abundance as a waste from the sugar mills at no cost except the handling charges for the collection and transportation. Thus, the total cost of BFA will be extremely low in comparison to those for ACC. Hence, adsorptive treatment of SDW with BFA can be a viable alternative for ACC.



(a) Loaded - ACC



(b) Loaded-BFA

Fig. 6.2.7. TGA-DTA graphs of SDW loaded ACC and BFA.

Chapter – 7

SBR TECHNOLOGY

7.0. GENERAL

SDW treatment by SBR technology has been reported in this chapter. Detail explanation about experimental set up, chemicals used and various analyses during the SDW treatment by aerobic SBR technology have been presented. Results obtained during the treatment have been interpreted and discussed in detail.

7.1. MATERIALS AND METHODS

7.1.1. Wastewater

Wastewater used in this study was same as described in section 4.1.1.

7.1.2. Seed Activated Sludge

The activated sludge (AS) used in the present study was collected from Haridwar sewage treatment plant, Haridwar, India. The AS was first screened for the removal of coarse and bigger particles, and then, it was acclimatized for one week in the SBR with SDW. Dissolved oxygen (DO) concentration inside the reactor was maintained over 2 mg/L during the acclimatization.

7.1.3. Analytical Methods

Various analytical methods have been described in section 4.1.3.

7.1.4. Experimental Setup

The experimental set-up consisted of a well-mixed cylindrical glass reactor having maximum volume of 10 L and a working volume of 5 L. The schematic diagram of the lab scale setup of SBR is shown in Fig. 1. Aeration was achieved by an air compressor pump with sintered-sand diffusers at the bottom of the reactor. Air flow rate was maintained constant through air rotameter to 30 LPM during the experiments, which maintained ≈6.0 mg/l Dissolved oxygen (DO) concentration inside the reactor before filling of SDW. The addition of SDW and the decanting of treated SDW were performed by peristaltic pumps.

A stirrer was used to keep reactor contents homogeneous. Temperature (T) and SRT were maintained constant 28±2 °C and 20 d, respectively, during all experimental runs.

7.1.5. Experimental Plan and System Operation

The reactor was operated on a fill-and-draw basis, with a t_C of 12 h, while, t_S, t_D and t_I were 1, 0.5 and 0.5 h, respectively. t_R were varied according to the fill and anoxic phases strategies to degrade the carbonaceous materials and nitrogen present in SDW. For the optimization of various operating parameters of SBR for the treatment of SDW, four phases study was carried out (Fig. 7.1.1).

In the phase-I of SBR operation, instantaneous filling strategy with $t_F = 0$ was implemented with varying VER and HRT from 0.40-0.80 and 0.63-1.25 d, respectively (Table 7.2.1 and Fig. 7.1.1). Aeration was started at start of the reaction time and closed when settle phase started.

Phsae-II was initiated by varying $t_F = 0.5\text{-}2$ h at optimum VER (VER_{opt}) and HRT (HRT_{opt}) obtained from phase-I study (Fig. 7.1.1). The filling of SDW to SBR was carried out under aerated and mixed fill strategy. Whereas, in phase-III and IV an anoxic phase (t_A) were introduced to enhance the nitrogen removal just after fill phase and react phase, respectively, at optimum t_F ($t_{F,\,opt}$) and VER_{opt} and HRT_{opt} (Fig. 7.1.1). t_A after fill ($t_{A\text{-}F}$) of 0.5-2 h was introduced in phase-III, while the effect of t_A after reaction ($t_{A\text{-}R}$) of 1-3 h were studied in phase-IV at optimum $t_{A\text{-}F}$ ($t_{A,opt\text{-}F}$). 187.50 ml of mixed liquor was wasted from the SBR just before start of settling phase in every cycle to preserve the SRT of 20 d, and this was utilized as a sample for the measurement of MLSS.

SBR was seeded initially with acclimatized AS and SDW of C_o = 3900 mg/l as per strategy explained above. DO and pH changes in the reactor were monitored during treatment with time. Samples were taken from the reactor at different time for finding residual COD measurement in the SBR during its operation. For this purpose, sludge and treated wastewater were separated from each other by centrifuging the sample at 10000 rpm for 15 min and then COD removal efficiency were measured.

