ADSORPTIVE REMOVAL OF AZOPHLOXINE DYE BEARING WASTEWATER

A DISSERTATION

Submitted in partial fulfillment of the
requirements for the award of the degree
of
MASTER OF TECHNOLOGY
in
CHEMICAL ENGINEERING
(With Specialization in Industrial Pollution Abatement)

By

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CANDIDATE'S DECLARATION

I hereby declare that the work which is being presented by me in this project report entitled. "**ADSORPTIVE REMOVAL OF AZOPHLOXINE DYE BEARING WASTEWATER** ", submitted in partial fulfillment of the requirement for the award of the degree of,"**Master of Technology in Chemical Engineering**" with specialization in "**Industrial Pollution Abatement**", and submitted to the Department of Chemical Engineering, Indian Institute of Technology, Roorkee, is an authentic record of the work carried out by me during the period June 2011 to June 2012, under the guidance of Prof. I.D. Mall, professor & Head of Chemical Engineering, Indian institute of Technology, Roorkee.

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CERTIFICATE

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

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ABSTRACT

Present study explores the adsorptive removal of azophloxine dye from aqueous solution onto bagasse fly ash (BFA), rice husk ash (RHA). Batch experiments were carried out to determine the influence of parameters like initial pH (pH_0), contact time (t), adsorbent dose (m), temperature (T) and initial dye concentration (C_0) on the removal of azophloxine. The optimum conditions have been found to be : For BFA pH_0=6, C_0= 100 mg/l, m=20g/l, t=5 h and T=60°C; For RHA: pH_0=6, C_0= 100 mg/l, m=25g/l, t=5 h and T=60°C. The removal efficiencies of BFA and RHA were found to be 97% and 95% .Results clearly shows that for the removal of azophloxine dye BFA is a better adsorbent as it gives more removal efficiency even at lower adsorbent dose in comparison to RHA. The various equilibrium isotherms have been studied and it has been found out that Langmuir isotherm fits better to the experimental data than other isotherms for azophloxine adsorption on BFA. For adsorption of azophloxine dye by RHA Freundlich isotherm isotherm fits better. For various Kinetic studies it has been found that for both BFA and RHA pseudo second order is the best fit observed. Since BFA and RHA is a waste material obtained at almost no cost, the spent BFA and RHA can be combusted to recover its energy value and the bottom ash can be blended with cementitious mixture for making building blocks.

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NOMENCLATURE

C_0	Initial dye concentration
C_e	Concentration of adsorbate solution at equilibrium (mg/l)
K_F	Freundlich constant (l/mg)
K_L	Constant related with the free energy of adsorption (l/mg).
k_R	R-P isotherm constant (l/g)
K_T	Temkin isotherm constant (l/mg)
K_f	Pseudo-first-order rate constant (min^{-1})
K_S	Pseudo-second-order rate constant (g/mg min).
$1/n$	Heterogeneity factor, dimensionless
q_t	Amount of adsorbate adsorbed per unit amount of adsorbent at time t,(mg/g)
q_e	Amount of adsorbate adsorbed per unit amount of adsorbent at time equilibrium,(mg/g)
K_{id}	Intra- particle diffusion rate constant
SSE	Sum of square of errors
TDS	Total dissolved solids
CPCB	Central Pollution Control Board
COD	Chemical oxygen demand
BOD	Biochemical oxygen demand
TSS	Total suspended solids
BFA	Bagasse fly ash
RHA	Rice husk ash
BET	Brunauer–Emmett–Teller
FTIR	Fourier Transform Infrared
XRD	X ray diffraction

CHAPTER 1

INTRODUCTION

The world is facing problems related to the management of wastewater. This is due to extensive industrialization, increasing population density and high urbanized societies [Akpor and Muchie., 2011].

The effluents generated from domestic and industrial activities constitute the major sources of the natural water pollution load. This is a great burden in terms of wastewater management and can consequently lead to a point-source pollution problem, which not only increases treatment cost considerably, but also introduces a wide range of chemical pollutants and microbial contaminants to water sources.

The applications of dyes and pigments have increased in a considerable way in recent years. A lot of industries have been set up to mitigate the continuously increasing demand of dyes and pigments. Dyes are used in textiles, food and beverage industries and printing processes. Approximately 1 million kg/yr of dyes is discharged in to water streams by the textile industry [Mane and Babu., 2011]. Dye producers and users are interested in stability and fastness and, consequently, are producing dyestuffs that are more difficult to degrade after use. Unless properly treated, the dyes present in wastewaters can affect photosynthetic activity due to reduced light penetration and may also be toxic to certain forms of aquatic life.

1.1 ENVIRONMENTAL ISSUES RELATED WITH TEXTILE SECTOR

There are large numbers of mechanical and chemical processes involved in the textile industry and each process has a different impact on the environment. This impact starts with the use of pesticides during the cultivation of natural fibres, the erosion caused by farming or the emissions during the production of synthetic fibres. From that moment on, a number of processes are applied, using thousands of different chemicals, to process the fibres and to reach the final stage of textile end product.

Presence of colour in the waste water is one of the main problems in textile industry. Colours are easily visible to human eyes even at very low concentration. Hence, colour from textile wastes carries significant importance. Most of the dyes are stable and has no effect of light or oxidizing agents. They are also not easily degradable by the conventional treatment methods.

Removal of dyes from the effluent is major problem in most of textile industries. [Advance methods for treatment of textile industry effluents, 2007].

1.1.1 Impact of colorants

Environmental problems associated with the textile industry are typically those associated with water pollution caused by the discharge of untreated effluent. Effluent are generally hot, alkaline, and strong smelling, and coloured by chemicals used in colouring process. Some of the chemicals, including dyes and pigments, are toxic or can lower the dissolved oxygen content of receiving waters, threaten aquatic life and damage general water quality downstream. Effects on organisms in the environment can be either short term (acute) or long term (chronic) [Environmental aspects of textile wet Processing].

In relation to the textile industry, four potential routes of colorants to enter the environment have to be considered.

- Through routine process effluent or emissions.
- Through disposal of surplus materials and process residues.
- Through accidental release.
- Through the disposal of used packages (Solid waste).

These pollutants are expressed in terms of chemical oxygen demand (COD), 5-day biochemical oxygen demand (BOD_5), total suspended solids (TSS), and total Kjeldahl nitrogen (TKN), as well as sulphur, phosphorus and chromium compounds[Sheikh et al., 2011].

1.1.2 Impact of the main solid wastes

The majority of textile solid wastes are fibres, yarns, fabrics, packaging waste, dye containers, chemical containers, dirt, waxes, wasted sludge and retained sludge, paper, cartons, etc. The hazardous solid wastes are the sludge, the dye and chemical containers, as they contain toxic material, and dealing with wastes for disposal may expose the workers to toxic effects.

1.1.3 Impact of noise

The noise level resulting from the machines used in the textile industry, especially from the dry processes, may violate the limit allowed by the law and cause hearing problems. The ring spinning machines, the open-end spinning machines, the winding machines, the looms, the sewing machines etc. Work at very high speeds, thus exceed the allowed level of noise (90 decibels) and cause hearing troubles to the production workers.

1.1.4 Impacts of pollutants on health

The major sources of pollution in the textile industry, causing either acute or chronic effect are the cotton dust and fibre particulates from the dry processes, oil and acid/alkaline mists; solvent vapours; odours; dust and lint in the wet processes, and the nitrogen and sulphur oxides and other particulates from boilers. The use of dyestuffs and pigments may cause a number of adverse effects to health. Health effects may be exerted directly at the site of application (affecting the workers) and later in the life cycle (affecting the consumers). Many chemicals used in textile processing have adverse effect on occupational and community health. The surrounding area is also affected by the fibre fuzz in case of facilities not using scavenging systems, and depending on ventilation through factory windows. This situation may have effect on the respiratory diseases of people living in the area.

Table 1.1 Summary of potential releases emitted during textile manufacturing (Management practices for pollution prevention in textile industry, EPA, office and research).

Process	Air emissions	Waste water	Residual waste
Fibre Preparation	Little or no air emission generated	Little or no waste water generated	Fibre waste, packaging waste and hard waste
Yarn spinning	Little or no air emission generated	Little or no waste water generated	Packaging waste, sized warn, fibre waste, cleaning and processing waste
Slashing	VOCs	BOD , COD, metals , cleaning waste, size	Fibre lint, yarn waste , packaging waste, unusual starch based sizes
Weaving	Little or no air emission generated	Little or no waste generated	Packaging waste , yarn and fabric scraps, off-spec fabric, used oil
Knitting	Little or no air emission generated	Little or no waste generated	Packaging waste, yarn and fabric scraps, off-spec fabric
Tufting	Little or no air emission generated	Little or no waste generated	Packaging waste, yarn and fabric scraps, off-spec fabric
Desizing	VOCs from glycol ethers	BOD from water soluble sizes, synthetic size, lubricant biocides , antistatic compounds	Packaging waste, fibre lint warn waste, cleaning material such as wipes, rags, filters, cleaning and maintenance waste containing solvents
Scouring	VOCs from glycol ethers and scouring solvents	Disinfectants and insecticide residues, NaOH, detergent, fats, oil, pectin, wax, knitting lubricants , spin finishers, spent solvents	Little or no residual waste generated
Bleaching	Little or no air emission generated	Hydrogen peroxide, sodium silicate or organic stabilizer, high pH	Little or no residual waste generated

Singeing	Small amount of exhaust gases from burners	Little or no waste generated	Little or no residual waste generated
Mercerizing	Little or no air emissions generated	High pH, NaOH	Little or no residual waste generated
Heat setting	Volatilization of spin finish agents applied during synthetic fibre manufacture	Little or no waste water generated	Little or no waste generated
Dyeing	VOCs	Metals, salt, surfactants, toxics, organic processing assistants, cationic materials, colour, BOD, COD, sulphide acidity/alkalinity, spent solvents	Little or no waste generated
Printing	Solvent, acetic acid from drying and curing oven emissions, combustion gases, particulate matter	Suspended solvents , urea, solvents, colours, metals, heat, BOD, foam	Little or no waste generated
Finishing	VOCS, contaminants in purchased chemicals, formaldehyde vapour, combustion gases, particulate matter	BOD, COD, suspended solids, toxic, spent solvents	Fabric scraps and packaging waste
Product fabrication	Little or no air emissions generated	Little or no waste generated	Fabric scraps

Table 1.2 Typical characteristics of dye used in textile dying operation (Management practices for pollution prevention in textile industry, EPA, office and research).

