PRETREATMENT OPTIONS WITH RO AS TERTIARY TREATMENT OF DISTILLERY SPENTWASH

Ph.D THESIS

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **"PRETREATMENT OPTIONS WITH RO AS TERTIARY TREATMENT OF DISTILLERY SPENTWASH"** in partial fulfilment of the requirements for the award of the Degree of Doctor of Philosophy and submitted in the Department of Hydrology of the Indian Institute of Technology Roorkee. Roorkee is an authentic record of my own work carried out during a period from July, 2010 to December, 2015 under the supervision of **Dr. Himanshu Joshi,** Professor, Department of Hydrology, Indian Institute of Technology Roorkee, Roorkee.

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

(PINKI SHARMA)

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

(HIMANSHU JOSHI)
Supervisor

Date:________, 2015.


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ABSTRACT

India is one of the leading country in the field of alcohol production. There are around 360 distilleries in India, producing 2300 liters of alcohol per annum. The wastewater generated (spentwash) per liter of alcohol production is 8-15 liters, characterized by high organic content (BOD and COD), high solids (TSS and TDS), low pH (3- 4) and dark brown color. Bio-methanation is currently employed as a primary treatment step in almost all distilleries to reduce organic pollution load. However, bio-methanation alone does not meet the discharge standards, irrespective of subsequent aeration, thus leaving a need of further treatment. At the tertiary level, reverse osmosis (RO) treatment units have already been installed in many distilleries as well as studied in a number of bench and pilot studies in India. However, fouling has the main problem associated with the membrane technology restricting its use in industrial application. Industrial wastewater is generally highly concentrated leading to rapid membrane fouling which results in reduced permeate water flux and increased trans-membrane pressure. In case of distilleries, as the organic content in the spentwash after biological treatment is quite high, direct application of biologically treated spentwash to RO generally results in choking of the membrane system.

The focus of the present study is to evaluate the effectiveness of different pretreatment methods for RO system. To begin with, performance of RO treatment plant of an existing distillery in the vicinity was evaluated. Detailed surface and chemical characterization (FE-SEM, AFM, FTIR and XRD) of the RO membrane, collected from the existing plant, was also performed. The EDX results identified Si, Fe, Ca and Na as the major inorganic foulants. AFM study also supported the deposition of colloids or other foulants on the membrane surface. The XRD results confirmed the presence of calcite and silica compounds in the foulant layer.

Low pressure membranes (MF and UF) and electrocoagulation (EC) were studied as pretreatment of RO. Optimization of operating parameter was done for these treatment options in isolation as well as with RO against the displayed response of removal of contaminants (COD, color, TDS and TOC). A comparative evaluation was done in terms of contaminants removal and total water production. Study revealed that EC is more effective in removing organic matter as compared to the UF and MF. Whereas, color and TDS removal was observed more in case of UF. The difference in organic matter removal between UF and EC treatment was around 10-12 % (EC>UF). However, the difference in removal of color and TDS was

around 5-6% (UF>EC). Permeate flux (recovery) with RO has showed a remarkable increase from 17.5 l/m^2/h (direct RO) to 40.5 l/m^2/h, 38.0 l/m^2/h and 32 l/m^2/h when used in combination with EC, UF and MF, respectively.

Economic assessment of the proposed treatment schemes was done on the lab scale on the basis of water production cost, which was estimated considering technical assumptions, specification and design parameters of different treatment system. The per cubic meter water production cost for RO system is 470 Rs./m^3/m^2. The pretreatment reduces the cost up to 50% than RO system alone. Among all pretreatment studies (MF, UF and EC), EC-RO (185 Rs./m^3/m^2) has been found to be more economical and efficient than UF-RO (220 Rs./m^3/m^2) and MF-RO (256 Rs./m^3/m^2) in terms of water production. The capital cost of RO system with pretreatment (MF-RO, UF-RO and EC-RO) observed to be 30% higher than RO system alone.

Possible reuse of sludge generated during the EC treatment was explored employing it as a partial replacement of cement while manufacturing the non-constructional building blocks. Mortar specimens with different proportions of sludge ranging from 0 to 15% by weight of cement were tested for density, compressive strength and leachability of heavy metals by standard methods. From mechanical as well as environmental point of view, it was successfully demonstrated that cement–sludge mortar containing 7.5% EC sludge could be used in different applications such as decoration tiles, pot making and fencing of garden without adversely affecting the environment.

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Pinki Sharma

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ABBREVIATIONS AND SYMBOLS

Acronyms

AFM	Atomic force microscopy
ANOVA	Analysis of variance
BOD	Biological oxygen demand
CCD	Central composite design
COD	Chemical oxygen demand
EC	Electro-coagulation
ED	Electrodialysis
EDX	Energy dispersive using X-Ray
FE-SEM	Field emission scanning electron microscopy
FTIR	Fourier transform infrared spectroscopy
FTIR	Fourier transform infrared spectroscopy
g	Electrode distance
IC	Ion Chromatography
ICP-MS	Inductive Coupled Plasma-Mass spectrometry
j	Current density
LPH	Liter per hour
MF	Microfiltration
MWCO	Molecular weight cut off
NF	Nano-filtration
NTU	Nephelometric turbidity units
O&M	Operation and maintenance
RO	Reverse osmosis
RSM	Response surface methodology
t	Time
TDS	Total dissolve solids
Temp	Temperature
TFC	Thin film composite
TMP	Trans membrane pressure
TOC	Total organic carbon

UF	Ultrafiltration
V	Voltage, Volts
XRD	X-Ray diffraction
ZLD	Zero liquid discharge

Abbreviations

A	Periodic amortization payment,
Al	Aluminum
As	Arsenic
B	Boron
C	Carbon
Ca	Calcium
Cd	Cadmium
C_f	Feed concentration
Cl	Chloride
C_p	Permeate concentration
Cr	Chromium
Cu	Copper
Da	Dalton
F	Fluoride
f	RO plant availability
Fe	Iron
Hg	Mercury
K	Potassium
Mg	Magnesium
Mn	Manganese
n	Number of variables
N	Total number of experiments required
Na	Sodium
n_c	Replicate number at the central point
NO_3	Nitrate
O	Oxygen
P	Principal amount borrowed

Pb	Lead
Q_f	Feed flowrate
Q_p	Permeate flowrate
r	Periodic interest rate
R^2	Coefficient of determination
R_q	RMS roughness
S	Sulphur
Si	Silica
SO_4	Sulphate
w	Weights
xi	Coded levels of input variables
y	Predicted response
Zn	Zinc

Greek Symbols

β_0	Constant term
β_i,	Linear regression coefficients
β_{ii}	Quadratic regression coefficients
β_{ij}	Interaction regression coefficients
°C	Degree Celsius
ε	Experimental error
μ	Micron
2θ	Scanning angle


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CHAPTER 1. INTRODUCTION

1.1 History and Background

After industrial revolution in India, the industries are growing at very faster rate so the waste generated by them also increasing considerably, thereby putting extra load on environment. Management of industrial effluent is one of the most important environmental problems faced worldwide nowadays. Limited availability of clean water suitable for direct use drives the need towards the purification of the industrial effluent and utilization of the waste by-products. Characteristics of effluents and level of contaminants vary from industry to industry significantly. Effluents may be characterized in two major categories on the basis of the nature of underlying impurities/contaminants viz. inorganic and organic. Out of the industries generating effluents rich in organic contaminants having potential to cause serious problems, distilleries, pulp and paper, textile, and tanneries are most important. Among these, distillery effluent is highly organic and dark brown in color, which shall play havoc with the fields and water bodies when dumped into water sources without treatment or with inappropriate treatment [1].

India is Asia’s second largest ethanol producer with about 2300 million liters of annual production in 2006-07 [2]. Distilleries are amongst the major agro-based industries. There are around 400 distilleries in India based on different feedstocks (molasses, sugar beet, grain etc.). 326 distilleries are molasses based (molasses as raw material), out of which 126 are attached with sugar industries while the rest are of stand-alone type as shown in Figure 1.1 [3]**.**Maharashtra and Uttar Pradesh are the states in India where maximum number of molasses based distilleries were established due to the irrigation facilities that existed for sugarcane cultivation. Alcohol based industry occupies an important place in the Indian chemical industry and is a key contributor to the growth of this sector. It also provides an alternative fuel over the conventional petroleum based fuels [4]. Pollution arising from alcohol distilleries has been recognized as one of the most difficult problems to be solved to the entire satisfaction of the Pollution Control Act [1]. In view of this, Indian distilleries were stipulated to achieve zero discharge of their effluent (also called spentwash) to inland surface water by December 2005

[5]. Due to the mounting pressure of the environmental regulations, it has become essential for the distilleries to treat and reuse their wastewater to comply with the zero discharge norm to avoid damage to the environment.

Figure 1.1. State wise distribution of molasses based distilleries in India [3].

1.2 Spentwash Characteristics and its Treatment

Spentwash originating from distilleries leads to extensive soil and water pollution. It forms the major part (77%) of the effluent generated by a distillery. For every liter of alcohol produced, the distilleries would usually generate about 8–15 L of effluent (spentwash), depending on the nature of the ethanol production process (continuous or batch) and quality of feedstock used. Spentwash is characterized by extremely high chemical oxygen demand (COD) falling in the range of 80,000 to 1,00,000 mg/L, biochemical oxygen demand (BOD) ranging from 40,000 to 50,000 mg/L, high dissolved inorganic solids, low pH, strong odor and dark brown color as shown in Table 1.1 [5]. Inorganic portion is mainly contributed by nitrogen (1,660-4,200 mg/l), phosphorus (225-3,038 mg/l) and potassium (9600-17,475 mg/l) [6]. Characteristics of the spentwash also varies depending on the raw material used (quality of molasses), unit operations and process used for alcohol recovery [7]. Generation of large amount of spentwash and the presence of recalcitrant compounds in it make its treatment by conventional methods challenging.

A number of techniques have been practiced and studied for the treatment of spentwash from time to time. Figure 1.2 shows the various combination of treatment approaches for spentwash treatment adopted in context of Indian distilleries.

Beingvery richin organic matter, spentwash has been proposed for use as a fertilizer, food supplement, biomass production agent, animal feed, and potash source [4] but the ground water contamination still being a matter of concern, so it is banned by the government. Bio-methanation is currently employed as a primary treatment step in almost all distilleries to reduce organic pollution load and recover energy in the form of biogas [8]. However, bio-methanation alone does not meet the discharge standards, irrespective of aeration, thus leaving a need of further treatment [9].

Bio-composting is also a popular option adopted by several Indian distilleries. The adverse effect of spentwash disposal, via bio-composting is magnified during the rainy season. In some parts, the color problem in ground water is so acute that distilleries have to provide potable water to surrounding villages. For land disposal, availability of land in nearby region of the distillery is the major necessity [10].

Table 1.1. Characteristics of untreated and anaerobically treated distillery effluent.

Parameters	**Values of distillery effluent**	**Values of anaerobically treated effluent**
pH	3.0–4.5	7.5–8
BOD_5 (mg/l)	50,000–60,000	8000–10,000
COD (mg/l)	110,000–190,000	45,000–52,000
Total solid (TS) (mg/l)	110,000–190,000	70,000–75,000
Total volatile solid (TVS) (mg/l)	80,000–120,000	68,000–70,000
Total suspended solid (TSS) (mg/l)	13,000–15,000	38,000–42,000
Total dissolved solids (TDS) (mg/l)	90,000–150,000	30,000–32,000
Chlorides (mg/l)	8000–8500	7000–9000
Phenols (mg/l)	8000–10,000	7000–8000
Sulphate (mg/l)	7500–9000	3000–5000
Phosphate (mg/l)	2500–2700	1500–1700
Total nitrogen (mg/l)	5000–7000	4000–4200

Source: [11]

Various physico-chemical and biological methods such as adsorption, coagulation-flocculation, wet air oxidation etc. are also in use for the removal of color and organic matter from the biodigestedspentwash at the tertiary level. Concentrating the spentwash in multiple effect evaporators and its subsequent incineration has also been tried in a few places [10], [12]. However, this was not found technically and economically feasible in majority of the cases [13].

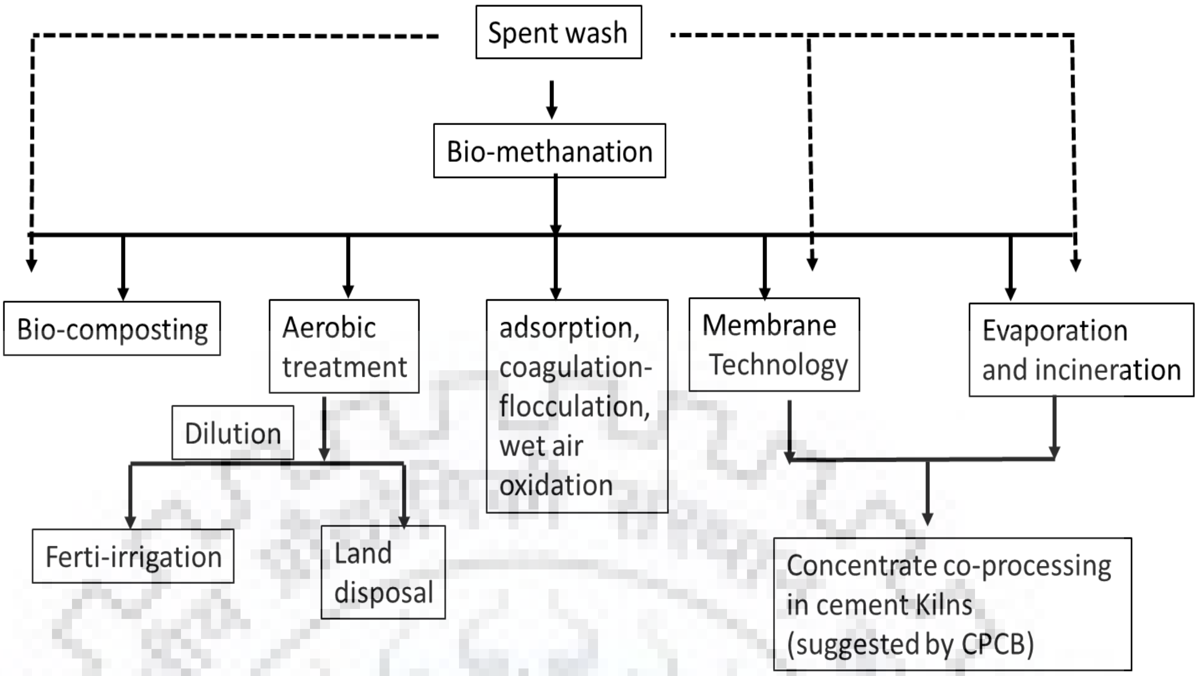

Figure 1.2. Spentwash treatment technologies.

In the recent years, there has been a growing interest in membrane technology for treatment of various type of effluents. Membrane separation techniques have grown from a simple laboratory tool to an industrial process with considerable technical and commercial impact [14].

The application of reverse osmosis (RO) process, particularly for industrial effluent treatment has been limited due to sensitivity of the RO membrane to fouling with suspended solids, colloidal material, organics, bacteria and scale from dissolved ions in the raw water. These can cause irreversible damage to the RO system if not removed through proper pretreatment. Treatment of raw spentwash with membrane system results in fouling of the membrane in a short span of time and also loss of biogas as an energy resource produced from the bio-methanation process. The major problem encountered in almost every membrane filtration plant is fouling.

At tertiary level, reverse osmosis (RO) treatment plants have already been applied in a number of bench and pilot studies in India [15][16]. Earlier work on the pilot scale using a hybrid nano-filtration (NF) and RO process demonstrated 80 to 95% rejection of the color and 55% transmission of monovalent salts at pressures of 30-50 atm[17]. The results with various membrane systems have been promising; however, significant challenges remain in selecting the appropriate pretreatment system. To make the membrane processes more reliable and effective, improvement in process designs by including proper pretreatment appears essential [18], [19]. Present study is projected to select an appropriate pretreatment process for RO along with waste utilization for tertiary treatment of distillery spentwash.

1.3 Research Gaps

In the light of existing situation, distilleries are exploring new approaches to make the membrane process effective for spentwash treatment. Followings research gaps were observed:

- In depth study on poor performance of existing RO treatment process for distillery spentwash needs to be evaluated.
- Pretreatment train before RO needs to be rectified as employing RO treatment directly after bio-methanation is not advisable.
- Various physicochemical pretreatment options (MF, UF and EC) for RO needs to be evaluated in terms of pollutant removal and water recovery at tertiary treatment.
- Refinement in economic assessment of RO with pretreatment (MF, UF and EC) systems is required to find a cost effective solution.

1.4 Objectives

The aim of the present study is to evaluate the effectiveness of different pretreatment methods for RO, treating bio-digested distillery spentwash by developing an effective treatment train. Following are the major objectives of the present study:

- Study of an existing tertiary RO treatment system for distillery spentwash.
- Performance evaluation of different pretreatment processes (micro-filtration, ultra-filtration and electro-coagulation) with RO membrane system.
- Economic assessment and comparison of proposed treatment schemes (MF-RO, UF-RO and EC-RO) with RO system.
- Reuse of waste generated from the pretreatment process.

1.5 Significance of Study

The present study concentrates on water recovery from distillery effluent and utilization of generated by products during treatment processes. The fouling issues in RO membrane system used in distillery at tertiary level is minimized by using different pretreatment processes (MF, UF and EC) in combination with RO during the present study.

Application of electrocoagulation as pretreatment of RO system for the tertiary treatment of distillery spentwash not only improves the RO performance but also cut down the water production cost significantly and generate good quality of water, which can be used as process water within the industry.

The knowledge based on the present study may be utilized to minimize the RO membrane fouling issues faced by the distillery and helps to bring the membrane treatment processes in a better practice.

1.6 Organization of Thesis

The thesis is divided into eight chapters.

Chapter One presents an introduction, problem statement, aims and objectives along with the significance of work.

Chapter Two presents the literature review, discussing the earlier studies carried in the field of spentwash treatment by RO membrane systems in isolation or with other pretreatment systems, and their limitations along with the research gaps.

Chapter Three presents the methodology related to the experimental work carried out *viz.* analytical techniques, laboratory scale experimental setup, and optimization of process parameters, membrane experiments and electro-coagulation experiments.

Chapter Four presents the study of spentwash treatment processes in existing distillery.

Chapter Five presents the Optimization and comparison of low pressure membranes MF, UF and EC as pretreatment options for RO process.

Chapter Six presents the economic assessment of the proposed configured systems.

Chapter Seven presents the waste management study related to the EC sludge.

Chapter Eight presents major findings and conclusions of the study. Future scope of the present study is also highlighted.


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CHAPTER 2: LITERATURE REVIEW

2.1 Pollution Potential of Distillery Spentwash

The wastewater generated from molasses based distillery (Spentwash) is primarily characterized by high organic matter, odorous and typical dark brown color. It is perceived as one of the prime polluters in the countries producing alcohol from the of sugar cane molasses.

Seasonal discharges of spentwash containing high nutrient and organic loading into water courses would result in eutrophication of contaminated water courses [20]. Its intense color does not allow sunlight to enter into water bodies which becomes detrimental to the aquatic life due to reduction in photosynthetic activity leading to reduction in oxygenation. Land disposal is also equally hazardous. Application of distillery effluent to soil without proper monitoring, perilously affects the groundwater quality by altering its physicochemical properties such as color, pH, electrical conductivity (EC) etc. due to leaching down of the organic and inorganic ions [21]. Reduction in the alkalinity of soil and manganese availability leading to suppression of seed germination have also been reported [22]. The indices indicating soil quality like Sodium Absorption Ratio (SAR), Soluble Sodium Percentage (SSP) and Kelly's ratio have also been reported to be adversely affected in the soil amended with distillery effluent [23]. Constant disposal/irrigation of the soil with the effluent also reportedly leads to deleterious effects on the soil properties. Soil microorganisms are essential components of the soil ecosystem and are involved in regulating various processes of nutrient recycling in soil. Any type of interference with their activity may affect soil productivity as they are the indices of soil fertility [24]. A number of studies have demonstrated the presence of genotoxic compounds in wastewater from distilleries [6], [25]. Raw spentwash discharge in rivers has also been observed to result in a highly deleterious effect on fish and other aquatic life. In view of the above, it appears necessary to take proper remedial measures for elimination of pollutants and color from distillery effluent from an environmental and also aesthetic points of view.

2.2 Issues with Spentwash Treatment

Spentwash is extremely toxic due to the presence of highly colored organic compounds i.e. melanoidin[4], [26], formed during the non-enzymatic chemical reaction (Maillard reaction) between carbohydrates (sugars) and amino acids (proteins) at high temperature [14] or thermal degradation and condensation reaction of sugars [27].Maillard reaction takes place during the heat treatment and a class of compounds is formed as Maillard product. At high temperature (>50˚C), reaction occurs effectively and is also favored at pH 4 to 7 [28]. Melanoidin is a widely distributed biopolymer in nature having a complex chemical structure and it is hardly decomposed by microorganisms. Suggested empirical formula for the melanoidin is $C_{17-18}H_{26-27}O_{10}N$ having molecular weight between 5,000 and 40,000 Da [29], [30]. Nature and concentration of the parent reacting compound along with the reacting conditions (pH, temperature, heating time etc.) affect the exact structure of the product compound. Increase in pH or temperature enhances the reaction rate between sugar and amino acids and molecular weight of colored compound also increase as browning proceeds [31]. The presence of skatole, indole and other sulphur compounds left un-decomposed during distillation, imparts unpleasant odor to the spent wash [32]. Antioxidant property of the melanoidin renders them toxic to microorganisms [33]. Due to the large volume of spentwash and presence of certain recalcitrant compounds, the treatment of this stream is rather challenging by conventional methods.

2.3 Spentwash Treatment Technologies

A number of technologies have been explored for the treatment of distillery spentwash from an earlier time. The reported studies can broadly be classified under biological and physico-chemical treatment.

2.3.1 Biological Treatment

Biological treatment is the primary treatment step generally employed by the distillery for treating spentwash to reduce organic pollution load. Biological treatment could be anaerobic as well as aerobic. These are discussed in the following sections:

2.3.1.1 Anaerobic Treatment

Anaerobic treatment is the first most treatment process which is generally used by distillery industries. Anaerobic treatment is often followed by aerobic treatment to further reduce the organic load. Treatment of wastewater having high organic load using anaerobic process is a very promising technology [34]. At first stage, aerobic treatment is not preferred due to high production of sludge (50% of the COD), high energy consumption without any resource recovery [35]. Anaerobic treatment is having so many advantages over aerobic treatment i.e. low sludge production, less energy consumption and generation of biogas as resource which can be used as fuel in boilers for steam generation etc.

Anaerobic system can be single or two phase system i.e. involving single reactor or two separate reactors for acidogenic and methanogenic phase respectively. Two phase system is most appropriate for the treatment of high strength of wastewater due to its capability of optimizing the fermentation steps of each phase in separate reactors, which results in higher overall methane generation efficiency [36], [37].

Simplest choice for the anaerobic treatment of distillery spentwash is anaerobic lagoons. Rao et al., (1972) [38], investigated the application of two stage anaerobic lagoon in series and found overall BOD reduction up to 92%. However, higher land requirement, odor problem due to open system and ground water contamination issue restrict its application [39], [40].

Conventional anaerobic systems such as continuous stirred tank reactor are found to be less feasible for the treatment of distillery spentwash treatment due to high HRT (hydraulic retention time) value [41], in-spite of its simple and high COD removal efficiency of 80-90% [40]. High rate anaerobic reactors have extensively been used. These have different categories such as suspended bed reactors, fixed bed reactor, fluidized bed reactor and hybrid reactor. UASB reactor is one of the popular high rate anaerobic reactor which has been successfully employed for the treatment of various types of wastewater including spentwash[42], [43]. A notable point is that after anaerobic treatment, spentwash cannot be directly discharged due to high organic load and darker color due to intensification of color causing pigment (melanoidin) under anaerobic conditions [44]. Performance of various types of anaerobic reactors for treating distillery spentwash is summarized in Table 2.1.

2.3.1.2 Aerobic Treatment

Anaerobic treatment is generally followed by aerobic treatment to further reduce the organic pollution load and for decolorization of spentwash. The most commonly used aerobic process is the activated sludge process. Sequencing Batch Reactor (SBR) has been reported to be quite promising for treating effluents of wineries [45]. Rotating biological reactor is another type of aerobic process, which is being used [46]. Different aerobic treatment process result in reduction of organic load (COD) significantly, but they are energy intensive and color removal is not adequate. Several culture of bacteria, fungi and algae have also been studied for treating distillery spentwash. Most of the reported studies are restricted to laboratory scale experiments and no pilot scale studies are reported yet. Table 2.2 presents the microbial culture based studies for the removal of COD and color from distillery spentwash.

Constructed wetlands have also been investigated for treating distillery spentwash treatment. Chandra et al., 2008 [25] studied the bi-phasic treatment using bacterium Bacillus thuringienesis and Typhaangustata for reducing the color and organic load. The reported organic load and color reduction was 98-99% in 7 days. In another laboratory scale investigation employing constructed wetland, Typhalatipholia was used to treat diluted distillery spentwash[47]. The results showed 78% of COD reduction in 7 days. Adequate land availability is the major issue for this treatment.

Bio-composting is another aerobic treatment process adopted by several Indian distilleries that are attached to sugar mill with land availability. Spentwash is sprayed in controlled way on sugarcane press mud (generated during sugar production) and resulting in a humus rich product which can be used as fertilizer. The adverse effect of spentwash disposal via bio-composting is magnified during the rainy season, which resulted in ground water contamination.

During the 1970s, land disposal was practiced as one of the main treatment options, since it was found to enhance yield of certain crops i.e., ferti-irrigation. But the downside of this method was that it contaminated both the ground water and surface water sources, as most often it was practiced in non-scientific manner.

Table 2.1. Anaerobic treatment of distillery spentwash.

Reactor type	Organic loading ($Kg/m^3/d$)	COD Removal (%)	BOD Removal (%)	HRT (days)	Reference
Upflow anaerobic sludge blanket (UASB) reactor	28	39-67	80	-	[48]
Diphasic fixed-film reactor (granular activated carbon (GAC) as support media)	21.3	67.1	-	4	[49]
Diphasic fixed-film reactor (Clay brick granules as support media)	22	71	-	3	[37]
Downflow fixed-film reactor	14.2-20.4	85-97	60-73	3.3-2.5	[50]
Hybrid anaerobic baffled reactor	20	70	-	-	[51]
Granular bed anaerobic baffled reactor (GRABR	2.37	90-96	80-92	4	[52]
Anaerobic contact filter	-	73-98	-	4	[53]
Hybrid Reactor (sludge blanket and filter)	8.7	79	-	5	[54]
Hybrid UASB and filter	36	80	-	0.25	[55]
Upflow blanket filter	9-11	70	-	9-11	[56]
Thermophillicupflow anaerobic fixed film reactor	6.29	76	-	2.5	[57]
Thermophillic anaerobic fluidized bed reactor	5.88	96	-	2.5	[57]

Table 2.2. Aerobic treatment with microbes (fungi, bacteria and algae).

Type of microorganism	COD removal (%)	Color Removal (%)	Time (days)	Reference
Fungi				
Aspergillus sp.	75-97	56-80	3-5	[58]–[61]
Coriolus sp.	53-90	53-80	4-10	[62]–[65]
Flavodonflavus	-	80	7	[66], [67]
Phanerochaetechrysosporium	73	53-80	7-10	[27], [68]
Trametes sp.	61-77	73-82	3-7	[69]
Geotrichumcandidum	-	80	3	[70]
Bacteria				
Bacillus thuringiensis	-	22-27.4		[71]
Bacillus brevis				
Bacillus sp.				
Xanthomonasfragariae	-	76	5	[72]
Bacillus megaterium		76	5	
Bacillus cereus		82	5	
Pseudomonas putida	-	60	1	[36]
Pseudomonas fluorescens	-	94	4	[73]
Pseudomonas aeruginosa	-	67	-	[74]

Cyanobacterial/ algal system				
Oscillatoriaboryana BDU 92181	60	75	30	[26]
Combine micro algae (Chlorella vulgaris) and amcro algae (Lemna Minuscule)	61	52	5	[75]

2.3.2 Tertiary Treatment

2.3.2.1 Physico-chemical Treatment

Apart from biological treatments, various physicochemical treatment schemes have also been investigated for distillery spentwash treatment. Activated carbon is a well-known adsorbent and widely used for the color and organic pollutant removal from wastewater. Color removal efficiency of commercial activated carbon and bagasse fly ash were compared by Mall and Kumar (1997) [76] who observed the color removal efficiency of activated carbon around 80.7% with a dose of 20 g/L and that of bagasse fly ash around 58% with a dose of 30 g/L. Advanced oxidation with ozone, H_2O_2, ultraviolet etc. has also been studied to degrade the organic matter and color from spentwash. Ozone is highly reactive but it only transforms the functional groups and doesn't degrade the melanoidin[44].

Researchers have also investigated the removal of COD and color from different types of wastewater like textile effluent, pulp and paper mill effluent etc., using various physicochemical processes like thermochemical precipitation, acid precipitation, chemical oxidation and coagulation [77]–[79]. In a study combination of chemical and physicochemical treatment (coagulation followed by adsorption) was investigated to remove COD and color from textile wastewater [80]. It was concluded that the salt of ferrous sulfate was most efficient for removing COD from the textile wastewater but the high dose of chemical and generated sludge was a matter of concern.

2.3.2.2 Membrane Technology

In recent years, membrane techniques have grown from a simple laboratory tool to an industrial process with considerable technical and commercial impact. Membrane processes with the greatest immediate application to water and wastewater treatment are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), and electrodialysis (ED). Membranes have been used at large scale to produce potable water from the sea by reverse osmosis, to clean industrial effluents (distillery wastewater) and to recover valuable constituents by (ED)[81]–[83].

2.3.2.3 Reverse Osmosis (RO)

During recent years, RO system has gained attention to treat various types of domestic and industrial wastewater. A number of applications have been investigated on water treatment [84], [85]. Into et al., (2004) [86] investigated the treatment of wastewater from an industrial park by using 5 stage RO system. Results revealed that the permeate flux decreases as the concentration increases, which in turn decreases the permeate flow at each stage. Linde et al., (1995) [87] investigated the different types of landfill leachate treatment by using RO. Reduction in the permeate flux with time was observed due to fouling.

2.3.2.4 Nano-filtration (NF)

Ciputra et al., 2010 [88] investigated the comparative study between ion exchange resin (IER), granular activated carbon (GAC) and nanofiltration (NF) to remove dissolved organic matter from paper mill effluent and achieved maximum removal using NF. Mrayed et al., (2011) [89] studied the effectiveness of NF and RO process to produce recycled water for irrigation from treated effluent having high salinity. The results revealed that the integration of NF as tertiary treatment has potential to reclaim water for irrigation purpose having enough nutrients. NF membrane for treating various effluents; electroplating wastewater [90], land fill leachate [91], leather plant wastewater [92], [93] and textile wastewater [82] were also been investigated by different researchers.

2.3.2.5 Electrodialysis (ED)

RO is a broad spectrum separation process. The concentrate of RO after treatment of distillery spentwash is highly rich in both salts and residual organics. The best opportunity to achieve high organic rejection (>90%) and high salt transmission (>90%) is to employ salt specific separation processes such as electro dialysis (ED). DC voltage is applied to the two different types of membrane stacked alternately and spaced apart by spacers. Salt ions are attracted by the membranes depending upon their polarity and clean water comes out of from other side [94], [95]. Wilde, (1987) [96] demonstrated a 55% recovery of potassium at the bench scale using ED with anion and cation exchange membranes. However, again, the key observation as reported by Vlyssides (1997) [97] was that the fouling increased and rejection decreased as the electrodes fouled.

2.3.2.6 Membrane Bio-reactors (MBR)

In an MBR, membrane filtration (MF/UF) is integrated with the biological treatment. The use of membrane system at tertiary stage is extended to secondary stage in MBRs. Brik et al., (2006) [98] investigated the treatment of textile effluent by MBR using tubular modules. Results of the study showed the COD and color removal between 60-95% and 30-99%, respectively. Zhang et al., (2006) [99] studied the treatment of simulated distillery waste water by aerobic MBR using 0.2 micron stainless steel membranes and reported 94.7% COD removal efficiency. Lu et al., (1999) [100] have also investigated the aerobic MBR with rotatory disk type UF membrane for treating high strength fermentation wastewater.

Various physiochemical treatment schemes for the treatment of distillery spentwash are summarized in Table 2.3

Table 2.3. Treatment employing physiochemical methods.