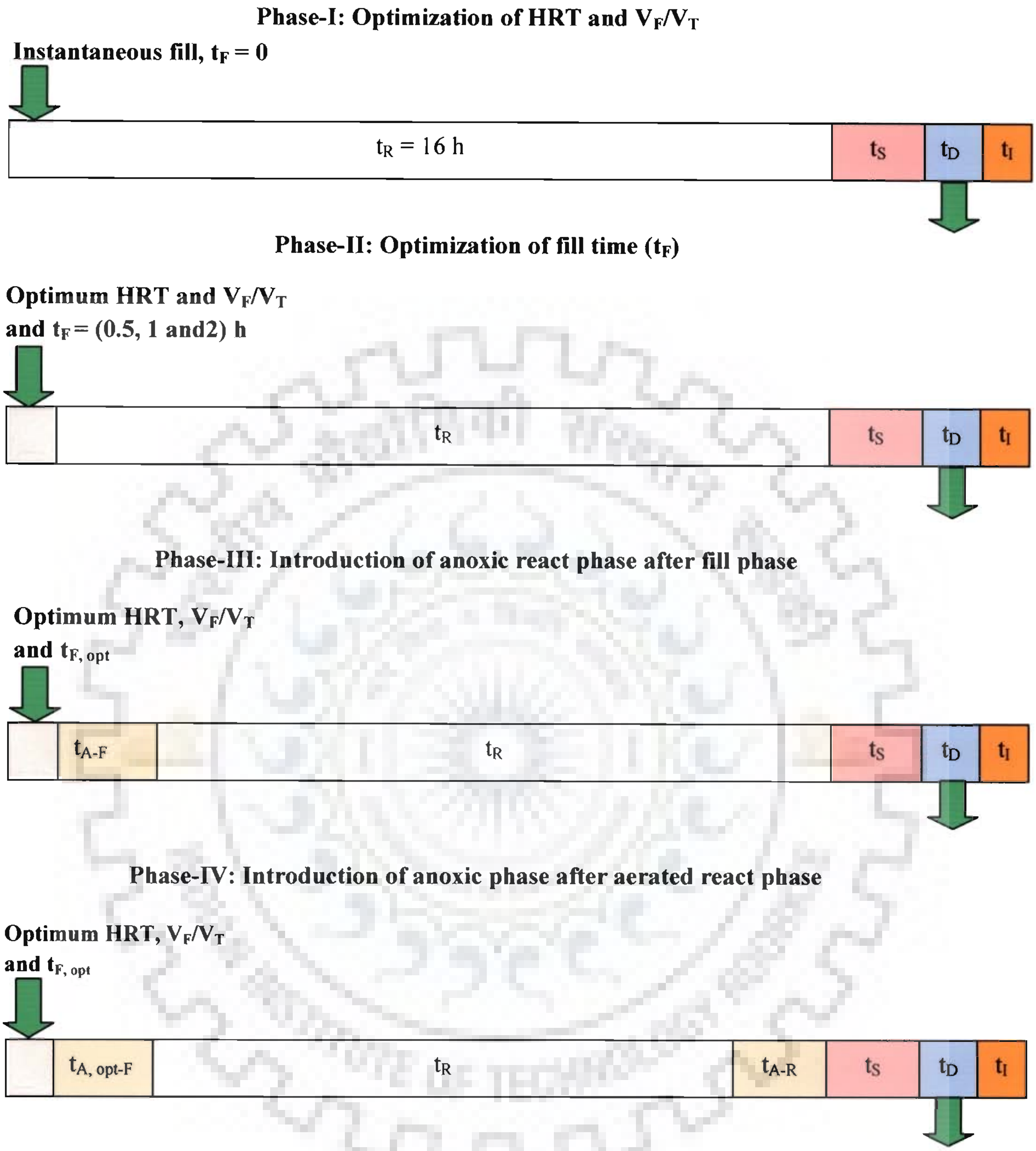


Fig. 7.1.1. Experimental programme during the SDW treatment by aerobic SBR technology.

7.2. RESULT AND DISCUSSION

7.2.1. Phase-I: Instantaneous Fill with Varying HRT

7.2.1.1. Effect of HRT on COD and TKN removal efficiency: Fig. 7.2.1 shows the effect of HRT on COD removal efficiency with time. Table 7.2.1 shows the effect of HRT on COD and TKN removal efficiency after treatment for 10 h. It may be seen that an increase in HRT from 0.625 to 1.25 d reduces the residual COD and TKN in the liquid effluent. Same trend of COD removal and TKN with HRT was also reported by Neczaj et al. (2008). Maximum COD removal efficiency of 97.05% was found at 1.25 d HRT. Table 7.2.1 also shows that there are no significant differences in COD removal efficiencies at higher HRTs. For HRT 1.0 and 1.25 d, COD removal efficiencies are 96.5 and 97.1%, respectively. At these HRTs, volume SDW being treated was 2.5 and 2.0 litre, respectively. Therefore, 1.0 d HRT with 2.5 litre of SDW treatment volume and 96.5% COD and 64.6% TKN removal efficiency was selected as HRT_{opt}.

7.2.1.2. Effect of HRT on MLSS and SVI: MLSS and SVI changes with change in HRT. Results are shown in Fig. 7.2.2. MLSS increases with an increase in HRT. This is due to the fact that increased HRT increased the COD removal rate and helped in achieving higher COD removal efficiency, which in turn increased the microbial growth rate. SVI was found to decrease with an increase in HRT from 0.625 to 0.83 d, however, further increase in HRT increased the SVI.

Table 7.2.1. Experimental programme and results during the phase-I study.

RUN	V_F	V_{SI}	VER (V_F/V_T)	HRT(d)	COD_{eff}	% COD removal	TKN_{eff} (mg/l)	% TKN removal
1	4	1	0.80	0.625	285	92.69	56.75	49.85
2	3.5	1.5	0.70	0.714	255	93.46	49.15	56.57
3	3	2	0.60	0.83	240	93.85	43.81	61.29
4	2.5	2.5	0.50	1.00	135	96.54	40.05	64.61
5	2	3	0.40	1.25	115	97.05	41.78	63.08

7.2.1.3. Effect of HRT on pH and DO: During the SDW treatment with SBR, pH and DO change due to microbial reactions taking place inside the reactor. Fig 7.2.3a shows change in pH with time at different HRTs. It may be seen that pH decreases very sharply and attains a minimum value then increases upto a maximum and becomes nearly constant. This trend was seen at all HRTs studied. Same trend of first decrease and then increase in DO with time can be seen in Fig. 7.2.3b. Under aerobic conditions decrease in pH is due to nitrification. The reduction of alkalinity by existing nitrification decreases the pH until it reaches minima. This minimum value in the pH profile is called ammonia valley and corresponds to the end of nitrification (Cho et al., 2001; Li et al., 2008). The time at which ammonia valley is attained, DO level is also minimum and nearly anoxic condition is attained. After the ammonia valley, the pH increases due to the stripping of CO_2, which is produced by oxidation of carbonaceous material, and ongoing denitrification. Thereafter, pH becomes nearly constant showing complete denitrification and end of CO_2 evolution. It may also be seen in Fig. 4 that as HRT is increased, the ammonia valley is attained in shorter time and at higher pH. Also, minimum DO level gets lower and this minimum DO value is attained in shorter time as HRT is increased.