Dye class	Description	Method	Fibers typically applied to	Typical fixation %	Typical pollutants associated with various dy
Acid	Water soluble anionic compounds	Exhaust, Continuous	Wool nylon	80-93	Colour, organic acids, unfixed dyes
Basic	Water soluble, applied in weakly acidic dye baths, very bright dyes	Exhaust	Acrylic, some polyesters	97-98	N/A
Direct	Water soluble, Anionic compounds can be directly applied to cellulosic without mordant's	Exhaust, Continuous	Cotton, rayon, other cellulosic	70-95	Colour, salt, unfixed dye, cationic fixing agents, surfactants, defoamer, leveling and retarding agents
Disperse	Not water soluble	High temperature exhaust continuous	Polyester acetate other synthetics	80-92	Colour, organic acids carriers, leveling agents, phosphates, defoamers , lubricants, dispersants, dilutents
Reactive	water soluble, anionic compounds, largest dye class	Exhaust, Continuous	Cotton other cellulosic wool	60-90	Colour, salt, alkali, unfixed dye, surfactants, defoamer, dilutents, finish
Sulphur	Organic compounds containing sulphur or sodium sulphide	Continuous	Cotton other cellulosic	60-70	Colour, alkali, oxidizing agents, reducing agent , unfixed dye
Vat	Oldest dyes, complex, water insoluble	Exhaust, Continuous	Cotton other cellulosic	80-95	Colour, alkali, oxidizing agents, reducing agent

Table 1.3 Standards of textile industry discharge (Ministry of environment and forest notification New Delhi, 2010)

	Parameter	Standards (limiting concentration in mg/l except for pH, temperature and color)
Dye and dye intermediate industry	pH	6.0-8.5
	Suspended solids	100
	BOD_3 days, 27°c	100
	Temperature	Shall not exceed 5°C above the ambient temperature of water in the receiving body
	Colour	400(hazen unit)
	Mercury (as Hg)	0.01
	Chromium (as Cr^{6+})	0.1
	Copper (as Cu)	3.0
	Zinc (as Zn)	5.0
	Nickel (as Ni)	3.0
	Lead (as Pb)	0.1
	Manganese (as Mn)	2.0
	Cadmium (as Cd)	2.0
	Chlorine (as Cl)	1000
	Sulphate	1000
	Phenolic compounds	1.0
	Oil and grease	10
	Bioassay test	90% survival of fish after 96 hr in 100% effluent

1.2 OBJECTIVE

The aim of the present work is to explore the possibility of utilizing BFA and RHA for the adsorptive removal of azophloxine dye from aqueous solution. The following objectives have been set for the present work.

1. Study the feasibility of using BFA and RHA as adsorbents for the removal of azophloxine dye from aqueous solutions.
2. Study the effect of initial pH, adsorbent dose, temperature and initial concentration of dye on the adsorption process.
3. Choose a suitable model among several adsorption isotherm models (i.e., Freundlich, Langmuir and Temkin) based on regression analysis.
4. Choose a suitable model among several adsorption kinetic models (i.e., Pseudo-First order, Pseudo-Second-order, Bangham and Intra-particle diffusion) based on regression analysis.

CHAPTER 2

LITERATURE REVIEW

In the present section literature review is presented on the removal of dyes present in the textile waste water using various low cost technologies and adsorbents. The dyestuff industry is one of the highly polluting industries .The discharge of dye bearing wastewater into the environment may cause various problems. Research and development is going on to search for the low and cost effective technique.

Rameshraja et al., [2011] investigated the adsorption of quinoline onto granular activated carbon (GAC) and bagasse fly ash (BFA) in a batch system. Various parameters such as pH, adsorbent dose (m), temperature (T), initial quinoline concentration (Co) and contact time (t) were optimised. Equilibrium contact time and optimum pH were found to be 8 h and 5.5 h, respectively, for both the adsorbents. The adsorbent dose for GAC and BFA were found to be of 5 g/l and 10 g/l, respectively. Pseudo-second-order kinetic model was found to fit the adsorption kinetic data.

Sidiras et al., [2011] investigated the use of untreated pine sawdust for wastewater cleaning. The effect of the auto hydrolysis time and temperature on the microstructure and the crystallinity of pine sawdust were investigated by means of: SEM, FTIR, XRD and BET, in order to obtain information at a higher granularity level, in comparison with previous studies. The BET surface area increased from 0.89 to 19.3 m^2g^{-1}. In the case of MB (methylene blue), the Freundlich's adsorption capacity K_F increased from 5.60 to 15.7 (mg g^{-1}) (L mg^{-1}), 1/n the amount of dye adsorbed when saturation is attained (Langmuir constant, q_m) increased from 38.7 to 88.0 mg g^{-1}.

Suresh et al .,[2011] studied the simultaneous adsorptive removal of phenol and aniline, and phenol and nitrophenol from aqueous solutions using granular activated carbon (GAC). The effect of operating parameters such as initial component concentrations, temperature, adsorbent dosage and contact time on the adsorption of mixtures of solutes in the binary aqueous solution were studied. Taguchi's method of design of experiments was used to study the effect of each parameter at three levels on the total amount of solutes adsorbed on GAC (q_{tot}, mmol/g).

Zhang et al., [2011] investigated that white mud prepared from waste material of soda production can be used in the removal of the model anionic dyes reactive bright red K-2BP, reactive light yellow K-6G, acid orange II and direct yellow R. In alkaline conditions, the leaching solution of white mud generates hydroxide precipitates, which have relatively high specific surface area and excess surface energy, and readily adsorb the dyestuffs. In this study, the chemical composition of the white mud was determined by X-ray fluorescence and the hydroxide precipitates were characterized by dynamic light scattering, transmission electron microscopy and Fourier-transform infrared spectroscopy.

Kushwaha et al., [2010] studied, the treatment of simulated dairy wastewater (SDW) by electro-chemical method using iron electrode. Full factorial central composite design (CCD) with four factors namely current density (J), dosage of sodium chloride (NaCl) (m), electrolysis time (t) and pH, with each factor at five levels, was used to optimize the factors for higher COD removal. Operational parameters J, m, t and pH were varied between 61.73–308.64 A/m^2, 0–2 g/l, 10–90 min and 5–11, respectively. Optimum value of J, t and pH were found 270 A/m^2, 50 min, and 7.0, respectively, while m was found to be zero.

Visaet et al., [2010] examined that modified fly ash is effectively used as a substrate for the removal of waste from textile industry. The main constituents of fly ash (silica, alumina, iron oxide and unburned carbon), are the priority compounds which favour the heavy metal adsorption and are active sites in dyes adsorption processes. Here the effect of MB (methylene blue) adsorbed on the fly ash surface on the removal efficiency of cadmium, copper and nickel ionic species from complex, multi-cationic dye solutions. The adsorption efficiency and kinetics are evaluated from the complex, multi component systems and possible influences are discussed. High efficiencies are obtained at low heavy metal concentrations (as it is the real case for the dyes industry) whereas at medium values, competitive processes lower the individual efficiencies of copper, nickel or cadmium from mixtures.

Ahmad and Hameed., [2009] investigated that activated carbon that was prepared from bamboo waste by chemical activation method using phosphoric acid as activating agent can effectively remove COD and colour from waste from dye industry. The activated carbon was evaluated for chemical oxygen demand (COD) and colour reduction of a real textile mill effluent. A maximum reduction in colour and COD of 91.84% and 75.21% respectively was achieved. The Freundlich isotherm model was found best to describe the obtained equilibrium adsorption data at 30. Various functional groups on the prepared bamboo activated carbon (BAC) were determined from the FTIR results.

Mahmoued., [2009] evaluated that cement kiln dust (CKD) and CKD + Coal filters can be used in removing colour, turbidity and organic substances (BOD and COD) and heavy metals from textile wastewater. The results showed that the negligible difference between the CKD filter at hydraulic loading 0.5 and 1.0 m^3/m^2h in the removal efficiency COD and colour and increasing of seed germination for treated of textile industrial effluents. The higher efficiency of CKD + Coal than CKD filters for COD and colour removal of textile wastewater at hydraulic loading of 1.0 m^3/m^2h. CKD + Coal filter could remove about 97% of colour, 76% of turbidity, 84% of COD. The experimental results confirmed that CKD + Coal filter can be adopted as a decolourization and heavy metals of textile industrial effluent.

Wanga and Peng., [2009] investigated the modifications of natural zeolites that have been widely used as adsorbents in separation and purification processes. Due to their high cation-exchange ability as well as to the molecular sieve properties, The recent development of natural zeolites as adsorbents in water and wastewater treatment as various natural zeolites around the world have shown varying ion-exchange capacity for cations such as ammonium and heavy metal ions. Some zeolites also show adsorption of anions and organics from aqueous solution. Modification of natural zeolite can be done in several methods such as acid treatment, ion exchange, and surfactant functionalisation, making the modified zeolites achieving higher adsorption capacity for organics and anions.

Batra et al., [2008] characterised the bagasse fly ash carbon by thermal analysis, electron microscopy and adsorption. The carbon particles can be separated from oxide fraction of fly ash by floating it in water. This process increases the loss on ignition from 20–30% to 80%. N_2 adsorption measurements give BET surface areas of near 200 m^2/g for the separated carbons. Analysis of the isotherms indicates a large fraction of pores in the size range of 10–12 Å.