Treatment method	COD removal (%)	Color removal (%)	Reference
Coagulation–flocculation			
Polyferrichydroxysulphate	-	95	[101]
Ferric chloride	-	96	
Ferric sulphate	-	95	
Aluminiumsulphate	-	83	
Calcium oxide	-	77	
Calcium chloride	-	46	
Ferric chloride	55	83	[102]
Aluminium chloride	60	86	
Polyaluminium chloride	72	92	
Iron chloride coagulation	38	47	[103], [104]
Iron chloride	65	69	
Aluminium chloride	61.3	74.4	
Calcium oxide	39.8	80.2	
Adsorption			
Chitosan	99	98	[105]
Chemically modified bagasse			[106]
DEAE bagasse	40	51	
CHPTAC bagasse	25	50	
Bagasse fly ash	50	58	[76]
Activated charcoal	-	98	[101]
Oxidation Processes			
Ozonation	15-25	80	[44]
Fenton’s oxidation	88	99	[107]

Electrocoagulation and electro Fenton	92.6		[108]
Ozone	13	76	[31]
Ozone + Hydrogen peroxide	23	89	
Other processes			
NF+RO	99	100	[17]
Emulsion liquid membrane	86	-	[109]
Electrochemical treatment	55-88	-	[97]
Ceramic UF membrane	50	-	[110]
Membrane bioreactor	94.7		[99]

2.4 Issues with RO Membrane Technology

Membrane technology has grown from a simple laboratory tool to industrial application. It has been widely used from sea water desalination to the treatment of various type of industrial wastewater. Fouling is the main problem associated with the membrane technology restricting its use in industrial application. Industrial wastewater is highly concentrated leading to rapid membrane fouling which results in reduced permeate water flux and increased trans-membrane pressure [111]. RO membrane fouling is mainly of two types: internal fouling and external (surface) fouling. In high pressure membranes (RO and NF), fouling is broadly classified in four categories: colloidal/particulate fouling (accumulation of colloidal/particulate matters), organic fouling (deposition of organic macromolecules), inorganic fouling (precipitation of inorganic salts) and biofouling (microbial colonization) [112]. Fouling can be mitigated by using anti scalant and appropriate pretreatment prior to RO [111].

2.4.1 Need of Pretreatment for RO Membrane

Before discharging the distillery spentwash in to any water body or on land, an appropriate treatment is imperative so as to meet the discharge standards. Recovery of the resources from the wastewater and reuse of the treated effluent would conserve the water resource as well as forbid the wastage of large amount of water used in dilution for meeting the disposal standards. For high strength wastewater like distillery spentwash, anaerobic treatment is generally practiced in Indian industries. Further, RO plants have been installed for tertiary treatment in many distilleries. As the organic content in the spentwash after biological treatment is quite high, direct application of biologically treated spentwash to RO generally results in choking of the membrane system within a short span of time. Without a proper pretreatment system, RO plant would need expensive and complicated cleaning and maintenance to sustain production, especially in industrial and municipal effluents reuse [113]. It is also quite clear that the issues related to an ineffective pretreatment with RO system like membrane fouling, high frequency of membrane cleaning and replacement, low water recovery and poor treated water quality; all directly influence the operational cost of the treatment plant.

In a number of bench and pilot studies in India on the RO systems intended to be used at the tertiary level, the results have been found promising [15], [16]. However, significant challenges remain in selecting the appropriate pretreatment system for achieving optimal performance as well as addressing the major issue of fouling. In depth assessment of nature and characterization of fouling has also been found lacking in literature with respect to distillery spentwash treatment. To make the membrane processes as a proven and reliable technology, recasting the process designs by integrating proper pretreatment appears to be mandatory.

2.4.2 Pretreatment Options for RO Membrane

2.4.2.1 Micro-filtration (MF) and Ultra-filtration (UF)

Low pressure membranes; micro-filtration and ultrafiltration (MF and UF) have been used as a pretreatment step in a number of applications in water and wastewater treatment. Ultrafiltration (UF) is widely used in various applications; such as ultrapure water production, in food industry for separation, wastewater treatment in pulp and paper industry, chemical industries etc. [114], [115]. UF and MF membranes have also been investigated for pretreatment of RO influent for desalination and recycling of wastewater by many researchers at laboratory as well as pilot scales. [116]–[119]. The results revealed that UF reduces the rate of membrane fouling, cost of chemicals for dosing and also extends the life of RO membrane modules. Into et al., (2004) [86] studied the feasibility of reuse of industrial effluent after RO treatment and were successful. Ruth et al., (2011) [120] evaluated the use of MF and UF for RO pretreatment to reclaim municipal wastewater in paper mill. Results revealed that the quality of the produced reclaimed water was good enough to be used as a substitute of fresh water in a paper mill but the system showed several problems due to unstable quality of the feed water. Bick et al., (2012) [98] also investigated the feasibility of an integrated approach to produce high quality of water by using UF in series with RO membrane from secondary effluent for unrestricted reuse. Aouni et al., (2012) [121] studied and compared the UF/ NF process for the removal of reactive dyes from textile wastewater. Results demonstrated the NF process to be effective and capable of elevating the treated water quality, and also offering a possibility of use of UF membrane as pretreatment to improve wastewater quality.

Chang et al., (1994) [110] demonstrated that ceramic ultrafiltration membranes could be used to reject 50% of the COD of spentwash prior to anaerobic digestion. The key finding of this study was the need for low trans-membrane pressures (0.5 atmospheres) and high velocity (>6 m/s) to maintain permeability and manage the fouling properties of the molasses. The authors also reported some improvement in anaerobic reactor performance due to the removal of inhibitors. The findings of this study suggested that the use of a tighter membrane (such as a nano-filtration membrane) in a configuration that decouples pressure drop from shear force (such as a vibrating membrane) would be more appropriate in these applications.

The need for a higher rejection membrane that is more selective for organics was demonstrated by Kumaresan et al., (2003) [109] in studies that demonstrated that use of an organic selective emulsion liquid membrane enabled the recovery of 86% of the COD. Recent work on the pilot scale using a hybrid nano-filtration (NF) and RO process demonstrated 80 to 95% rejection of the color and 55% transmission of monovalent salts at pressures of 30-50 atm. [17]. Further treatment of the NF permeate using RO at an applied pressure of 50 atm removed 99% of the residual salt and produced high quality water containing negligible amounts of salt and organics that was suitable for discharge or industrial reuse. *Again, the key lessons from these studies were the need to control fouling, as indicated by the high operating pressures (35-50 atm), the requirement to achieve better separation of the salt from organics, conducting further work to characterize the nature of the organics and identify appropriate cleaning protocols to maintain permeability and separation.*

2.4.2.2 Electro-coagulation (EC)

Electro-coagulation (EC) has been utilized for the various types of wastewater by different researchers [122]–[126]. It has been widely used for removing the color from industrial wastewater [127]–[130]; and for the removal of COD and color from paper mill effluents [131]–[133], laundry wastewater [134], refinery wastewater [135]–[137], biodiesel wastewater [138], tannery wastewater [139], electroplating wastewater[140] and restaurant wastewater [141]. EC technology has also been used for the treatment of potable water. Emamjomeh et al., (2009a and 2009b) [142], [143] showed the effectiveness of EC process for de-fluoridation of potable water and could also be utilized for the de-fluoridation of industrial wastewater. A complete review on removal of pollutants by electro-coagulation and electro-coagulation/flotation processes was given. Results have demonstrated that pollution parameters can be effectively removed via EC treatment provided that operating parameters and experiment conditions are carefully optimized [144]. EC process optimization with different operating parameters has been done by many researchers by using parametric and multiple response optimization for treatment of textile printing wastewater [145], [146] and acrylic dye bearing textile wastewater [147]**.** EC has also been used for treatment of distillery spentwash as shown in Table 1.

Manisankar et al., (2003 and 2004) [29], [148] investigated the effect of pH and current density on the treatment of distillery effluent by EC process using graphite anode electrode in the presence of supporting electrolytes (sodium chloride, sodium flouride and sodium bromide). They showed 85.2% COD removal Piya-areetham et al., (2006) [149]carried out the EC study using graphite particles and titanium sponge as the voluminous anodes and Ti/RuO_2 as cathode placed above anode particles. They reported 89.62% COD and 92.24% color removal efficiency. Prasad et al., (2008) [150] reported 95% color removal from distillery spentwash by EC process using Fe anode. Prasad et al., (2009) [151] employed ruthenium oxide coated titanium mesh as anode and stainless steel (SS) as cathode for distillery spentwash treatment. COD and color removal were found to be 37% and 81%, respectively, at optimal conditions. Krishna et al., (2010) [152] reported 72.3% COD removal efficiency at optimum condition using Al electrodes. They also suggested further treatment of effluent before discharging. Khandegar and Saroha (2012) [153]studied EC treatment process by Al and Fe electrodes in various combinations and observed maximum 81.3% COD removal by Al-Al electrodes. Asaithambi et al., (2012) [154] investigated the synergistic effect of ozone assisted EC treatment on distillery effluent. Results concluded that combined technique was more efficient than either technique alone. Yavuz et al., (2007) [108] studied the effect of H_2O_2 on electro chemical treatment of distillery spentwash. They showed 92.6% removal of COD by electro-fenton study. In few previous studies, EC treatment of bio-digested effluent from the distillery were reported using Fe, SS and Al electrodes [155]–[157]. Ponselvan et al., (2008) [155] reported maximum COD removal efficiency of 52.23% at optimized condition using Al electrodes. Kumar et al., [2009] [156] used Fe electrode and studied the effect of pH, current density, inter-electrode distance and time on COD and color degradation. Maximum COD and color removal of 50.5% and 95.2% respectively was reported at optimized conditions. Thakur et al., (2009) [157]reported COD and color reduction of 61.6% and 98.4%, respectively, using SS electrodes. Aouni et al., (2009) [158] investigated the hybrid EC/ NF process for the treatment of textile wastewater. Results confirmed the hybrid EC followed by NF process was effective and capable of elevating the treated water quality.

Table 2.4. Comparison of various studies on electrochemical treatment of distillery spentwash.

Spent-wash used	Electrode used	Parameters studied	Optimization procedure	Optimized parameters	Performance			Reference
					COD (%)	Color (%)	TOC (%)	
Raw spentwash	(RuO_2–Ti) as anode, SS as cathode	j: 1.5 -5.5 A dm^{-2}.	One at a time	-	92%	100	-	[148]
Actual effluent from alcohol plant	Graphite	j: 1-6 Adm^{-2}; pH_o: 2-13.5; C_o: 12000–15000mg/l; type of additive: NaCl, NaBr, NaF	One at a time	-	85.2	100	-	[29]
Raw spentwash	Graphite + titanium particles	i: 1–10 A; pH_o; 1–5; type of additive: H_2O_2 and NaCl.	One at a time	i: 9 A; pH_o: 1; type of additive: 1.0 M NaCl	89.62	92.24	-	[149]
Raw spentwash	Fe	j: 12.5-37.5 Am^{-2}; dilution: (10- 30%); t: 120-240 min	BB design	j: 31 Am^{-2} dilution: 17.5% and t: 240 min	-	93.5		[150]
Diluted distillery spentwash	ruthenium oxide coated titanium mesh acting as anode and SS as cathode	j: 7.142 to 57.142 Am^{-2}; pH_o: 4–10; dilution: (5-30%); t: 60-300 min	factorial design	j: 14.285 Am^{-2} dilution; pH_o: 5.5; 10% and t: 180 min	37	81		[151]
Biodigestereffl	Al	j: 44.65–223.25 Am^{-2};	Pareto	j: 120 Am^{-2}; pH_o:	52.23	-		[155]

uent		pH$_o$: 2–8; g: 1–3 cm; t: 30–150 min; Co: 15,600 mg/l.	analysis	6.0; g: 1 cm; and t:150 min.				
Biodigester effluent	Fe	j: 44.65–223.25 Am^{-2}; pH$_o$: 2–8; g: 1–3 cm and t: 30–150 min; C$_o$: 15,600 mg/l	CCD	j: 44.65Am^{-2}; pH$_{o:}$ 8; g: 2 cm; t: 120 min	50.5	95.2		[156]
Biodigester effluent	SS	j: 39.06–195.31Am^{-2}; pH$_o$: 3.5–9.5; g: 1–2 cm and t: 30–150 min; C$_o$: 9310 mg/l	CCD	j: 146.75 Am^{-2}; pH$_o$ 6.75; g: 1 cm t: 130 min	61.6	98.4		[157]
Anaerobically treated distillery wastewater	Al	j: 10–30 Am^{-2}; pH$_o$: 3–9; and t: 30–180 min; C$_o$: 42240-46440 mg/l	One at a time	j: 30 Am^{-2}; pH$_o$ 3; cm t: 120 min	72.3	-		[152]
Raw spentwash	Al and Fe	j: 6.25- 18.75 Am^{-2}, pH$_o$: 3-9; agitation speed: 200-600 rpm; t: 20-120 min; and g: 2-4 cm; C$_o$:120000 mg/l	One at a time	j: 18.7 Am$^{-2;}$pH$_o$: 3; agitation speed: 500 rpm; t: 120 min; g: 3 cm	81.3	-		[153]
Raw spentwash	Ozonation + Fe and Al	j: 1–5 Am^{-2}; pH$_o$: 2–10; g: 1–3 cm; C$_o$: 1250–5000 mg/l	One at a time	j: 3 Adm^{-2}; pH: 6 ; g: 1 cm; C$_o$: 2500 mg/l	83.0	100		[154]
Biomethanated spentwash	SS	j: 30.86-154.32 Am^{-2}; pH$_o$: 2–10; g: 0.5–2.5 cm; t: 30–150 min; C$_o$: 10,500-12,000 mg/l	CCD	SS: j: 154.32 Am^{-2}; pH$_o$: 7.8; g: 2.2 cm; t: 135 min	69.63	92.73	72.30	[159]

Biomethanated spentwash	Al	j: 30.86-154.32 Am^{-2}; pH_o: 2–10 and 4-10; g: 0.5–2.5 cm; t: 30–150 min; C_o: 10,500-12,000 mg/l	CCD	Al: j: 154.32 Am^{-2}; pH_o: 6.6; g: 0.5 cm; t: 120 min	58.82	80.07	55.03	[159]
Biomethanated spentwash	SS and Al (Two-stage process)	j: 30.86-154.32 Am^{-2}; pH_o: 2–10 and 4-10; g: 0.5–2.5 cm; t: 30–150 min; C_o: 10,500-12,000 mg/l	CCD	For SS: j: 154.32 Am^{-2}; pH_o: 7.8; g: 2.2 cm; t: 135 min For Al: j: 154.32 Am^{-2}; pH_o: 6.6; g: 0.5 cm; t: 120 min	80.86	94.28	77.85	[159]

Notes: j: current density; i: current intensity; g: electrode gap; C_o: initial COD concentration; CCD: central composite design; BB: box–behnken design RSM: response Surface methodology; SS: stainless steel.

2.4.3 Economic Assessment of Combined Treatment Systems

For any technology, economic assessment and comparison is important from the commercialization point of view. In case of MF-RO, UF-RO and EC-RO combined systems, unit water production is mainly affected by the recovery ratio, equipment cost (membrane and EC system), interest rate, operation cost etc. In general, the total cost is evaluated as the sum of the cost of different components such as the cost of pumps, pipes, membranes, instruments, establishment etc. [160]. Although pretreatment increases the installation cost of total treatment plant, but the reduced RO membrane cleaning frequency and replacement cost compensate its higher installation cost [161], [162].

2.4.4 Reuse of ECGenerated Sludge

For industries using large quantities of water such as distilleries, it is essential to treat and reuse their wastewater for achieving zero discharge. Electrocoagulation (EC) technology, discussed in an earlier section, is one of the promising technologies for the treatment of this high-strength industrial wastewater. An important issue associated with the EC treatment is the generation of large volume of sludge that is semisolid and bulky. EC sludge is very complex in nature having organic and inorganic matter; oil and grease; toxic heavy and trace metals [163]. It also contains hydroxide of metals used as sacrificial anode dissociated during wastewater treatment [164]. These metal hydroxides are hazardous in nature and cannot be discharged as such to water bodies. This residual solid waste is considered as a nuisance to the distilleries as well as to the environment because of various handling and management issues [165]–[167]. Sludge treatment and disposal are an expensive operation and have negative impact on environment. The land application of metal containing sludge leads to soil and ground water contamination [168]. Leaching of heavy metals (e.g., Cd, Zn, Cu, Cr, Co, Fe, Pb, Mn, Ni, Hg) into ground water is of main concern because of its non-biodegradable nature and potential to bio-accumulate in vegetation and animal body parts, which can also potentially affect food quality and health safety [169]–[171]. Landfills are generally used for waste disposal. Rapid urbanization makes disposal of sludge in landfills difficult due to shortage of suitable landfill sites. Incineration is another conventional option used for the sludge disposal, but the residues generated after incineration cause secondary pollution, and the process is not economically viable also many a times. The above points highlight the need to find some cost-effective and eco-friendly reuse or disposal methods for the sludge disposal.

Solidification/stabilization has been a potential long-term solution and an attractive alternative for the remediation and disposal of improperly discarded hazardous waste as the solidification of waste material in reusable form reduces the risk of environment pollution and also helps in conservation of natural resources. Sludge solidification is an effective strategy to overcome the disposal problem and also to reduce leaching potential of hazardous constituents [172]. It stabilizes the waste material by mixing with cement, clay and sand as binder material producing a solid mass with improved physical properties [173]. The stabilized waste material can be used in various building materials if it meets the standards otherwise it may be disposed to a secure landfill site with a reduced storage volume requirement [165]. Various researchers have done research on solidification of sludge emanating from different sources viz. sewage treatment plants; and effluent treatment plants of textile industry, electroplating industry, and oil and petroleum industry [174]–[181]. Industrial wastes have also been used in different building materials (e.g., flooring tiles, bricks, wall materials) as partial replacement of cement and clay. Disposal of industrial by-products, e.g., fly ash, ground bottom ash and silica fume in concrete have been investigated earlier in various studies [182], [183]. Effective use of electrocoagulated metal hydroxide sludge (EMHS) as soil substitute has been reported (up to 30 %) for making different types of building materials such as pavement block, hollow block and brick [165], [175]. Balasubramania et al., (2006) [166] found that the textile effluent treatment plant (ETP) sludge could be substituted for cement up to a maximum of 30 % in manufacturing of non-structural building materials. Utilization of arsenic-contaminated sludge for making ornamental bricks was also studied by the researchers [184]. Result revealed that up to 4 % arsenic-contaminated sludge could be used safely. Rouf and Hossain (2003) [185] have also recommended the use of contaminated sludge up to 15–25 % by weight in brick formation. The clay in the brick making material can be effectively replaced by textile sludge up to 15 % [186]. Adyel et al., (2012b) [187] studied the reusability of EC-generated sludge from textile industry by substituting it with the soil in bricks making. They found that the soil could be substituted up to 30 % with sludge. Sogancioglu et al., (2013) [188] investigated the utilization of andesite processing wastewater treatment sludge as admixture in concrete mix. Results of the study concluded that cement could be replaced by up to 0.5 % of physicochemical sludge for making non-load-bearing structures. However, environmental aspects of sludge usage have not been considered.

No study has been reported regarding potential reuse of EC-generated sludge from distillery effluent treatment in building or non-building materials considering their detrimental effects on environment.The present study comprehends the utilization of the EC-generated sludge from distillery spentwash treatment as a non-construction building material, employing cement-based solidification and also its potential effect on environment.


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CHAPTER 3: MATERIAL AND METHODS

3.1 Material

3.1.1 Collection and Characterization of Raw/ Treated Spentwash and Fouled Membrane from Existing Treatment Plant

Spentwash samples from different sampling points (Raw spentwash, after bio-methanation, after aerobic treatment and after RO membrane treatment) were collected from the treatment plant of an existing nearby distillery. Characterization of the spentwash samples was done for following parameters:

Onsite characterization: pH, electrical conductivity and temperature.

Offsite characterization: COD, color, TS, TDS, TOC, cations (Ca^{2+}, Mg^{2+}, K^{+}), and anions (Cl^{-}, SO_4^{2-}).

Disc tube membranes were reportedly used in the studied RO plant (make: ROCHEM, TFC type and hexagonal shape). The reported duration of replacement of the membranes in the plant was 6 monthsor earlier depending upon the performance of the system. Membrane samples were collected for autopsy after 3 and 6 months of use. The increase in pressure drop through the membrane modules subsequently decreasing the performance in a short span of time was reported as the major problem**.** Surface characterization of the collected membranes was conducted through FESEM and AFM in order to study the structure of both the foulants and the membrane layer; and to determine the membrane roughness. Chemical characterization was also done employing FTIR and XRD to determine the nature of the organic foulants.

3.1.2 MF, UF and RO Membranes

Flat membranes were used in the laboratory experiments. MF, UF and RO membranes were procured from the local supplier of GE Osmonics manufacturing company. Operating range of input parameter for each membrane was considered on the basis of their operating specification from the company as shown in Table 3.1. Membranes were dipped in milliQ water prior to use. MilliQ water was also run through the system prior to the experimental run with wastewater.

3.1.3 Stainless and Aluminum Electrodes

In the electro-coagulation experiments, stainless steel (SS) and aluminum (Al) electrodes were used for the treatment. Metal sheets of respective electrodes were procured from the open market and then resized as per the required form and dimensions (90 mm × 105 mm).

3.1.4 Ingredient for Mortar Preparation

Sludge generated from EC experiment was used as the additive in the cement mortar as a substitute to cement. Prior to use, it was dried in a hot air oven at 100 °C until its weight became constant and then grounded manually to reduce the size of larger particles. The grounded EC sludge was then directly used as a substitute of the cement in mortar preparation. It was characterized for assessment of physico-chemical properties. Cement used in mortar formation was ordinary Portland cement (43-grade) complying with Indian Standard Specifications, IS: 8112-1989 [189]. Sand of particle size 16 micron was used.

3.2 Experimental Setup and Operation

3.2.1 MF, UF and RO Membrane Setup

A laboratory scale membrane unit (NilshanNischotech Pvt. Ltd, India) was used to perform different experiments during this study i.e. in isolation and combined mode with EC. Actual picture of RO membrane unit is shown in Figure 3.1. The type of membrane setup used was GE SEPA flat plate system with thin film composite membranes (MF, UF and RO). The effective surface area of the membrane was 0.0155 m^2. Pure water was used to determine the permeability of the membrane. At different pressures, pure water flux was calculated and plotted against trans-membrane pressure. After completion of the experimental run, system was thoroughly cleaned by pure water and permeability was reassessed. It was found to be almost the same throughout all the experimental runs. MF, UF and RO systems were optimized using central composite design (CCD) (discussed later). Optimization experiments were carried out to maximize the permeate flux (recovery) and percentage removal of COD, color and TDS using initial pH (pH_o), feed temperature (Temp) and trans membrane pressure (TMP) as input operating parameters [190]. The operating parameters were pH_o: 2 to10, Temp: 15 to 43°C and

TMP: 10 to50 bars for RO system. For MF and UF systems, however, the TMP range was 2 to 5 bars and 4 to 20 bars, respectively. Feed water was pumped into the module by means of a centrifugal pump and the transmembrane pressure was controlled by the pressure valve. Temperature of the system was maintained by running the hot and cold water through a jacketed tank as per requirement. The pH of the solutions was initially measured and then adjusted as per the designed runs by adding 0.1 N NaOH or 0.1 N H_2SO_4 solutions. Percentage removal of COD, color, TDS and permeate flux were taken as responses of the system. Samples were collected before and after each experimental run and analyzed for COD, color and TDS.

COD was analyzed using digestion unit (make: HACH, DRB 200, USA) and UV visible spectrophotometer (make: HACH, DR 5000, USA). TDS was measured using a conductivity meter (make: HACH, HQ40D, USA) and color by using double beam UV-visible spectrophotometer (make: HACH, DR 890, USA).Percentage removal of these contaminants were calculated by using Eq.:

$$\text{Percentage removal } Y\ (\%) = \left(\frac{C_i - C_f}{C_i}\right) / \, 100 \qquad (3.1)$$

Where, Y is percentage removal of contaminants (COD, color and TDS), C_i is initial concentration of contaminants (COD, color and TDS) in feed (mg/l) and C_f is the concentration of contaminants (COD, color and TDS) in permeate (mg/l).

Permeate flux (J) is the amount of sample collected per unit area per unit time. It was calculated by dividing the permeate volume (V) divided by the product of effective membrane area (A) and time (t)[191] given in Eq.:

$$\text{Permeate flux } (J) = \left(\frac{V}{A * t}\right) \qquad (3.2)$$

Where, J is permeate flux, V is permeate volume, A is effective membrane surface area and t is the time.

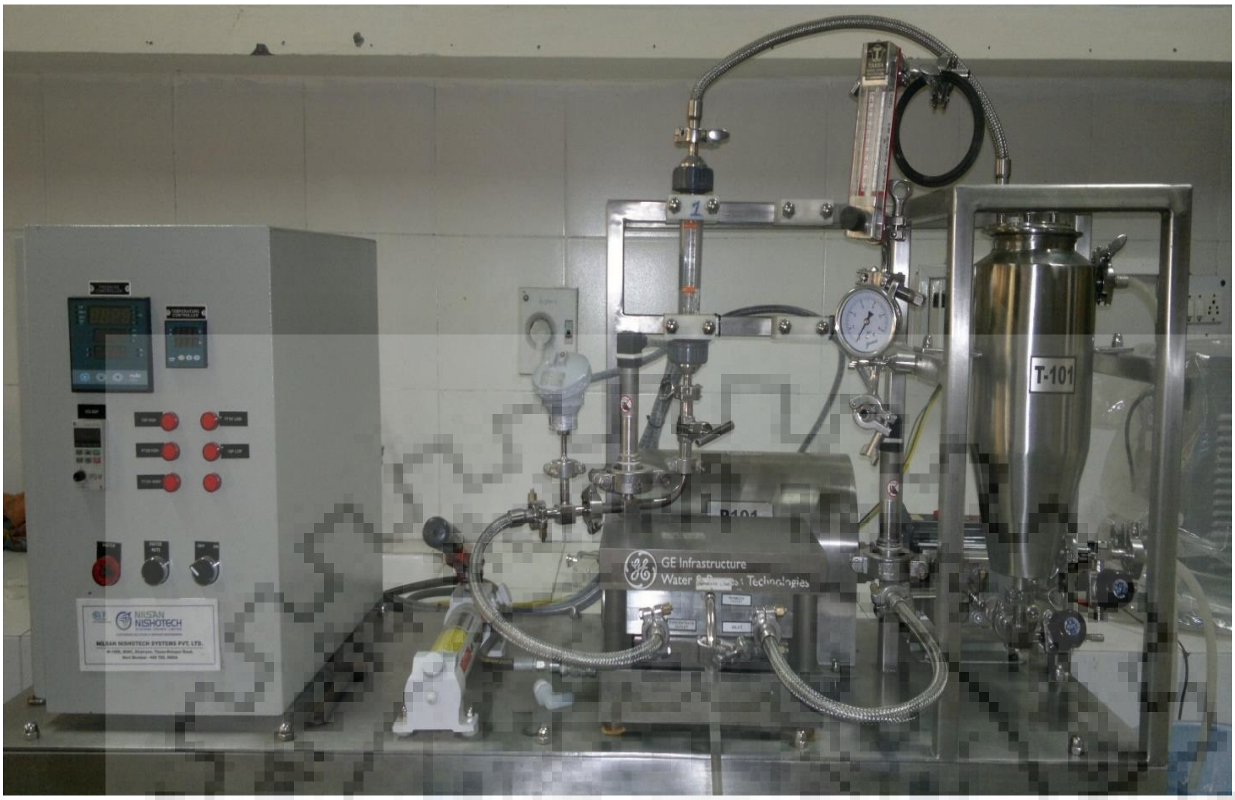


Figure 3.1. Experimental setup of membrane system.

3.2.2 Electro-coagulation (EC) Setup

The experimental setup used for EC study was similar to previous studies [157] (Figure 3.2). The experimental reactor was cubical in shape having dimensions (110 mm × 110 mm × 140 mm) and was made of Perspex glass. The capacity of the reactor was 1.5 L. A digital direct current (DC) power of 0–18 V, 0–5 A was used to supply regulated current to the EC cell. Four mono-polar aluminum (Al) and stainless Steel (SS) electrodes connected in parallel were used in the EC experiments. The area of the electrodes exposed to the wastewater was 90 mm × 90 mm. The gap between anodes and cathodes was varied in the range of 0.5 to 2.5 cm. To maintain the uniformity throughout the reactor, magnetic stirrer was used for providing proper stirring.

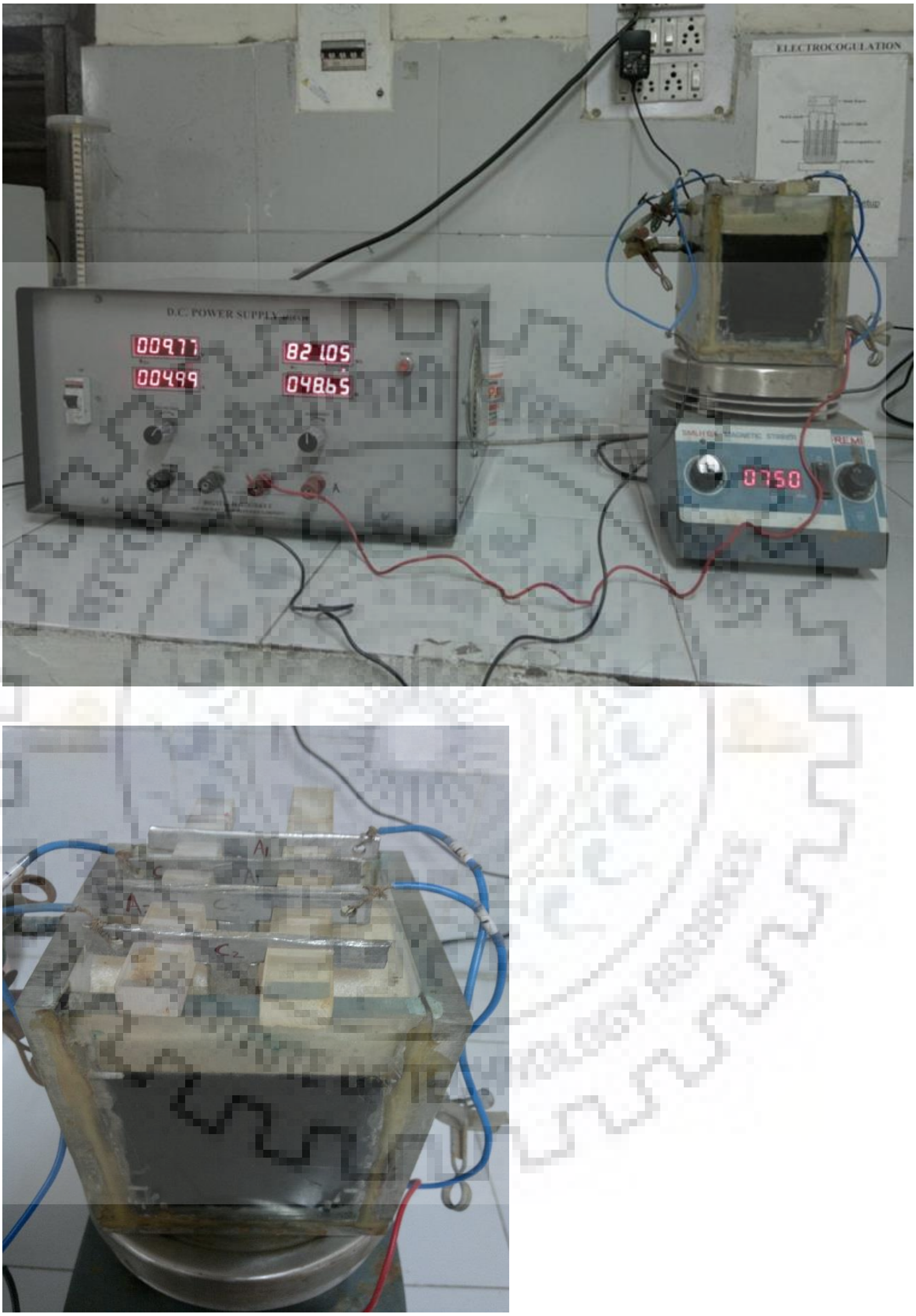


Figure 3.2. Electro-coagulation experimental setup.

3.2.3 Casting Module for Mortar Preparation

The cement solid blocks (mortar) were formed by using different proportions of EC sludge ranging from 5%, 7.5%, 10%, 12.5% and 15% by weight of cement as per Indian Standard Specifications, IS: 10262-1982 [192]. A control sample i.e. 0% EC sludge was also prepared for comparison purpose. Steel molds of 25 × 25 × 25 mm size were used for the preparation of mortar cubes (Figure 3.3). Cement to sand ratio used for the preparation of mortar was 1:4. Mortars were prepared using hand mix method with glass rod to remove the entrapped air. Compaction was provided by putting the steel molds on vibration table. Mortar samples were demolded after 48 h of demolding time. Thereafter, the mortars were cured in water for different curing periods i.e. 7, 14 and 28 days. After specified curing period, mortar cubes were subjected to different physico-chemical tests (wet and dry densities, compressive strength, leachability test, TGA and XRD.