7.2.2. Phase-II: Effect of t_F of Varying Length

7.2.2.1. Effect of t_F on COD and nitrogen removal: During the fill phase, aerated and mixed fill strategy was followed to achieve more COD removal efficiency and nitrification and to reduce t_R. Increased COD removal rate was found during filling of SDW to the SBR as t_F was increased from 0.5-2.0 h. For t_F = 0.5, 1.0 and 2.0 h, COD removal efficiencies were found to be 72.7, 83.7 and 90.5%, respectively, at the end of filling phase (shown by solid line in Fig. 7.2.4), but at the end of reaction phase (shown by dotted line in Fig. 7.2.4) nearly same COD removal efficiency of ≈96% was observed.

For instantaneous filling strategy, 96.5% COD removal efficiency was achieved at HRT_{opt} = 1.0 d at the end of reaction phase (Table 7.2.1). In instantaneous filling with HRT_{opt} = 1.0 d, for achieving COD removal efficiencies of 72.7, 83.7 and 90.5% (which were observed at the end of various t_F = 0.5, 1.0 and 2.0 h, respectively), the corresponding time required was approximately 1, 2.5 and 3 h, respectively. Therefore, it may be concluded that introduction of fill phase helps in achieveing the same COD removal efficiency in shorter time. Also an increase in t_F increases the COD removal rate, and hence, reduces the t_R (Fig. 7.2.5).

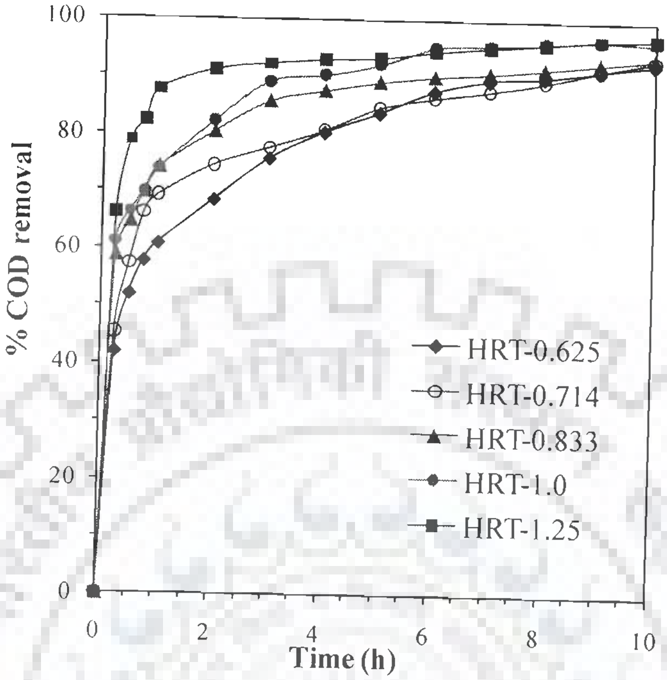


Fig. 7.2.1. Effect of HRT on COD removal efficiency as per strategy of phase-I.

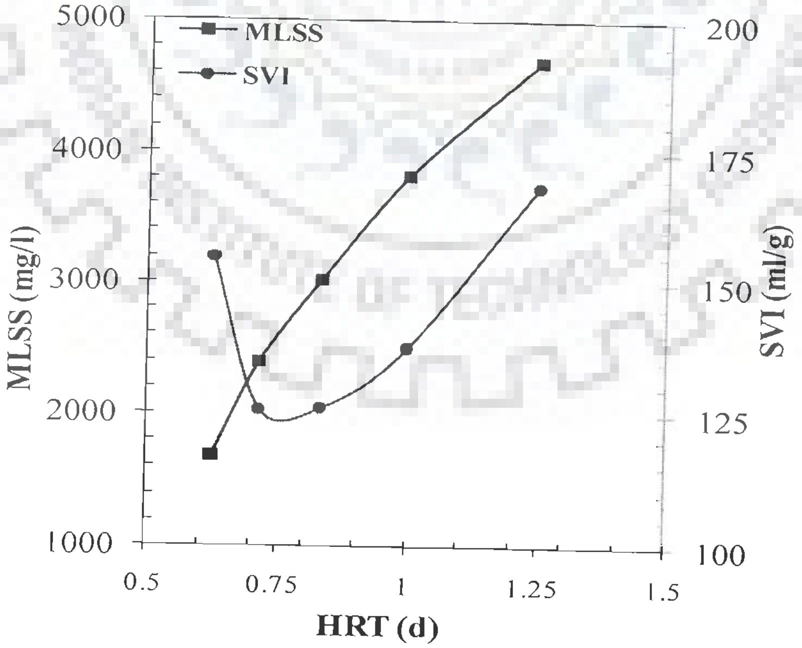


Fig. 7.2.2. Effect of HRT on MLSS and SVI.