Hassana et al., [2008] investigated that Sorel's Cement can be used for removal of some reactive dyes from textile wastewater effluents. Parameters affecting dye uptake including contact time, reagent dosage and pH are examined and optimized. Dye adsorption equilibrium data are fitted well to the Langmuir isotherm rather than Freundlich isotherm. The adsorption isotherm indicates that the adsorption capacities are 107.67, 120.89 and 103.14 mg dye per gram of Sorel's cement for RY-145, RR-194 and RB-B reactive dyes, respectively. The sorption of the dyes is enhanced by increasing the pH, reaching a maximum at pH 6–11. Experimental runs were conducted to measure the chemical oxygen demand (COD) of textile wastewater loaded with reactive dyes, reveals~96% removal of the COD contents within 30 min under optimized conditions.

Demirbas., [2008] investigated that a number of different low cost adsorbents derived from agricultural wastes have demonstrated outstanding capabilities for the removal of dyes from wastewater. Therefore, low cost agricultural waste adsorbents can be viable alternatives to activated carbon for the treatment of contaminated waste water. The use of cheap and eco-friendly adsorbents have been studied as an alternative substitution of activated carbon for the removal dyes from waste water. The dye adsorption capacities of agricultural waste adsorbents vary, depending on the characteristics of the individual adsorbent, the extent of surface modification and the initial concentration of adsorbate.

Fatma et al., [2006] examined that the adsorption of Reactive Blue 19, Reactive Red 195 and Reactive Yellow 145 onto wheat bran increased with increasing temperature and initial dye concentration while the adsorbed RB 19, RR 195 and RY 145 amounts decreased with increasing initial pH and adsorbent concentration. The Langmuir and Freundlich isotherm models were applied to the experimental equilibrium data depending on temperature and the isotherm constants were determined by using linear regression analysis. The monolayer coverage capacities of wheat bran for RB 19, RR 195 and RY 145 dyes were obtained as 117.6, 119.1 and 196.1 mg/g at 60°C, respectively. It was observed that the reactive dye adsorption capacity of wheat bran decreased in the order of RY 145 >RB 19 >RR 195.

Dincer et al., [2006] examined that locally available CBBA (coal based bottom ash) waste material can be used as adsorbent for removal of reactive dyes from synthetic textile wastewater. His study presents the results of investigation on colour removal from synthetic wastewater containing Vertigo Blue 49 and Orange DNA13 by adsorption onto CBBA waste material. The effectiveness of CBBA waste material in adsorbing reactive dyes from aqueous solutions was studied as a function of contact time, initial dye concentration and pH by batch experiments. Leachability of waste material was also evaluated using standard leaching test with deionised water.

Matheswaran et al., [2006] studied the effective utilization of fly ash as adsorbent for the removal of Chrysoidine R from the aqueous solution. The fly ash is a major by product generated in coal-based thermal power plants and has good potential for use as an adsorbent. A series of experiments were carried out in a batch adsorption technique to obtain the effect of process variables viz. contact time, pH (2, 4, 6 and 8) initial concentration of the dye (400, 600, 800 and 1000 mg L^{-1}), amount of the adsorbent (125, 250, 375 and 500 mgL^{-1}), and temperature (303, 313, 323 and 333 K) on adsorption.

Iqbal and Ashiq., [2006] investigated the adsorption of industrially important dyes namely bromophenol blue, alizarine red-S, methyl blue, methylene blue, malachite green, phenol red and methyl violet from aqueous media on activated charcoal. The effect of shaking time, pH and temperature on the adsorption behaviour of these dyes has been studied. It was noted that adsorption of all the dyes on activated charcoal decreases with an increase in the pH and the temperature. The adsorption isotherms at different temperatures were found to be of L-type. Adsorption data was fitted to Freundlich, BET and Langmuir isotherms and various adsorption parameters have been calculated.

Figueiredoa et al., [2005] examined that three natural waste materials containing chitin were used as adsorbents for textile dyestuffs, namely the Anodonta shell, the Sepia and the Squid pens. The selected dyestuffs were the Cibacron green, and the Solophenyl green, both from CIBA, commonly used in cellulosic fibres dyeing; the most used fibres in the textile industry. Batch equilibrium studies showed that the materials, adsorption capacities increase after a simple and in expensive chemical treatment, which increases their porosity and chitin relative content. Kinetic studies suggested the existence of a high internal resistance in both systems. Fixed bed column experiments performed showed an improvement in adsorbents behaviour after chemical treatment.

Kargi., [2005] evaluated that acid pretreated powdered waste sludge (PWS) can be used for removal of textile dyestuffs from aqueous medium by adsorption as an alternative to the use of powdered activated carbon (PAC). The rate and extent of dyestuff removals were determined for four different dyestuffs at different PWS concentrations varying between 1 to 6 g/L. Biosorbed dyestuff concentrations at equilibrium decreased with increasing PWS concentration for all dyestuffs tested. More than 80% percent dyestuff removal was obtained for all dyestuffs at PWS concentrations above 4 g/L after 6 h of incubation. Similar to percent dyestuff removal, the rate of adsorption was maximum at a PWS concentration of 4 g/L. Kinetics of adsorption of dyestuffs was investigated by using the first and second-order kinetic models and the kinetic constants were determined. Second-order kinetics was found to fit the experimental data better than the first-order model for all dyestuffs tested.

Rao and Rao., [2005] examined that fly ash has potentiality for use as an adsorbent. In the present work, adsorption studies were made in treating the dye solutions of methylene blue (M-B) and Congo red (CR) textile dyes by using fly ash. Effects of quantity of adsorbent, time of contact, initial effluent concentration, pH and temperature have been investigated experimentally and the results were compared with those obtained by using activated carbon. The first-order adsorption rate constants were determined and found decreasing with temperature. The results obtained were fitted by Langmuir model since monolayer formation observed.

Srivatava et al., [2005] studied the competitive adsorption of cadmium (Cd(II)) and nickel (Ni(II)) ions onto bagasse fly ash (BFA) from single component and binary systems. BFA is a waste material obtained from the flue gas of the bagasse-fired boilers of sugar mills. Equilibrium adsorption is affected by the initial pH (pH_0) of the solution. The $pH_0 \approx 6.0$ is found to be the optimum for the individual removal of Cd(II) and Ni(II) ions by BFA. The pH of the system, however, increases during the initial sorption process for about 20 min and, thereafter, it remains constant. The equilibrium adsorption data were obtained at different initial concentrations (C_0= 10-100 mg/l), 5 h contact time, 30°C temperature, BFA dosage of 10 mg/l at pH_0=6.

Erdem et al., [2004] investigated that the adsorption of some textile dyes by batch adsorption techniques at 30°C by diatomite earth, Everzol Brill Red, and Int Yellow5GF (IY)). The adsorption behaviour of textile dyes on diatomite samples was investigated using a UV via spectrophotometric technique. The effect of particle size of diatomite, diatomite concentration, the effect of initial dye concentrations, and shaking time on adsorption was investigated. Adsorption coverage over the surface of diatomite was studied using two well-known isotherm models: Langmuir and Freundlich.

Forgacsa et al., [2004] investigated various methods of removal such as adsorption on various sorbents, chemical decomposition by oxidation, photo degradation, and microbiological decolouration, employing activated sludge, pure cultures and microbe consortiums are described. The advantages and disadvantages of the various methods are discussed and their efficacies are compared.

Robinson et al., [2002] investigated the adsorption of five reactive dyes in a synthetic textile dye effluent onto barley husks in static-batch mode and in a continuous flow, packed-bed, reactor (CFPBR). Effective adsorption, thermodynamics and various initial concentrations (C_0) were studied for static batch conditions. The effect of C_0 and retention time(s), by varying height and weight of packing, along with the kinetics of dye adsorption in CFPBR, were studied. The Langmuir isotherm was used to predict saturation capacities. The barley husks were found to remove 8 mg/l of dyes at C_0=100 mg/l in CFPBR with a residence of 11 min, with 90% adsorption being achieved.

Robinson et al., [2001] examined barley husk, for dye removal is compared to corncob. The effectiveness of adsorption as a means of dye removal has made it an ideal alternative to other more costly treatments. This paper deals with two low-cost, renewable biosorbents, which are agro-industrial by-products for textile dye removal. Experiments at total dye concentrations of 10, 20, 30, 40, 50, 100, 150 and 200 mg/l were carried out with an artificial effluent consisting of an equal mixture of five textile dyes. The effects of initial dye concentration, biosorbent particle size, dose of biosorbent, effective adsorbance, and dye removal kinetics were examined.

CHAPTER 3

TREATMENT METHODS AND AZOPHLOXINE DYE

Textile waste water includes a large variety of dyes and chemical additions that make the environmental challenge for textile industry not only as liquid waste but also in its chemical composition. Biological methods such as biodegradation have been proposed. However, due to the low biodegradability of dyes, conventional biological wastewater treatment processes are not very efficient for the treatment of dyeing wastes [Ahmad and Hameed., 2009]. Therefore various primary, secondary and tertiary treatment methods are used in some cases even they are unable to remove the dyes present in waste water there we go for the advanced treatment methods.

3.1 PRIMARY AND SECONDARY TREATMENT

The conventional treatment systems like physio-chemical treatment followed by biological treatment system are installed in majority of textile industries. The first step in the waste water treatment is to mix and equalize the wastewater streams that are discharged at different time and different intervals from different stages in the processes. Some industries also prefer screening, oil trap prior to equalization for removal of solids and oil and grease. Equalization ensures that the effluent have uniform characteristics in terms of pollution load, pH and temperature [Advance methods for treatment of textile industry effluents, 2007].

The effluent is then subject to flash mixing for the addition of coagulants such as lime, alum, ferrous sulphate, ferric chloride. The chemical treatment helps in reduction of colour and suspended solids. A significant reduction in BOD and COD values is also observed. This physio-chemical treatment is followed by biological treatment process, with settling which further reduces BOD and COD values. The textile process houses, which undertake chemical processing, do not have much organic load in their effluents.