Figure 3.3. Steel mould for mortar casting.

3.3 Design of Experiments and Model Fitting

3.3.1 Predictive Modelling using Response Surface Methodology (Central Composite Design)

In the present study, the operating parameters of the laboratory scale membrane setup (MF,UF and RO) and EC system were optimized to maximize the contaminant removal (COD, color, TDS and TOC) and permeate flux. Spentwash collected after biological treatment from the distillery was used for all the experiments. RSM is a good modelling tool and is generally used for the experimental design and optimization. It helps in minimizing the experimental cost and time by reducing the total number of experiments to be performed [193], [194]. In the present study, RSM was employed for the optimization of membrane (MF, UF and RO) and EC process by using CCD method. Furthermore, to validate the RSM model predictions, experiments were carried out employing the optimized input variable parameter values derived from the model. RSM also yielded the surface graphs, which provided a good visual assessment of the relation between different operating variables.

CCD is the most commonly used design method of response surface methodology (RSM). This design determines both the first and second order terms very efficiently [195]–[197]. This design consists of two-level full factorial (cubic) design; a set of center points (for which all the factor values are at the zero (or midrange) value), in order to improve the precision of the experiments this point is often replicated; a set of axial points (for which all but one factor is set at zero (midrange) and one factor is set at outer (axial) values) [193], [198]. The input variable parameters value (x_1, x_2, $x_3 \ldots x_n$) vary from their minimum (-1) to maximum (+1) level in coded scale. The levels were coded according to the following relationship:

$$X_i = (X_i - X_o)/\delta X \tag{3.3}$$

Where, X_o is value of the X_i at the center point and δX presents the step change.

Second order model with quadratic terms was used to determine the critical point and the equation in a general form can be presented as:

$$y = \beta_0 + \sum_{i=1}^{n} \beta_i x_i + \sum_{i=1}^{n} \beta_{ii} x_i^2 + \sum_{i<j}^{n} \beta_{ij}\, x_i x_j + \varepsilon \tag{3.4}$$

Where, y denotes the predicted response, x_i and x_j are the coded levels of design variables, β_0, β_i , β_{ii}, β_{ij} are the regression coefficients (constant term, linear, quadratic and interaction parameter), n is the number of variables and ε is the experimental error [198]. For the model fitting and graphical analysis, Design-Expert software (Stat-Ease Inc., version 6) was used. The number of experiments designed can be calculated from the given equation as:

$$N = 2^n + 2n + n_c \tag{3.5}$$

Where, N is the total number of experiments required, n is the number of numeric factors and n_c is replicate number at the central point.

3.3.1.1 *Design of Membrane Experiments*

In the present study, individual and interactive effects of three operating input variables viz. pH (pH_o), temperature (Temp) and trans-membrane pressure (TMP) on the membrane performance was evaluated. Experiments were carried out at different range of operating parameters designed by design-expert model with CCD. The total number of experiments that were designed by the design-expert software was 20. Different ranges of input variable parameters for different membrane systems (MF, UF and RO) are given in Table 3.2. Optimization experiments were carried out to maximize the permeate flux and percentage removal of COD, color and TDS using pH, feed temperature and TMP as input parameters.

3.3.1.2 *Design of EC Experiments*

For the EC experiments, individual and interactive effects of four independent input parameters viz. initial pH, current density (j) inter-electrode distance (g) and electrolysis time (t) on the COD, color and TOC removal efficiency were evaluated for both the electrodes (SS and Al). A total of 30 experiments were designed for both the electrodes. Range of different input variable parameters for both the electrodes (SS and Al) is given in Table 3.3. Designed experiments were carried out to maximize the permeate flux and percentage removal of COD, color and TOC using pH, current density, inter-electrode distance and electrolysis time as input parameters.

Further, multi-parameter non-linear regression models as actual and coded factors were developed [199] for both the membrane and EC system. To analyze the deviation of experimental values from predicted value of the responses, statistical study of CCD model was done. Analysis of variance (ANOVA) was used to develop a predictive model and to show that the chosen model explains the factor response interaction correctly[198], [200], [201].R-square (co-efficient of determination) was also applied to test the satisfactory adjustment and fit of the model [199]. Three dimensional surface graphs were generated from the developed CCD model equation of RSM. After optimization, validation experiments were performed at optimized input parameters and the results were verified against the predicted values from the model.

3.4 Combined RO Experiments with Pretreatments

In the present study, combined experiments of RO employing different pretreatment schemes (MF-RO, UF-RO and EC-RO) were conducted at laboratory scale. Experiments with MF, UF and EC at optimized operating conditions were performed and the treated water from each pretreatment type (MF, UF and EC) was used as the feed for RO system. At optimized operating conditions, the removal efficiencies of the contaminants (COD, color and TDS) along with the permeate flux (water recovery) was measured.

3.5 Predictive Modelling of RO Permeate Flux Decline Profile with and without Pretreatment

Depending on membrane type, wastewater characteristics and operating conditions, membrane performance declines with time. Permeate flux is a measure of membrane performance and it continuously decreases due to fouling of the membranes. Fouling not only decreases the flux but also changes the retention [202]. Permeate flux assessment with time is the most common method to study the fouling and performance of membrane system. Effect of filtration time on permeate flux of RO system was studied at optimized conditions (pH, temperature and TMP). To investigate the mechanism of flux decline, a modified form of Hermia's model was used to analyse flux-time curves. Intermediate blocking filtration model is reportedly best suited for RO membranes [191], which assumes that all the particles donot block the membrane pores and they may settle on other particles. Its equation is given as:

$$\frac{1}{Q} = K_t t + \frac{1}{Q_o} \tag{3.6}$$

Where, Q is the permeate flow rate, Q_o is the initial permeate volume, t is time and K_t is the filtration constant.

The permeate flux data of RO alone and with each pretreatment (MF, UF and EC) was fitted into the intermediate blocking filtration model equation to calculate the value of filtration constant, K_t and intercept, Q_o, and further to extrapolate the graph and to find out the filtration pattern for RO with and without pretreatment. This study was conducted for 3 hrs to show the effect of pretreatment on permeate flux. Reduction in flux indicated the fouling potential of the wastewater with time [202].

3.6 Economic Assessment of Proposed Treatment Schemes

Cost analysis was attempted for RO treatment alone and RO with different pretreatments (MF, UF and EC) for per cubic meter water production with the data generated from the laboratory scale experiments. Following cost components were included:

Capital cost: It includes onetime fixed expenses incurred on procurement of machinery. It is specific for the different technologies, considered at current market rate. This cost is distributed annually to determine the production costs.

Operation, maintenance and other costs: It presents a variable value, dependent on the components like consumption and cost of chemicals used, membranes replacement rate, electrode consumption rate and electricity consumption for different processes. Annual water production rate is affected by per unit water production rate, cost of experimental setup, rate of interest etc.

3.7 Analytical Procedures and Characterization

3.7.1 Analysis of Fresh and Used Membranes, Electrodes and Cement EC Sludge-mortar

Characterization of the membranes, electrodes, cement and EC sludge was done by following techniques:

Field Emission Scanning Electron Microscopy (FESEM)

The surface morphology of the membranes and electrode were studied by FESEM (make: Quanta FEI-200). The FESEM is equipped with energy depressive X-ray analyzer (EDAX) (make: Penta FET Precision), that allows analysis of the elemental composition of the samples. The excitation energy was set at 20 kV.

Atomic Force Microscopy (AFM)

The AFM technique was chosen for the morphological characterization of the membrane surface roughness [203], representing the average of the mean roughness (Ra—arithmetic average of the deviation from the center plane) of different spots and scanning sizes. AFM provided the change in the surface structure or roughness using NanoScope III scanning probe microscope (make: NT-MDT NTEGRA) in the tapping mode.

Fourier Transform Infrared Spectroscopy (FTIR) Spectrometry

FTIR facilitates the identification of functional groups that may be present in the sample and was performed using a fourier transform infrared spectrometer (make: Thermo Fisher Scientific Inc.). Results appear in the form of spectra, ranges from wavelength 600 to 4000 cm^{-1}, which shows different bands at different wavelengths corresponding to different functional groups. Each spectra was corrected for penetration depth and background subtraction using OMNIC 8.0 software (Thermo Fisher Scientific Inc.)

Particle Size of Sludge

The particle size distribution was measured with particle size analyzer (make: Zeta sizer, NANO S90), using mechanism of Dynamic light scattering. Samples of 0.5–1.0 g of EC sludge and cement was suspended in 100 ml deionized water and this suspension was used for analysis. Each measurement was done in triplicates.

Compressive Strength

Compressive strength of control mortar and various sludge added mortar samples were analyzed using a hydraulic type testing machine (make: Shimadzu, UH-1000 kNI) according to American Society for Testing and Materials C109-92 (ASTM, 1992) [204], for different curing days (7, 14 and 28 days). Gradual and steady load was applied to the mortar till the time when it got crushed. The average strength of three cubes was taken as the result in kN/s unit. The compressive strength of mortars was calculated by dividing the maximum load applied to the cross-sectional area of the mortar.

Leaching Test

Leaching test was conducted to predict the chemical stability of the waste material (sludge) when it came in contact with the acidic aqueous solution. Both whole and crushed mortar samples were subjected to leaching test to simulate worst case scenario. The extraction procedure was performed according to the United States Environmental Protection Agency (USEPA) protocol [205]. For the whole mortar leachability (WML) test, complete mortar pieces (25 × 25 mm) were subjected to extraction using 1 N acetic acid for 24 h with 1:10 solid-liquid ratio by weight. Then, the EC sludge–acid suspension was filtered through Whatman filter paper no.1 and filtrate was subjected to heavy metal extraction in the presence of strong acids using direct digestion method using 10 ml nitric acid and 5 ml per-chloric acid. The solution was made up to 100 ml with distilled water [206] and then analyzed for heavy metals using inductively coupled plasma mass spectrometry (ICP-MS) as per APHA [207]. For the crushed mortar leachability (CML), the core portion of the crushed mortar was taken. The solid-liquid ratio of 1:20 by weight was taken using acetic acid as an extractant. EC sludge–acid suspension was agitated mechanically for 18 h and then filtered. Then, the sludge–acid suspension was digested as in CML test and analyzed using inductively coupled plasma mass spectrometry (ICP-MS) (make: Perkin Elmer, ELAN DRC-e). Initial heavy metal content in EC sludge and cement were also analyzed.

Wet and Dry Density

Block density was measured by taking the ratio of constant mass of the mortar after oven drying at 100°C followed by cooling to the volume of the dried mortar by measuring its dimensions. Density was measured by taking the average of triplicate.

X-ray Diffraction (XRD)

Compound analysis of membranes and oven dried EC sludge and cement was performed by using X-ray diffraction (XRD) analysis (make: Bruker, D8 ADVANCE) with Cu Kα target. The peaks in the spectrum were marked, compared, and identified from the joint committee on powder diffraction standards (JCPDS) data file.

Thermo-gravimetric (TGA)

Thermo-gravimetric (TG) analysis of oven dried EC sludge and cement was carried out using TG/DTA (make: Perkin Elmer Diamond, SII 6300 EXSTAR) in air at a heating rate of 10°C/min.

Table 3.1. Different operating parameters and specification of membranes used in experiments (RO, UF and MF).

Membrane make and type	**Model**	**Rejection NaCl (%)**	**MWCO**	**Typical flux/ psi gfd@psi**	**Membrane filtration area (m^2)**	**Max operating Temp. (^{o}C)**	**Max P (bar)**	**pH range**
RO (GE Osmonics)	SE	98.9	-	22/425	0.0155	80	80	1-11
UF (GE Osmonics)	GE	-	1K-PEG	20/400	0.0155	70	40	1-11
MF (GE Osmonics)	JX	-	0.3μm	130/30	0.0155	70	5	1-11

Table 3.2.Process variables and their levels for membrane system (UF, MF and RO).

Variable unit	**Factors**	**Membrane**	**Level**				
For membrane System	X		-∞	-1	0	1	+∞
Initial pH, pH_o	X_1	MF, UF and RO	2	4	6	8	10
Temperature (C)	X_2	MF, UF and RO	15	22	29	36	43
Trans-membrane pressure (bar)	X_3	RO	10	20	30	40	50
		UF	4	8	12	16	20
		MF	1	2	3	4	5

CHAPTER 4: CRITICAL EVALUATION OF TERTIARY RO TREATMENT SYSTEM

4.1 General

Spentwash samples were collected from different sampling points of the identified treatment plant and were then characterized. To study the existing RO treatment plant in the distillery, the membrane samples were collected from the treatment plant after 3 and 6 months, as per the stated replacement frequency of the membranes. Autopsy was performed on the collected membranes to find out the reason for poor performance of RO plant and high frequency of the membrane replacement. Fresh membrane samples were also collected and characterized for the reference. As mentioned earlier in chapter 3 (Material and Methods), surface characterization was done employing FESEM and AFM. To determine the nature of the organic foulants, chemical characterization was performed employing FTIR and XRD.

4.2 Evaluation of Tertiary RO Treatment System in an Existing Distillery

4.2.1 Collection and Characterization of Distillery Spentwash

Spentwash samples were collected at different sampling points from the treatment plant. Schematic flow diagram of existing distillery spentwash treatment plant is depicted in Figure 4.1 showing different sampling points. Collected samples were characterized for pH, EC, temperature, COD, Color, TS, TDS, TOC, Cations (Ca^{2+}, Mg^{2+}, K^{+}), and Anions (Cl^{-}, SO_4^{2-}). Typical characteristics of spentwash at different treatment points are presented in Table 4.1.

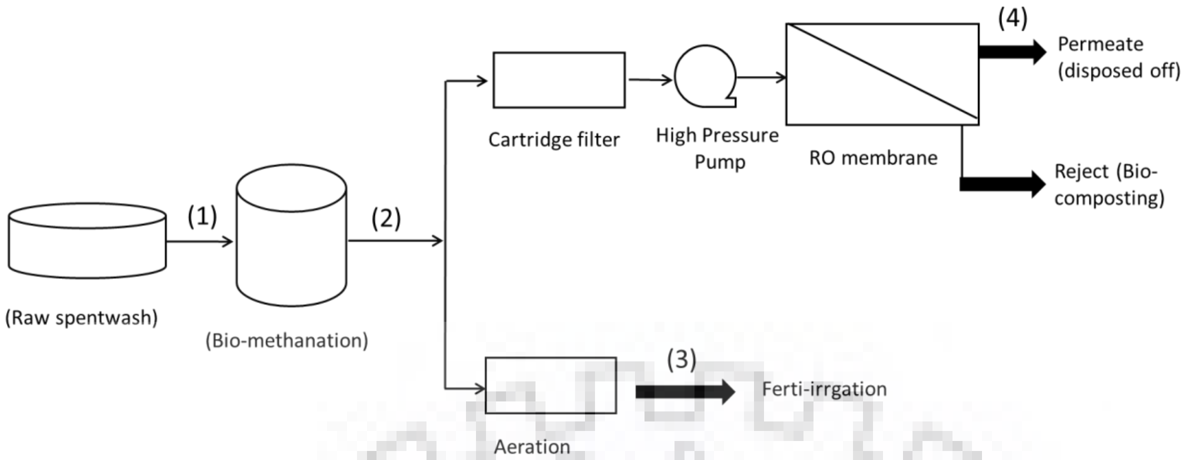


Figure 4.1. Schematic flow diagram of existing distillery spentwash treatment plant with different sampling points: Raw spentwash (1), after bio-methanation (2), after aerobic treatment (3) and after RO membrane treatment (4).

Removal efficiencies of COD, TOC and TDS with bio-methanation were observed as 52.4%, 46.1%, and 58.9% respectively, whereas, aeration further removed 65.5%, 54.5%, and 5.4% respectively. RO plant showed removal efficiency over 70% for COD, TOC and TDS, but permeate still did not meet the discharge standards due to high organic load after bio-methanation. Direct feeding of bio-methanatedspentwash into the RO system contributed towards odor problem and also the compromised efficiency of treatment. RO process removed 82.9%, 74.9% and 72.8% of COD, TOC and TDS, respectively. Mg, Ca and sulphate were apparently observed to contribute a lot towards membrane fouling and scaling problems. Permeate of RO still contained high concentration of these ions after RO treatment. Further, autopsy based assessment of the membranes was done to obtain more information about the membrane foulants.

Table 4.1. Spentwash Characterization.

Parameters	Raw Spentwash	After biomethanation	After Aerobic treatment	After RO treatment
pH	4.57	8.07	7.86	6.85
Temp	34.4	35.6	28.7	28.9
EC (mS/cm)	21.3	35.3	31.4	1.67
color	75000	79000	63000	343
TS (mg/l)	101308	51670	41630	364
TDS (mg/l)	83860	34500	32640	374
COD (mg/l)	100800	48000	16600	4000
TOC (mg/l)	36360	19420	8820	1250
K^+ (mg/l)	8425	8201	7986	3576
Ca^{2+} (mg/l)	3077	6866	1603	1176
Mg^{2+} (mg/l)	1465.43	1083	979	271
Cl^- (mg/l)	5700	4889	4393	1820
SO^{2-}_4 (mg/l)	4136	2323	1413	632

4.3 Autopsy Based Assessment of RO Membrane Used in Treatment Plant

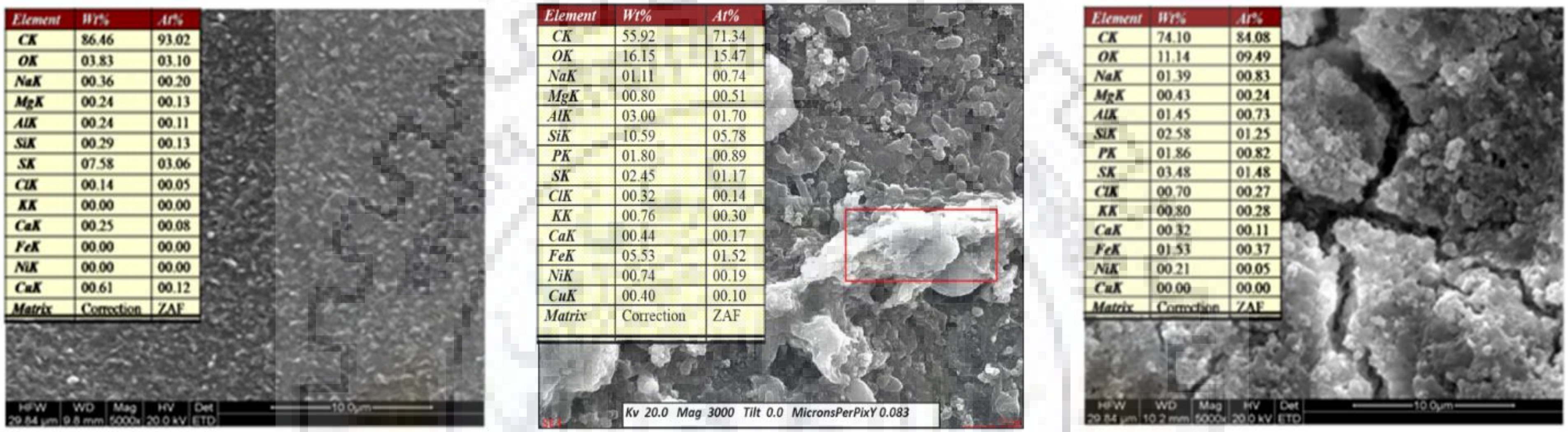
4.3.1 Field Emission Scanning Electron Microscopy (FESEM) analysis

Collected samples of membrane from the existing treatment plant (fresh, 3 months and 6 months used) were subjected to surface characterization. Direct visual observation of the fouled membrane surface revealed a strong discoloration with a reddish fouling layer without imparting any sign of damage compared to the fresh membrane which was clean and slightly yellow in color. The reddish color could be due to the presence of iron in the spentwash. An electron microscopic picture of the clean or fresh membrane (as reference) surface of the same magnification is shown in Figure 4.2a, which shows a significant change in the surface morphology of the fouled membranes (Figure 4.2b and 4.2c).

The FE-SEM images showed the presence of very thick firm cake layer deposits on the surface of fouled membranes (Figure 4.2b and 4.2c) as compared to the clean surface of fresh membrane (Figure 4.2a). This cake layer was probably made up of organic matter or colloidal particles, or a combination of both. Scaling was also common in RO processes because of the presence of monovalent and divalent ions in the waste stream [208]. The reddish color of the membrane sample could reflect the presence of iron oxide in the waste stream. Elemental analysis by EDX of 3 months and 6 months old membranes didn’t show much difference. Elemental analysis of the surface of the fouled membranes revealed the presence of a significant amount of silica. Other metallic elements such as iron, aluminum, calcium, sulphate and magnesium were also observed, which apparently contributed to the inorganic fouling deposits on the membrane surface [209]. The presence of a substantial amount of oxygen in the fouled membrane in comparison to the fresh membrane could be attributed to organic matter which is present in the fouling layer, although it could also be from the membrane polymer.

4.3.2 Atomic Force Microscopy (AFM)

The micrographs of AFM showed the change in the membrane surface structure by fouling [203]. AFM images (Figure 4.3a and 4.3b to 4.3c) clearly show the differences between the surface morphology of fresh and fouled membranes respectively. The fresh membrane showed uniformly distributed grains throughout the surface having a ridge and valley structure, while the fouled membrane exhibited large-scale roughness with organic and colloidal matter filled between the ridges and valleys, as also confirmed by the variable grain size distribution over the surface. Roughness mean of fouled membrane 3 and 6 months old was 138nm and 241 nm respectively, while that of the fresh membrane was 75 nm. This noteworthy difference in the surface roughness shows the deposition rate of colloids and other foulants on the membrane surface. Rough surfaces are more vulnerable to fouling which causes decline in pollutant removal [210]. As the surface roughness increases, total surface area of the membrane also increases contributing to accumulation of more foulants. SEM micrographs (Figure 4.2b to 4.3c) also confirmed the deposition on the surface due to sticking of the organic and colloidal particles between the uniformly distributed grains on the surface of the membrane.



Element	*Wt%*	*At%*
CK	86.46	93.02
OK	03.83	03.10
NaK	00.36	00.20
MgK	00.24	00.13
AlK	00.24	00.11
SiK	00.29	00.13
SK	07.58	03.06
ClK	00.14	00.05
KK	00.00	00.00
CaK	00.25	00.08
FeK	00.00	00.00
NiK	00.00	00.00
CuK	00.61	00.12
Matrix	Correction	ZAF

(a)

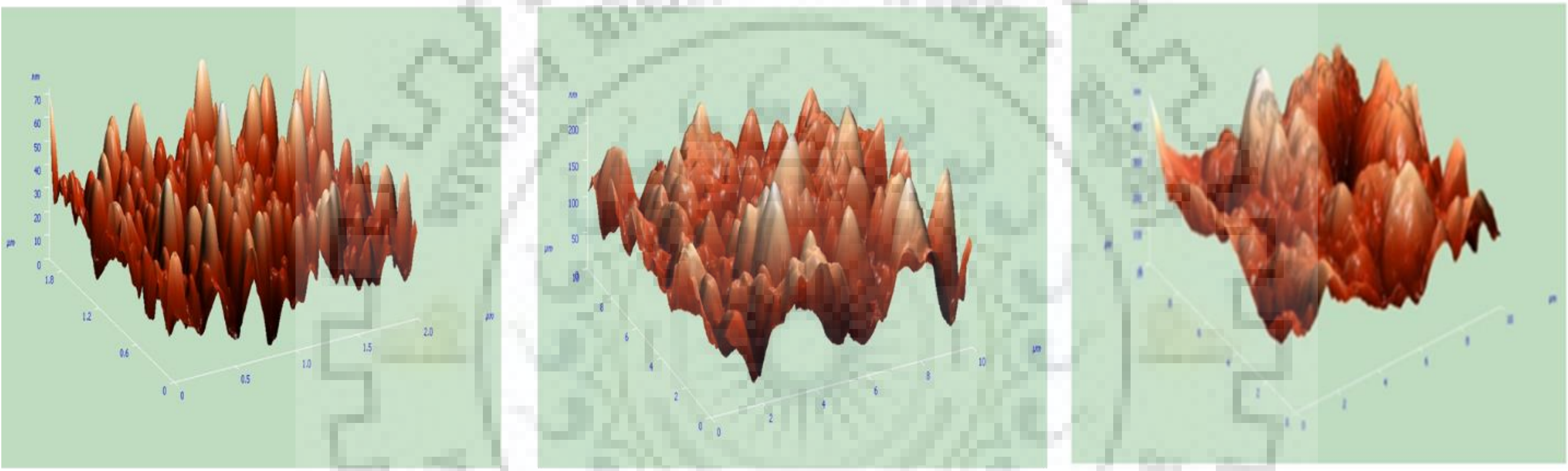
Element	*Wt%*	*At%*
CK	55.92	71.34
OK	16.15	15.47
NaK	01.11	00.74
MgK	00.80	00.51
AlK	03.00	01.70
SiK	10.59	05.78
PK	01.80	00.89
SK	02.45	01.17
ClK	00.32	00.14
KK	00.76	00.30
CaK	00.44	00.17
FeK	05.53	01.52
NiK	00.74	00.19
CuK	00.40	00.10
Matrix	Correction	ZAF

(b)

Element	*Wt%*	*At%*
CK	74.10	84.08
OK	11.14	09.49
NaK	01.39	00.83
MgK	00.43	00.24
AlK	01.45	00.73
SiK	02.58	01.25
PK	01.86	00.82
SK	03.48	01.48
ClK	00.70	00.27
KK	00.80	00.28
CaK	00.32	00.11
FeK	01.53	00.37
NiK	00.21	00.05
CuK	00.00	00.00
Matrix	Correction	ZAF

(c)

Figure 4.2. FESEM images of (a) fresh, (b) 3 months and (c) 6 months used membranes.



(a) (b) (c)

Figure 4.3.AFM images of (a) fresh, (b) 3 month and (c) 6 month used membranes.

4.3.3 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopic analysis demonstrated the functional groups present in the membrane foulant sample. Results presented as graph that. FTIR graph for composite foulant layer (scrapped from the surface of fouled membranes) as shown in Figure 4.4 shows different bands at different wavelengths corresponding to different functional groups. The spectrum (Figure 4.4) shows the presence of a sulphate band located at 1151.54 cm^{-1} depicting the presence of sulphate and its role in the clogging of membranes. Peaks localizing at 1650 cm^{-1} and 1530 cm^{-1} represent typical bands of proteins and amides, respectively [211], [212].

Alcohols and amines showed OH or NH stretching absorption at 3000–3700 cm^{-1} [212]. The presence of nitrate salts in the samples was also evident by the presence of a nitrate band at 1383 cm^{-1}. The IR bands characteristic of sodium chloride, located at 3400 cm^{-1} and 2089 cm^{-1}, appeared quite clearly [213]–[215]. Polysaccharides contain CH and OH functional groups having a peak at 2930 cm^{-1} and broad absorption bands at 3000 cm^{-1} and 3400 cm^{-1}, respectively. Peak observed at 1380 was also representative of polysaccharides [211]. The peaks of FTIR spectra of the fouled membranes demonstrated that the major constituents in the foulants were polysaccharides, colloids and sulphides.

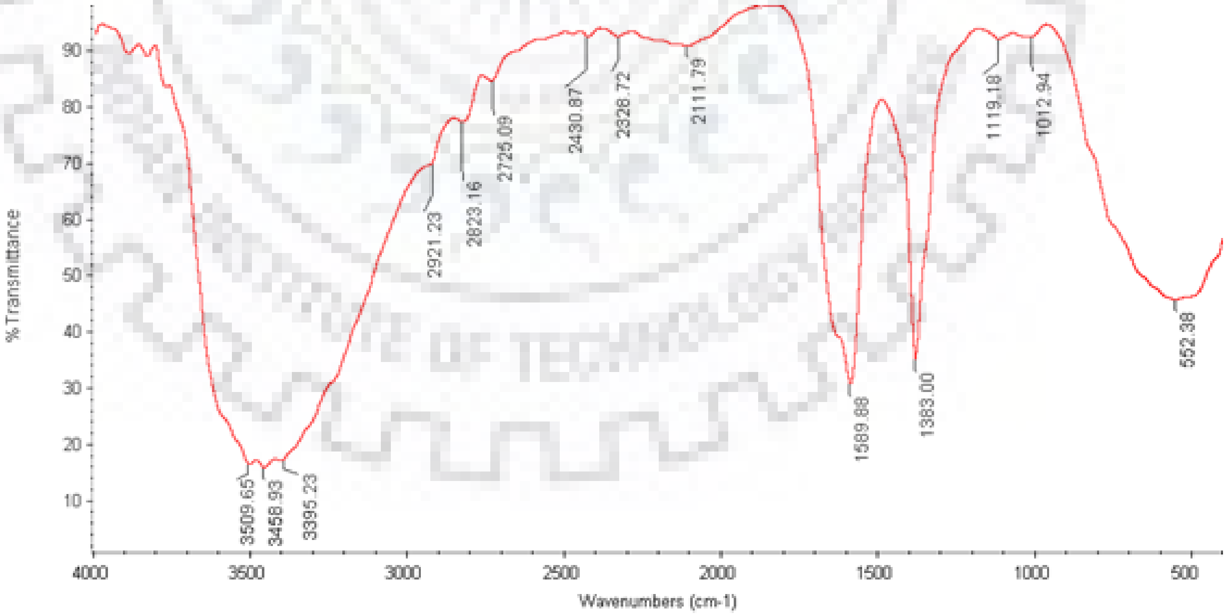


Figure 4.4. FTIR graph for composite foulant layer.

4.3.4 X-Ray Diffraction Analysis (XRD)

XRD analysis was performed for compound analysis of the deposits on the fouled membrane surface (composite foulant layer scrapped from the surface of fouled membranes). XRD data base was used to search every possible compound. Figure 4.5 shows analysis of the qualitative as well as quantitative compounds by using XRD with reference codes. Results showed that a large proportion of the foulant layer comprised of carbon sulphur. The rest of the layer comprised mostly of calcite, silicon oxide chloride, potassium persulphate, zinc sulphide and iron oxide chloride. Spentwash is highly organic in nature, which contributes to a good amount of carbon present in the foulant layer. XRD data demonstrated that the major fouling constituents in the deposit were organic, calcite and silica.

Compound	Ref. code	% in the foulant layer
$C76.59(S_8)_6$	01-084-2400	37
$CaCO_3$	00-005-0586	15
$Ca(CO_3)$	01-086-2334	10
$Si_3O_3Cl_6$	01-087-0313	12
$Ca(Al_2Si_2O_8)$	01-073-0265	16
$K_2S_2O_8$	00-032-0846	7
ZnS	01-089-2172	1
FeOCl	01-076-2300	1

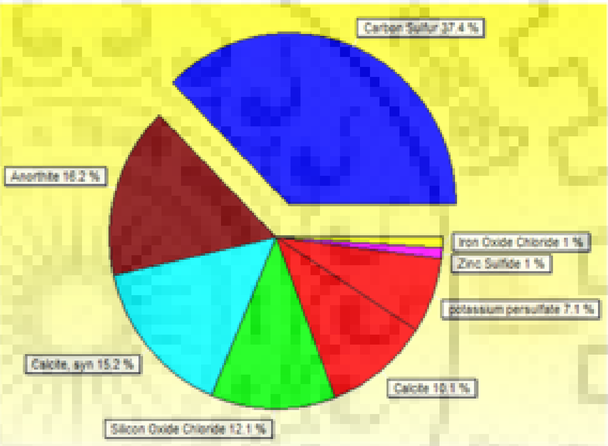


Figure 4.5. XRD analysis for composite foulant layer.

4.4 Findings

Organic matter apparently got significantly reduced after aeration but a substantial amount still remained in effluent, which needed treatment before feeding to the RO membrane system, for its efficient performance. Characterization of the fouled membrane using different analyses (FESEM, AFM, FTIR and XRD) demonstrated that the fouling was mainly caused by a combination of colloidal particles, organic matter and multivalent ions. Results of the FTIR analysis showed that the major organic components in the foulant layer were found to be polysaccharides and amine groups. The EDX results identified Si, Fe, Ca and Na as the major inorganic foulants. AFM study also supported the deposition of colloids or other foulants on the membrane surface. The XRD results confirmed the presence of calcite and silica compounds in the foulant layer. Considering the above outcomes of the study, an upgraded pretreatment train for RO system was proposed to improve the treated water quality and membrane life (Figure 4.6).