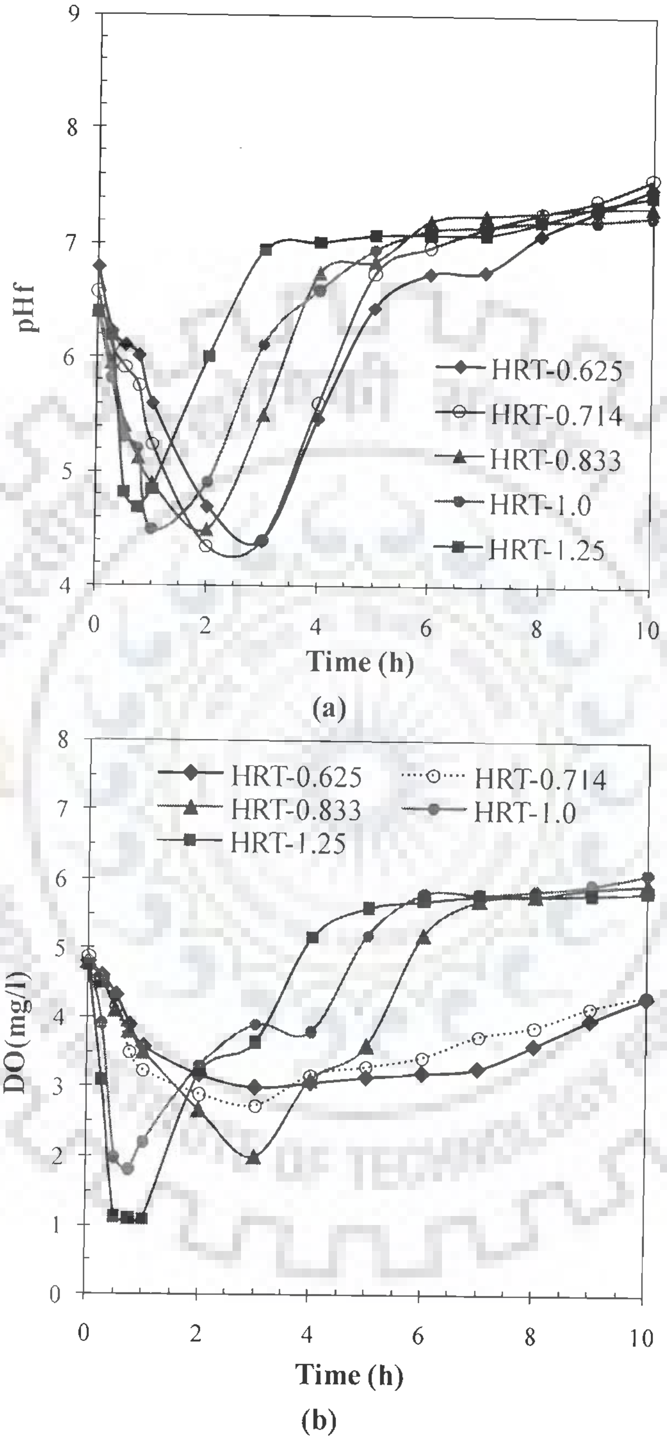


Fig. 7.2.3. Effect of HRT on (a) pH and (b) DO during phase-I study.

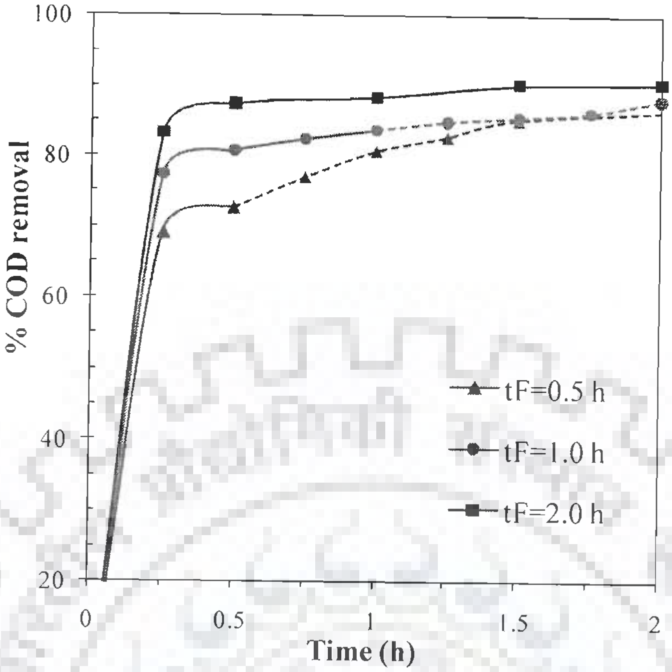


Fig. 7.2.4. Effect of various t_F on COD removal efficiencies. Solid line shows filling time and dotted line reaction time.