3.2 TERTIARY TREATMENT

Textile effluents may require tertiary or advance treatment methods to remove particular contaminant or to prepare the treated effluent for reuse. Some common tertiary operations are removal of residual organic colour compounds by adsorption and removal of dissolved solids by membrane filtration. The waste water is also treated with ozone or other oxidizing agent to destroy many contaminants. Evaporation and crystallization are other methods to minimize effluent disposal problems.

3.2.1 Adsorption

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (the adsorbate) [http://en.wikipedia.org/wiki/Adsorption]. It is different from absorption, in which a substance diffuses into a liquid or solid to form a solution. The term sorption encompasses both processes, while desorption is the reverse process. The adsorption process is used to removes colour and other soluble organic pollutants from effluent. The process also removes toxic chemicals such as pesticides, phenols, cyanides and organic dyes that cannot be treated by conventional treatment methods. Dissolved organics are adsorbed on surface as waste water containing these is made to pass through adsorbent.

Most commonly used adsorbent for treatment is activated carbon. Fixed bed adsorption columns using activated carbon have been widely used in industrial processes for the removal of contaminants from textile effluents. This study present the modelling of an adsorption process applied to textile dyes, using fixed bed columns [Guelli et al., 2007]. This model permits the prediction of the dye concentration at the adsorption column outlet, considering the influence of various operational parameters. The adsorption isotherms of the dye Basic Green 4, over granular activated carbon at 25°C in an aqueous solution, were determined experimentally through a comprehensive series of tests.

Adsorption is an effective alternative process for the treatment of contaminated wastewater. Currently, activated carbon is the most popular and extensively used commercial biosorbent material due to its high adsorption capacity, surface area and degree of surface reactivity as well as micro porous structures. However, it shows some disadvantages such as high operating costs and regeneration problems [Akar et al., 2009].

Therefore, in the recent year's considerable amount of researches have been done on the development of effective, low cost and easily available alternative biosorbents. Different agricultural biomasses such as tree fern, peat and rice husk, peanut, sugarcane dust, apple and wheat straw, bark, palm kernel fibre, banana peel and orange peel, linseed cake and sawdust have been previously tried for the removal of different types of dyes, but high effective and more economical biosorbent materials are still needed to search.

Different Adsorbents

It is necessary to establish the rate law of adsorbate-adsorbent interactions to understand the mechanism by which the solute accumulates on the surface of a solid and gets adsorbed to the surface [Sen Gupta et al., 2011]. A number of theoretical models and equations are available for the purpose and the best fit of the experimental data to any of these models is interpreted as giving the appropriate kinetics for the adsorption process. In this review, an attempt has been made to discuss the kinetics of adsorption of metal ions on inorganic solids based on published reports. A variety of materials like clays and clay minerals, zeolites, silica gel, soil, activated alumina, inorganic polymer, inorganic oxides, fly ash etc. have been considered as the adsorbents and cations and anions of As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se and Zn as adsorbate have been covered in this review.

3.2.2 Ion Exchange

Ion exchange process is normally used for the removal of inorganic salts and some specific organic anionic components such as phenol. All salts are composed of a positive ion of a base and a negative ion of an acid. Ion exchange materials are capable of exchanging soluble ions and cations with electrolyte solutions. The chemical or electrocoagulation treatment process followed by ion-exchange process is effectively used in textile dye effluent [Raghu and Basha., 2007]. The dye effluent was treated using polymeric coagulant (cationic dye-fixing agent) or electrocoagulation (iron and aluminium electrode) process under various conditions such as various current densities and effect of pH. Efficiencies of COD reduction, colour removal and power consumption were studied for each process.

3.2.3 Reverse Osmosis

The process of reverse osmosis is based on the ability of certain specific polymeric membranes, usually cellulose acetate or nylon to pass pure water at fairly high rates and to reject salts. To achieve this, water or waste water stream is passed at high pressures through the membrane. The applied pressures has to be high enough to overcome the osmotic pressure of the stream, and to provide a pressure driving force for water to flow from the reject compartment through the membrane into the clear water compartment. The recent advances in reverse osmosis technology as related to the major issues of concern in this rapidly growing desalination method [Malaeb and Ayoub., 2010]. These issues include membrane fouling studies control techniques, membrane characterization methods as well as applications to different water types and constituents present in the feed water.

3.2.4 Nanofiltration

Nanofiltration is essentially a lower pressure version membrane where the purity of permeate water less important this process is used where the high salt rejection of reverse osmosis is not necessary. The nanofiltration is capable of removing hardness elements such as calcium or magnesium together with bacteria, viruses, and colour. Removal of dye compounds from colour baths used in the textile industry is a possible application of nanofiltration. However, the mechanisms involved in this process are not clearly understood and the practical application of the process is facing many problems such as fouling and flux decline [Bruggen et al., 2001].

3.2.5 Ozonation

Ozone is one of the strongest oxidizers commercially available and popular for disinfection of potable water. Besides this it has multiple applications. Large, complex organic molecules, detergents, phenols etc. can be broken into simpler compounds by ozonation. Among the industrial applications, oxidation of organics and inorganic, deodorisation and decolourisation are the main usages. Ozone is an unstable gas at temperature and pressure encountered in water and waste water treatment plants. Advanced oxidation processes (AOPs) have been widely used in water and wastewater treatment for the removal of organic and inorganic contaminants as well as to improve biodegradability of industrial wastewater. Unfortunately, the partial oxidation of organic contaminants may result in the formation of intermediates more toxic than parent compounds [Rizzo., 2011].

3.3 AZOPHLOXINE DYE [Santa Cruz Biotechnology, Inc. material safety data sheet]

Table 3.1 Physiochemical properties of azophloxine dye

PROPERTY	DATA
Common name	Azophloxine
Other names	amidonaphthol red G
C.I. number	18050
C.I. name	acid red 1
Class	Azo
Ionisation	Acid
Solubility aqueous	Soluble
Solubility ethanol	Slightly
Absorption maximum (λ_{max})	531, 540
Colour	Red
Empirical formula	$C_{18}H_{13}N_3O_8S_2Na_2$
Formula weight	509.44

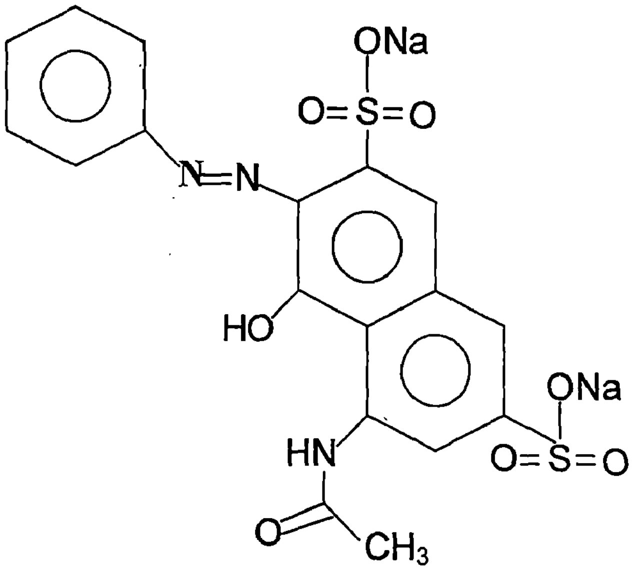


Figure 3.1 Azophloxine dye structure

3.3.1 Potential health effects

- Inhalation - May be harmful if inhaled. May cause respiratory tract irritation.
- Skin - May be harmful if absorbed through skin. May cause skin irritation.
- Eyes -May cause eye irritation.
- Ingestion -May be harmful if swallowed [Aldrich chemical catalogue, 1992].

3.3.2 First aid measures

- If inhaled, if breathed in- move person into fresh air. If not breathing, give artificial respiration.
- In case of skin contact -Wash off with soap and plenty of water.
- In case of eye contact -Flush eyes with water as a precaution.
- If swallowed -Never give anything by mouth to an unconscious person. Rinse mouth with water.

3.3.3 Fire fighting measures

- Suitable extinguishing media -Use water spray, alcohol-resistant foam, dry chemical or carbon dioxide.
- Special protective equipment for fire fighters -Wear self contained breathing apparatus for fire fighting if necessary.
- Hazardous combustion products -Hazardous decomposition products formed under fire conditions – Carbon oxides, nitrogen oxides (NO_x), Sulphur oxides, and Sodium oxides.

3.3.4 Accidental release measures

- Personal precautions -Avoid dust formation. Avoid breathing vapors, mist or gas.
- Environmental precautions- Do not let product enter drains.
- Methods and materials for containment and cleaning up- Sweep up and shovel. Keep in suitable, closed containers for disposal.

3.3.5 Handling and storage

- Precautions for safe handling -Provide appropriate exhaust ventilation at places where dust is formed. Normal measures for preventive fire protection.
- Conditions for safe storage -Keep container tightly closed in a dry and well-ventilated place. Keep in a dry place. Store at room temperature.

3.3.6 Exposure controls/personal protection

- Contains no substances with occupational exposure limit values.
- Personal protective equipment
- Respiratory protection is not required.
- Hand protection- Handle with gloves. Gloves must be inspected prior to use. Use proper glove removal technique (without touching glove's outer surface) to avoid skin contact with this product. Dispose of contaminated gloves after use in accordance with applicable laws and good laboratory practices. Wash and dry hands.
- Eye protection-Use equipment for eye protection tested and approved under appropriate government standards.
- Skin and body protection- Choose body protection in relation to its type, to the concentration and amount of dangerous substances, and to the specific work-place. The type of protective equipment must be selected according to the concentration and amount of the dangerous substance at the specific workplace.
- Hygiene measures -General industrial hygiene practice.

3.3.7 Stability and reactivity

- Chemical stability -Stable under recommended storage conditions.
- Materials to avoid- Strong oxidizing agents.

CHAPTER 4

MATERIAL AND METHODS

4.1 GENERAL

In the present study, bagasse fly ash (BFA) and rice husk ash (RHA) has been utilised for the removal of azophloxine dye bearing synthetic sample. Experimental details of study have been presented in the chapter.

4.2 CHARACTERIZATION OF ADSORBENT

The characteristics of both BFA and RHA have been determined using standard procedures as described below:

4.2.1 Density

The bulk density of BFA and RHA is determined using MCA bulk density meter.