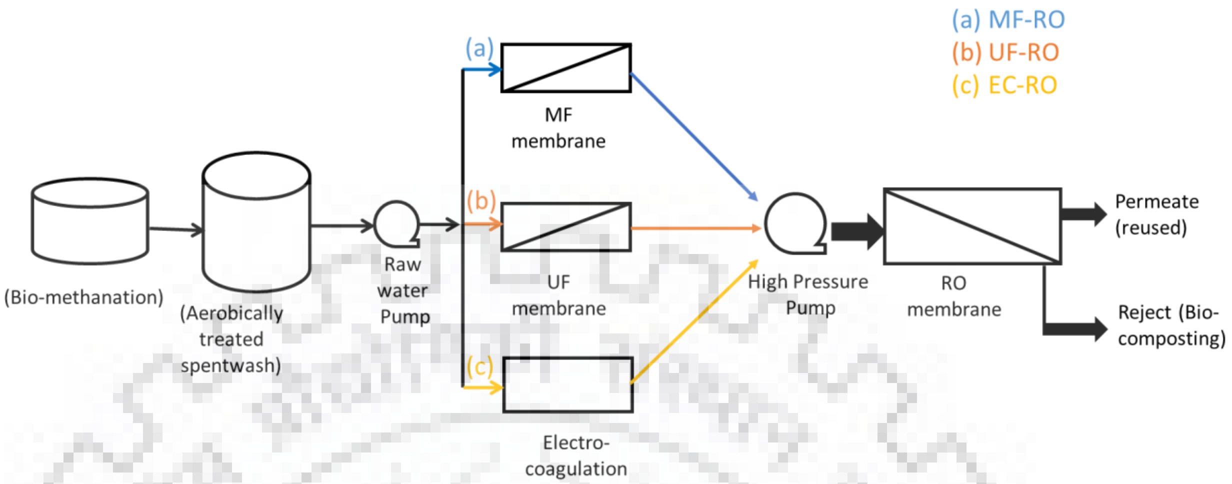


Figure 4.6. Schematic flow diagram of proposed treatment schemes.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CHAPTER 5: OPTIMIZATION OF PROPOSED TREATMENT PROCESSES

5.1 General

In this chapter, details regarding optimization of various input parameters for pretreatment processes (MF, UF and EC) employed for RO have been presented. Optimization experiments were designed by RSM method using central composite design (CCD). The total number of experiments that were designed by the design-expert software was 20 for the MF and UF membranes respectively, whereas, it was 30 for EC experiments. In order to find optimal values of the variable operating parameters, were linear, interactive and quadratic regression models were fitted to the generated experimental data. ANOVA was used to analyze efficacy of the derived experimental response models.

5.2 Optimization of Process Parameters for MF

5.2.1 Statistical Analysis and Modelling

pH, temperature and trans-membrane pressure are important factors which affect the performance of the membrane process. MF membrane system was optimized with three operating parameters, initial pH (pH_o: 2-10); temperature (Temp: 15-43°C) and trans-membrane pressure (TMP: 2-5 bars). Effect of different operating parameters on permeate flux and contaminant removal (COD, color, and TDS) was studied by conducting different combinations of experiments using CCD. Actual and predicted flux and percent removal of COD, color and TDS by MF membrane are shown in Table 5.1. Among the linear, interactive, quadratic and cubic regression models, quadratic model was found to be the best for the experimental data.

Final equations in terms of coded factors are as:

$$COD\ removal = +31.89 - 2.34 \times \mathrm{A} + 2.25 \times \mathrm{B} - 0.66 \times \mathrm{C} - 3.90 \times \mathrm{A2} - 1.19 \times \mathrm{B2} - 3.33 \times \mathrm{C2} + 1.75 \times \mathrm{A} \times \mathrm{B} + 1.45 \times \mathrm{A} \times \mathrm{C} + 0.14 \times \mathrm{B} \times \mathrm{C} \tag{5.1}$$

$$Color\ removal = +52.26 + 3.12 \times \mathrm{A} + 2.78 \times \mathrm{B} + 7.98 \times \mathrm{C} + 1.79 \times \mathrm{A2} - 2.26 \times \mathrm{B2} + 0.15 \times \mathrm{C2} + 2.36 \times \mathrm{A} \times \mathrm{B} + 2.56 \times \mathrm{A} \times \mathrm{C} - 1.67 \times \mathrm{B} \times \mathrm{C} \tag{5.2}$$

$$\mathrm{TDS}\ removal = +14.36 - 1.00 \times \mathrm{A} - 0.081 \times \mathrm{B} + 1.08 \times \mathrm{C} - 1.68 \times \mathrm{A2} - 5.00 \times \mathrm{B2} - 4.62 \times \mathrm{C2} + 0.12 \times \mathrm{A} \times \mathrm{B} - 0.021 \times \mathrm{A} \times \mathrm{C} - 7.908\mathrm{E} - 004 \times \mathrm{B} \times \mathrm{C} \tag{5.3}$$

$$\text{Permeate flux} = +59.43 + 1.62 \times \mathrm{A} + 0.78 \times \mathrm{B} + 0.93 \times \mathrm{C} - 1.52 \times \mathrm{A2} - 1.27 \times \mathrm{B2} + 1.41 \times \mathrm{C2} - 1.94 \times \mathrm{A} \times \mathrm{B} + 1.45 \times \mathrm{A} \times \mathrm{C} + 1.84 \times \mathrm{B} \times \mathrm{C} \tag{5.4}$$

For MF optimization, the ‘p’ value and value of regression coefficient for different responses are given in Table 5.2. The value of p is less than 0.05 (<0.0001), which indicates that the model is statistically significant [157], [200], [216]. The F-values from the ANOVA results for permeate flux and removal of COD, color, TDS are 3.5, 10.9, 22.9, and 8.7 respectively. If the value of F is large and the value of ‘p’ is small, then the terms of coefficient are more significant [217]. The ‘p’ values of the model for permeate flux and removal of COD, color, TDS are significantly low (0.0367, 0.004, 0.0001 and 0.0011, respectively), which indicates that the model fits the experimental results well [150]. The R^2 values for permeate flux and removal of COD, color, TDS are 0.751, 0.907, 0.954 and 0.887, respectively, given in Table 5.2. The ‘p’ values shown in Table 5.3 can be used to find the pair of parameters among various parameters which have most-significant interaction [150]. Interaction between pH and Temp was appeared as more significant among all.

ANOVA results for MF system given in Table 5.2 show that the chosen model explains the factor response interaction correctly[200]. The actual and predicted values of responses are shown in Table 5.1. It shows that the residuals for the prediction of each response are minimum, which indicate that the results of ANOVA analysis are acceptable [155], [157].

Table 5.1. Experimental inputs and responses for MF.

Run	pH	Temp. (°C)	Pressure (bar)	%COD removal		%Color removal		%TDS removal		Permeate flux	
				Actual	Predicted	Actual	Predicted	Actual	Predicted	Actual	Predicted
1	8	20	1	26.04	27.56	41.77	41.32	1.09	3.16	57.29	56.08
2	4	30	3	16.45	16.47	35.68	37.71	1.06	0.95	60.00	60.28
3	6	25	1	25.58	28.28	44.94	45.48	1.19	2.76	59.61	57.83
4	4	20	3	25.94	24.20	53.22	51.33	1.45	1.03	53.42	54.29
5	6	25	2	20.42	23.06	53.63	55.49	3.78	5.37	53.42	51.35
6	6	30	2	19.58	17.78	62.70	62.12	3.47	3.08	60.77	61.36
7	6	25	2	23.47	24.35	55.06	52.99	3.68	4.97	61.94	60.46
8	6	25	2	26.68	26.07	68.65	69.07	4.05	3.16	62.71	62.73
9	4	20	1	24.41	20.99	53.13	53.17	12.32	9.65	47.45	50.12
10	6	25	2	9.10	11.62	65.66	65.65	4.15	5.63	58.06	56.59
11	10	25	2	30.82	28.45	50.08	47.22	12.62	9.45	54.97	57.38
12	6	20	2	34.18	32.95	49.78	52.78	10.84	9.29	56.58	58.94
13	6	25	2	31.70	29.21	44.67	44.43	11.78	8.66	58.06	59.91
14	4	30	1	29.02	27.90	60.00	60.38	12.43	10.82	58.84	61.77
15	2	25	2	32.04	31.89	50.67	52.26	14.21	14.36	61.94	59.43
16	6	25	3	29.37	31.89	52.00	52.26	15.33	14.36	60.00	59.43
17	8	20	3	31.19	31.89	49.98	52.26	11.78	14.36	61.81	59.43
18	8	30	3	32.88	31.89	55.33	52.26	12.80	14.36	57.68	59.43
19	6	25	2	31.81	31.89	52.00	52.26	13.83	14.36	61.94	59.43
20	8	30	1	29.56	31.89	53.75	52.26	12.34	14.36	59.23	59.43

Table 5.2.Analysis of variance for %COD, color, TDS removal and permeate flux by MF.

	COD					Color					TDS					Permeate flux				
Source	**SS**	**DF**	**MS**	**F**	**P**	**SS**	**DF**	**MS**	**F**	**P**	**SS**	**DF**	**MS**	**F**	**P**	**SS**	**DF**	**MS**	**F**	**P**
Model	683.5	9	75.9	10.9	0	1099.1	9	122.1	22.8	0	475.3	9	52.82	8.71	0	200.5	9	22.28	3.35	0.03
Residual	69.9	10	6.9			53.4	10	5.34			60.61	10	6.06			66.5	10	6.66		
Lack of fit	60	5	12.0	6.1	0.03	33.86	5	6.77	1.73	0.28	51.94	5	10.39	5.99	0.03	50.9	5	10.18	3.26	0.11
Pure error	9.9	5	1.98			19.53	5	3.91			8.67	5	1.73			15.6	5	3.13		
Total	753.4	19				1152.5	19				535.9	19				267.0	19			
R^2			0.907					0.954					0.888					0.751		

Notes: SS: Sum of squares; MS: Mean Square; F: F value; P: P value; R^2: R-square.

5.2.2 Effects of Various Operating Parameters

Figure 5.1 to Figure 5.3 show the three-dimensional response surface graphs for all responses with different variables. They show that the performance of the MF membrane is affected by a change in pH, temperature and trans-membrane pressure.

Figure 5.1 shows the effect of pH versus Temp on contaminant removal. At each value of Temp, as the pH increases, the removal efficiency increases till pH value reaches 7-8. Further increase in pH decreases COD removal efficiency. Separation performance of the membrane is thus affected by a change in pH. The reason might be that the change in pH affects the hydration and absorption capacity of solution on the membrane surface [110]. At highly acidic and basic pH, the COD removal is low, whereas the color and TDS removal is high at acidic pH. The permeate flux increases with increase in temperature and pH value.

At each value of pH, as the TMP increases (Figure 5.2), permeate flux also increases. Removal efficiency of the contaminants increases as the TMP increases to an optimum value after which it starts decreasing. This may be due to the fact that pressure increases the driving force for the solvent and decreases the osmotic pressure. This results in passage of more amount of water through the membrane and high rate of salt rejection [218], [219].

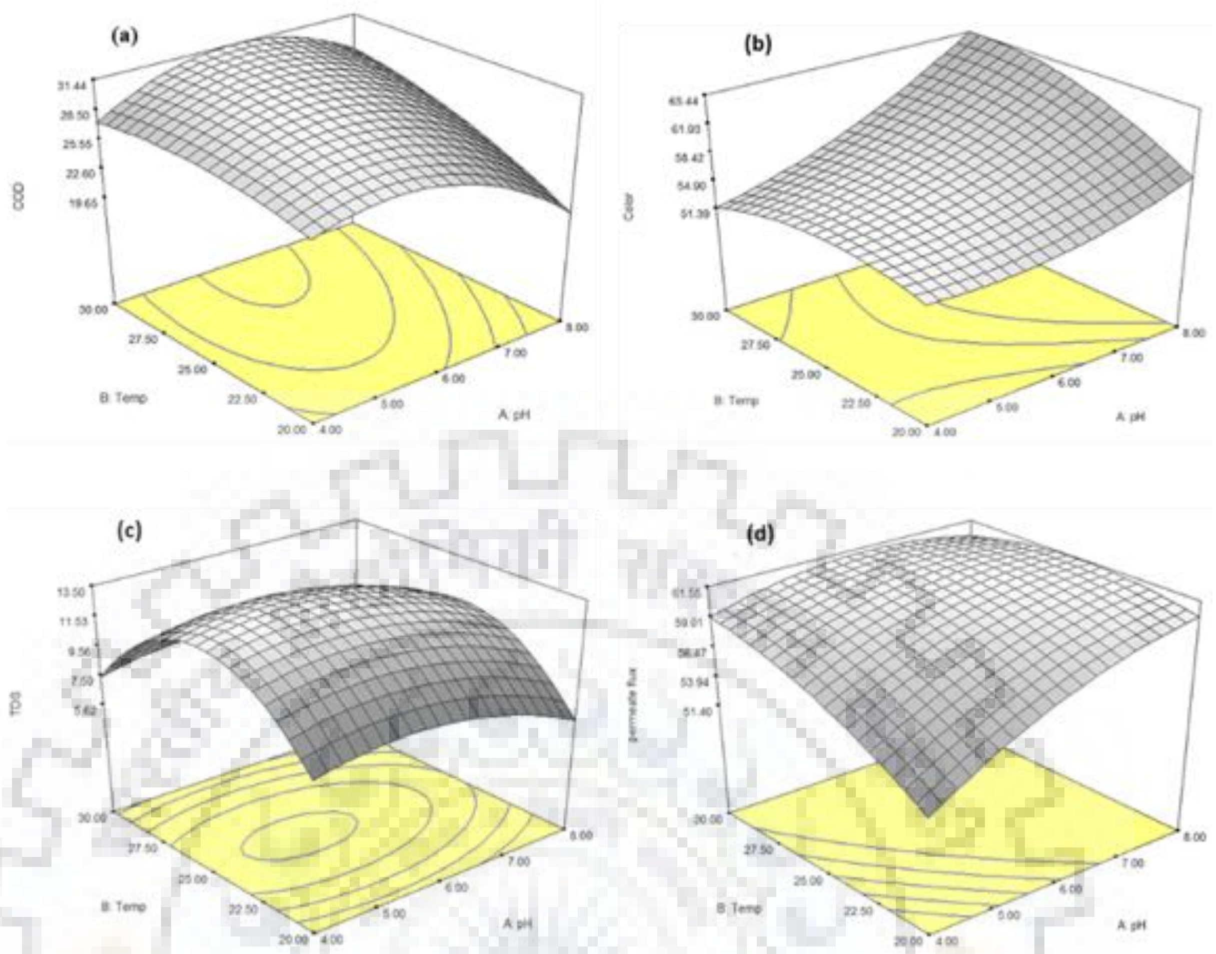


Figure 5.1. Effect of pH and Temp on (a) %COD removal (b) %color removal (c) %TDS removal and (d) permeate flux.

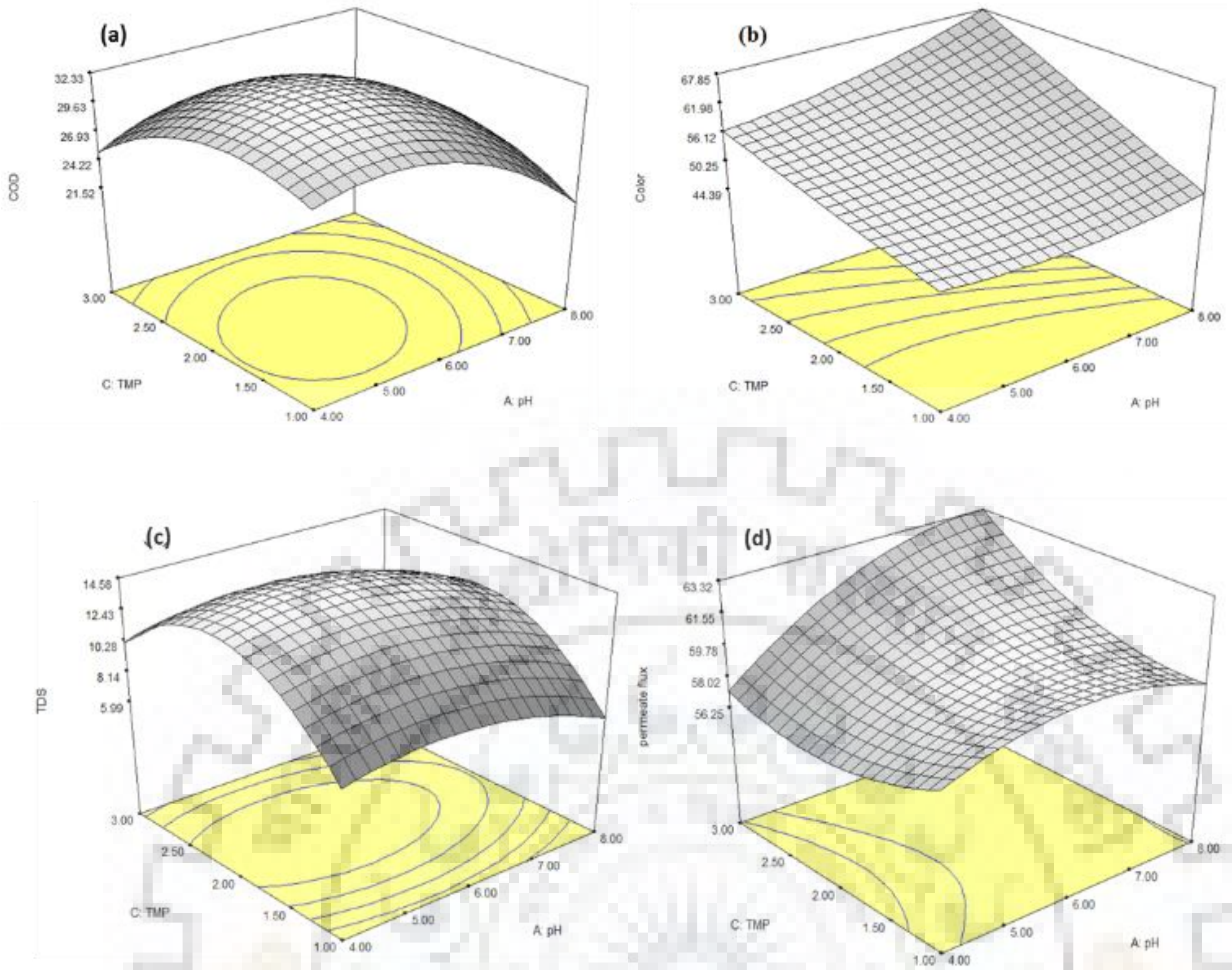


Figure 5.2. Effect of pH and TMP on (a) %COD removal (b) %color removal (c) %TDS removal and (d) permeate flux.

Interaction between Temp and TMP shown in Figure 5.3 depicts that at each value of temperature, as the value of TMP increases, the COD removal also increases. The reason could be the formation of concentration polarization at the membrane interface [220], [221]. Effect of temperature on TDS removal is not much but as the value of temperature increases, decrease in TDS removal is observed, because increase in the temperature results in decreased viscosity and higher rate of water passage through the membrane. Solubility of the solute also increases as the temperature increases, which may result in higher diffusion rate of the solute through the membrane [219], [222], [223]. At each value of temperature, increase in pH results in permeate flux increase. Effect of temperature on permeate flux is not significant due to the low susceptibility of polyamide membrane to structural variations in response to change in temperature [197].

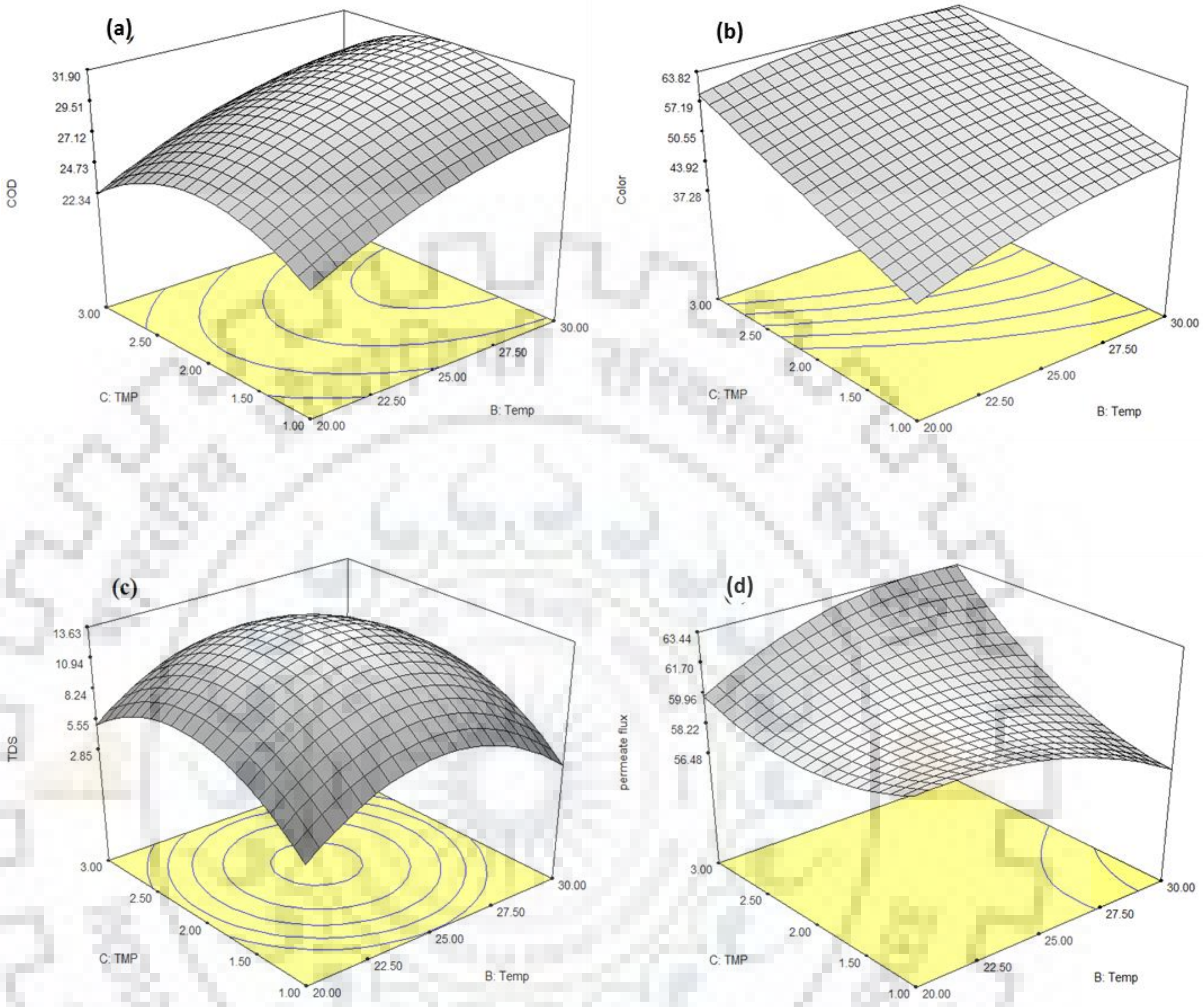


Figure 5.3.Effect of TMP and Temp on (a) %COD removal (b) %color removal (c) %TDS removal and (d) permeate flux.

Table 5.3. Coefficients, standard deviation and P for COD, color, TDS removal and permeate flux by MF.

Factor	**COD**			**Color**			**TDS**			**Permeate flux**		
	Coefficient Estimate	**Standard deviation**	**Prob> F**	**Coefficient Estimate**	**Standard deviation**	**Prob> F**	**Coefficient Estimate**	**Standard deviation**	**Prob> F**	**Coefficient Estimate**	**Standard deviation**	**Prob> F**
Intercept	31.89	0.98		52.26	0.85		14.36	0.91		59.43	0.95	
A-pH	-2.34	0.66	0.005	3.12	0.58	0	-1.00	0.62	0.133	1.62	0.64	0.031
B-Temp	2.25	0.84	0.022	2.78	0.73	0.003	-0.081	0.78	0.919	0.78	0.82	0.361
C-TMP	-0.66	0.84	0.451	7.98	0.73	0	1.08	0.78	0.194	0.93	0.82	0.281
A2	-3.90	0.51	0	1.79	0.44	0.002	-1.68	0.47	0.005	-1.52	0.49	0.011
B2	-1.19	1.48	0.439	-2.26	1.29	0.111	-5.00	1.38	0.004	-1.27	1.44	0.398
C2	-3.33	1.48	0.047	0.15	1.29	0.911	-4.62	1.38	0.007	1.41	1.44	0.352
AB	1.75	0.94	0.090	2.36	0.82	0.016	0.12	0.87	0.892	-1.94	0.91	0.059
AC	1.45	0.94	0.151	2.56	0.82	0.010	-0.021	0.87	0.981	1.45	0.91	0.142
BC	0.14	0.94	0.883	-1.67	0.82	0.068	-0.0007	0.87	0.999	1.84	0.91	0.071

5.2.3 Multi-response Optimization for MF

Multi-objective optimization of operating parameters of MF system was done using desirability function approach, ranging from 0 to 1 i.e. least to the highest probability so as to maximize the COD, color and TDS removal efficiencies with maximum permeate flux. The values of operating parameters (pH, temperature, TMP) after examining the response curves were found to be 6.9 (pH), 25°C (Temp) and 2.6 bars (TMP), respectively at the optimum condition. The maximum predicted removal efficiencies of COD, color and TDS were 31.5%, 42.7% and 27.6% respectively, with permeate flux being 63.8 $l/m^2/h$. Three ratification experiments were carried out at optimum conditions to support the results.

5.3 Optimization of Process Parameters for UF

5.3.1 Statistical Analysis and Modelling

Optimization of the operating parameter plays an important role in the effectiveness of a process. UF membrane system was optimized with three operating parameter pH_o (2-10), Temp (15-43°C) and TMP (4-20 bars). Central composite design was used to study the effect of different operating parameters on permeate flux and contaminant removal (COD, color, and TDS) by conducting different combination of experiments. Actual and predicted values of permeate flux and percentage removal of COD, color and TDS by UF process are shown in Table 5.4. To obtain the regression equations from the linear, interactive, quadratic and cubic model, quadratic model was found to be best fit with the experimental data.

Final equations in terms of coded factors:

$$COD\ removal = +47.74 - 0.51 \times \mathrm{A} - 4.50 \times \mathrm{B} + 5.08 \times \mathrm{C} - 4.75 \times \mathrm{A2} + 1.32 \times \mathrm{B2} + 2.55 \times \mathrm{C2} + 3.04 \times \mathrm{A} \times \mathrm{B} + 3.85 \times \mathrm{A} \times \mathrm{C} - 6.27 \times \mathrm{B} \times \mathrm{C} \tag{5.5}$$

$$Color\ removal = +96.07 - 0.58 \times \mathrm{A} - 0.098 \times \mathrm{B} + 0.41 \times \mathrm{C} - 0.058 \times \mathrm{A2} + 8.687\mathrm{E} - 003 \times \mathrm{B2} + 0.11 \times \mathrm{C2} + 9.055\mathrm{E} - 003 \times \mathrm{A} \times \mathrm{B} - 0.22 \times \mathrm{A} \times \mathrm{C} - 0.076 \times \mathrm{B} \times \mathrm{C} \tag{5.6}$$

$$\mathrm{TDS}\ removal = +28.15 - 0.22 \times \mathrm{A} - 0.46 \times \mathrm{B} + 4.03 \times \mathrm{C} + 1.82 \times \mathrm{A2} + 0.82 \times \mathrm{B2} + 0.73 \times \mathrm{C2} - 1.18 \times \mathrm{A} \times \mathrm{B} + 0.53 \times \mathrm{A} \times \mathrm{C} - 1.22 \times \mathrm{B} \times \mathrm{C} \tag{5.7}$$

$$\text{Permeate flux} = +30.52 + 1.26 \times \mathrm{A} + 2.91 \times \mathrm{B} + 8.95 \times \mathrm{C} - 2.71 \times \mathrm{A2} - 0.55 \times \mathrm{B2} - 0.87 \times \mathrm{C2} - 0.48 \times \mathrm{A} \times \mathrm{B} - 0.29 \times \mathrm{A} \times \mathrm{C} + 1.35 \times \mathrm{B} \times \mathrm{C} \tag{5.8}$$

Regression coefficient and ‘p’ values for different responses with UF optimization is given in Table 5.4. The value of F from the analysis of variance (ANOVA) for COD, color, TDS removal and permeate flux is 6.7, 6.4, 10.7, and 46.25, respectively. The ‘p’ values of model for COD, color, TDS removal and permeate flux are significantly low (0.003, 0.0039, 0.0005 and 0.0001, respectively), less than 0.05, indicating that model fits close to the experimental results [150]. The R^2 values for COD, color, TDS removal and permeate flux are 0.8575, 0.8511, 0.9056 and 0.9765, respectively given in Table 5.5.Table 5.3 can be used to find the pair of parameters among various parameters which have most-significant interaction [150]. Interaction between pH and TMP; Temp and TMP were appeared as more significant among all.

Results of ANOVA for UF system show that the selected model explains the factor response interaction correctly. The values of permeate flux and removal efficiencies for COD, color and TDS are found close to optimum values. The actual and predicted values of responses show that the residuals for the prediction of each response is minimum (Table 5.4). It indicates that the results of ANOVA analysis are correct [155], [157].

Table 5.4.Experimental inputs and responses for UF.

Run	pH	Temp. (°C)	Pressure (bar)	%COD removal		%Color removal		%TDS removal		Permeate flux	
				actual	predicted	actual	predicted	actual	predicted	actual	Predicted
1	6	20	12	42.07	47.42	94.61	94.71	24.27	26.31	13.55	13.85
2	6	25	12	34.03	32.63	96.50	96.33	28.33	27.18	16.65	17.91
3	6	33	12	39.11	44.87	95.02	94.68	31.77	30.20	18.58	17.93
4	6	25	12	41.56	42.23	96.01	96.26	24.20	26.34	18.97	20.05
5	4	20	8	58.48	62.40	96.40	96.12	38.21	35.75	29.03	29.62
6	4	20	16	64.18	63.01	96.57	96.88	37.46	38.72	30.19	32.52
7	8	30	16	28.80	34.79	95.65	95.79	33.92	34.75	38.71	39.12
8	6	25	12	48.31	47.55	96.64	96.51	35.36	33.00	38.71	40.09
9	6	25	20	37.98	29.77	94.50	94.67	35.47	35.88	16.65	17.16
10	8	30	8	24.13	27.75	97.15	97.01	35.09	34.99	24.39	22.20
11	6	25	12	57.30	53.56	96.16	96.18	29.38	29.44	30.97	27.05
12	4	30	16	49.07	43.89	95.90	95.93	29.28	29.71	34.84	33.85
13	6	25	12	50.70	47.80	94.73	94.79	23.92	23.04	9.29	9.13
14	2	25	12	69.79	68.10	96.48	96.45	37.94	39.14	46.45	44.94
15	8	20	16	43.44	47.74	95.83	96.07	27.11	28.15	30.97	30.52
16	4	30	8	41.81	47.74	95.83	96.07	26.08	28.15	30.97	30.52
17	6	25	4	49.24	47.74	96.16	96.07	28.25	28.15	30.97	30.52
18	6	25	12	48.82	47.74	95.51	96.07	27.94	28.15	29.03	30.52
19	8	20	8	52.50	47.74	96.88	96.07	30.10	28.15	30.19	30.52
20	10	25	12	50.91	47.74	96.22	96.07	29.28	28.15	29.42	30.52

Table 5.5. **Analysis of variance for %COD, color, TDS removal and permeate flux by UF.**

Source	COD				Color				TDS				Permeate Flux			
	SS	**DF**	**F**	**P**	**SS**	**DF**	**F**	**P**	**SS**	**DF**	**F**	**P**	**SS**	**DF**	**F**	**P**
Model	2043.05	9	6.68	0.003	9.08	9	6.35	0.003	379.30	9	10.66	0	1620.17	9	46.25	0
Residual	339.62	10			1.59	10			39.53	10			38.93	10		
Lack of fit	249.92	5	2.79	0.142	0.48	5	0.43	0.809	29.04	5	2.77	0.144	35.20	5	9.46	0.013
Pure error	89.70	5			1.11	5			10.49	5			3.72	5		
Total	2382.67	19			10.67	19			418.82	19			1659.09	19		
R^2	0.8575				0.8511				0.9056				0.9765			

Notes: SS: Sum of squares; DF: Degree of freedom; F: F value; P: P value; R^2: R-square.

Table 5.6. Coefficients, standard deviation and P for COD, color, TDS removal and permeate flux by UF.