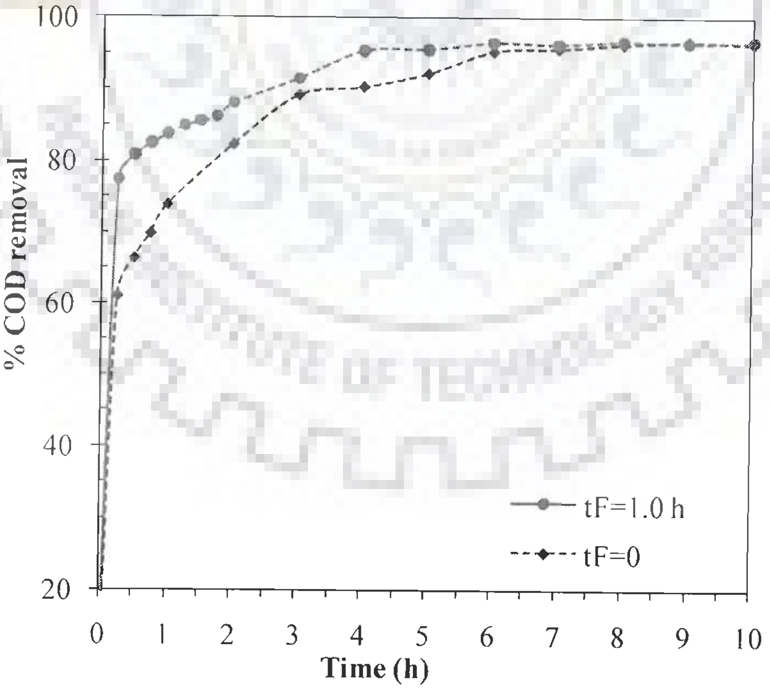


Fig. 7.2.5. Comparison of COD removal efficiencies at $t_{F,\ opt}$ = 1.0 h and t_F = 0 at HRT_{opt} = 1.0 d. Solid line shows filling time and dotted line reaction time.

For t_F of 0.5, 1.0 and 2.0 h, TKN at the end of filling phase (TKN_F) was found to 76.4, 43.0, 40.5 mg/L and TKN at the end of t_R (TKN_{eff}) was 41.4, 39.0 and 36.0 mg/L, respectively (Table 7.2.2). There is no significant difference in TKN_F values for t_F of 1.0 and 2.0 h. Therefore, from the point of view of COD as well as TKN removal, it may be concluded that t_F = 1.0 h is sufficient to treat SDW. Therefore, t_F = 1 h was taken as optimum ($t_{F,opt}$) for further study.

7.2.2.2. Effect t_F on pH and DO: pH and DO of SDW was also found to vary during filling of SDW in SBR (Fig. 7.2.6). It is clear from Fig. 7.2.6a that as the t_F was increased, decrease in pH was little sharper indicating higher rate of nitrification at higher t_F values. It may also be seen that minimum pH attained was lower for higher t_F. This implies higher nitrification at higher t_F values. For t_F = 1 and 2 h, there is no significant difference in minimum pH attained, but pH decrease rate is higher for t_F = 2 h. This trend of pH variation with t_F also indicates that the t_F = 1 h is optimum. Level of DO in the SBR also changed as the t_F was varied. On increasing the t_F, level of minimum DO reached increased, however, for t_F = 1 and 2 h change in minimum reached DO is marginal (Fig. 7.2.6b). For the t_F = 0.5 h, it can be seen that decrease in pH and DO continues after the end of filling time, however, for t_F = 1 and 2 h, minimum pH and DO is attained at the end of fill phase itself (Fig. 7.2.6). Therefore, it may be concluded that t_F = 0.5 h is not sufficient for nitrification and oxidation of COD.

7.2.3. Phase-III and IV: Effect of t_{A-F} and t_{A-R} of Varying Length

Anoxic phases were introduced after filling phase (t_{A-F}) and reaction phase (t_{A-R}) of varying length to enhance the nitrogen removal. t_{A-F} was varied from 0.5-2 h. It may be seen in Table 7.2.3 that an increase t_{A-F} increases the nitrogen removal. The difference in TKN_{A-F} values for t_{A-F} of 1 and 2 h is marginal, therefore, t_{A-F} = 1 h was taken as optimum ($t_{A,opt-F}$) for further studies. t_{A-R} after reaction phase has no effect on nitrogen removal (Table 7.2.4) and it cannot be used for nitrogen removal. At the end of reaction phase with $t_{A,opt-F}$ = 1 h, 76.7% TKN removal was found. Grady et al. (1999) reported that the COD:TN ratio should be greater than 9.5 for good nitrogen removal. At the start of t_{A-F} and t_{A-R} phase, COD:TN ratio were 14.8 and 5.8, respectively. Therefore, introduction of t_{A-R} phase showed no effect on nitrogen removal.

Table7.2.2. Effect of varying t_F on TKN during phase-II study

t_F (h)	TKN_F (mg/l)	% TKN_F removal	TKN_{eff} (mg/l)
0.5	76.4	32.52	41.4
1	43	62.18	39.0
2	40.5	64.26	36.0

Table7.2.3. Effect of varying t_{A-F} during phase-III study

t_{A-F} (h)	TKN_{A-F} (mg/l)	TKN_{eff} (mg/l)	% TKN Removal
0.5	38.3	31	72.61
1	30.79	26.31	76.75
2	29.79	25.91	77.11