4.2.2 Surface area

Brunauer–Emmett–Teller (BET) method is used for the determination of surface area of sample. The BET method is based on adsorption of gas on a surface. The amount of gas adsorbed at a given pressure allows determine the surface area. It is a cheap, fast and reliable method.

4.2.3 FTIR

Fourier Transform Infra red (FTIR, Nicolet 6700, USA) analysis provides spectral information that is essentially a molecular fingerprint for organic, polymeric, and in some case inorganic materials. This technique is extremely useful for identifying base polymer compositions and organic contaminants. The FTIR spectrum of the unknown material can be compared for "best matches" with libraries of spectra that have been catalogued for known materials. Pellet technique was used for this purpose.

4.2.4 XRD

X-ray diffraction analysis of blank BFA and RHA was carried out with Phillips diffraction unit, using copper target with nickel as filter media, and K radiation maintained at 1.542 ° A. XRD can provide additional information beyond basic identification. If the sample is a mixture, XRD data can be analysed to determine the proportion of the different minerals present. Other information obtained can include the degree of crystallinity of the minerals present, possible deviations of the minerals from their ideal compositions (presence of element substitutions and solid solutions), the structural state of the minerals (which can be used to deduce temperatures and (or) pressures of formation), and the degree of hydration for minerals that contain water in their structure.

4.2.5 TGA

The thermo gravimetric analysis (TGA, Perkin Elmer, Japan) of blank and dye loaded BFA and RHA is carried out from 25 °C to 1000 °C. TGA measures the amount and rate (velocity) of change in the mass of a sample as a function of temperature or time in a controlled atmosphere. The measurements are used primarily to determine the thermal and/or oxidative stabilities of materials as well as their compositional properties. The technique can analyse composition of multicomponent Systems, thermal Stability of materials, oxidative Stability of materials, estimated lifetime of a product, and decomposition kinetics of materials, the effect of reactive or corrosive atmospheres on materials, moisture and volatiles content of materials.

4.3 ADSORBATE

Azophloxine dye is mainly used for dyeing cloths in textile industry. It is an azo class dye manufacture by Santa Cruz Biotechnology, Inc. It has molecular weight of 509.44 and molecular formula $C_{18}H_{13}N_3O_8S_2Na_2$. It is red in colour.

4.4 ANALYTICAL MEASUREMENT

Concentrations of dyes were determined by finding out the absorbance at the characteristic wavelength using a double beam UV spectrophotometer. A standard solution of the dye was taken and the absorbance was determined at different wavelengths to obtain a plot of absorbance versus wavelength. The wavelength corresponding to maximum absorbance (λ_{max}) as determined from this plot was 531 nm. This wavelength was used for preparing the calibration curve between absorbance and the concentration of the dye solution. The calibration curve is shown in figure 4.1.

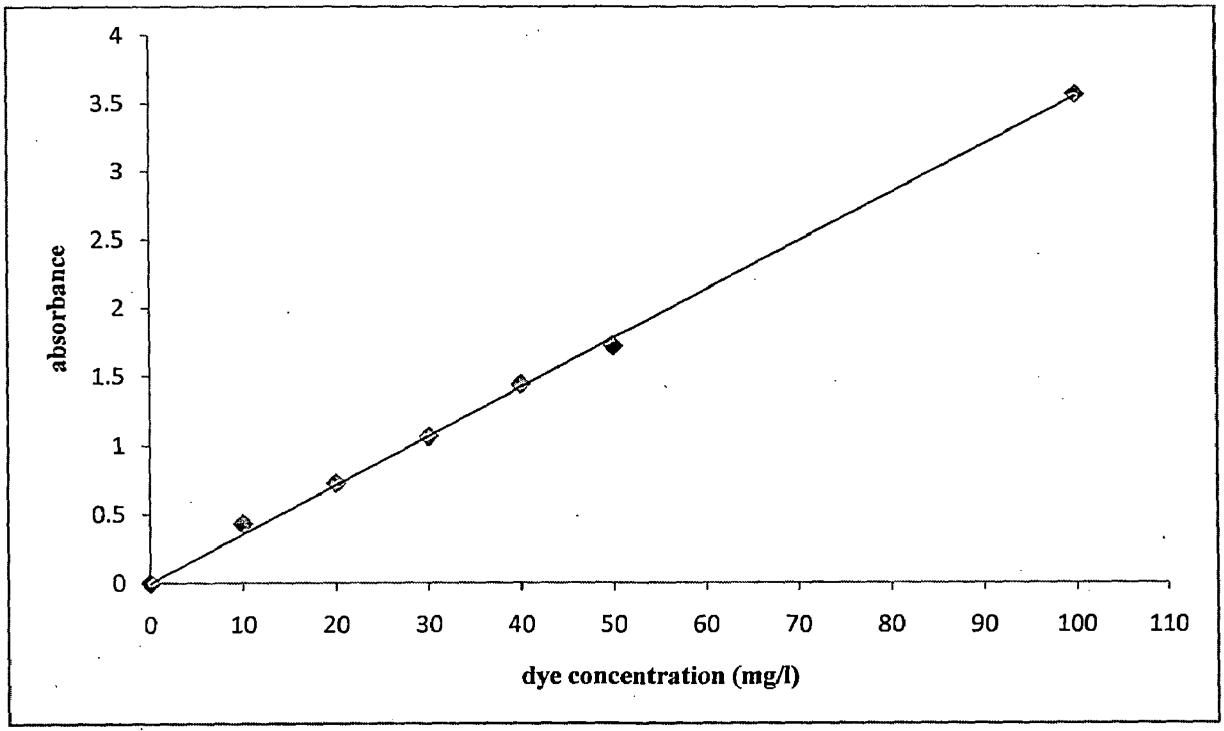


Figure 4.1 Calibration curve between concentration of azophloxine and absorbance

4.5 EXPERIMENTAL PROGRAMME

To study the effect of important parameters like pH, m, C_0 and t on the adsorptive removal of azophloxine, batch experiments were conducted at 30±1°C. For each experimental run, 100 ml of azophloxine solution of known concentration, pH and a known amount of the adsorbent were taken in a 100 ml stoppered conical flask. This mixture was agitated at a constant speed of 150 rpm at 30±1°C. Samples were withdrawn at appropriate time intervals. Therefore, all the samples were centrifuged at 6400 rpm for 5 min and analysed for the residual dye concentration using double beam UV spectrophotometer.

The effect of pH on dye removal was studied over a pH range of 3–9. pH was adjusted by the addition of dilute aqueous solutions of HCl or NaOH (0.10M). For the optimum amount of adsorbent per unit mass of adsorbate, a 100 ml dye solution was contacted with different amounts of adsorbents till equilibrium was attained. The kinetics of adsorption was determined by analysing adsorptive uptake of the dye from the aqueous solution at different time intervals. For adsorption isotherms, dye solutions of different concentrations were agitated with the known amount of adsorbent till the equilibrium was achieved. The residual dye concentration (C) of the solution was then determined.

Batch tests were carried out to compare the adsorptive capacity and intensity of the adsorbents. The percentage removal of azophloxine and equilibrium adsorption uptake, q_e (mg/g), was calculated using the following relationships:

% removal = $100 \times (C_o - C_e)/C_o$.

Amount adsorbed, $q_e = (C_o - C_e)\, V/m$,

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

4.6 MODELLING STUDIES

To optimize the design of an adsorption system for the removal of adsorption of adsorbates, it is important to establish the most appropriate correlation for the equilibrium curves. Freundlich, Langmuir and Temkin isotherm equations have been used to describe the equilibrium nature of adsorption of azophloxine onto BFA and RHA.

4.6.1 **Freundlich isotherm**

The Freundlich isotherm is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface [Mall et al., 2007]. The monolayer freundlich isotherm is given by:

$q_e = K_F C^{1/n}$

Or

$\ln q_e = \ln K_F + 1/n \ln C_e$

Where K_F is the Freundlich constant (l/mg) and 1/n the heterogeneity factor.

4.6.2 Langmuir Isotherm

In the Langmuir theory the basic assumption is that the sorption takes place at specific homogeneous sites within the adsorbent [Srivastav et al., 2005].The Langmuir isotherm equation is given as:

$q_e = K_L q_m C_e / (1 + K_L C_e)$

Or

$C_e/q_e = C_e/q_m + 1/K_L q_m$

Where q_e is the amount of solute adsorbed per unit weight of adsorbent at equilibrium (mg/g).C_e is the equilibrium concentration of the solute in the bulk solution (mg/l), q_m the maximum monolayer adsorption capacity (mg/g) of azophloxine, K_L is the constant related with the free energy of adsorption (l/mg).

4.6.3 Temkin Isotherm

Temkin isotherm assumes that (i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbate–adsorbent interactions and (ii) adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. The Temkin isotherm is represented by following equation:

$$q_e = RT/b \ \ln(K_T C_e)$$

Or

$$q_e = B_1 \ln K_T + B_1 \ln C_e$$

Where $B_1 = RT/b$, b is the tempkin energy constant (j/mole), K_T that explicity takes into account the interaction between adsorbing species and the adsorbent [Lataye et al., 2007].

4.7 KINETIC AND DIFFUSION STUDIES

4.7.1 Pseudo first order

The pseudo first order, proposed by Lagergren (1898) for adsorption analysis, is expressed in the form

$$dq_t/dt = K_f(q_e - q_t)$$

Where q_t is the amount of adsorbate adsorbed at time t (mg g^{-1}), q_e the adsorption capacity at equilibrium (mg g^{-1}), k_f the pseudo-first-order rate constant (min^{-1}) and t is the contact time (min) [Lin et al., 2007]. The integration of above equation with the initial condition, $q_t = 0$ at $t = 0$ leads to:

$$\log(q_e - q_t) = \log q_e - k_f t/2.303$$

The values of adsorption rate constant (k_f) for azophloxine adsorption on BFA, RHA are determined from the plot of log ($q_e - q_t$) against t.