Factor	COD			Color			TDS			Permeate flux		
	Coefficient Estimate	Standard deviation	P value	Coefficient Estimate	Standard deviation	P value	Coefficient Estimate	Standard deviation	P value	Coefficient Estimate	Standard deviation	P value
Intercept	47.74	2.32		96.07	0.16		28.15	0.79		30.52	0.79	
A-pH	-0.51	1.46	0.73	0.58	0.100	0.003	-0.22	0.50	0	1.26	0.49	0
B-Temp	-4.50	1.78	0.03	-0.098	0.12	0	-0.46	0.61	0.66	2.91	0.60	0.02
C-TMP	5.08	1.46	0.005	0.41	0.100	0.43	4.03	0.50	0.46	8.95	0.49	0
A2	-4.75	1.14	0.002	-0.058	0.078	0.001	1.82	0.39	0	-2.71	0.39	0
B2	1.32	1.95	0.51	0.008	0.13	0.47	0.82	0.67	0	-0.55	0.66	0
C2	2.55	1.14	0.04	-0.11	0.078	0.94	0.73	0.39	0.24	-0.87	0.39	0.42
AB	3.04	2.06	0.17	-0090	0.14	0.17	-1.18	0.70	0.08	-0.48	0.70	0.04
AC	3.85	2.06	0.09	-0.22	0.14	0.95	0.53	0.70	0.12	-0.29	0.70	0.50
BC	-6.27	2.06	0.01	-0.076	0.14	0.15	-1.22	0.70	0.47	1.35	0.70	0.68

5.3.2 Effects of Various Operating Parameters

The three-dimensional response surface graphs for all responses with different variables are shown in Figure 5.4 to Figure 5.6. pH, temperature and trans-membrane pressure of the system affect the membrane performance. Removal efficiency of COD, color and TDS increases as the pH approaches to the neutral. The reason could be that at highly acidic and basic condition, pollutants have maximum solubility which results in their easy passage through the membrane. Effect of pH versus Temp on contaminants removal is shown in Figure 5.4. At the optimum temperature, around 25 °C, removal efficiency is maximum. Further increase in temperature results in decreased removal efficiency of the pollutants. This could be due to increased solubility and diffusion of the solute with increase in temperature. Permeate flux increases as the pH and temperature increases due to increase in the solubility of solute and permeability of water through the membrane [222], [223].

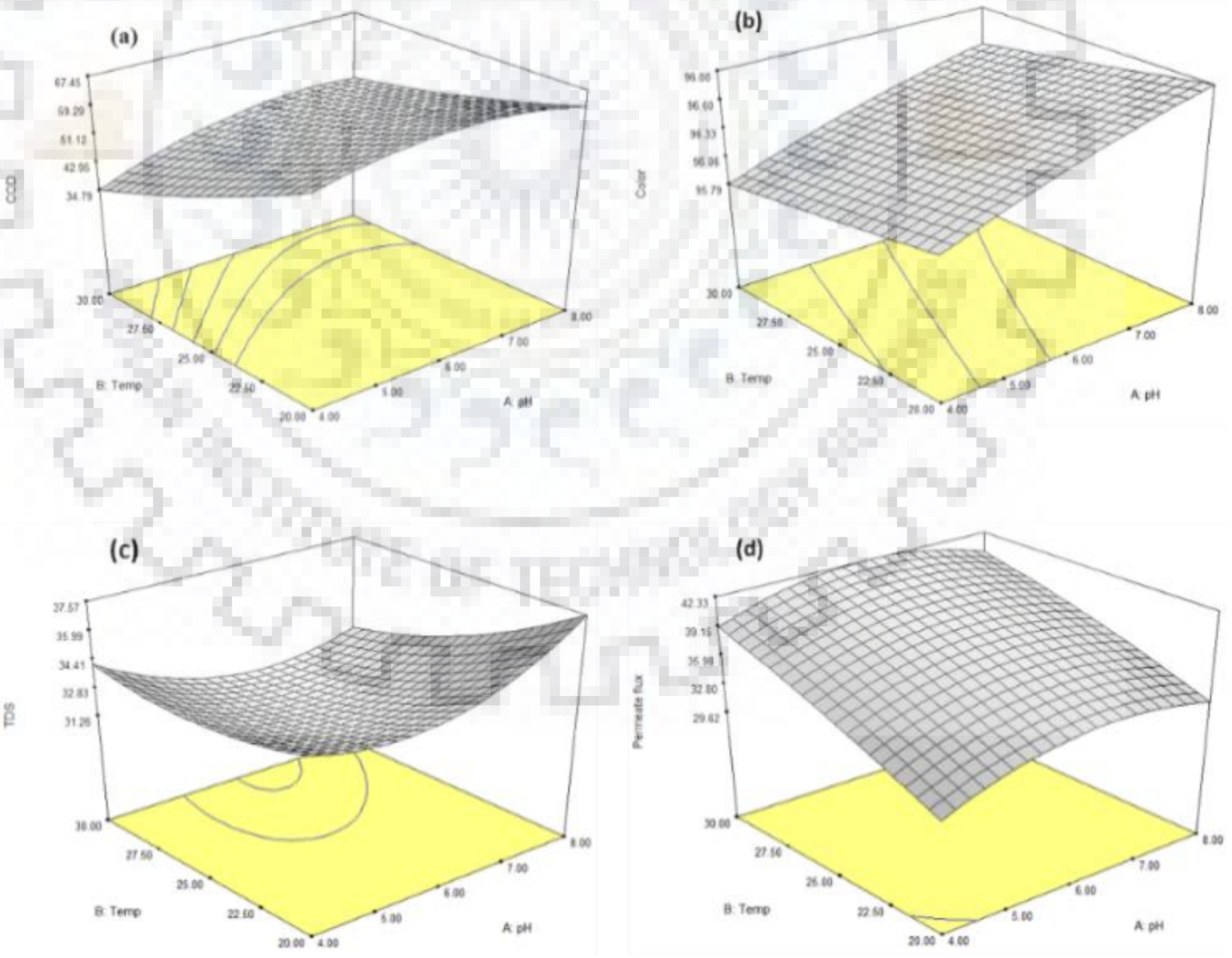


Figure 5.4.Effect of pH and Temp on (a) %COD removal (b) %color removal (c) %TDS removal and (d) permeate flux.

With the increase of the TMP, removal efficiency of COD, color and TDS also increases (Figure 5.5) [224]. As the UF membrane has lower pore size compared to MF, at higher pressure formation of concentration polarization at membrane surface could result in higher pollutant removal. Permeate flux also increases as the TMP increases due to an increase in permeability of water through the membrane [218], [219]. However, at high values of temperature, as the trans-membrane pressure increases, the removal efficiency of the contaminants decreases but the permeate flux increases (Figure 5.6). It could be due to the low viscosity of water at high temperature which results in to increased solubility of solute and also higher rate of water passage through the membrane [219], [222], [223].

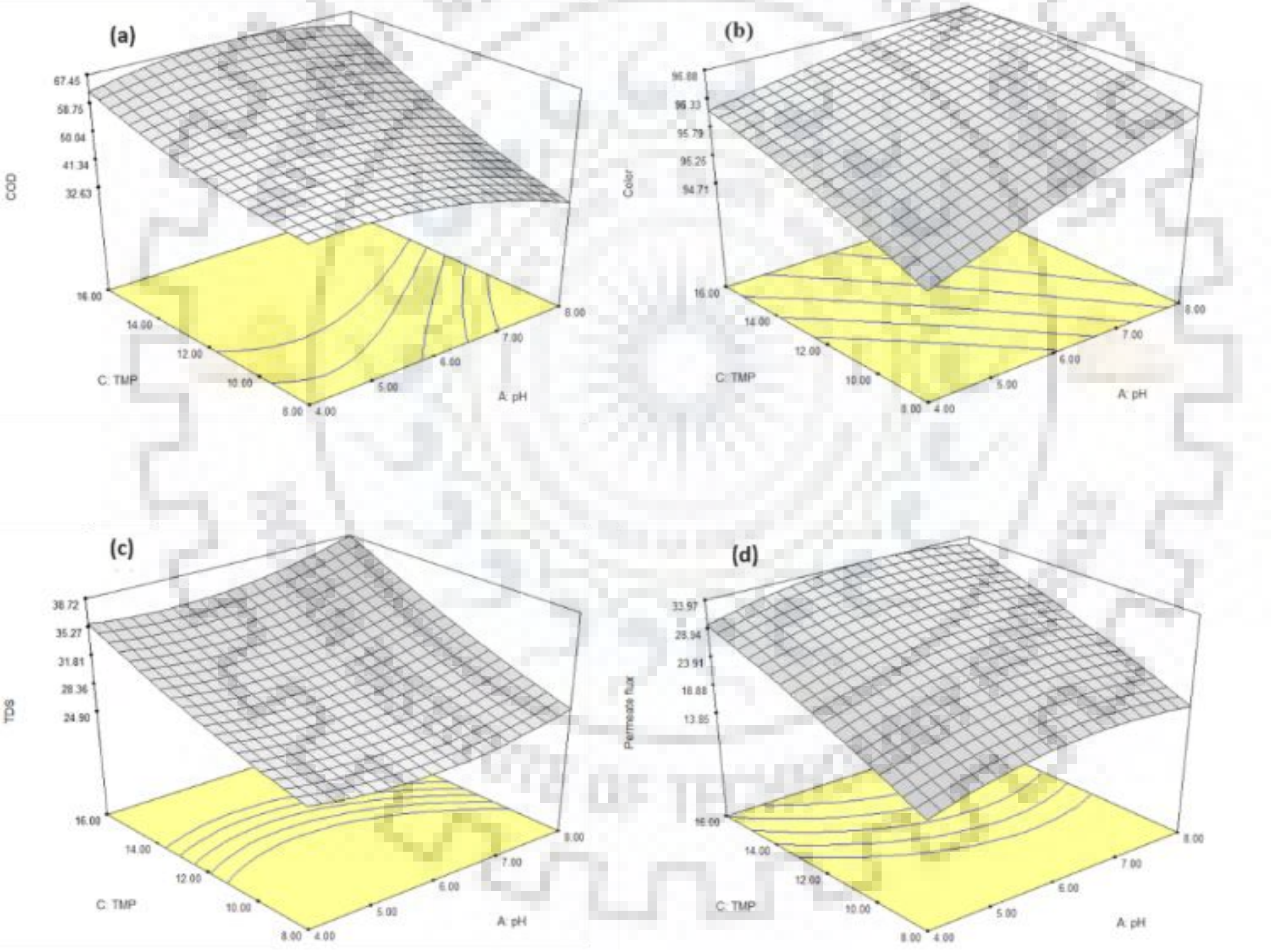


Figure 5.5. Effect of pH and TMP on (a) %COD removal (b) %color removal (c) %TDS removal and (d) permeate flux.

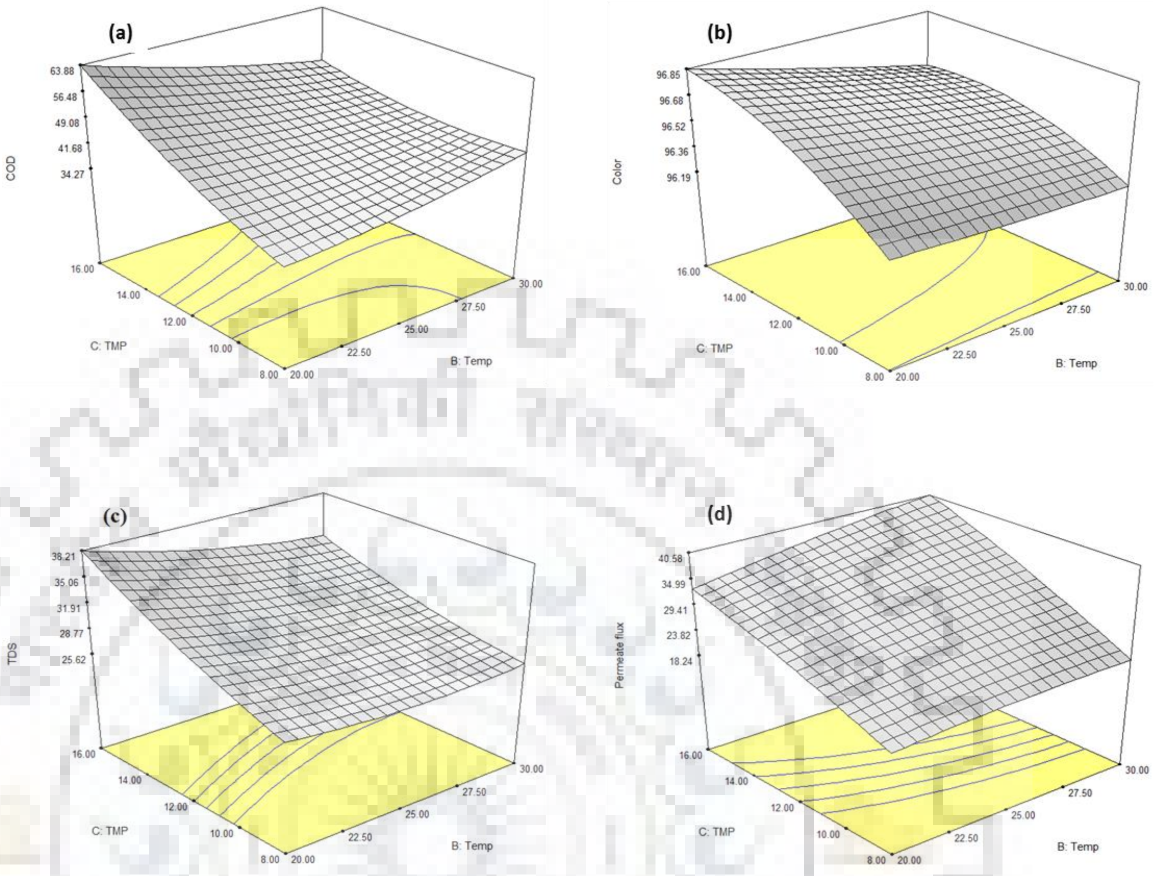


Figure 5.6. Effect of TMP and Temp on (a) %COD removal (b) %color removal (c) %TDS removal and (d) permeate flux.

5.3.3 Multi-response Optimization for UF

To maximize the COD, color and TDS removal efficiencies with maximum permeate flux, multi-objective optimization of operating parameters of UF system was done using desirability function approach. The optimum value of operating parameters after examining the response curves were as: pH=6.9; T=20°C; and TMP=16 bar for UF respectively. The maximum predicted COD, color, TDS removal were 62%, 93.5% and 75.5%, respectively with permeate flux of 33 l/m^2/h. At optimum conditions, three ratification experiments were carried out to support the results.

5.4 Optimization of Process Parameters for EC

5.4.1 Statistical Analysis and Modelling

Current density (j), pH (pH_o), electrode distance (g) and time (t) are important factors which affect the performance of EC process. To study the combined effects of these factors on SS and Al electrodes performance, experiments with different combinations were conducted by using CCD. The actual design matrixes along with actual and predicted percent removal of COD, color and TOC by SS and Al electrodes are given in Tables 5.7 and 5.8, respectively. Out of linear, interactive, quadratic and cubic models, quadratic model was found to be best fitted for the experimental data to obtain the regression equations.

The final equations in terms of coded factors for COD, color and TOC removal by SS electrode are given as:

$$COD\ removal = +48.82 + 3.01 \times A + 4.08 \times B - 0.58 \times C + 7.71 \times D\ 1.91 \times A2 + 2.88 \times B2 + 2.55 \times C2 + 1.40 \times D2 - 0.21 \times A \times B - 2.46 \times A \times C + 2.50 \times A \times D + 3.94 \times B \times C - 1.98 \times B \times D + 0.86 \times C \times D \tag{5.9}$$

$$Color\ removal = +89.57 - 1.27 \times A + 9.66 \times B + 0.13 \times C + 5.69 \times D - 14.81 \times A2 - 0.83 \times B2 - 1.16 \times C - 2.18D2 + 0.067 \times A \times B + 5.70 \times A \times C - 2.47 \times A \times D + 0.65 \times B \times C + 1.07 \times B \times D + 1.40 \times C \times D \tag{5.10}$$

$$\text{TOC}\ removal = +57.64 + 1.22 \times A + 6.70 \times B - 3.30 \times C + 8.16 \times D - 4.75 \times A2 + 1.33 \times 2 - 0.57 \times C2 - 1.24 \times D2 - 1.04 \times A \times B - 0.66 \times A \times C + 0.036 \times A \times D + 3.18 \times B \times C - 1.06 \times B \times D + 1.71 \times C \times D \tag{5.11}$$

The final equations in terms of coded factors for COD, color and TOC removal by Al electrode are given as:

$$COD\ removal = +48.25 - 2.50 \times A + 1.38 \times B - 0.64 \times C + 2.82 \times D + 0.39 \times A2 + 0.56 \times B2 + 1.23 \times C2 + 1.08 \times A \times B + 1.35 \times A \times C - 2.35 \times B \times C + 0.67 \times B \times D + 1.04 \times C \times D \tag{5.12}$$

$$Color\ removal = +72.71 - 7.99 \times A + 5.73 \times B + 0.22 \times C + 5.48 \times D - 1.82 \times A2 - 0.45 \times B2 + 0.54 \times C2 - 0.89 \times D2 - 1.35 \times A \times B + 4.54 \times A \times C - 1.75 \times A \times D + 3.22 \times B \times C - 2.06 \times B \times D + 3.15 \times C \times D \tag{5.13}$$

$$\text{TOC}\ removal = +45.20 - 3.43 \times A + 3.64 \times B + 1.30 \times C + 4.37 \times D + 1.77 \times A2 - 0.29 \times B2 + 0.87 \times C2 - 1.61 \times D2 + 2.54 \times A \times B + 0.42 \times A \times C - 0.79 \times A \times D - 2.48 \times B \times C + 0.13 \times B \times D + 0.77 \times C \times D \tag{5.14}$$

The values of the regression coefficient and ‘p’ values for the analysis by SS and Al electrode are given in Tables 5.9 and 5.10, respectively. The analysis of variance results for COD, color and TOC removal show F-values of 3.19, 23.20 and 4.48, respectively, for SS electrode; and F-values of 2.71, 8.93 and 6.45, respectively, for Al electrode. If the value of F is larger and the value of ‘p’ is smaller, then the terms of coefficient are more significant [217]. These values indicate that the regression equations are able to explain the variation in responses properly. Values of p i.e. $p < 0.05$ indicate that the factor or interaction of factors play a significant role. If the probability p (<0.0001) is less than 0.05or close to zero, then it indicates that the model terms are significant at 95% of probability level and factors play significant role which indicates that the model is statistically significant [157], [200], [216]. Analysis of variance (ANOVA) results by SS and Al electrode are shown in Tables 5.7 and 5.8, respectively. The ‘p’ values of lack of fit for COD, color and TOC are 0.0034, <0.0467 and 0.0362, respectively, for SS electrode; 0.1806, 0.0012 and 0.0004, respectively, by Al electrode which are significantly low, indicating that the model fits close to the experimental results [150].

The R^2 values for COD, color and TOC removal are 0.82, 0.91 and 0.86, respectively by SS electrode and 0.66, 0.89 and 0.86, respectively by Al electrode given in Tables 5.11 and 5.12, respectively. The ‘p’ values as shown in Tables 5.9 and 5.10 can be used to find the pair of parameters among various parameters which have most-significant interaction [150]. In case of SS electrode, among different operating parameters the value of p for parameter ‘t’ is <0.0001 followed by j (0.0093), pH (0.049) as shown in Table 5.11. Thus, t, j and pH_o are most significant parameters affecting COD removal. Interaction among j and g shows more impact than other operating parameters. For color removal, j is the most controlling parameter having least value of p (0.0001) followed by t (0.004), pH (0.455) and g (0.939). In case of Al electrode, parameter ‘t’ followed by pH shows the least values for p (Table 5.12) which expressed their level of importance in COD removal. Interaction among j and g show more impact than other operating parameters.

Table 5.7. **Experimental inputs and responses for SS electrode.**

Run	**pH**	**j (A m^{-2})**	**g (cm)**	**t (min)**	**% COD removal**		**% color removal**		**% TOC removal**	
					actual	**predicted**	**actual**	**predicted**	**actual**	**predicted**
1	4	60.72	1	60	34.50	42.09	58.60	63.02	32.76	41.87
2	8	60.72	1	60	50.50	48.45	55.93	53.88	48.67	47.60
3	4	123.45	1	60	54.78	47.81	84.48	79.24	59.12	54.02
4	8	123.45	1	60	56.17	53.28	77.02	70.38	58.22	55.39
5	4	60.72	2	60	36.49	36.43	47.80	47.82	22.86	26.98
6	8	60.72	2	60	38.17	32.96	59.17	61.48	30.00	30.05
7	4	123.45	2	60	57.80	58.62	76.85	66.74	50.11	52.42
8	8	123.45	2	60	56.21	54.26	76.29	80.69	51.74	51.14
9	4	60.72	1	120	61.50	54.65	83.80	74.44	58.46	56.76
10	8	60.72	1	120	68.53	71.01	45.31	55.44	62.08	62.63
11	4	123.45	1	120	43.62	52.09	97.37	95.14	61.42	64.47
12	8	123.45	1	120	76.32	67.55	81.32	76.42	72.17	65.99
13	4	60.72	2	120	45.98	52.45	58.24	64.83	42.55	48.72
14	8	60.72	2	120	61.17	58.97	68.00	68.63	49.36	51.94
15	4	123.45	2	120	73.41	66.35	91.00	88.23	71.21	69.73

16	8	123.45	2	120	75.94	71.98	97.00	92.31	74.39	68.59
17	2	90.6	1.5	90	39.23	35.26	26.14	33.04	44.23	36.39
18	10	90.6	1.5	90	37.78	47.29	30.00	27.97	34.13	41.18
19	6	30.86	1.5	90	55.09	51.97	76.51	67.29	59.40	49.61
20	6	154.23	1.5	90	62.09	70.75	92.51	106.42	69.40	78.10
21	6	90.6	0.5	90	58.38	60.11	79.35	84.85	59.49	61.97
22	6	90.6	2.5	90	54.30	58.11	86.04	85.41	52.31	49.04
23	6	90.6	1.5	30	36.56	39.16	65.60	69.61	39.15	36.55
24	6	90.6	1.5	150	66.90	69.84	91.58	92.44	67.29	69.10
25	6	90.6	1.5	90	45.89	48.90	95.77	89.76	53.08	57.78
26	6	90.6	1.5	90	48.63	48.90	86.70	89.76	59.80	57.78
27	6	90.6	1.5	90	50.23	48.90	87.80	89.76	60.11	57.78
28	6	90.6	1.5	90	47.50	48.90	94.30	89.76	54.10	57.78
29	6	90.6	1.5	90	49.35	48.90	85.35	89.76	60.11	57.78
30	6	90.6	1.5	90	51.80	48.90	88.45	89.76	59.15	57.78
					SD=4.48		SD=14.24		SD=5.02	

Table 5.8. Experimental inputs and responses for Al electrode.

Run	pH	j (A m^{-2})	g (cm)	t (min)	% COD removal		% color removal		% TOC removal	
					actual	predicted	actual	predicted	actual	predicted
1	5.5	61.72	1	60	52.16	51.21	72.72	72.78	37.89	40.87
2	8.5	61.72	1	60	41.75	41.47	54.70	53.78	30.16	29.96
3	5.5	123.45	1	60	58.61	55.50	84.98	84.81	50.75	47.88
4	8.5	123.45	1	60	45.25	50.20	66.66	60.25	42.47	47.43
5	5.5	61.72	2	60	52.60	49.59	59.26	51.78	44.20	45.77
6	8.5	61.72	2	60	40.90	45.25	53.06	50.92	34.38	36.53
7	5.5	123.45	2	60	43.29	44.21	72.69	77.06	43.09	42.56
8	8.5	123.45	2	60	49.41	44.30	73.91	70.65	47.88	43.79
9	5.5	61.72	1	120	46.47	53.51	81.09	84.82	45.02	49.42
10	8.5	61.72	1	120	47.34	43.78	68.51	58.80	36.13	35.33
11	5.5	123.45	1	120	65.70	60.54	91.57	88.37	60.43	56.94
12	8.5	123.45	1	120	52.13	55.24	48.84	56.80	54.58	53.32
13	5.5	61.72	2	120	61.80	56.05	75.36	76.43	63.67	57.38

14	8.5	61.72	2	120	48.50	51.71	67.90	68.55	41.79	44.97
15	5.5	123.45	2	120	51.20	53.41	91.84	93.24	54.20	54.70
16	8.5	123.45	2	120	55.19	53.50	85.21	79.81	57.07	52.75
17	4	92.6	1.5	90	51.19	54.74	84.45	82.13	57.65	59.00
18	10	92.6	1.5	90	47.95	45.11	42.51	49.69	46.47	46.15
19	7	30.86	1.5	90	48.60	47.72	54.71	59.65	40.89	36.88
20	7	154.32	1.5	90	52.21	53.80	83.00	82.93	46.62	51.66
21	7	92.6	0.5	90	56.37	54.99	72.47	74.37	49.19	46.82
22	7	92.6	2.5	90	49.54	51.63	73.42	76.38	47.75	51.15
23	7	92.6	1.5	30	42.30	42.62	53.51	59.05	32.83	30.33
24	7	92.6	1.5	150	54.64	54.13	80.93	80.25	44.31	47.84
25	7	92.6	1.5	90	48.30	48.38	74.20	73.21	46.70	45.51
26	7	92.6	1.5	90	42.80	48.38	74.60	73.21	44.60	45.51
27	7	92.6	1.5	90	48.50	48.38	73.70	73.21	45.90	45.51
28	7	92.6	1.5	90	49.46	48.38	72.24	73.21	45.29	45.51
29	7	92.6	1.5	90	47.10	48.38	70.90	73.21	44.80	45.51
30	7	92.6	1.5	90	53.20	48.38	73.60	73.21	45.78	45.51
					SD=1.28		SD=2.04		SD=2.63	

Table 5.9.Analysis of variance for %COD, color and TOC removal with SS electrode.

	COD				Color				TOC			
Source	**SS**	**DF**	**MS**	**F**	**SS**	**DF**	**MS**	**F**	**SS**	**DF**	**MS**	**F**
Mean	84781.7	1	84781.69		167893.1	1	167893.1		87142.3	1	87142.29	
Linear	2152.6	4	538.2	7.22	3162.1	4	790.5	2.55	3084.9	4	771.23	11.6
2FI	549.4	6	91.6	1.32	676.3	6	112.7	0.303	269.6	6	44.9	0.61
Quadratic	603.9	4	150.9	3.19	6086.1	4	1521.5	23.20	757.8	4	189.5	4.48
Cubic	533.9	9	59.3	2.03	869.8	9	96.6	5.095	551.3	9	61.3	4.44
Residual	175.7	6	29.3		113.8	6	18.9		82.8	6	13.8	
Total	887970.2	30	2959.9		178801.2	30	5960.0		918880.8	30	3062.9	

Notes: SS: Sum of squares; DF: Degree of freedom; MS: Mean Square; F: F value; P: P value.

Table 5.10. Analysis of variance for %COD, color and TOC removal with Al electrode.

	COD				**Color**				**TOC**			
Source	**SS**	**DF**	**MS**	**F**	**SS**	**DF**	**MS**	**F**	**SS**	**DF**	**MS**	**F**
Mean	75446.6	1	75446.6		151590.9	1	151590.9		63709.2	1	63709.2	
Linear	410.4	4	102.6	4.72	3070.8	4	767.7	4.26	1063.5	4	265.9	9.57
2FI	170.4	6	28.4	1.45	815.9	6	136.0	0.98	236.3	6	39.4	1.63
Quadratic	49.6	4	12.4	0.57	126.04	4	31.5	6.73	207.9	4	51.9	3.11
Cubic	259.2	9	28.8	2.68	437.8	9	48.7	13.48	244.7	9	27.2	28.60
Residual	64.6	6	10.8		43.4	6	7.23		5.7	6	0.95	
Total	76400.7	30	2546.7		156084.9	30	5202.8		65467.4	30	2182.3	

Notes: SS: Sum of squares; DF: Degree of freedom; MS: Mean Square; F: F value; P: P value.

Table 5.11. Coefficients, standard deviation, t and P for COD, color and TOC removal by SS electrode.

Factor	COD			Color			TOC		
	Coefficient	Standard deviation	Prob> F	Coefficient	Standard deviation	Prob> F	Coefficient	Standard deviation	Prob> F
Intercept	48.82	2.81	0.0019	89.57	3.30	< 0.0001	57.64	2.65	0.0003
A-pH	3.01	1.41	0.049	-1.27	1.66	0.455	1.22	1.33	0.374
B- j	4.08	1.37	0.009	9.66	1.61	< 0.0001	6.70	1.29	0.0001
C- g	-0.58	1.41	0.686	0.13	1.66	0.939	-3.30	1.33	0.026
D- t	7.71	1.41	< 0.0001	5.69	1.66	0.004	8.16	1.33	0
A2	-1.91	1.31	0.167	-14.81	1.55	< 0.0001	-4.75	1.24	0.002
B2	2.88	1.24	0.034	-0.83	1.46	0.575	1.33	1.17	0.272
C2	2.55	1.31	0.071	-1.16	1.55	0.465	-0.57	1.24	0.654
D2	1.40	1.31	0.303	-2.18	1.55	0.178	-1.24	1.24	0.334
AB	-0.21	1.64	0.898	0.07	1.94	0.973	-1.04	1.55	0.513
AC	-2.46	1.72	0.174	5.70	2.02	0.013	-0.66	1.63	0.689
AD	2.50	1.72	0.168	-2.47	2.02	0.242	0.04	1.63	0.983
BC	3.94	1.64	0.030	0.65	1.94	0.743	3.18	1.55	0.059
BD	-1.98	1.64	0.247	1.07	1.94	0.588	-1.06	1.55	0.505
CD	0.86	1.72	0.623	1.40	2.02	0.501	1.72	1.63	0.308
	R-Squared: 0.823			R-Squared: 0.909			R-Squared: 0.866		

Table 5.12.Coefficients, standard deviation, t and P for COD, color and TOC removal by Al electrode.

Factor	COD				Color			TOC		
	Coefficient	Standard deviation	Prob> F	Factor	Coefficient	Standard deviation	Prob> F	Coefficient	Standard deviation	Prob> F
Intercept	48.25	1.51	0.029	Intercept	72.71	2.31	< 0.0001	45.20	1.67	0.0005
A-pH	-2.50	0.90	0.013	A-pH	-7.99	1.16	< 0.0001	-3.43	0.84	0.001
B- j	1.38	0.88	0.136	B- j	5.73	1.14	0.0001	3.64	0.82	0.0005
C- g	-0.64	0.90	0.488	C- g	0.22	1.16	0.849	1.30	0.84	0.143
D- t	2.82	0.90	0.006	D- t	5.48	1.16	0.0003	4.37	0.84	0.0001
A2	0.39	0.83	0.647	A2	-1.82	1.08	0.112	1.77	0.78	0.039
B2	0.56	0.78	0.482	B2	-0.45	1.02	0.664	-0.29	0.74	0.696
C2	1.23	0.83	0.155	C2	0.54	1.08	0.623	0.87	0.78	0.283
AB	1.08	1.07	0.327	D2	-0.89	1.08	0.424	-1.61	0.78	0.057
AC	1.35	1.10	0.236	AB	-1.35	1.38	0.343	2.54	0.99	0.022
BC	-2.35	1.07	0.042	AC	4.54	1.42	0.006	0.42	1.02	0.687
BD	0.67	1.07	0.541	AD	-1.76	1.42	0.234	-0.79	1.02	0.449
CD	1.04	1.10	0.357	BC	3.22	1.38	0.034	-2.48	0.99	0.025
				BD	-2.06	1.38	0.155	0.13	0.99	0.899
				CD	3.15	1.42	0.042	0.77	1.02	0.464
	R-Squared: 0.656				R-Squared: 0.892			R-Squared: 0.857		

For the present study, ANOVA analysis for treatment by both SS and Al electrode show that the model selected correctly explicates the factors and response relationship [200]. The removal efficiencies of COD, color and TOC by SS electrode are found to be higher than by Al electrode at optimum conditions. The relationship between the actual and predicted values of responses are shown in Tables 5.7 and 5.8. It may be seen that the residuals for the prediction of each response are minimum indicating that the results of ANOVA analysis are correct [155], [157].

5.4.2 Effects of Various Operating Parameters

During the EC process dissolution of Al and SS electrode generates respective ions in situ as coagulant. Generation of metal hydroxide flocs helps in removal of soluble compounds by adsorption onto large surface areas flocs by trapping the colloidal particles [225].Formation of gas bubble (hydrogen gas) at cathode help in removal of less dense particles present in the solution by floatation process. The layer formed at the top of solution by floatation i.e. scum, can be skimmed. Presence of chloride ions in the solution results in generation of various chlorine species (Cl_2, HOCl and ClO^-) at anode depending on the solution pH during the EC process. These chlorine species indirectly causes the oxidation of organic material present in wastewater [226].

Three-dimensional response surface graphs for all responses with SS and Al electrodes are shown in Figures 5.7 and 5.8, respectively. pH of the medium changes during the process which is governed by the material of the electrode being used [141], [227].In an attempt to compare the effect of pH_o on the EC process using SS and Al electrode in term of COD, color and TOC removal, pH_o of the effluent was varied in the range of 2 to 10 and 4-10 for SS and Al electrodes, respectively, by adding 0.1 N NaOH or 0.1 N H_2SO_4 solution [155]. The results from the graph obtained by design expert depicted that COD, color and TOC removal showed same trend by both the electrode. Maximum removal efficiency of COD, color and TOC by SS electrode was obtained at pH 7.8, whereas, Al electrode showed the maximum removal efficiency at pH 6.6. Bensadok et al., (2008)[228]reported that aluminum hydroxide precipitates work more efficiently at pH 6-7, and its solubility increases as the solution becomes either more acidic or alkaline [136]. SS electrode showed greater removal efficiency than Al electrode at optimum conditions obtained through central composite design of RSM.