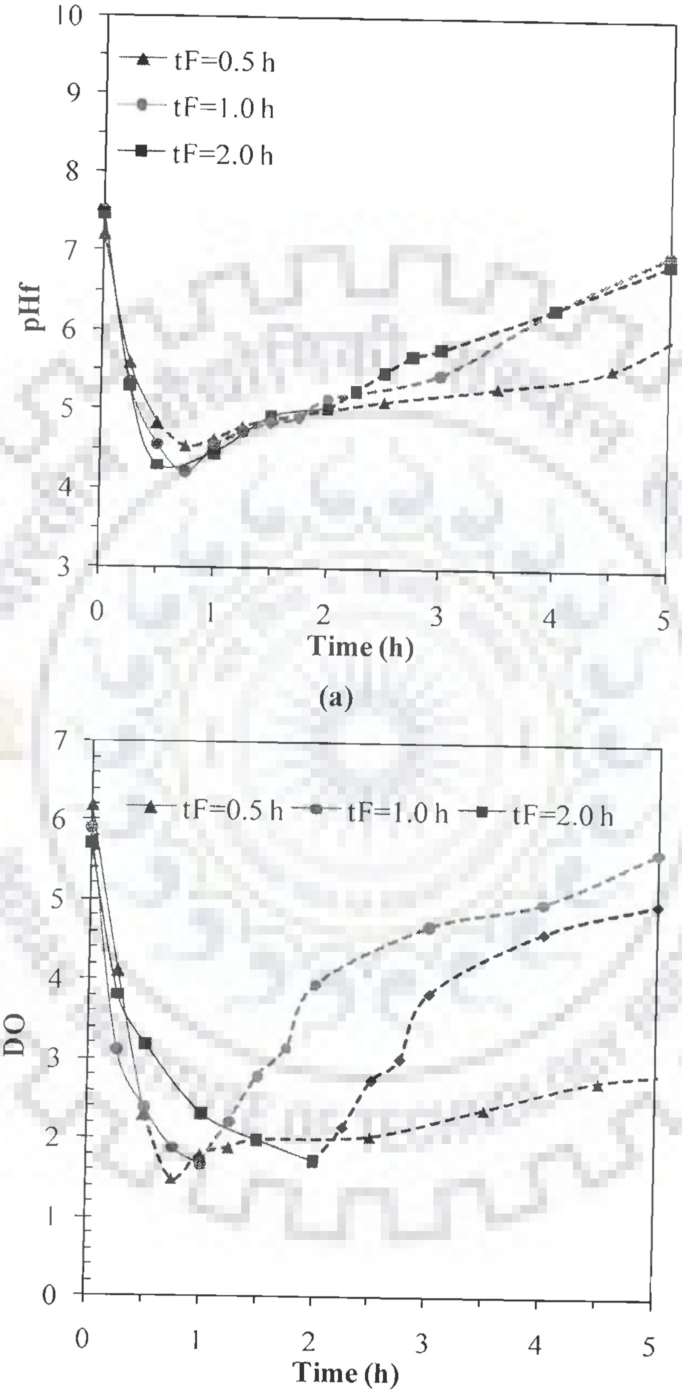
Table7.2.4. Effect of varying t_{A-R} during phase-IV study

t_{A-R} (h)	TKN_{eff} (mg/l)	%TKN Removal
1	25.8	77.20
2	27.4	75.79
3	28.1	75.17

7.2.4. Physico-Chemical Analysis of Sludge

Fig. 7.2.7 shows SEM images of dried sludge before and after its use in SBR with SDW. Fig. 7.2.7 shows harder surface texture of the sludge after its use in SBR (Fig. 7.2.7b) in comparison to before its use (Fig. 7.2.7a). There are fewer pores on the surface of sludge after its use in SBR; however, pores of varying sizes can be seen on the surface of sludge before its use in SBR.

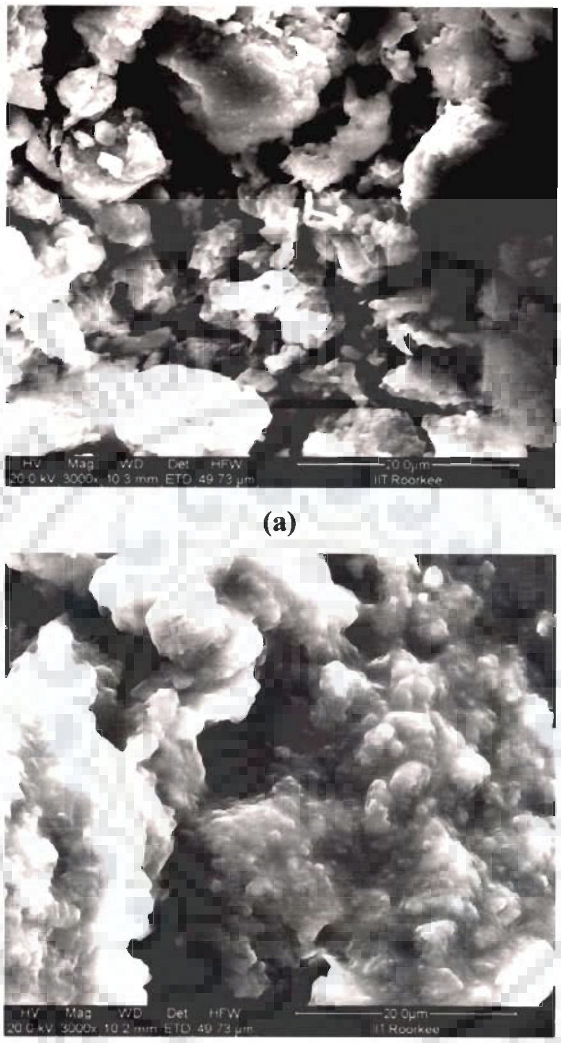
EDX analysis was done so as to study the distribution of the elements in sludge. EDX analysis showed the presence of 77.5% and 86.6% carbon, 16.11% and 8.13% oxygen, 0.58% and 1.85% aluminum, 2.28% and 0.69% silica, 1.64% and 0.38% calcium, and 1.47% and 0.36% iron in sludge before and after their use in SBR, respectively. Other elements like sulphur, potassium and magnesium were observed in trace amount. Sludge after its use in SBR was found to contain higher amount of carbon.



(a)

(b)

Fig. 7.2.6. Effect of t_F on (a) pH$_f$ (b) DO. Solid line shows filling time and dotted line reaction time.



(a)

(b)

Fig. 7.2.7. SEM image of sludge (a) without treating with SDW (b) Treated with SDW in SBR.