4.7.2 Pseudo second order

The pseudo -second- order model is represented as [Mane et al., 2006]:

$dq_t/dt = K_S (q_e - q_t)^2$

where K_S is the pseudo-second-order rate constant (g/mg min).Integrating above equation and noting that $q_t=0$ at $t=0$, the following equation is obtained:

$q_t = t K_S q_e^2 / (1 + t K_s q_e)$

The initial sorption rate, h (mg/g min), at t =0 is defined as: $h = K_S q_e^2$

4.7.3 Bangham Equation

Bangham's equation is given as:

$\log(\log(C_o/C_o - q_t m)) = \log(k_o m / 2.303V) + \alpha \log(t)$

Where V is the volume of the solution (ml), and α (<1) and k_0 are constants.

4.7.4 Intra-particle diffusion study

The adsorbate transport from the solution phase to the surface of the adsorbent particles occurs in several steps. The overall adsorption process may be controlled by one or more either steps, e.g. film or external diffusion, pore diffusion, surface diffusion and adsorption on the pore surface, or a combination of more than one-step [Srivastava et al., 2005]. The possibility of intra-particle diffusion resistance affecting adsorption was explored by using the intra-particle diffusion model as:

$q_t = K_{id} t^{1/2} + I$

Where k_{id} is the intra-particle diffusion rate constant.

4.8 THE SUM OF SQUARE OF ERRORS (SSE)

This most commonly used error function has one major drawback. The function will result in the calculated isotherm parameters providing a better fit at the highest end of liquid phase concentration range. This is because the magnitude of the errors and hence the square of errors will increase as concentration increases.

$$SSE = \sum_{i=1}^{n} (q_{e,cal} - q_{e,meas})_i^2$$

4.9 POINT OF ZERO CHARGE

The point of zero charge of the RHA and BFA was determined by the solid addition method. To a series of 100 ml conical flasks 45 ml of KNO_3 solution of known strength was transferred. The pH_0 values of the solution were roughly adjusted from 2 to 12 by adding either 0.1N HNO_3 or NaOH. The total volume of the solution in each flask was made exactly to 50 ml by adding the KNO_3 solution of the same strength. The pH_0 of the solutions were then accurately noted. One gram of RHA of BFA was added to each flask, which were securely capped immediately. The suspensions were then manually shaken and allowed to equilibrate for 48 h with intermittent manual shaking. The pH values of the supernatant liquid were noted. The difference between the initial and final pH (pH_f) values ($\Delta pH = pH_0 - pH_f$) was plotted against the pH_0. The point of intersection of the resulting curve at which $\Delta pH=0$ gave the the value of point of zero charge. The procedure was repeated for different concentrations of KNO_3.

CHAPTER 5

RESULT AND DISCUSSIONS

Detailed discussion of the experimented results is given in this chapter:

5.1 CHARACTERIZATION OF BFA AND RHA

Characterization includes determination of surface area, bulk density etc.

5.1.1 Bulk density

The bulk density of BFA and RHA was found to be 446 and 300 kg/m^3.

5.1.2 Surface area

The BET surface area of BFA and RHA has been found to be 180 and 139 m^2/g.

5.1.3 FTIR

The FTIR spectrum for blank and azophloxine loaded BFA and RHA are shown in Figures 5.1-5.4. For RHA figure, shows that typical peaks are observed at 3474 cm^{-1}, 2819 cm^{-1}, 1563 cm^{-1},1353 cm^{-1} and 564 cm^{-1}. The region from 2800-3500 cm^{-1} corresponds to the presence of free oxygen and hydrogen bonded -OH group, silicon hydroxide group. Peak around 1600 cm^{-1} indicates the presence of aldehyde and ketone group. Peak at 1353 cm^{-1} indicates the presence of methyl group. Peaks in the region 500-800 cm^{-1} indicates the presence of -SiH. In case of loaded RHA, there is a slight shift in the peaks. The shifting occurs both at higher and lower wave numbers this increase signifies decrease in the amount of functional group at this wave number, indicating the participation of this functional group during the sorption process [Lakshmi et al., 2008].

For BFA characteristic peaks are observed at 3468 cm^{-1}, 1592 cm^{-1}, 1383 cm^{-1},759 cm^{-1} and 594 cm^{-1}. The peaks are mainly due to -NH, -CN and -OH stretching. The peak at 3468 cm^{-1} signifies the OH stretching in primary, secondary or tertiary alcohol. The region from 2800-3500 cm^{-1} corresponds to the presence of free oxygen and hydrogen bonded -OH group, silicon hydroxide group. Peak at 1383 cm^{-1} indicates the presence of methyl group. Peaks in the region 500-800 cm^{-1} indicates the presence of -SiH. In case of loaded BFA there is some shift in the peaks this must be due to the -CO, -CHO, -OH, -SiH and -SiOH groups that are effective in adsorption.

5.1.4 XRD

The d-spacing values obtained from the X-ray spectra of RHA reflects the presence of cristobalite (SiO_2), margaritasite ($(Cs,K,H_3O)_2(UO_2)_2V_2O_8$), macedonite ($PbTiO_3$) and on the other hand for BFA it reflects the presence of alumina (Al_2O_3), Silica (SiO_2), CaO and $Ca_8Si_5O_{18}$.

5.1.5 TGA

The TGA analysis for blank and loaded BFA and RHA was done and the results are shown in Fig 5.5 and Fig 5.6. For blank RHA about 10% weight loss takes place between 25-300°C. The maximum weight loss takes place between 400-500 °C nearly 27%. This may be due to the oxidation of silica and decomposition of carbon to various components. A strong exothermic reaction takes place at temperature of 462°C. Generally, when the carbonaceous compounds are heated at higher temperatures, the surface groups decompose, producing CO (200–600°C), CO_2 (450–1000 °C), water vapour and free hydrogen (500–1000°C) [Mall et al., 2006]. Therefore, the weight loss in second oxidation zone may be due to the evolution of CO_2 and CO. A third oxidation zone with weight loss <1% can be envisaged at higher temperatures up to 1000°C. At 472°C maximum weight loss takes place per unit time. For loaded RHA the maximum weigh loss takes place between 400-575°C, this must be due to the adsorption of azophloxine dye which must have changed the properties of silica and carbon present in the RHA. The exothermic reaction takes place at 502°C. The maximum weight loss per unit time takes place at 500 °C.

The blank BFA sample nearly 14% weight loss takes between 20-400°C.The maximum weight loss nearly 66.6% takes place between 400-537°C, this must be due to the oxidation or decomposition of silica, alumina and magnesium compounds. A strong exothermic reaction takes place at 493°C.The maximum weight loss per unit time is found at 488°C. In loaded BFA maximum 15% weight loss takes place between 25-400°C. In between 400-600°C nearly 72% weight loss takes place. This must be due to the change in the properties of silica, alumina and magnesium compounds due to adsorption of azophloxine dye. The exothermic reaction takes place at 530°C. The maximum weight loss per unit time takes place at 549°C.

5.1.6 Point of zero charge: Point of zero charge for RHA and BFA was found to be at pH values of 8.43 and 8.88. The pKa value of azophloxine dye was found to be 4.3.

5.2 BATCH EXPERIMENTAL STUDY

The effect of various parameters such as pH, concentration, dye concentration, adsorbent dose, and temperature is shown below:

5.2.1 Effect of pH

The pH of the solution affects the surface charge of the adsorbents as well as the degree of ionization of the materials present in the solution. The hydrogen ion and hydroxyl ions are adsorbed quite strongly, and therefore, the adsorption of other ions is affected by the pH of the solution. The change of pH affects the adsorptive process through dissociation of functional groups on the active sites of the adsorbent. This subsequently leads to a shift in reaction kinetics and equilibrium characteristics of the adsorption process.

It is a common observation that the surface adsorbs anions favourably at lower pH due to presence of H^+ ions, whereas, the surface is active for the adsorption of cations at higher pH due to the deposition of OH^- ions. pH is, also, known to affect the structural stability of azophloxine, and therefore, its colour intensity. Hence, the effect of pH was studied with blank solutions of azophloxine of concentration 100 mg/l having natural $pH_0=6$ for 300 minutes. Azophloxine breaks at lower pH and forms negative anion. Consequently, the dye molecule has high negative charge density at lower pH. Therefore, at pH below 6 electrostatic attraction exists between the positively charged surface and the negatively charged dye molecule. This illustrates as to why adsorption increases with decrease in pH as shown in figure 5.7 and 5.8. From experiment, it has been found that the maximum removal efficiencies for both BFA and RHA is found maximum at normal pH ($pH_0=6$).

5.2.2 Effect of adsorbent dosage (m)

The effect of m on the removal of azophloxine by BFA and RHA at $C_0=100$ mg/l, pH 6 and T=30°C is shown in Fig. 5.9 and fig 5.10. It is observed that the azophloxine removal increases up to a certain limit and then it remains almost constant. An increase in the adsorption with the adsorbent dosage can be attributed to greater surface area and the availability of more adsorption sites. For BFA at m<10 g/l, the adsorbent surface becomes saturated and the residual concentration in the solution is large. With increase in the m, the azophloxine removal increases due to increased azophloxine uptake by the increased amount of adsorbent as shown in figure 5.9. At m>20 g/l, the incremental azophloxine removal becomes very low, as the surface azophloxine concentration and the solution azophloxine concentration come to equilibrium with each other. At about m=25g/l, the removal efficiency becomes almost constant. The above process also takes place in case of RHA only the concentration varies.

5.2.3 Effect of initial dye concentration (C_0)

The effect of C_0 on the removal of azophloxine by adsorbents BFA and RHA is shown in Fig 5.11 and Fig 5.12. The effect was analysed at given conditions, For BFA: $pH_0 = 6$, m=20 g/l, T=30°C; For RHA: $pH_0 = 6$, m=25g/l and T=30°C. From the figure, it is evident that the percent azophloxine removal decreased with the increase in C_0, although, amount of azophloxine adsorbed per unit mass of adsorbent (q_e) increased with the increase in C_0. The q_e increased with the increase in C_0 as the resistance to the uptake of azophloxine from the solution decreases with the increase in azophloxine concentration. The rate of adsorption also increases with the increase in C_0 due to increase in the driving force.