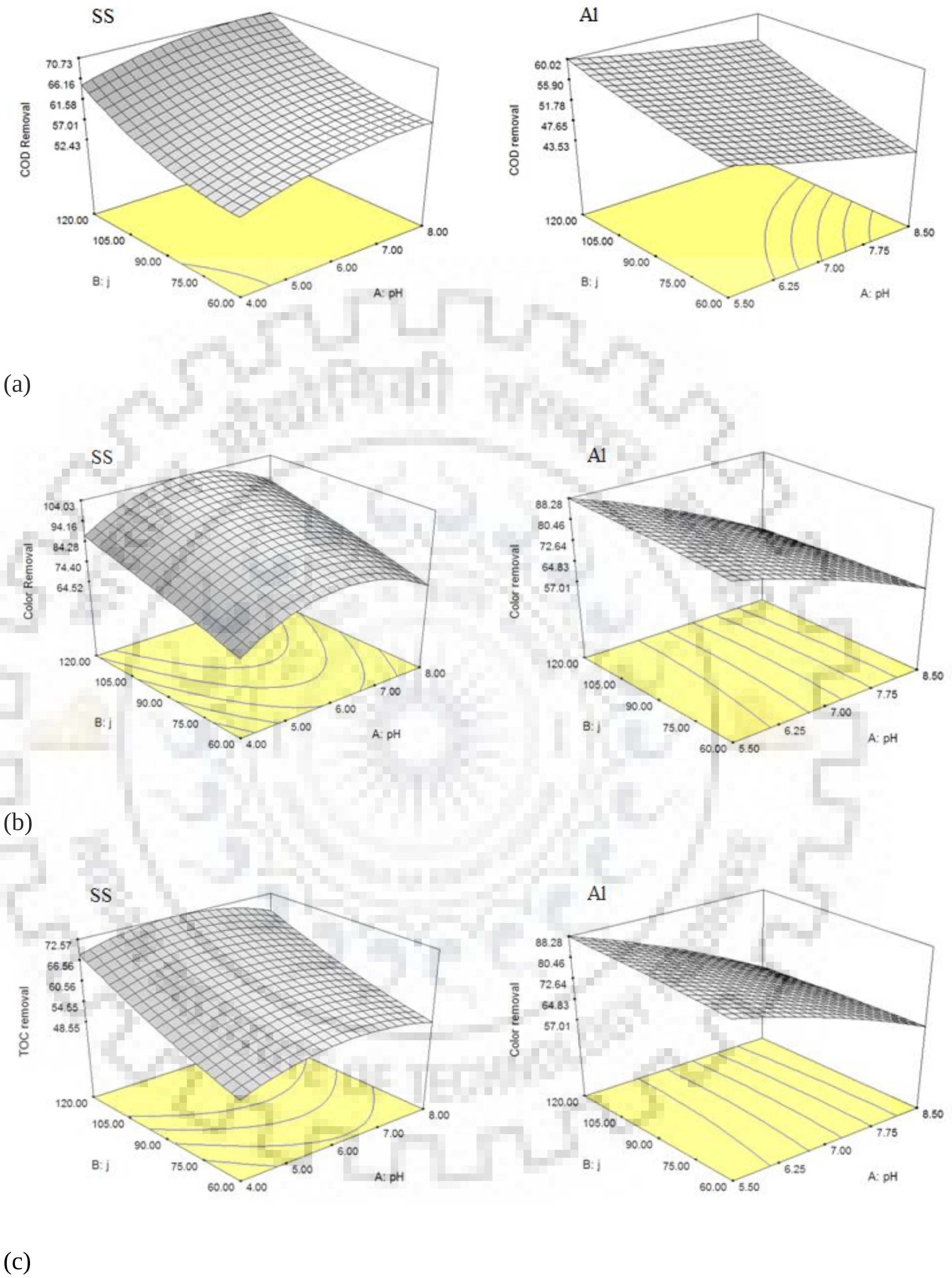


Figure 5.7.Three-dimensional response surface graphs of EC treatment of distillery spent wash for COD, color and TOC removal versus j and pH;
(a) Effect of pH and j on %COD removal by SS and Al electrodes,
(b) Effect of pH and j on %color removal by SS and Al electrodes,
(c) Effect of pH and j on %TOC removal by SS and Al electrodes.

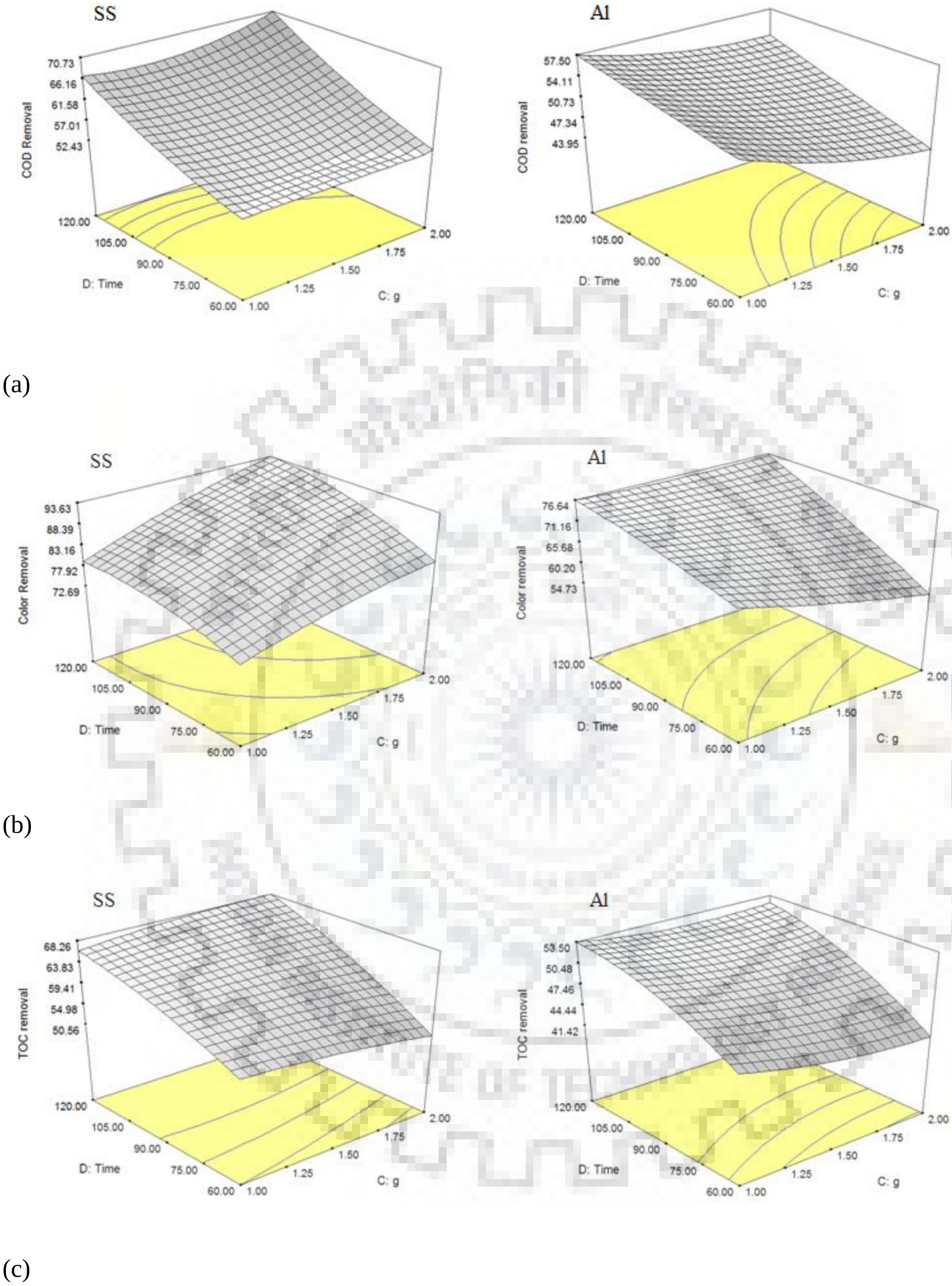


Figure 5.8.Three-dimensional response surface graphs of EC treatment of distillery spent wash for COD, color and TOC removal versus g and time;
(a) Effect of g and t on %COD removal by SS and Al electrodes,
(b) Effect of g and t on %color removal by SS and Al electrodes,
(c) Effect of g and t on %TOC removal by SS and Al electrodes.

Figure 5.7 (a)-(c) shows the effect of pH and j on the percent removal of COD, color and TOC respectively by SS and Al electrode. As the j increases, removal efficiency of COD, color and TOC increases [130]. This is due to increased rate of formation of metal hydroxides of respective electrodes due to dissolution of corresponding electrode material at higher j values. This resulted into higher rate of removal of pollutants due to process of co-precipitation process [229].Furthermore, with an increase in j, the bubble density increases and their size decreases which in turn accelerates the removal of pollutants [230], [231]. There is hydroxide generation which is followed by an electrophoretic concentration of colloids (usually negatively charged), which traverse towards the anode by the electric field [151], [232]. The particles later interact with the hydroxides generated and removed by electrostatic attraction. Higher rate of dissolution of electrode materials results in higher production of sludge which in turn increases the removal efficiency due to sweep coagulation at higher j value [155], [158]. The probability of coagulation in the region close to anode is more due to the high concentration of hydroxides formed close to anode [233].For both the electrodes, there is a continuous increase in removal of the contaminants with an increase in the j value. The removal efficiency of SS was more than that of Al at same j value. This was probably due to differences in mechanism of the pollutant removal by SS and Al electrode. In case of Al electrode, pollutant removal mainly occurred due to charge neutralization process by Al cation while in case of SS electrode removal of pollutants took place by combined effect of charge neutralization and sweep coagulation by Fe cations and $Fe(OH)_3$, respectively [234].

Figure 5.8 (a)-(c) depicts the effect of g and time on the removal efficiency of COD, color and TOC by EC process using SS and Al electrode, respectively. Generally, with an increase in the distance (*g*) between the anode and the cathode, resistance offered by the cell also increases. In the present case for SS electrode, the pollutant removal increased with an increase in g up to a certain distance and further increase in the g decreased the removal efficiency. This could be due to the fact that there was an optimum distance up to which there was a proper flow and movement of the hydroxide flocs throughout the reactor. In case of Al electrode, the maximum removal of the pollutant was found at g value of 0.5 cm.

ANOVA analysis showed that presence of interaction among the four factors. For SS electrode, the two way interactions among j and g for the COD and TOC removal (p=0.030 and p=0.059) and interaction among pH and j (p=0.242) were observed to be statistically more significant than the interaction between other factors. In case of Al electrode, interaction between j and g for the COD, color and TOC removal (p=0.042, p=0.034 and p=0.025) was found to be statistically more significant than the interaction between other factors [150].

5.4.3 Multi-response Optimization for Single Stage EC

Multi-objective optimization of operating parameters was done using desirability function approach so as to maximize all the three COD, color and TOC removal efficiencies. Details of desirability function approach are given in our previous studies [146], [147], [226].After examining the response curves, the optimum values for different operating parameters were found to be pH=7.8; j=154.32 A m^{-2}; g=2.2 cm and t=135 min for SS electrode and pH=6.6; j=154.32 A m^{-2}; g=0.5 cm and t=120 min for Al electrode, respectively. Maximum COD, color and TOC removal predicted at these optimal conditions were 69.6%, 92.7% and 72.3%, respectively, by SS electrode. In comparison, Al electrode showed maximum percent removal of COD, color and TOC as 58.8%, 80.1% and 55%, respectively, at optimized conditions. Three ratification experiments were carried out at these optimum conditions to support the results. The removal efficiencies obtained by ratification experiments were within 95% confidence interval of the predicted value [157].

These results conclude that SS electrode performs better than Al electrode in terms of COD, color and TOC removal. Analysis of Table 3.4 shows that various investigators reported lower COD removal efficiency as compared to the present study using SS and Al electrodes [155]–[157]. Many of the investigators had reported higher COD removal efficiency also [150], [152]–[154].Removal efficiencies by EC process depend on many factors such as initial concentration, chemical characteristics of wastewater being treated, operating parameters and experiment conditions optimization. The difference in removal efficiencies may be because of these factors.

5.4.4 Two-stage EC Treatment

In this part of the present study, two-stage treatment of bio-digested distillery spentwash by SS and Al electrodes was studied with and without pH adjustment between the two-stages. Distillery spentwash was treated by SS electrode in the 1st stage followed by Al electrodes in 2nd stage; and in reverse order of the electrodes too. Conditions in both the stages were kept at the optimized conditions as obtained from the RSM study. Results of the two-stage EC treatment are shown in Table 5.13. It may be seen that when pH adjustments were done in both the stages, treatment by SS followed by Al electrode showed 80.9, 94.3 and 77.8% of COD, color and TOC removal efficiencies, respectively, while treatment by Al followed by SS electrode showed 78.3, 88.8 and 75.6% of COD, color and TOC removal, respectively at optimized conditions. In both the combinations, the removal efficiency was higher in the

1^{st}stage than the 2^{nd} stage [235], [236]. Results show that efficiency of both the combinations was nearly same but the SS-Al combination was comparatively more efficient than Al-SS combination. Experiments were also conducted at optimized j, g and t values but without pH adjustment before both stages of treatment, and the results are shown in Table 5.13. Overall removal efficiencies decreased by maximum ≈11% with respects to experiments with pH adjustment for both combinations of electrodes. However, it may be noted that the final pH of the effluent in experiments without pH adjustment is 12.6 for SS-Al combination whereas it is 11.4 for Al-SS combination. These final pH values are much higher than the experiments with pH adjustment in which final pH values were 8.1 and 9.2 for SS-Al and Al-SS combinations, respectively. Therefore, it seems that pH adjustment before the experiments is more beneficial as not only higher treatment efficiencies can be achieved but also final pH in these experiments is within the manageable range.

Table 5.13.Effect of the two-stage electrocoagulation on distillery spent wash treatment.

Parameters	**SS followed by Al electrode**			**Al followed by SS electrode**		
	% removal at 1st stage	**% removal at 2nd stage**	**Total removal**	**% removal at 1st stage**	**% removal at 2nd stage**	**Total removal**
	With pH adjustment			With pH adjustment		
COD	69.9	39.7	80.9±1.2	59.19	57.14	78.34±1.4
Color	91.6	48.31	94.2±1.6	78.93	48.89	88.80±2.2
TOC	71.8	36.97	77.85±1.8	57.62	54.68	75.56±2.0
Initial pH	7.8	6.6	-	6.6	7.8	-
Final pH	9.3	8.1	-	8.5	9.2	-
	Without pH adjustment			Without pH adjustment		
COD	60.0	30.76	77.5±1.6	30.32	54.12	68.04±1.6
Color	81.9	17.18	83.5±2.1	69.44	43.69	79.58±2.0
TOC	64.9	9.2	71.5±2.8	48.6	35.68	66.80±2.3
Initial pH	8.8	9.8	-	8.8	11.3	-
Final pH	9.8	12.6	-	11.3	11.4	-

5.5 Comparison of MF, UF and EC processes

From the above analyses, EC process emerged as better pretreatment process than others (MF and UF). Figure 5.9 shows the comparative graph between MF, UF and EC with respect to the percentage removal of different contaminants (COD, Color, TDS and TOC). Results from the graph confirmed that the EC was found to be more effective in removing organic matter (COD and TOC) as compared to the UF and MF. Removal of color and TDS was, however, found to be more in case of UF. In view of the above results, it is inferred that the effectiveness of studied pretreatment options follow the trend as EC>UF>MF.

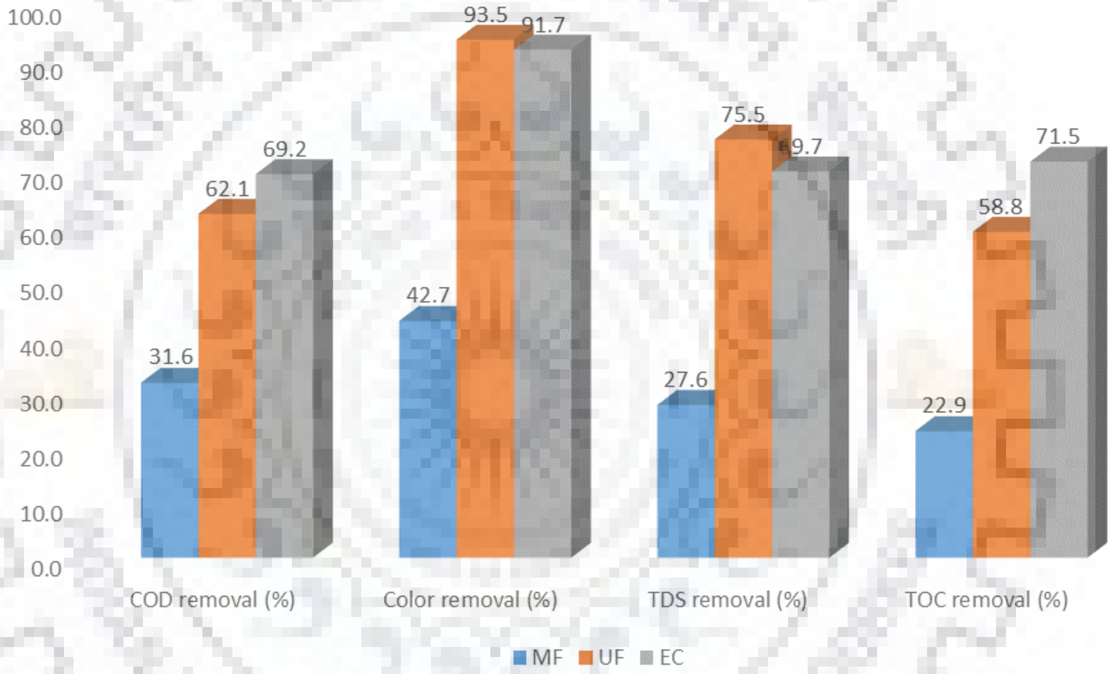


Figure 5.9.Comparative graph between MF, UF and EC in response to percentage removal of COD, color, TDS and TOC.

5.6 Optimization of Process Parameters for RO Membrane

5.6.1 Statistical Analysis and Modelling

After optimization of operating parameters of different pretreatment options (MF, UF and EC) with RSM, the treated water from best one was selected as feed for the optimization of RO process parameters. RO system was optimized with three operating parameter pHo (2-10), Temp (15-43°C) and TMP (10-50 bars) by conducting 20 set of experiments designed by CCD design. Effect of different operating parameters on permeate flux and removal percentage of COD, color and TDS were studied by conducting different combination of experiments. Actual and predicted permeate flux and percent removal of COD, color and TDS for all the 20 set of experiments by RO were obtained and shown in Table 5.14. To obtain the regression equations from the linear, interactive, quadratic and cubic model, quadratic model was found to be best fitted to the experimental data.

The final equations in terms of coded factors for permeate flux and percent removal of COD, color and TDS with RO are given as:

$$COD\ removal = +98.05 - 0.19 \times \mathrm{A} + 0.079 \times \mathrm{B} + 0.43 \times \mathrm{C} - 0.37 \times \mathrm{A2} + 0.14 \times \mathrm{B2} + 0.11 \times \mathrm{C2} + 6.207\mathrm{E} - 003 \times \mathrm{A} \times \mathrm{B} + 0.19 \times \mathrm{A} \times \mathrm{C} + 0.11 \times \mathrm{B} \times \mathrm{C} \tag{5.15}$$

$$Color\ removal = +99.55 - 0.18 \times \mathrm{A} - 0.11 \times \mathrm{B} - 0.097 \times \mathrm{C} - 0.067 \times \mathrm{A2} - 0.058 \times \mathrm{B2} - 0.081 \times \mathrm{C2} - 0.086 \times \mathrm{A} \times \mathrm{B} - 0.13 \times \mathrm{A} \times \mathrm{C} - 0.15 \times \mathrm{B} \times \mathrm{C} \tag{5.16}$$

$$\mathrm{TDS}\ removal = +97.69 - 0.35 \times \mathrm{A} + 0.28 \times \mathrm{B} + 1.23 \times \mathrm{C} - 0.78 \times \mathrm{A2} - 0.37 \times \mathrm{B2} - 0.79 \times \mathrm{C2} + 0.27 \times \mathrm{A} \times \mathrm{B} + 1.12 \times \mathrm{A} \times \mathrm{C} - 0.38 \times \mathrm{B} \times \mathrm{C} \tag{5.17}$$

$$\text{Permeate flux} = +19.65 + 4.51 \times \mathrm{A} + 3.55 \times \mathrm{B} + 6.81 \times \mathrm{C} - 0.78 \times \mathrm{A2} + 0.44 \times \mathrm{B2} - 0.11 \times \mathrm{C2} - 0.24 \times \mathrm{A} \times \mathrm{B} + 5.96 \times \mathrm{A} \times \mathrm{C} - 2.67 \times \mathrm{B} \times \mathrm{C} \tag{5.18}$$

For RO optimization the value of the regression coefficient and ‘p’ values for different responses are given in Table 5.15. The F-values from the analysis of variance results for COD, color, TDS removal and permeate flux are 25.7, 15.2, 42.34 and 45.27, respectively. The ‘p’ values of lack of fit for COD, color, TDS removal and for flux are significantly low (0.0596, 0.2904, 0.0005 and 0.003, respectively), less than (<0.0001) 0.05, which indicates that the model fits close to the experimental results [150].

The R^2 values for COD, color, TDS removal and permeate flux are 0.9586, 0.9320, 0.9744 and 0.9853, respectively (Table 5.15). The ‘p’ values shown in Table 5.16 can be used to find the pair of parameters among various parameters which have most-significant interaction [150]. For COD removal the value of p for the parameter TMP is <0.0001 followed by pH (0.0015) and temperature (0.1023) shown in Table 5.16. Thus, TMP and pH are the most significant parameters affecting the COD removal efficiency and also the interaction among TMP and pH shows more impact compared to others. For the permeate flux all the operating parameters i.e. TMP, pH and temperature have the value of p <0.0001, which explicate that all the operating parameters significantly affect the permeate flux value. Interaction between pH and TMP was most significant among all for rest of the responses too.

Table 5.14. Experimental inputs and responses for RO experiments.

Run	pH	Temp. (°C)	Pressure (bar)	%COD removal		%Color removal		%TDS removal		Permeate flux	
				actual	predicted	actual	predicted	actual	predicted	actual	predicted
1	4	22	40	98.34	97.92	99.86	99.37	96.93	95.60	5.82	3.47
2	8	22	40	98.14	97.15	99.26	99.44	97.27	92.11	14.25	1.96
3	4	22	20	97.74	97.84	99.38	99.61	95.90	96.39	2.98	7.83
4	6	29	30	98.14	97.10	99.54	99.34	97.81	93.98	8.05	6.39
5	8	22	20	97.11	98.18	99.54	99.74	92.12	96.57	3.01	5.73
6	6	17	30	98.34	98.16	99.48	99.28	95.97	97.57	5.98	13.91
7	4	36	40	98.56	98.56	99.34	99.38	95.88	95.84	6.00	6.69
8	6	29	30	98.04	98.56	99.44	98.58	97.69	97.91	7.90	14.95
9	6	29	30	97.96	97.33	99.62	99.67	97.62	96.08	7.74	3.38
10	6	41	30	98.61	96.69	99.20	99.05	97.25	94.89	10.84	9.05
11	6	29	30	98.19	98.31	99.46	99.58	97.76	96.17	7.90	6.39
12	6	29	13	97.89	98.58	99.43	99.19	93.21	97.12	3.12	10.93
13	2	29	30	97.34	97.64	99.59	99.48	95.48	93.39	4.18	3.46
14	4	36	20	97.81	99.09	99.70	99.16	96.74	97.51	7.86	12.56
15	6	29	47	98.91	98.05	99.12	99.55	97.62	97.69	12.39	7.86
16	6	29	30	97.95	98.05	99.60	99.55	97.59	97.69	7.74	7.86
17	8	36	20	96.89	98.05	99.28	99.55	93.66	97.69	6.66	7.86
18	6	29	30	98.00	98.05	99.64	99.55	97.71	97.69	7.90	7.86
19	8	36	40	98.70	98.05	98.63	99.55	97.66	97.69	15.79	7.86
20	10	29	30	96.74	98.05	99.04	99.55	95.42	97.69	7.74	7.86

Table 5.15. Analysis of variance for %COD, color, TDS removal and permeate flux by RO.

	COD					**Color**					**TDS**					**Permeate flux**				
Source	SS	DF	MS	F	P	SS	DF	MS	F	P	SS	DF	MS	F	P	SS	DF	MS	F	P
Model	6.16	9	0.68	25.75	0	1.32	9	0.15	15.2	0	52.19	9	5.80	42.3	0	1438.5	9	159.8	74.6	0
Residual	0.27	10	0.027			0.09	10	0.009			1.37	10	0.14			21.41	10	2.14		
Lack of fit	0.22	5	0.044	4.60	0.05	0.06	5	0.012	1.69	0.29	1.34	5	0.27	38.8	0	20.98	5	4.20	49.4	0
Pure error	0.047	5	0.009			0.03	5	0.007			0.034	5	0.006			0.42	5	0.08		
Total	6.43	19				1.41	19				53.56	19				1459.9	19			
R^2	0.9586					0.9320					0.9744					0.9853				

Notes: SS: Sum of squares; DF: Degree of freedom; F: F value; P: P value; R^2: R-square.

Table 5.16. Coefficients, standard deviation and P for COD, color, TOC removal and permeate flux by RO.

Factor	COD			Color			TDS			Permeate flux		
	Coefficient Estimate	Standard Error	P value	Coefficient Estimate	Standard Error	P value	Coefficient Estimate	Standard Error	P value	Coefficient Estimate	Standard Error	P value
Intercept	98.05	0.067		99.55	0.04		97.69	0.15		19.65	0.60	
A-pH	-0.19	0.044	0.001	-0.18	0.027	0	-0.35	0.1	0.005	4.51	0.40	0
B-Temp	0.079	0.044	0.102	-0.11	0.027	0.001	0.28	0.1	0.017	3.55	0.40	0
C-TMP	0.43	0.044	0	-0.097	0.027	0.004	1.23	0.1	0	6.81	0.40	0
A2	-0.37	0.043	0	-0.067	0.026	0.027	-0.78	0.097	0	-0.78	0.39	0.07
B2	0.14	0.043	0.008	-0.058	0.026	0.049	-0.37	0.097	0.003	0.44	0.39	0.27
C2	0.11	0.043	0.02	-0.081	0.026	0.010	-0.79	0.097	0	-0.11	0.39	0.78
AB	0.006	0.058	0.91	-0.086	0.035	0.032	0.27	0.13	0.06	-0.24	0.52	0.65
AC	0.19	0.058	0.008	-0.13	0.035	0.003	1.12	0.13	0	5.96	0.52	0
BC	0.11	0.058	0.07	-0.15	0.035	0.001	-0.38	0.13	0.015	-2.67	0.52	0

ANOVA results for RO system show that the model chosen explains the factor response interaction correctly [200]. The permeate flux and removal efficiency for COD, color and TDS were found to be close to the optimum conditions. The actual and predicted values of responses are shown in Table 5.14. It shows that the residuals for the prediction of each response are minimum which indicates that the results of ANOVA analysis are correct [155], [157]. A high R-square coefficient (close to unity) for all contaminant removal supports a satisfactory adjustment of the quadratic model to the experimental data (Table 5.15).

5.6.2 Effects of Various Operating Parameters

Figure 5.10 -5.13 shows the three-dimensional response surface graphs for COD, color, TDS and permeate flux respectively, with different input variables (pH, Temp and TMP) for RO treatment of EC pre-treated distillery spent wash. Performance of the RO membrane is affected by change in pH. Figure 5.10 (a-c) shows effect of pH, temperature and TMP on COD removal. At each value of temperature as the pH increases, the removal efficiency increases up to pH 7-8. Further increase in the pH results in decreased COD removal efficiency. Separation performance of the membrane affected by change in pH could be the reason for this observation. As the change in pH affects the hydration and absorption capacity of solution on membrane [110], the COD removal is low at highly acidic and basic pH, whereas the color and TDS removal was high at acidic pH. Interaction between temperature and TMP (Figure 5.11 and 5.12) shows that at each value of temperature as the TMP increases, the COD removal increases. At low pH, removal efficiency increases as the temperature and TMP increases. Further increase in pH decreases the removal efficiency of color. With increase in temperature, color removal decreases with increase of TMP.

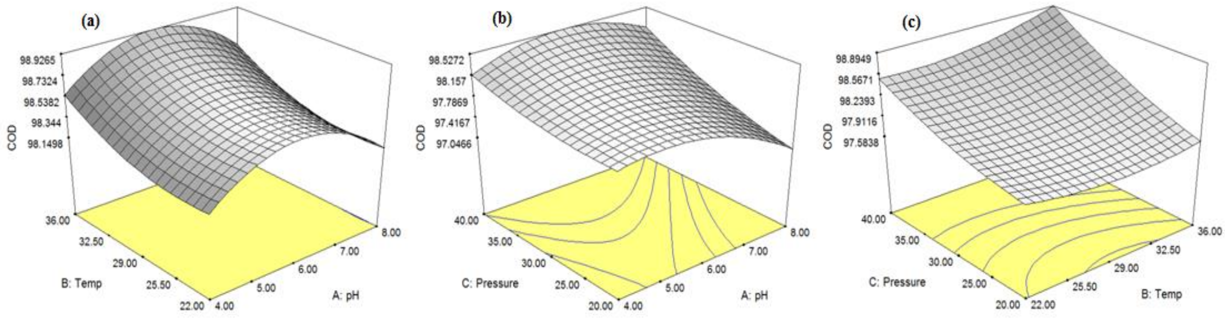


Figure 5.10. %COD removal (a) temp vs pH, (b) TMP vs pH and (c) TMP vs Temp.

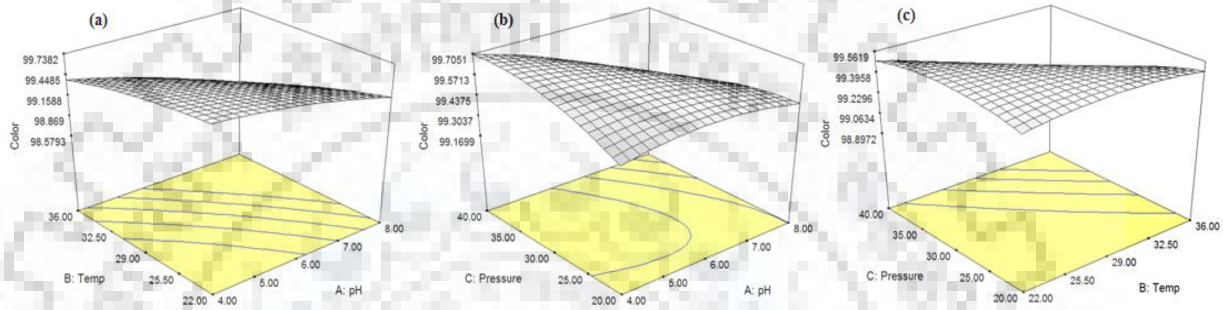


Figure 5.11. %Color removal (a) Temp vs pH, (b) TMP vs pH and (c) TMP vs Temp.

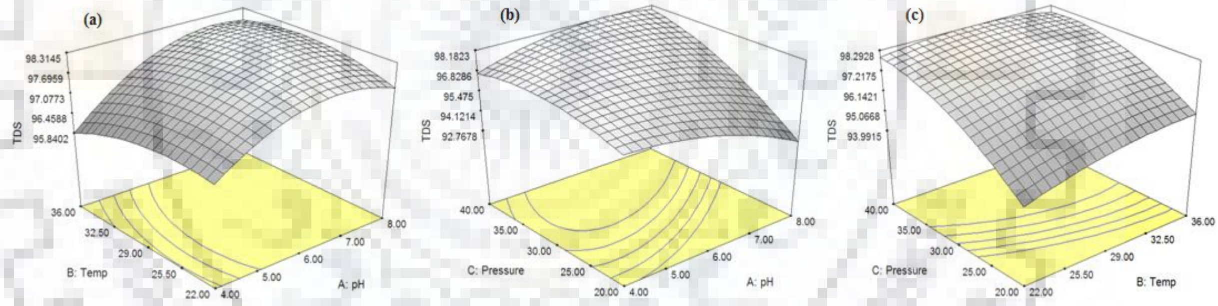


Figure 5.12. %TDS removal (a) Temp vs pH, (b) TMP vs pH and (c) TMP vs Temp.