7.2.5. Disposal of Residues

With respect to disposal of sludge wasted during treatment of SDW by SBR technology, thermal degradation characteristics of the sludge was studied by thermo-gravimetric (TG) instrument in air environment. Thermographs of the sludge are shown in Fig. 7.2.8. Three thermal breakdowns can be seen on thermograph of sludge. There is loss of moisture and low boiling point organic matters up to 150 °C and due to this weight loss of ≈5% were observed. A sharp decrease in weight loss can be seen from 150 °C. Highest weight loss of ~73% within the entire temperature range of study was established in temperature zone 150-550 °C. The maximum rate of weight loss of 0.76 mg/min was obtained at 528 °C (Table 7.2.5). A high exothermic peak at temperature 532 °C can also be seen on DTA plot indicating evolution of high amount of heat (Table 7.2.5). The exothermic peak starts at 475 °C and ends at 535 °C indicating ignition point being 475 °C. Weight loss of ≈2.4% can be envisaged at higher temperature oxidation from 550 up to 1000 °C.

Lower heating value of the sludge was also estimated using standard adiabatic bomb calorimeter equipped with a digital firing unit and was found to be 19.1 MJ/kg. Thus, the sludge wasted during treatment of SDW by SBR technology can be dried and used as a fuel in the boilers/incinerators, or can be used for the production of fuel-briquettes. The bottom ash may be blended with fire clay to make fire bricks.

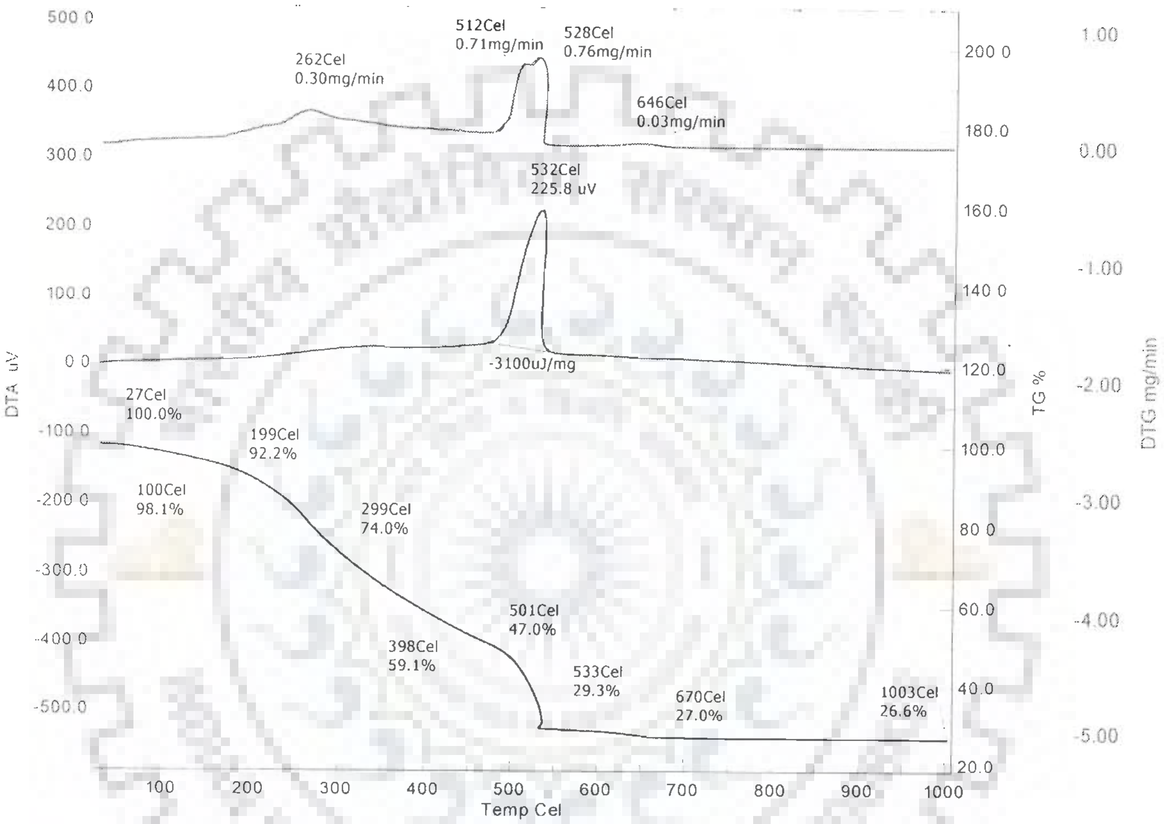


Fig. 7.2.8. TG/DTA/DTG of waste sludge during SDW treatment by SBR

Chapter – 8

CONCLUSIONS

8.0. CONCLUSIONS

On the basis of the results and discussion presented heretofore for the treatment of simulated dairy wastewater (SDW) by various physico-chemical methods (coagulation, electro-chemical treatment and adsorption) and sequential batch reactor (SBR), following major conclusions can be drawn:

Coagulation

- Optimum initial *pH* ($pH_{i\text{-}in,op}$) for the COD removal from SDW by three inorganic coagulants viz. PAC, $FeSO_4$ and $KAl(SO_4)_2.12H_2O$ was found to be ≈8.0.
- Effective *pH* ($pH_{in\text{-}effective}$) for the coagulation of SDW by inorganic coagulants were found to be 5.4, 4.7 and 4.5 for PAC, $FeSO_4$ and $KAl(SO_4)_2.12H_2O$, respectively.
- Optimum PAC, $FeSO_4$ and $KAl(SO_4)_2.12H_2O$ dosage ($m_{in\text{-}op}$) was found to be 300, 800 and 500 mg/l, respectively.
- COD removal by inorganic coagulants was mainly due to charge neutralisation and adsorption.
- Maximum COD removal efficiency by PAC, $FeSO_4$ and $KAl(SO_4)_2.12H_2O$ was found to be 69.2, 66.5 and 63.8%, respectively.
- Study on use of organic coagulants like guar gum, sodium salt of carboxy methyl cellulose (Na-CMC) and Na-alginate showed that they function as flocculation-aid only.