5.2.4 Effect of contact time (t)

The contact time between the pollutant and the adsorbent is of significant importance in the wastewater treatment by adsorption. A rapid uptake of pollutants and establishment of equilibrium in a short period signifies the efficiency of that adsorbent for its use in wastewater treatment. In physical adsorption most of the adsorbate species are adsorbed within a short interval of contact time. However, strong chemical binding of adsorbate with adsorbent requires a longer contact time for attainment of equilibrium. Available adsorption studies for both BFA and RHA reveals that the uptake of adsorbate is fast at the initial stages of the contact period, and thereafter, it becomes slower near the equilibrium as shown in Fig 5.13 and 5.14. This is due to the fact that a large number of vacant sites are available for adsorption during initial stage, and after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive force between the solute molecules on solid and bulk phases. For BFA the $pH_0 = 6$ and m=20 g/l and for RHA the $pH_0 = 6$ and m=25 g/l.

5.2.5 Effect of temperature

The effect of change of temperature has been analysed with respect to the percentage removal of azophloxine. The other parameters are for BFA the $pH_0 = 6$ and m=20 g/l and for RHA the $pH_0 = 6$ and m=25g/l. Graph clearly shows that with an increase in temperature the value of percentage removal of azophloxine increases as shown in Fig 5.15 and Fig 5.16. In general, an increase in temperature is followed by an increase in diffusivity of dye ion, and consequently by an increase in the adsorption rate if diffusion is the rate controlling step.

5.3 ADSORPTION ISOTHERM STUDY

Experiments are conducted on azophloxine dye solution where it is treated with both BFA and RHA at a constant temperature, optimised value of pH and adsorbent dose. The adsorption equilibrium data for azophloxine on to BFA and RHA are analysed by linear curve fitting analysis using Microsoft Office Excel. Various values of q_e is calculated using the various isotherm models. The values of parameters for all the three isotherms are given in Table 5.1. The mono-component Langmuir constant, q_m is the monolayer saturation at equilibrium. Wide variation is seen in the q_m values. Since the adsorbate concentration range (50-250 mg/l) are taken in the present study the q_m values are small as compared to other dye systems. This is due to the fact that unit adsorption per gram of adsorbent is higher in the higher dye concentration range and lower in lower dye concentration range. While removal is higher for lower concentration adsorbate solution and lower for higher adsorbate solution. A high K_L value indicates a higher affinity. The obtained data given in table 5 also indicate that the amount of azophloxine adsorbed on BFA to form a complete monolayer on the surface is higher than RHA.

K_F and 1/n, the mono-component Freundlich constants are indicators of adsorption capacity and adsorption intensity, respectively. Higher the value of 1/n, higher will be the slope expressed by 1/n and thus higher the affinity. Moreover, closer the 1/n value of Freundlich is to 0 the less heterogeneous is the system. The data obtained in this study (Table 5.1) indicated that the BFA represents more heterogeneous surface for azophloxine. Table 5.1 also showed that $1/n<1$, indicating that all the adsorbents favourably adsorbed azophloxine at pH 6. The magnitude of K_F also showed the higher uptake of azophloxine by BFA than RHA. As seen, Langmuir isotherm fits better to the experimental data than other isotherms for azophloxine adsorption on BFA as the value of R^2 is near unity in this case. For adsorption of azophloxine dye by RHA the Freundlich and Langmuir isotherm fits better as the value of R^2 is near unity in both cases. Various isotherm plots are given in figures 5.17-5.22.

5.4 ADSORPTION KINETIC STUDY

Experiments are conducted for the removal of azophloxine dye by both BFA and RHA at optimised conditions of adsorbent dose, pH etc. The values of q_t are calculated using various kinetic models. In selecting the best fit models both the value of correlation coefficient (R^2) and SSE (Sum of square of Errors) have been taken into consideration. The values of various kinetic parameters are shown in table 5.2. The $q_{e,exp}$ and $q_{e,cal}$ values for pseudo-second-order kinetic model are very close to each other. The calculated correlation coefficients are also closer to unity for pseudo-second-order kinetics than that for the pseudo first order kinetic model. Therefore, the sorption can be approximated more approximately by pseudo-second-order kinetic model than the pseudo first order kinetic model. For both BFA and RHA pseudo-second -order is considered as the best fit.

In case of intra-particle diffusion for Weber- Morris plot the value of I gives an idea about the thickness of the boundary layer. The thickness of the boundary layer is more for BFA than for RHA. The deviation of the straight lines from the origin may be due to the difference in the rate of rate of mass transfer during the initial and final stages of adsorption. It also indicates the pore diffusion is not the rate controlling step. The double logarithmic plots are nearly coming linear hence with increase in the contact time the diffusion process increases. For removal of BFA the value of correlation coefficient are nearly same for Bangham equation and Weber Moriss plot, hence both the models can be assumed to describe the intra particle diffusion. For removal of RHA, the value of correlation coefficient is near unity for Bangham equation and can be assumed as suitable fit for intra-particle diffusion study for removal of azophloxine dye. Various kinetic and diffusion plots are shown in figures 5.23-5.28.

Table 5.1 Isotherm parameters for removal of azophloxine dye by different adsorbents

Freundlich constants				
Adsorbent	K_F ((mg g^{-1})(mgl^{-1})$^{-1/n}$)	1/n	R^2	SSE
BFA	.787	.49	.93	2.98
RHA	.166	.83	.990	10.77

Langmuir constants				
Adsorbent	K_L (l mg^{-1})	q_m(mg g^{-1})	R^2	SSE
BFA	.052	8.87	.990	2.58
RHA	.0097	18.14	.995	0.36

Temkin constants				
Adsorbent	K_T (l mg^{-1})	B_l	R^2	SSE
BFA	.847	1.6	.9179	3.68
RHA	.30	2.36	.9347	5.95

Table 5.2 Kinetic parameters for removal of azophloxine dye by different adsorbents

Pseudo first order

Adsorbent	$q_{e,exp}$ (mg g^{-1})	$q_{e,cal}$ (mg g^{-1})	K_f (min^{-1})	R^2
BFA	4.475	3	.0135	.97
RHA	3.5	3.59	.007	.90

Pseudo second order

Adsorbent	$q_{e,exp}$ (mg g^{-1})	$q_{e,cal}$ (mg g^{-1})	h(mg g^{-1} min^{-1})	K_S (g mg^{-1} min^{-1})	R^2
BFA	4.475	4.56	0.4946	.0247	.993
RHA	3.5	3.68	.0624	.0051	.9968

Bangham equation

Adsorbent	K_0 (g)	A	R^2
BFA	2.88	.087	.9622
RHA	1.68	.309	.9404

Intra-particle diffusion

Adsorbent	K_{id} (mg g^{-1} min $^{-1/2}$)	I (mg g^{-1})	R^2
BFA	.07	3	.9638
RHA	.135	1.03	.892

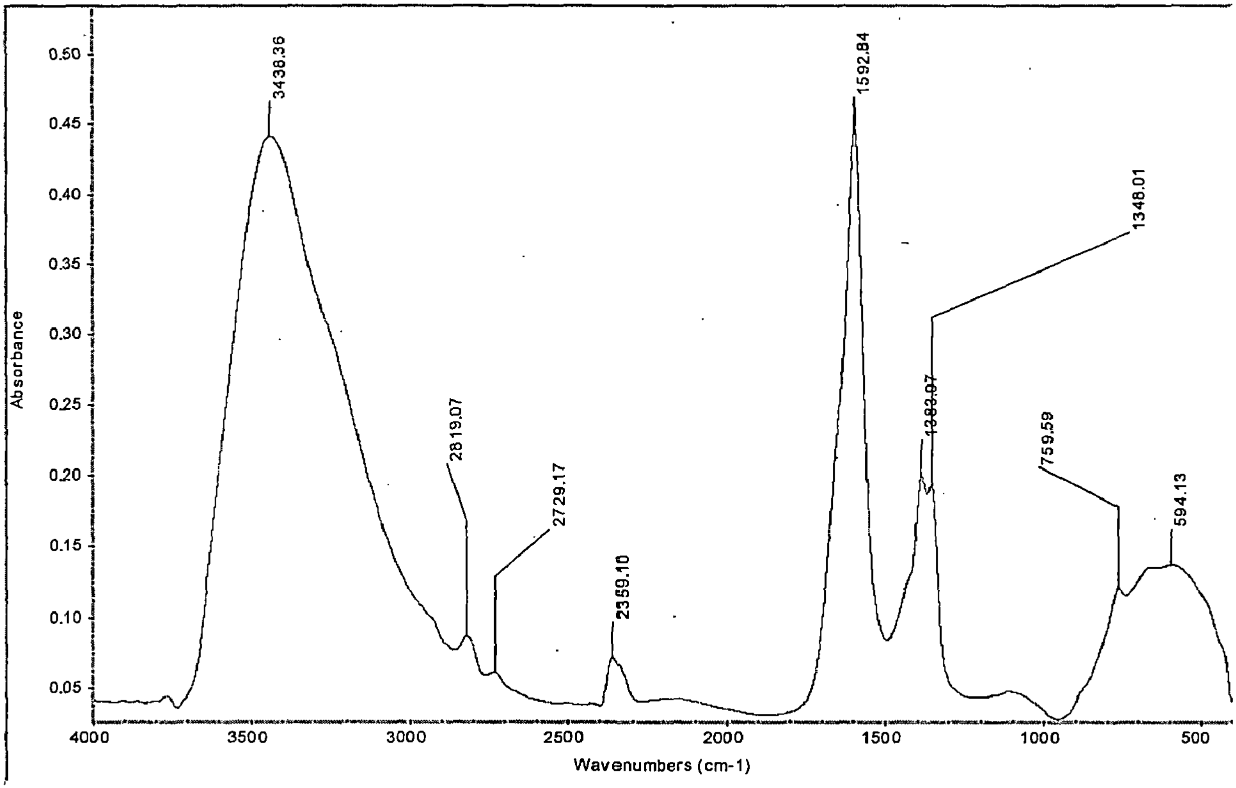


Figure 5.1 - FTIR spectra of BFA before adsorption of azophloxine dye.