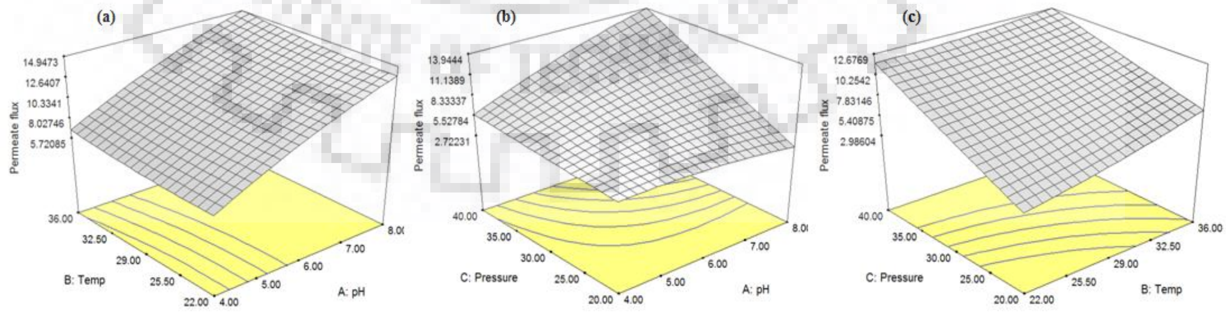


Figure 5.13. Permeate flux (a) Temp vs pH, (b) TMP vs pH and (c) TMP vs Temp.

Figure 5.12 (a-c) shows that the effect of temperature on TDS removal is not much but as the value of temperature increases, decrease in TDS removal is observed because, increase in the temperature results in decrease in viscosity and high rate of water passage through the membrane. Solubility of the solute also increases as the temperature increases which could result in higher diffusion rate of solute through the membrane [219]**.** At low and high value of temperature, increase in TDS (salt) removal was observed with increase in TMP, which could be due to formation of concentration polarization at the membrane interface [221].

At each value of temperature, as the pH increases the permeate flux also increases (Figure 5.13 (a-c). Effect of temperature on permeate flux was not significant, due to the low susceptibility of polyamide membrane to structural variations in response to change in temperature [197]. At each value of temperature and pH, as the TMP increases, permeate flux also increases. This could be due to the fact that pressure increases the driving force for the solvent and subsequently decrease osmotic pressure, which results in passage of more amount of water through the membrane and high rate of salt rejection [218], [219].

ANOVA analysis showed the presence of interaction among the three factors. The two way interaction between the pH and TMP for COD, color, TDS removal (p=0.0087, 0.0036 and <0.0001 respectively) and permeate flux (p= <0.0001) was found to be statistically more significant than the interaction between other factors [150].

5.6.3 Multi-response Optimization for RO

Multi-objective optimization of operating parameters for RO membrane system was done using desirability function approach so as to maximize the permeate flux and removal efficiency of COD, color and TOC. The value of operating parameters after examining the response curves were found out to be pH=6.1; temperature=20°C; and TMP=45.7 bars at optimum condition. The maximum predicted COD, color, TDS removal was 98.94, 99.37 and 97.74, respectively and permeate flux was 17.5 l/m^2/h. Model predictions were validated by ratification runs at these optimal process operating conditions.

5.7 Comparison of Proposed Pretreatment Schemes

5.7.1 MF, UF and EC Process Combined with RO at Optimized Conditions

After optimization of input parameters for MF, UF and EC system, combined experiments of RO with different pretreatment schemes (MF, UF and EC) were conducted at their optimized conditions as derived from CCD of RSM. Results showed that the removal efficiency of different pollutants with MF membrane alone is <50%, whereas, with UF membrane it's significantly better (>50 %). Removal efficiency of EC treatment for all pollutants is significantly high (>60%) as compared to MF and UF process depicted in graphs (Figure 5.14 to Figure 5.16).

5.7.2 Comparison of RO Process with and without Pretreatment (MF-RO, UF-RO and EC-RO)

Experimental results showed that the removal efficiency with MF and UF alone and in combination with RO (MF-RO, UF-RO) follows the trend MF<RO<MF-RO and UF<RO<UF-RO with MF and UF, respectively. Removal efficiency of combined MF-RO and UF-RO was observed to be marginally better than RO system alone. However, the permeate flux (water recovery) significantly increased from 17.5 (direct RO) to 32.0 l/m^2/h and 38.0 l/m^2/h, respectively while employing MF and UF prior to the RO treatment. In case of combined EC-RO system, removal efficiency for all pollutants was observed to be similar to marginally better than RO system alone and the permeate flux (water recovery) significantly increased from 17.5 (direct RO) to 40.5 l/m^2/h when EC is used prior to RO treatment. Visual experimental results for the color removal withRO process and in combination of different pretreatments (MF-RO, UF-RO and EC-RO) are presented in Figure 5.17.

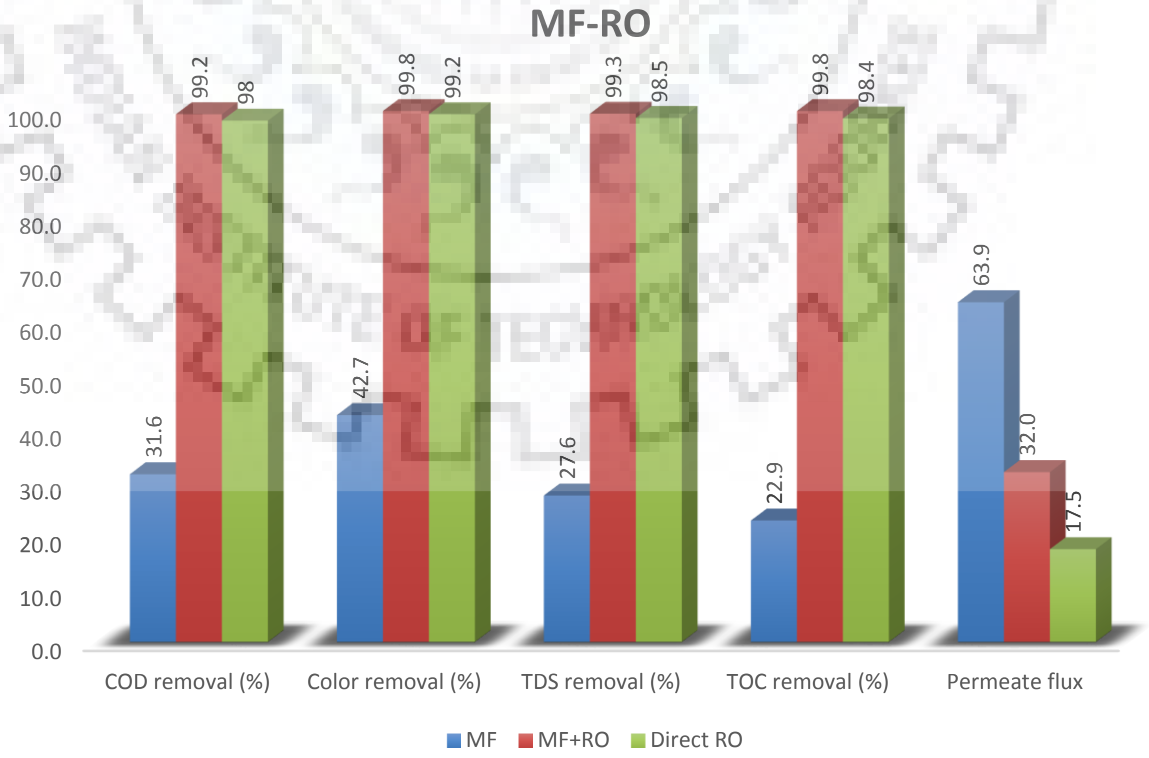


Figure 5.14.Combined experiments of RO with MF.

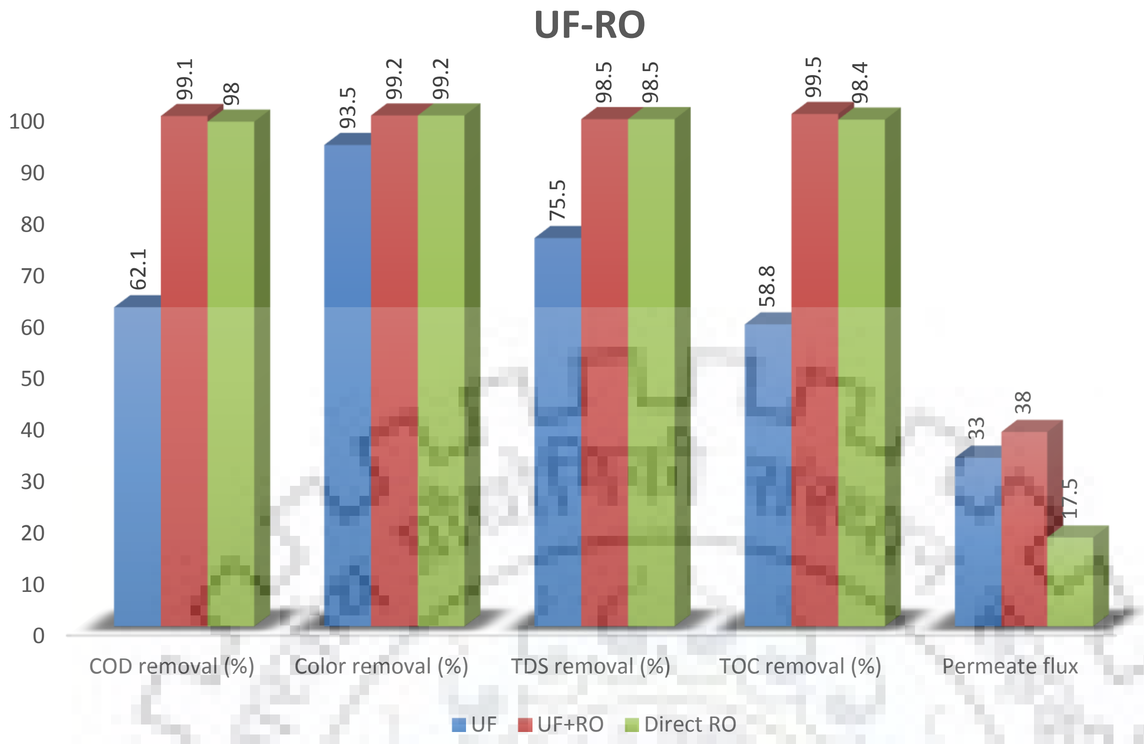


Figure 5.15. Combined experiments of RO with UF.

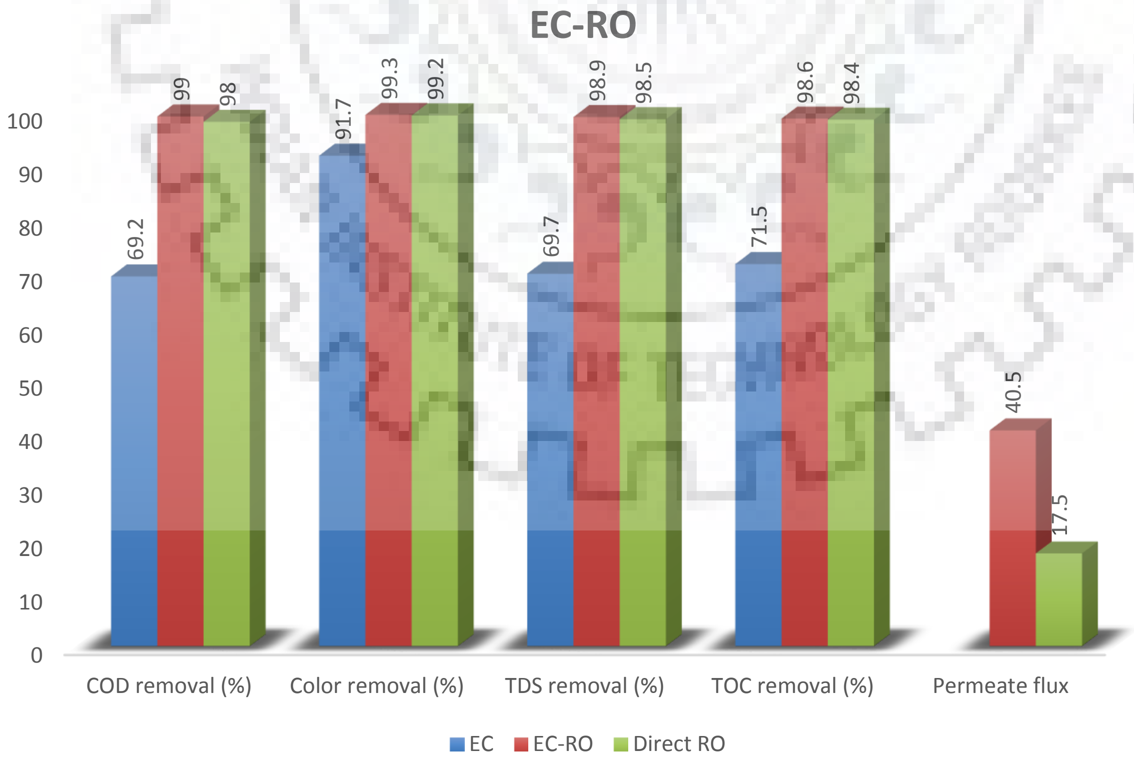


Figure 5.16. Combined experiments of RO with EC.

(a)

(b)

(c)

(d)

Figure 5.17. Color removal with (a) MF and MF-RO (b) UF and UF-RO (c) EC and EC-RO and (d) Direct RO.

5.7.3 Flux Decline Profile of RO with and without Pretreatment

Membrane technology has been employed for treating various types of waste water. Membrane loses its performance with time depending upon the type of membrane used, type of waste water and operating conditions [202]. Membrane flux modelling is generally done to access the fouling study (i.e. flux decline with time). Membrane permeate flux reduction is attributed to either concentration polarization at upstream process or membrane fouling [81]. In the present study, flux decline profile of RO membrane was studied by membrane flux modelling (comparing the model prediction with experimental data). In general, permeate flux increase with increase in pressure, but there are various forms of resistance i.e. internal fouling resistance, external fouling resistance and membrane resistance which influence the membrane permeate flux [237].Various categories of constant pressure filtration models used to study the effect of fouling on membrane flux are briefly presented below, which depend upon the type and process of the membrane [191]:

- Complete blocking filtration (assumes that particles arrive at the membrane and seal the membrane pores such that the particles are not superimposed upon one another).
- Intermediate blocking filtration (assumes that not every particle necessarily blocks the pores. Particles may settle on other particles)
- Standard blocking filtration (the particle diameter is much less than the pore diameter, thus, the particles can enter most pores, deposit on the pore walls, and thus reduce the pore volume.
- Cake filtration (for large particles, which cannot enter most pores and hence, deposit forms a cake on the membrane surface).

The intermediate blocking model is considered best for RO membranes [191]. Intermediate blocking filtration model equation is as:

$$\frac{1}{Q} = K_t t + \frac{1}{Q_o} \qquad (5.19)$$

Where, Q is permeate flow rate, Q_o is initial permeate volume, t is time and K_t is the filtration constant. $K_t$is directly related to the blocked surface area per unit permeate volume.

To obtain the value of slope (K_t) and intercept ($1/Q_o$), we modified the above equation in the form of flux. The modified and rearranged equation is presented as below:

$$\frac{1}{Q} = K_t t + 1/Q_o$$

$$\frac{A}{Q} = A.K_t t + A/Q_o$$

$$J = Q/A$$

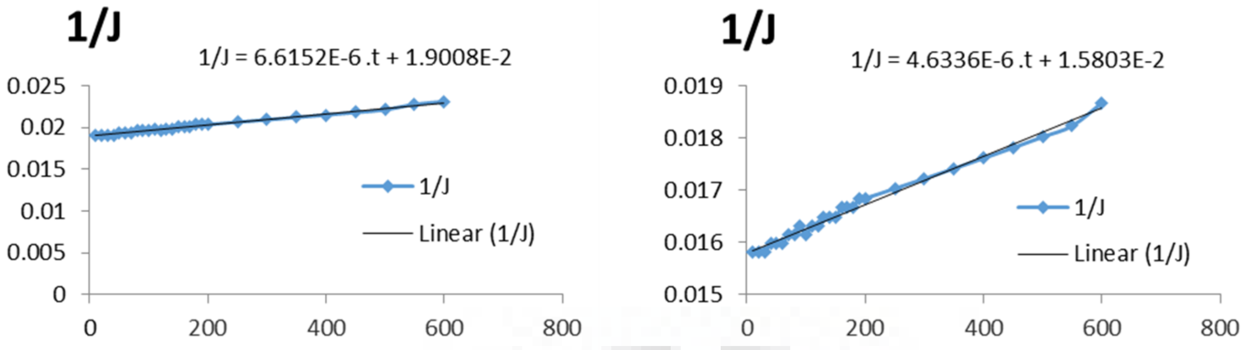
$$J = 1/(A.K_t t + \frac{A}{Q_o})$$

$$1/J = A.K_t t + \frac{A}{Q_o}$$

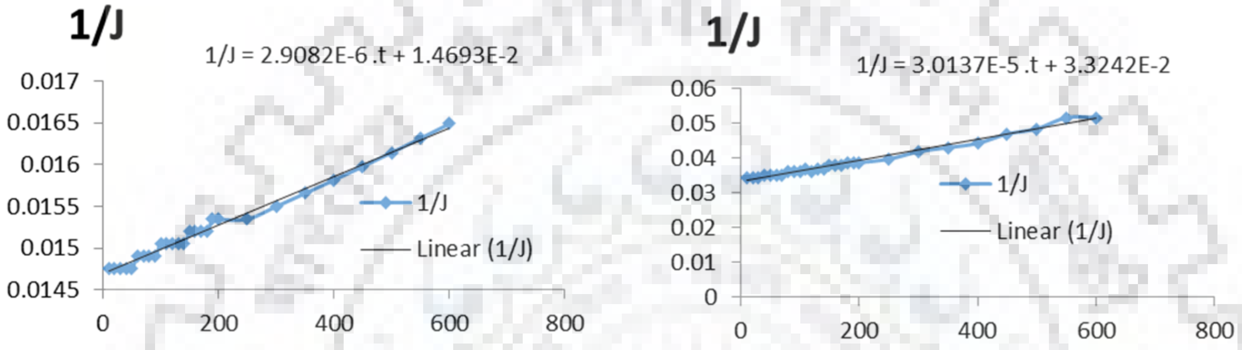
Then, values of 1/J were plotted with time in the above linear equation (Fig. 5.18). The values of the slope (K_t) and intercept ($1/Q_o$) obtained for different processes were used in intermediate filtration model equation for model fitting and extrapolation are shown in Table 5.17.

Table 5.17. The value of slope and intercept for MF, UF, EC and RO derived from the graphs.

Treatment process	Slope		Intercept	
	$A.K_t$	K_t	A/Q_o	$1/Q_o$
MF	6.62E^{-06}	4.27E^{-04}	0.01900	1.2263
UF	4.63E^{-06}	2.99E^{-04}	0.01580	1.0195
EC	2.91E^{-06}	1.88E^{-04}	0.01469	0.9479
RO	3.01E^{-05}	0.00265	0.03324	2.2045



(a) MF membrane (b) UF membrane



(c) EC (d) RO membrane

Figure 5.18. Intermediate blocking model for (a) MF membrane, (b) UF membrane, (c) EC and (d) RO membrane.

Permeate flux data was fitted into Intermediate blocking filtration model equation and extrapolation of graph was done to find out the filtration pattern of RO alone and with pretreatment (MF, UF and EC). Model prediction and experimental data for permeate flux decline profile of RO, with and without pretreatment is shown in graph (Fig 5.19). Results revealed that the pretreatment (MF, UF and EC) improves the RO flux compared to RO system alone. The permeate flux was found to be more in case of EC-RO combination than UF-RO, MF-RO and RO alone.

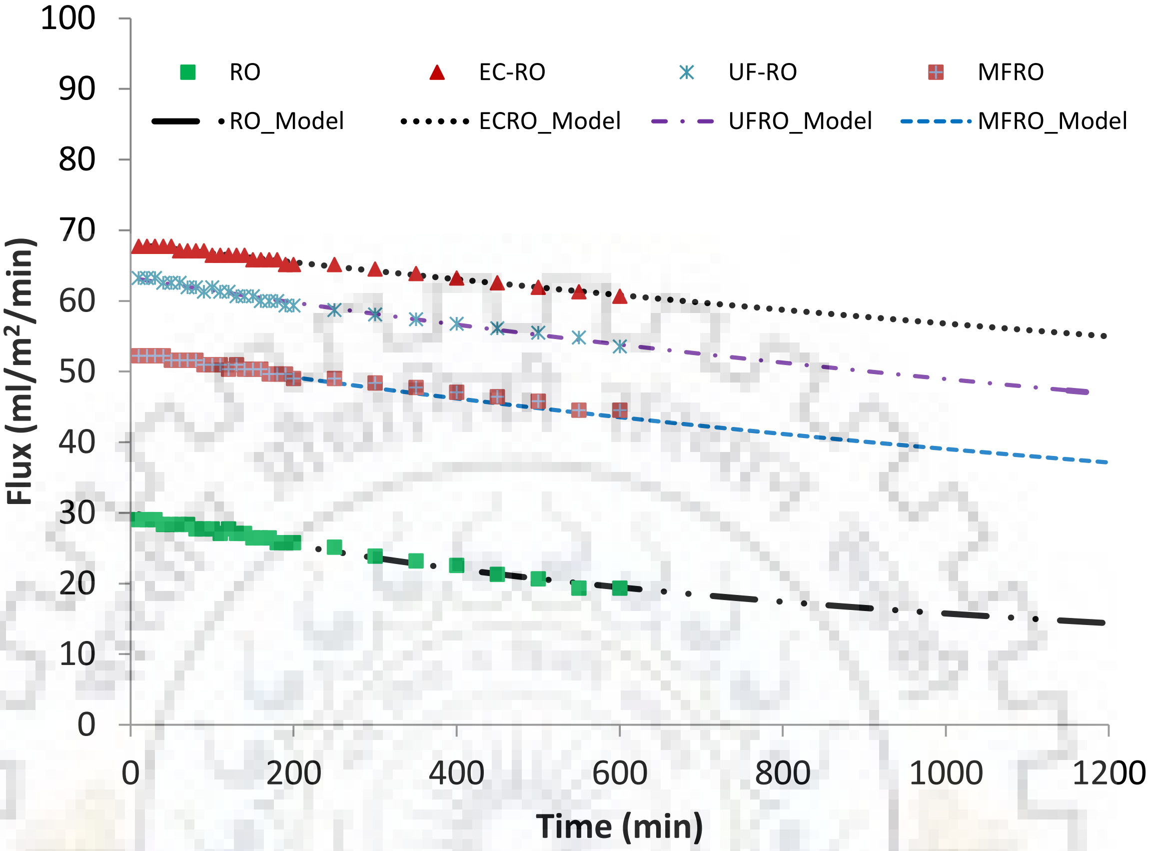


Figure 5.19. Permeate flux decline profile of RO alone and with pretreatment.

5.8 Findings

The comparison among MF, UF and EC treatment processes as pretreatment of RO was done on the basis of removal efficiency of the contaminants (COD, color, TDS and TOC) and permeate flux (water recovery) generated. Results were presented in Table 5.18.

Table 5.18. Comparison of RO process with and without pretreatment (MF-RO, UF-RO and EC-RO).

Parameters	Treatment processes						
	EC	UF	MF	RO	EC-RO	UF-RO	MF-RO
COD (%removal)	69.2	62.1	31.6	98	99	99.1	99.2
Color (%removal)	91.7	93.5	42.7	99.2	99.3	99.2	99.8
TDS (%removal)	69.7	75.5	27.6	98.5	98.9	98.5	99.3
TOC (%removal)	71.5	58.8	22.9	98.4	98.6	99.5	99.8
Permeate flux ($l/m^2/h$)	-	33	63.9	17.5	40.5	38	32

From the results it is revealed that EC was found to be more effective in removing organic matter as compared to the UF and MF. Whereas, color and TDS removal was observed more in case of UF. The difference in organic matter removal between UF and EC treatment was around 10-12 % (EC>UF). However, the difference in removal of color and TDS was around 5-6% (UF>EC). MF showed least effectiveness towards contaminants removal in comparison to UF and EC. Permeate flux data modelling inferred that the permeate flux was significantly improved with pretreatment as compared to RO system alone. Permeate flux (recovery) with RO has showed a remarkable increase from 17.5 $l/m^2/h$ (direct RO) to 40.5 $l/m^2/h$, 38.0 $l/m^2/h$ and 32 $l/m^2/h$ when used in combination with EC, UF and MF, respectively. Economic assessment of proposed treatment schemes is presented in the next chapter.

CHAPTER 6: ECONOMIC ASSESSMENT OF PROPOSED TREATMENT SCHEMES

In this chapter, findings of the economic assessment of the proposed treatment schemes and their comparison done on the basis of per unit water production cost are presented. Water production cost for RO plant with or without pretreatment (employing MF, UF and EC) was estimated on the basis of technical assumptions, specifications and design parameters presented in Table 6.1. For estimation of per cubic meter water production, the cost components included considering the laboratory scale experiments were capital cost, operation and maintenance cost and other costs for the process, as presented below:

6.1 Capital Cost

Total capital cost for the RO membrane system alone and in combination with different pretreatment systems (MF, UF and EC) is given in Table 6.2. The total annual water production cost is depicted in Table 6.3. The annual amortized cost was calculated by using the following equation:

$$A = P * r(1+r)^n/(1+r)^{n-1} \qquad (6.1)$$

Where, A is the periodic amortization payment, P is the principal amount borrowed, r is the periodic interest rate divided by 100 and n is the total number of payments.

Table 6.1 shows that the main components contributing to the total capital cost of the MF and UF systems were the membrane modules and the power supply unit for EC system respectively. The total capital cost of the combined RO system with pretreatment is higher than RO system alone.

6.2 Operation and Maintenance Cost

6.2.1 Membrane System

In membrane systems (MF and UF), the major component that needs regular replacement is membranes. In water treatment system, membranes are generally replaced once in two years [238], [239]. In case of industrial effluent treatment, this period has been assumed as 6 months as per the industrial survey data of current study.

6.2.2 EC System

During the Electrocoagulation treatment, as the electrode material is consumed throughout the process, the major component that will need regular replacement is electrode material.

6.3 Water Production Cost

The water production cost includes the annual amortized cost, operation and maintenance cost for the process and annual operating cost. Annual operating cost was estimated using the relation given by Bilton et al. (2011) [240] presented below:

$$C = (A1 + A2) \tag{6.2}$$

Where A1 is the annual amortized capital cost and A2 is the annual O&M costs.

The unit production cost was calculated by dividing the sum of the amortized capital costs and annual O&M costs by the annual water production and plant availability as given by Abraham and Luthra (2011) [241] and presented below:

$$C/(f * v) \tag{6.3}$$

Where, C is the annual operating cost, f is the plant availability, v is the annual product volume.

The total per cubic meter water production cost for RO system is 470 Rs./m^3/m^2. Whereas, cost with different pretreatment found to be as: MF-RO (256 Rs./m^3/m^2), UF-RO (220 Rs./m^3/m^2) and EC-RO (185 Rs./m^3/m^2).

Table 6.1. Technological specifications and design parameters for proposed treatment schemes.

Design Parameters	**MF**	**UF**	**EC**	**RO**	**MF-RO**	**UF-RO**	**EC-RO**
Membrane life(month)	6	6	-	6	6	6	6
Membrane Cost (Rs.)	2000	3000		5000	7000	8000	5000
Hours of operation (per day)	20	20	20	20	20	20	20
Water production/hour (LPH)	1	0.52	0.70	0.27	0.496	0.59	0.63
Annual product volume (m^3/year), v	7.3	3.8	5.1	1.2	3.62	4.3	4.58
Electrode consumed (kg/m^3)	-	-	3.2	-	-	-	3.2
Electrode consumed (kg/year)	-	-	16.3	-	-	-	16.3
Electrode price in India per kg (Rs.)	-	-	300	-	-	-	300
Capital Recovery period (Years), n [241], [242]	25	25	25	25	25	25	25
Interest rate (%), r [241], [242]	5	5	5	5	5	5	5
Operation availability % , f [241], [242]	90	90	90	90	90	90	90
Cost of consumed electrodes/year (Rs.)	-	-	4890	-	-	-	4890
Electricity price in India (Rs./ KWh)	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Electrical energy consumed (KWh.m^3/ year)	2313	2105	1010	3326	5639	5431	4336
Cost of electricity/m^3 water production/ year (Rs.)	9252	8420	4040	13304	22556	21724	17344
Total Cost/m^3 water production/year (A2)	13252	14420	8930	23304	36556	37724	32234

Table 6.2. Capital cost of proposed treatment schemes.

Systems cost (Rs.)	MF	UF	EC	RO	MF-RO	UF-RO	EC-RO
Low pressure pump (with ½ HP motor)	7000	7000	-		7000	7000	
High pressure pump (with ½ HP motor)	-	-	-	15000	15000	15000	15000
Connecting pipes	2000	2000	-	5000	7000	7000	5000
Membrane module	100000	100000	-	100000	200000	200000	100000
Membrane cost	2000	3000	-	5000	7000	8000	5000
Feed/ permeate tank	1000	1000	-	1000	2000	2000	1000
Temperature control unit	2000	2000	-	2000	2000	2000	2000
Membrane installation cost	5000	5000	2000	5000	5000	5000	7000
DC power supply	-	-	100000	-			100000
EC Reactor	-	-	5000	-			5000
Total capital cost (Rs)	119000	120000	107000	133000	245000	245000	240000

Table 6.3. Calculation of annual per cubic meter water production cost (Rs.).

	MF	UF	EC	RO	MF-RO	UF-RO	EC-RO
Total capital cost, P	119000	120000	107000	133000	245000	245000	240000
Annual amortized capital cost, A1	8443	8514	7592	9437	17383	17383	17029
O & M annual cost, A2	13252	14420	8930	23304	36556	37724	32234
Annual Operating cost C = (A1+A2)	21695	22934	16522	32741	53939	55107	49263
Unit Production cost = C/(f*v), Rs./m^3	3302	6705	3600	30315	16555	14240	11991
Unit Production cost = C/(f*v), Rs./m^3/m^2	51	104	56	470	256	220	185

6.4 Cost Comparison of Proposed Treatment Schemes

The per cubic meter water production cost for RO system is 470 Rs./m^3/m^2. Whereas, pretreatment reduces the cost up to 50% than RO system alone. Among all pretreatment studies (MF, UF and EC), EC-RO (185 Rs./m^3/m^2) found to be more economical and efficient than UF-RO (220 Rs./m^3/m^2) and MF-RO (256 Rs./m^3/m^2) in terms of water production. The capital cost of RO system with pretreatment (MF-RO, UF-RO and EC-RO) observed to be 30% higher than RO system alone. Although pretreatment facility adds an extra unit. However, maintenance, cleaning and frequency of membrane replacement gets reduced and a good quality of permeate is obtained which can be used as a resource.

In the present study the cost assessment was done considering the laboratory scale experiments in terms of total water production cost. This cost will certainly differ when applied at field scale, as the production cost may not necessarily vary with the increase in plant capacity in a linear fashion, its rational assessment may be needed after upscaling.

An important issue associated with the EC treatment is the generation of semisolid and bulky sludge, having hydroxide of metals used as sacrificial anode dissociated during wastewater treatment. Utilization of the EC-generated sludge from distillery spentwash treatment as a non-construction building material, employing cement-based solidification and also its potential effect on environment is presented in the next chapter.

CHAPTER 7: REUSE OF EC GENERATED SLUDGE

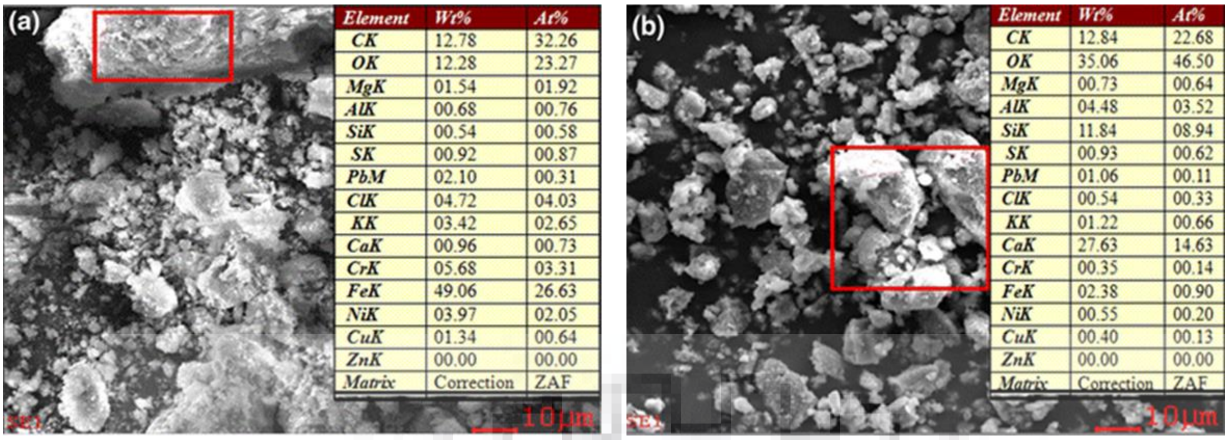
7.1 General

Sludge generated during the treatment of distillery spentwash by electrocoagulation process is highly complex in nature and requires proper disposal. However, it is advisable to explore possible ways in which it may be reused or recycled to close the loop. In this context, the present study was conducted to explore employment of this sludge as a partial replacement of cement while manufacturing the non-constructional building blocks. Various physicochemical and thermo-gravimetric characterization studies were carried out on the sludge and cement. Mortar specimens with different proportions of sludge ranging from 0 to 15% by weight of cement were tested for density, compressive strength and leachability of heavy metals by standard methods.