Electro-chemical treatment

- Maximum COD removal efficiency by electro-chemical treatment (ECT) with Al and Fe electrodes at optimum condition was found to be 68% and 70%, respectively.
- Specific energy consumption by Al and Fe electrodes was found to be 1.22 and 2.76 kWh/kg of COD removed, respectively.

- Electro-coagulation, electro-oxidation by hypochlorite which indirectly oxidises the COD, and electro-floatation were found to be the mechanisms of ECT of SDW by both Al and Fe electrodes.
- Combined electrical energy cost (C_{energy}) and electrode cost ($C_{electrode}$) for the removal of one Kg of COD from SDW having initial COD of 3.9 kg/m^3 by Al and Fe electrodes at optimum condition was found to be ₹ 19.3 and ₹ 10.75, respectively.

Adsorption

- Optimum conditions for the adsorptive treatment of SDW by activated carbon-commercial grade (ACC) and bagasse fly ash (BFA) were found to be: initial pH ≈ 4.8, adsorbent dose of 20 g/l for ACC and 10 g/l for BFA and contact time ≈8 h.
- Pseudo-second order kinetic model was found to fit the kinetic data.
- Adsorption process was found to be endothermic in nature and Redlich–Peterson isotherm model was generally found to best represent the equilibrium data.
- The change in entropy and enthalpy for SDW adsorption onto ACC and BFA were estimated as 125.85 kJ/mol K and 91.53 kJ/mol; and 25.71 kJ/mol K and 17.26 kJ/mol, respectively. The negative values of change in Gibbs free energy indicated the feasibility and spontaneous nature of the adsorptive treatment.
- ACC was found to be a better adsorbent than BFA in terms of amount of COD removed per unit weight of adsorbent.

Treatment in SBR

- In the present study, SBR was optimized for various operating parameters for the treatment of SDW. For this purpose, four phase study was carried out by varying hydraulic retention time (HRT), filling time of SDW to the reactor, anoxic phase introduction after filling phase and react phase.
- Optimum hydraulic retention time (HRT_{opt}) of 1 d with volume exchange ratio of 0.5 was found to sufficient to treat SDW.
- COD removal rate increased during filling of SDW in the SBR as filling time (t_F) was increased from 0.5 to 2.0 h.

- Filling time of 1 h and an anoxic phase of 1 h after filling phase were found to be optimum for the treatment of SDW in SBR.
- At optimum condition, COD and TKN removal were found to be 96.7% and 76.7%, respectively.
- Due to the high heating value of residues generated during various treatment processes, they can be dried and used as a fuel in the boilers/incinerators, or can be used for the production of fuel-briquettes.

Finally, optimum conditions for the treatment of SDW by various treatment methods studied in the present work and their treatment efficiencies are as follows:

Parameters	**Average Value of SDW**								
	Untreated SDW	**Coagulation**			**ECT**		**Adsorption**		**SBR**
		PAC	**$FeSO_4$**	**Potash Alum**	**Al**	**Fe**	**ACC**	**BFA**	
Dosage (g/l)	-	0.3	0.8	0.5	-	-	20	10	-
Treatment time (h)	-	0.5	0.5	0.5	1.23	0.83	8	8	10
Optimum initial pH	-	8.0	8.0	8.0	6.5	7.0	4.8	4.8	-
pH	6.5	5.4	4.7	4.5	8.6	8.5	5.2	6.7	7.3
COD (mg/l)	3900	1200	1305	1410	1245	1170	1220	2886	128
Total solids (mg/l)	3090	1930	2160	1970	1410	1485	-	-	2050
Turbidity (NTU)	1740	1.6	0.8	1.0	2.0	3.5	8	-	2.5
Conductivity (µs/cm	220	500	749	525	955	1035	-	-	200
Chloride (mg/l)	31	47	20	23	24	23	15	-	11
Total N (mg/l)	113	8.7	8.3	9.3	10.3	8.2	-	-	26.3
Heating value of residue	-	20.7	29.6	17.3	$16.5^{@}$ $19.2^{\#}$	$17.7^{@}$ $18.7^{\#}$	19.8	15.2	19.1

$^{@}$Sludge; $^{\#}$Scum

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PUBLICATIONS FROM THESIS

Papers Published/Accepted in SCI (International) Journals

1. Kushwaha JP, Srivastava VC, Mall ID. Treatment of dairy wastewater by inorganic coagulants: parametric and disposal studies. *Water Research 2010; 44/20: 5867-5874. Impact factor: 4.355.*
2. Kushwaha JP, Srivastava VC, Mall ID. Studies on electrochemical treatment of dairy wastewater using aluminum electrode. *AIChE Journal (In Press) DOI: 10.1002/aic.12463. Impact factor: 1.955*
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1. Kushwaha JP, Srivastava VC, Mall ID. A Review of various technologies for the treatment of dairy wastewater. Recent Advances in Waste Management (RAWM-2009), Organized by Department of Chemical Engineering, IT, BHU, Varanasi, India, February 20-21, 2009.

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3. Kushwaha JP, Srivastava VC, Mall ID. Equilibrium isotherm modeling for dairy wastewater treatment by activated carbon. 4th Uttarakhand State Science and Technology Congress, Organized by GBPUAT, Pant Nagar, Uttarakhand, India, November 10-12, 2009.