7.2 Cement and Sludge Characterization

7.2.1 Field Emission Scanning Electron Microscopy (FESEM) analysis

Figure 7.1 shows the FESEM images along with the elemental distribution of dried EC sludge (7.1a) and ordinary Portland cement (7.1b). It can be observed from the images that the particle size of EC sludge seems to be higher and more agglomerated than that of the cement. The average particle size of EC sludge measured was 1652 nm. EC sludge produced was dark brown and fluffy in appearance. The presence of calcium and silica defines the binding property of any material. Elemental analysis showed that cement contains relatively high content of calcium and silica compared to the sludge. In addition, as the EC sludge fraction increases, setting time gets delayed due to organic fraction present in the sludge.



Element	Wt%	At%
CK	12.78	32.26
OK	12.28	23.27
MgK	01.54	01.92
AlK	00.68	00.76
SiK	00.54	00.58
SK	00.92	00.87
PbM	02.10	00.31
ClK	04.72	04.03
KK	03.42	02.65
CaK	00.96	00.73
CrK	05.68	03.31
FeK	49.06	26.63
NiK	03.97	02.05
CuK	01.34	00.64
ZnK	00.00	00.00
Matrix	Correction	ZAF

Element	Wt%	At%
CK	12.84	22.68
OK	35.06	46.50
MgK	00.73	00.64
AlK	04.48	03.52
SiK	11.84	08.94
SK	00.93	00.62
PbM	01.06	00.11
ClK	00.54	00.33
KK	01.22	00.66
CaK	27.63	14.63
CrK	00.35	00.14
FeK	02.38	00.90
NiK	00.55	00.20
CuK	00.40	00.13
ZnK	00.00	00.00
Matrix	Correction	ZAF

Figure 7.1. FESEM images of cement and EC-generated sludge. (a) FESEM image of EC-generated sludge. (b) FESEM images of cement.

7.3 Cement-Sludge Mortars Characterization

7.3.1 Wet and dry densities

Figure 7.2 shows variation in wet and dry densities for various cement–sludge mortar samples (cured for 28 days). Water/cement ratio increased from 0.47 (without sludge) to 0.56 (with EC sludge) as the percentage of sludge increased from 5 to 15%. Results showed that both wet and dry density of the mortar samples decreased with the increase in sludge addition from 5 to 15%. The results are closely related to the fine particle size of EC sludge and water absorbed. As the sludge proportion increased, water absorption also increased, resulting in larger pore size and lower density [165]. Up to 7.5% EC sludge addition did not give much difference between the densities of cement–sludge mortar and control mortar.

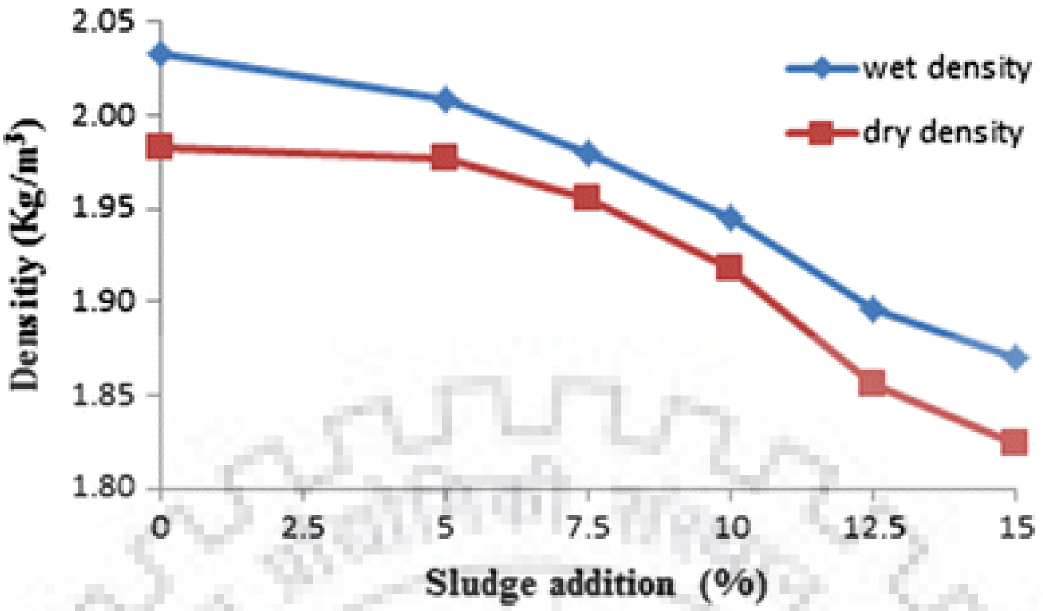


Figure 7.2.Wet and dry densities of sludge mortars versus percentage sludge addition.

7.3.2 Compressive strength

All construction materials must resist stress. To study the strength of the mortar and its ability to resist the forces at failure, compressive strength of mortar samples was determined. Figure 7.3 shows the variation of compressive strength with respect to dried sludge percentage in the mortar samples cured for different curing periods (7, 14 and 28 days). It may be seen that the strength of EC sludge-added mortar is generally lower than that of the control mortar and it greatly depends on the amount of sludge present in the mortar and the curing period. The strength decreased with an increase in the percentage of EC sludge in the mortar. The reason could possibly be the presence of heavy metals in the EC sludge, which causes retardation of cement hydration [243]. This could also be due to very fine particle size of EC sludge, large surface area and lower density, which might reduce the overall amount of cement available for binding the structure [244]. Change in the chemical reactions or bonding characteristic of the cement, water and admixture with addition of sludge could be another reason for the decreased compressive strength of mortars [188]. Maximum compressive strength was observed for samples which were cured for 28 days. For mortar samples containing up to 7.5% sludge, decrease in compressive strength was <5% against the control mortar (without sludge), thereafter the reduction was substantial. Thus, 7.5% sludge addition could be considered as optimum dosage for compressive strength and also acceptable with respect to control mortar.

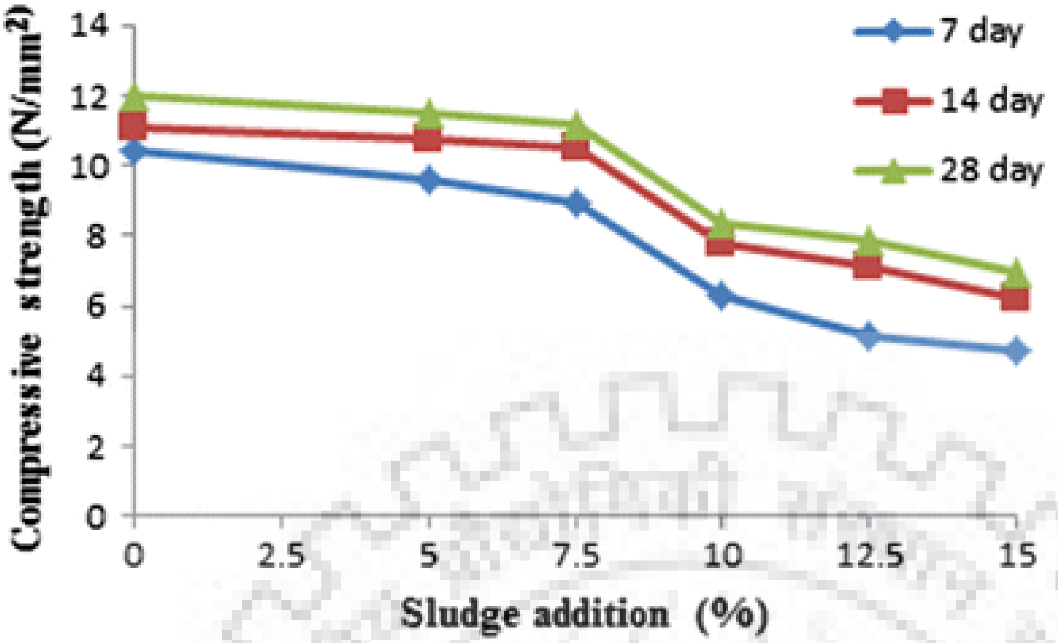


Figure 7.3. Effect of sludge accession on compressive strength of mortars as a function of curing time (7, 14 and 28 days).

7.3.3 Leaching test

At the end of the 28-day curing period, the mortar samples with different proportions of sludge (5, 7.5, 10, 12.5 and 15%) and control (without sludge) were subjected to the leaching test. Mortars were found to contain various metals such as chromium (Cr), lead (Pb), zinc (Zn), nickel (Ni), copper (Cu), manganese (Mn) and iron (Fe). These metals were initially present in the sludge, calling for their proper handling. Acetic acid extraction method has generally been used for heavy metal extraction [245] as the use of acetic acid as an extractant simulates the leachability conditions quite similar to the long detention periods (years) within the landfills. The findings were compared to the discharge limits of different heavy metals into inland surface water and land as prescribed by Environmental protection agency and Indian Standards [246], [247].

The leaching test was conducted for the whole and crushed mortar samples to predict the chemical stability of the waste in aqueous solution. The heavy metal contents in cement and sludge were also analyzed. EC sludge was found to contain Cr, Mn and Fe in higher concentration than their permissible limits. The effect of acidic conditions on the leaching from intact structure of sludge mortar was studied by WML (whole mortar leachability) test (as per procedure given in "Analytical procedures" section). The results of WML test are presented in Table 7.1. These results revealed that the mortar samples with various sludge percentages leach heavy metals within regulatory discharge limits set by EPA and Indian Standard [246], [247].

Table 7.1. WML leachability of different heavy metals and regulatory discharge and for various heavy metals by EPA and Indian standards.

Heavy metals (mg/l)	Replacement % of sludge						Regulatory discharge limits	
	0%	**5%**	**7.5%**	**10%**	**12.5%**	**15%**	**For Inland surface water** [247]	**For soil by Indian standard (mg kg^{-1})** [246]
Cu	0.007	0.014	0.009	0.006	0.006	0.008	3.0	-
Pb	0.014	0.015	0.013	0.009	0.013	0.010	0.1	250-500
Fe	0.533	0.628	0.647	0.660	0.661	0.671	3.0	-
Cr	0.019	0.039	0.078	0.089	0.077	0.078	0.2	-
Mn	0.048	0.049	0.063	0.044	0.057	0.059	2.0	-
Zn	0.077	0.103	0.137	0.153	0.170	0.214	5.0	300-600
Ni	0.014	0.060	0.076	0.078	0.107	0.107	3.0	75-150

To simulate the worst case scenario where the mortar gets mashed or broken down, CML test was conducted. The results of CML (crushed mortar leachability) test are shown in Table 7.2. Leaching test for CML showed that the concentration of heavy metals in the crushed mortar was comparatively more than that in whole mortar. Out of all the heavy metals studied, iron (Fe) showed a higher concentration than others in both WML and CML tests. Cr and Mn had shown very less concentration in the cement–sludge mortar leachate compared to the EC sludge leachate. The reason could be that during solidification, many metals are trapped within the pores of the cement matrix and converted to insoluble precipitates [248]. In view of this, no significant leaching of heavy metals from the prepared cement–sludge mortars could be established which could be harmful to the environment.

Table 7.2.CML leachability of different heavy metals.

Heavy metals (mg/l)	Replacement % of sludge							
	0%	**5%**	**7.5%**	**10%**	**12.5%**	**15%**	**Cement**	**Sludge**
Cu	0.017	0.045	0.024	0.026	0.031	0.031	0.009	0.086
Pb	0.009	0.006	0.008	0.006	0.007	0.008	0.019	0.012
Fe	1.051	1.215	1.224	1.231	1.374	1.557	3.531	4.331
Cr	0.102	0.296	0.344	0.506	0.561	0.813	0.101	5.889
Mn	0.094	0.109	0.112	0.119	0.137	0.150	0.013	1.397
Zn	0.141	0.200	0.200	0.196	0.223	0.225	0.208	0.361
Ni	0.035	0.180	0.245	0.312	0.360	0.543	0.033	8.813

7.3.4 Thermo-gravimetric analysis (TGA)

Thermal stability of any material is directly dependent on its decomposition temperature. Thermal characteristics and degradation kinetics of sludge, cement and mixtures with different proportions of sludge were studied by thermal gravimetric analysis (TGA). Sludge has both organic and inorganic compounds. At higher temperatures, organic matter decomposes into CO, CO_2 and free hydrogen [249]. Thermo-gravimetric analysis curves (TGA, DTA and dTG) for sludge, cement and mixtures with different proportions of sludge with cement are shown in Figure 7.4a to c, respectively. From the TG curve (Figure 7.4a), three different degradation zones could be envisaged. First zone exists from room temperature to 350 °C corresponding to the weight loss mainly due to moisture and light volatile compounds. Second zone ranges from 350 to 750 °C wherein the major weight loss occurred, while third zone from 750 to 1000 °C corresponded to the minor weight losses [167]. The TG graph of cement showed 5–7 % of weight loss on thermal treatment up to 1000 °C, whereas TG graph of EC sludge showed around 35–40% weight loss, which showed that the EC sludge contains up to 40% organic content. The difference in the weight loss for EC sludge-added mixture (up to 10%) was only 3–5% when compared to the control sample mixture (without sludge), whereas the weight loss difference was more than 15 % when the sludge addition increased (10–15%). DTA and dTG graphs (Figure 7.4b to c) for control (0%) and 5–10% sludge-added mixture, respectively, do not show much difference. Thermo-gravimetric analysis showed that the thermal stability of the mixture up to 5–10% EC sludge was comparable to the mixture without addition of sludge (control mortar).

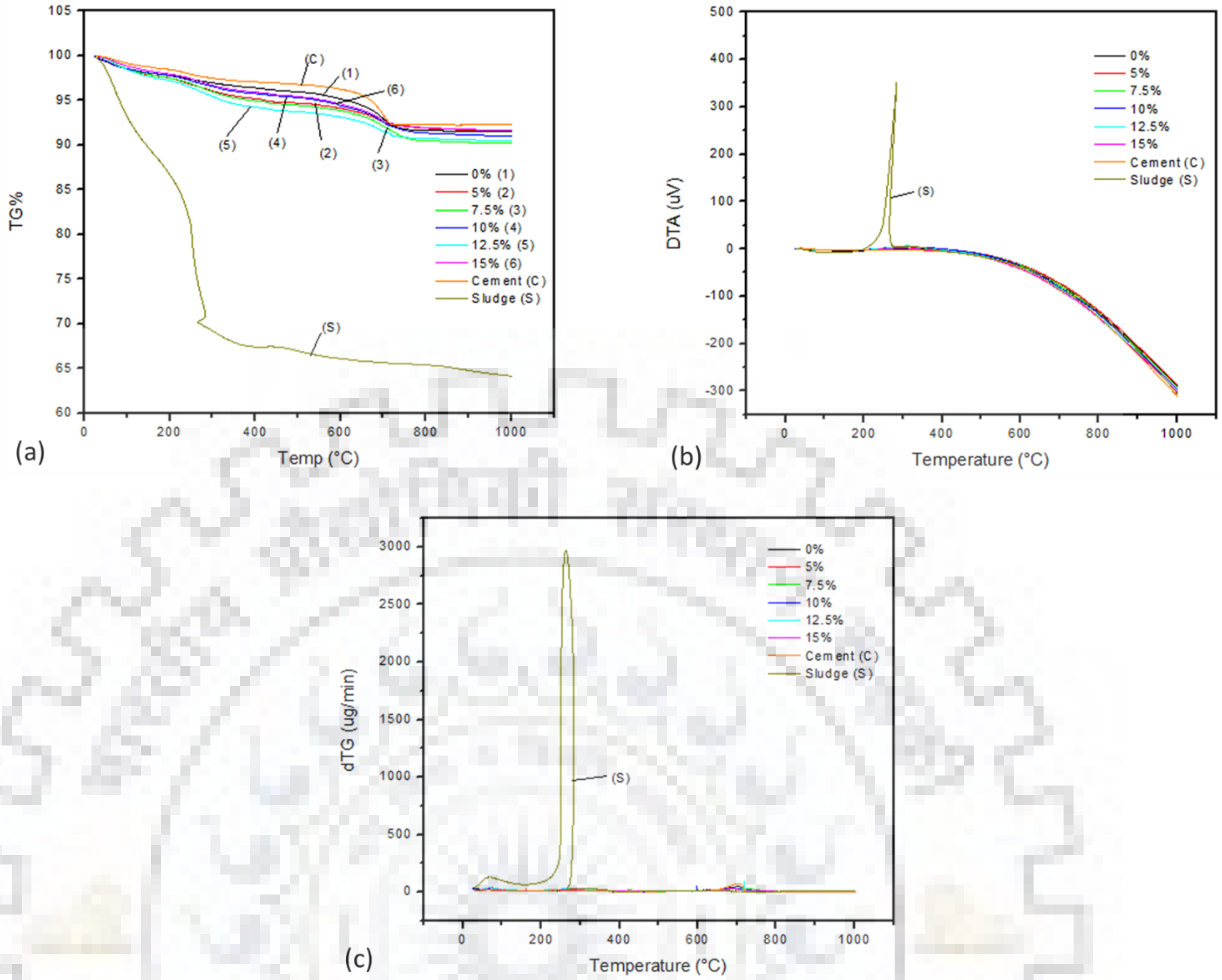


Figure 7.4. TGA, DTA and dTG plots for sludge, cement and different percentage of sludge mixtures (0–15 %). (a) TGA plot (b) DTA plot (c) dTG plot.

The difference in the weight loss for EC sludge-added mixture (up to 10%) was only 3–5% when compared to the control sample mixture (without sludge), whereas the weight loss difference was more than 15 % when the sludge addition increased (10–15%). DTA and dTG graphs (Figure 7.4b to 7.4c) for control (0 %) and 5–10% sludge-added mixture, respectively, do not show much difference. Thermo-gravimetric analysis showed that the thermal stability of the mixture up to 5–10% EC sludge was comparable to the mixture without addition of sludge (control mortar).

7.3.5 X-ray diffraction (XRD) analysis

XRD graph of sludge (Figure 7.5) does not show any prominent peaks due to its amorphous nature except very few low-intensity peaks. XRD analysis of ordinary Portland cement used in the formation of mortar showed the salient peaks of calcium aluminum silicate along with silicon dioxide peaks (Figure 7.5). Peaks in the XRD graph of cement demonstrate its crystalline nature. XRD analysis of the mixtures with different percentage of sludge (0–15%) is shown in Figure 7.6. Graph for the control sample without addition of sludge (0%) shows the prominent peaks of calcium aluminum silicate and silicon dioxide with few silicate peaks [250]. Up to 7.5% sludge addition, no remarkable change in the peaks was noticed in comparison with the control mortar except addition of few peaks of iron oxides and iron silicate which could be due to the presence of iron oxide in the sludge. Beyond 7.5% sludge addition, there are salient changes in the peak pattern and intensity. The peaks were started diminishing which might be the result of chemical reaction within the mixture. The nature of the underlying reactions in the mixtures needs to be further explored for explaining this behaviour.

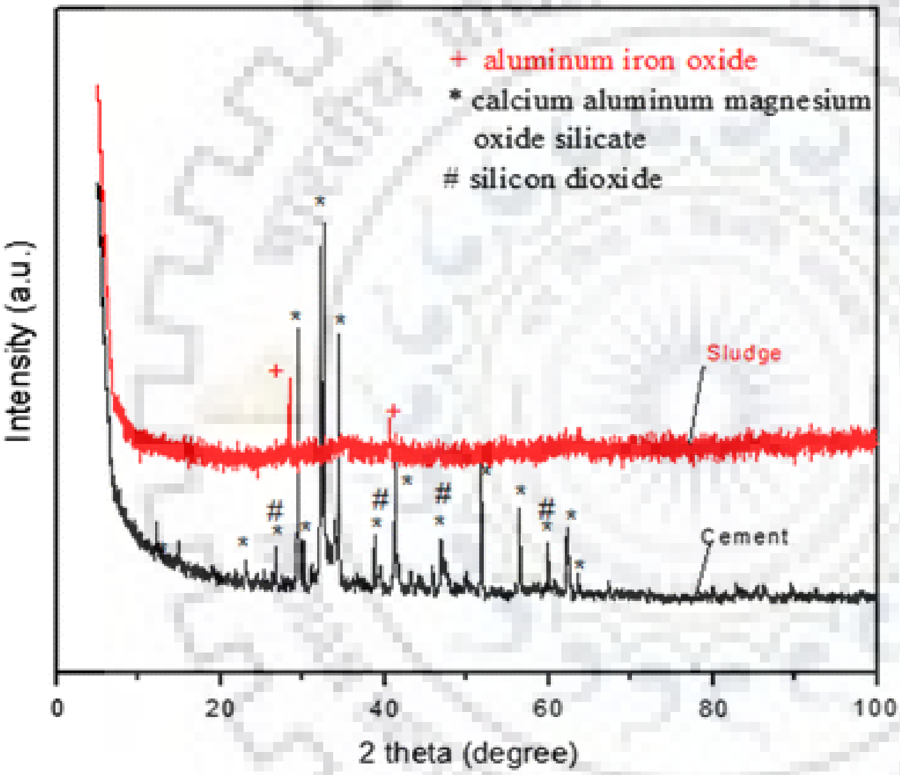


Figure 7.5. XRD graphs of sludge and cement.

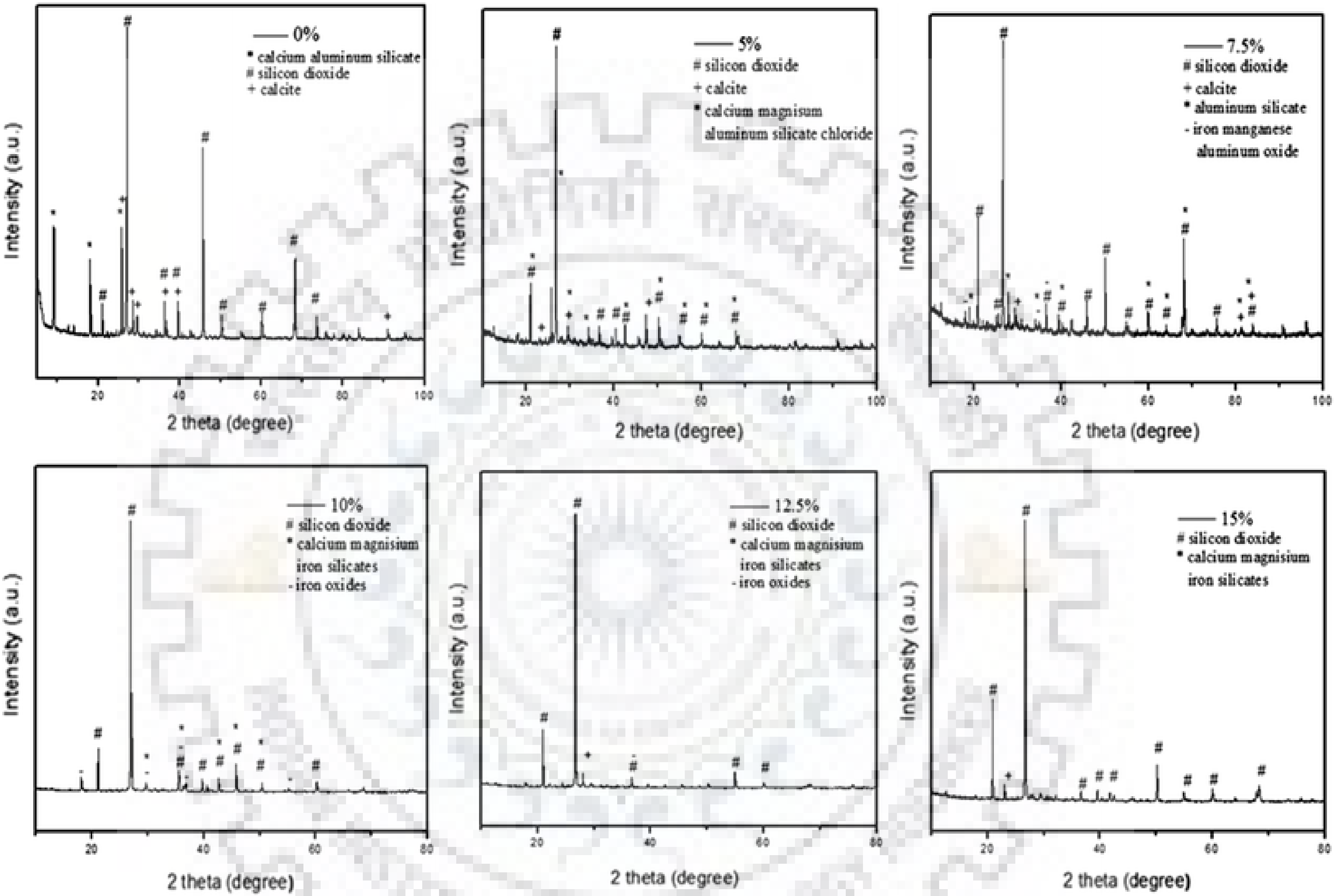


Figure 7.6.XRD graphs of different percentage of sludge mixtures (0–15 %).

7.4 Findings

The feasibility of utilization of EC sludge as a substitute of cement in non-construction materials was estimated in view of the environmental concerns regarding its disposal and exploring the possibility of reusing it as a resource. The experiments conducted to find out the optimum combination of cement and EC sludge displayed that the cement-based stabilization/solidification is an effective solution for the reuse of sludge generated during electrocoagulation process. Thermo-gravimetric analysis showed that the EC sludge, which has up to 40% organic content, and is mixed with the cement up to 7.5%, the thermal stability of the mixture is not significantly affected. Compressive strength of sludge–cement mortar samples decreased with an increase in the proportion of EC sludge. The compressive strength results indicated that a maximum amount of EC sludge of 7.5% could be added. The decrease in the compressive strength with 7.5% replacement was <5% with respect to the control mortar (without sludge). Cement-based solidification of EC sludge seemed to apparently reduce the heavy metal concentration in the leachate from mortars which could be due to their entrapment within the pores of the cement matrix and possible conversion to insoluble precipitates compared to the EC sludge alone [244]. All the heavy metals studied in the leachate were below the discharge limits of effluent as per the Indian standards. Leaching pollution potential of cement–sludge mortar also met the regulatory limits set by EPA. From mechanical as well as environmental point of view, it could be successfully demonstrated that cement–sludge mortar containing 7.5% EC sludge could be used safely within the industry itself in different applications such as decoration tiles, pot making and fencing of garden without adversely affecting the environment.

CHAPTER 8: CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

The derived conclusions and proposed recommendations for future work are briefly presented in the following sections.

8.1 Critical Evaluation of Tertiary RO Treatment System in an Existing Distillery

To find out the reason for poor performance of the tertiary RO plant and high frequency of the membrane replacement in an existing distillery unit, characterization of the spentwash at different stages in the treatment scheme followed by the autopsy of the used and discarded membranes (after 3 months and 6 months) were done. Surface characterization, membrane roughness, presence of functional groups and nature of the organic foulants were determined by using field emission scanning electron microscopy (FESEM), atomic force microscopy (AFM), fourier transform infrared spectroscopy (FTIR) and X-Ray diffraction analysis (XRD). The observations are presented below:

- Organic matter was found significantly reduced after aeration but a substantial amount remained in the effluent, which needed treatment before feeding to the RO membrane system.
- The fouling was observed to be mainly caused by a combination of colloidal particles, organic matter and multivalent ions.
- The FE-SEM results demonstrated Si, Fe, Ca and Na as the major inorganic foulants. AFM study also supported the deposition of colloids or other foulants on the membrane surface.
- Considering the above outcomes of the study, upgraded pretreatment train for RO was proposed to improve the treated water quality and membrane life.

8.2 Optimization of Proposed Treatment Processes

Experimental investigations were carried out to study the effect of selected operating parameters (feed water pH, temperature and trans-membrane pressure) on the membranes (MF, UF and RO) and a different set of parameters (temperature, current density, inter-electrode distance and time) on the EC system respectively. Input operating parameters were optimized in terms of increased permeate flux (water recovery) and contaminant removal (COD, color, TDS and TOC) by using response surface methodology (RSM) approach with central composite design (CCD). Multi parameter optimization was done and experiments were conducted employing optimized input parameter values to validate the RSM predictions. The observations are presented below:

- EC treatment with SS electrode was observed to offer better pretreatment than MF and UF for treating distillery spentwash with pollutant removal efficiency for COD, color and TOC at 69.63%, 92.73% and 72.30% respectively at optimized conditions.
- The pollutant removal efficiencies for COD, color, TDS and TOC with MF were 31.6%, 42.7%, 27.6% and 22.9%, and 62.1%, 93.5%, 75.5% and 58.8% with UF, respectively.
- EC was found to be more effective in removing organic matter as compared to the MF and UF, but the color and TDS removal was found to be more in case of UF. The difference in organic matter removal between UF and EC treatment was 10-20% (EC>UF).
- The experimental results were closer to the predicted values obtained by RSM.
- Among the proposed treatment schemes, EC-RO was found more superior compared to MF-RO and UF-RO for tertiary treatment of distillery spentwash. Permeate flux (recovery) with RO has showed a remarkable increase from 17.5 $l/m^2/h$ (direct RO) to 40.5 $l/m^2/h$, 38.0 $l/m^2/h$ and 32 $l/m^2/h$ when used in combination with EC, UF and MF, respectively

8.3 Economic Assessment of Proposed Treatment Schemes

Economic assessment of RO system was performed on stand-alone basis and in combination with different pretreatment schemes (with MF, UF and EC) for tertiary treatment of distillery spentwash. Estimation of per cubic meter water production cost was the main basis of the cost analysis. Conclusions drawn from the results are given below:

- The total water production cost for RO system came out as 467 Rs./m^3/m^2. The pretreatment reduced the cost up to 50%.
- EC-RO combinationwas found more economical (at 185 Rs/m^3/m^2) and efficient than MF-RO (256 Rs./m^3/m^2) and UF-RO (220 Rs./m^3/m^2) in terms of water production cost.

8.4 Reuse of Electro-coagulation Generated Sludge

Sludge generated during EC treatment process is highly complex in nature and requires proper disposal. In this context, the present study was conducted to employ the electrocoagulation generated sludge as a partial replacement of cement while manufacturing the non-constructional building blocks. Following interpretations and conclusions could be drawn from this study:

- The compressive strength results indicated that a maximum amount of EC sludge upto 7.5% could be added. The decrease in the compressive strength with 7.5% replacement was <5% with respect to control mortar (without sludge).
- Cement-based solidification of EC sludge reduces the heavy metal concentration in the leachate from mortars which could be due to their entrapment within the pores of the cement matrix and converted to insoluble precipitates compared to the EC sludge alone. All the heavy metals studied in the leachate were below discharge limits of effluent as per the Indian standards.
- From mechanical as well as environmental point of view, it could be successfully demonstrated that the optimum combination of cement and EC sludge was found to be 7.5%, which could be used safely within the industry itself in different applications such as decoration tiles, pot making and fencing of garden without adversely affecting the environment.

8.5 Recommendations and Future Scopes

i) Present study has been performed at the laboratory scale. Feasibility of this study at pilot scale could also be evaluated in the next stage.

ii) In the present study the cost assessment was done considering the laboratory scale experiments in terms of total water production cost. As the production cost may not necessarily vary with the increase in plant capacity in a linear fashion, its rational assessment may be needed after upscaling.

iii) Beyond 7.5% sludge addition during the mortar preparation, salient diminishing trend in the XRD graphs has been observed in the peak pattern and intensity of compounds. The nature of the underlying reactions in the mixtures needs to be further explored for explaining this behaviour.

iv) In view of the calorific content of the organic rich stream, it can be engaged in combustion or used as a feedstock in an anaerobic process to generate methane, while the stream of salts and low molecular weight organics can be processed to recover potassium salts and produce high quality water.

v) Spentwash contains 5 to 8 g/L of potassium. Reject of RO contains large fraction of TDS. So, recovery of the nutrient (Potash) from the RO reject could also be thought off.

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PUBLICATIONS

Publications out of this thesis work:

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