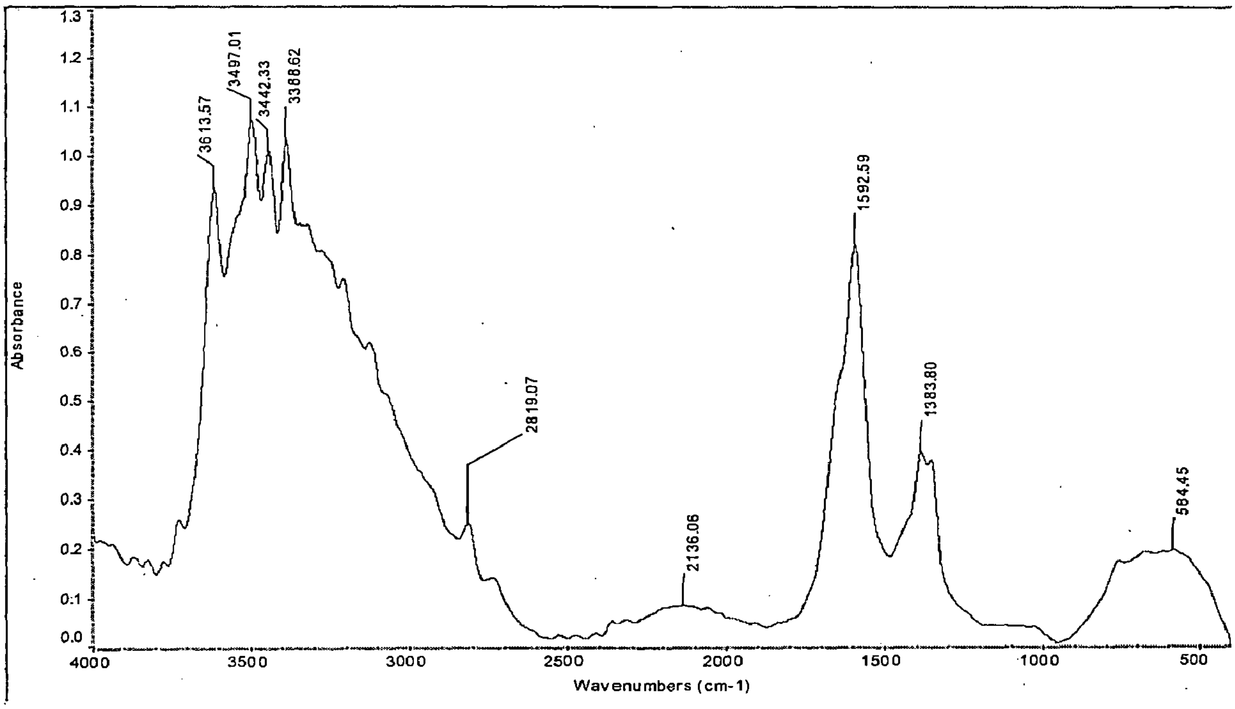


Figure 5.2 FTIR spectra of BFA after adsorption of azophloxine dye.

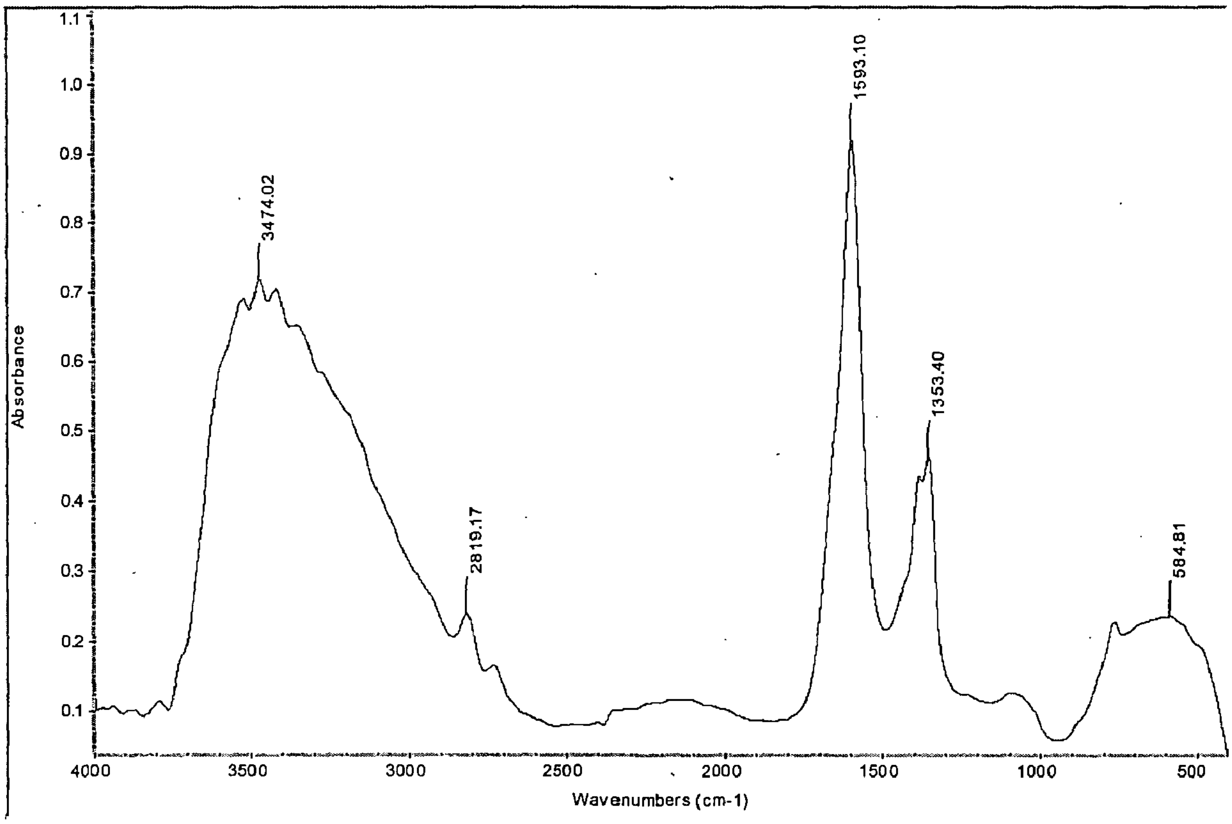


Figure 5.3 FTIR spectra of RHA before adsorption of azophloxine dye.

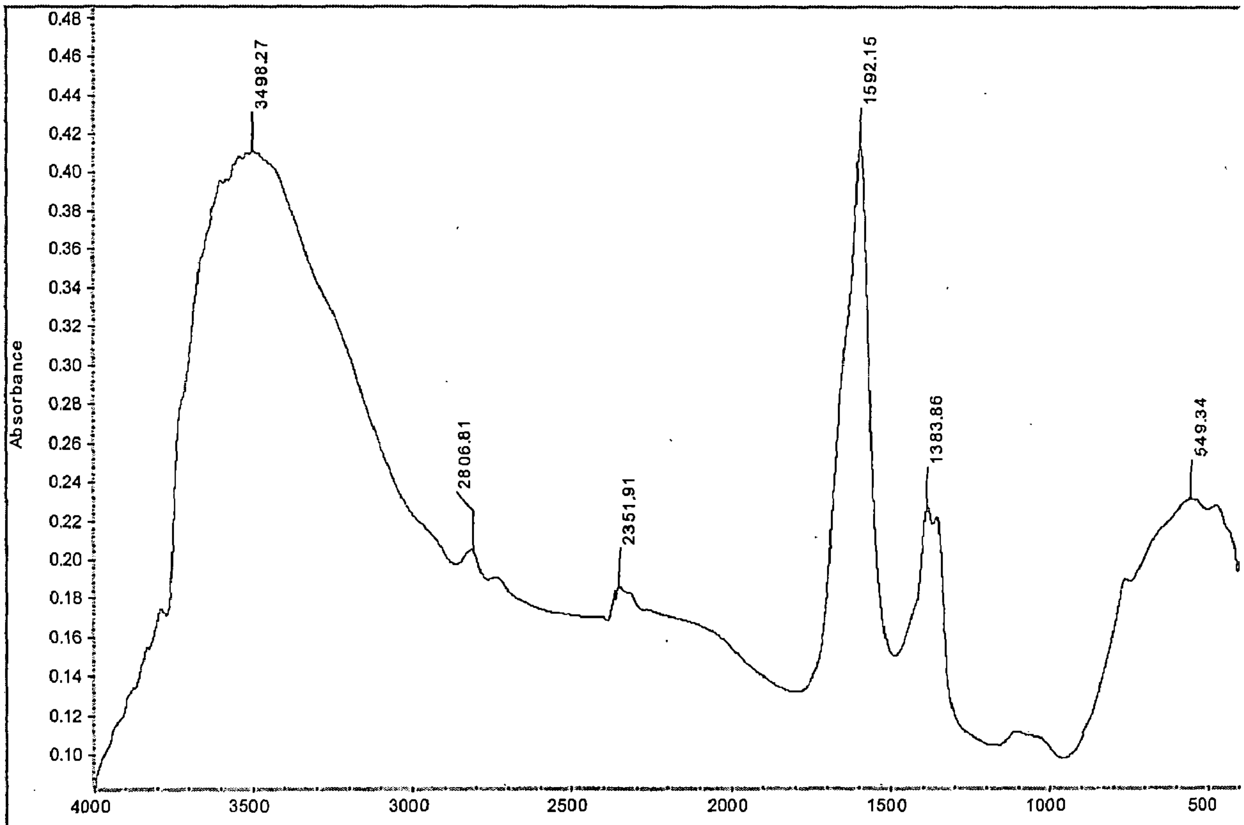
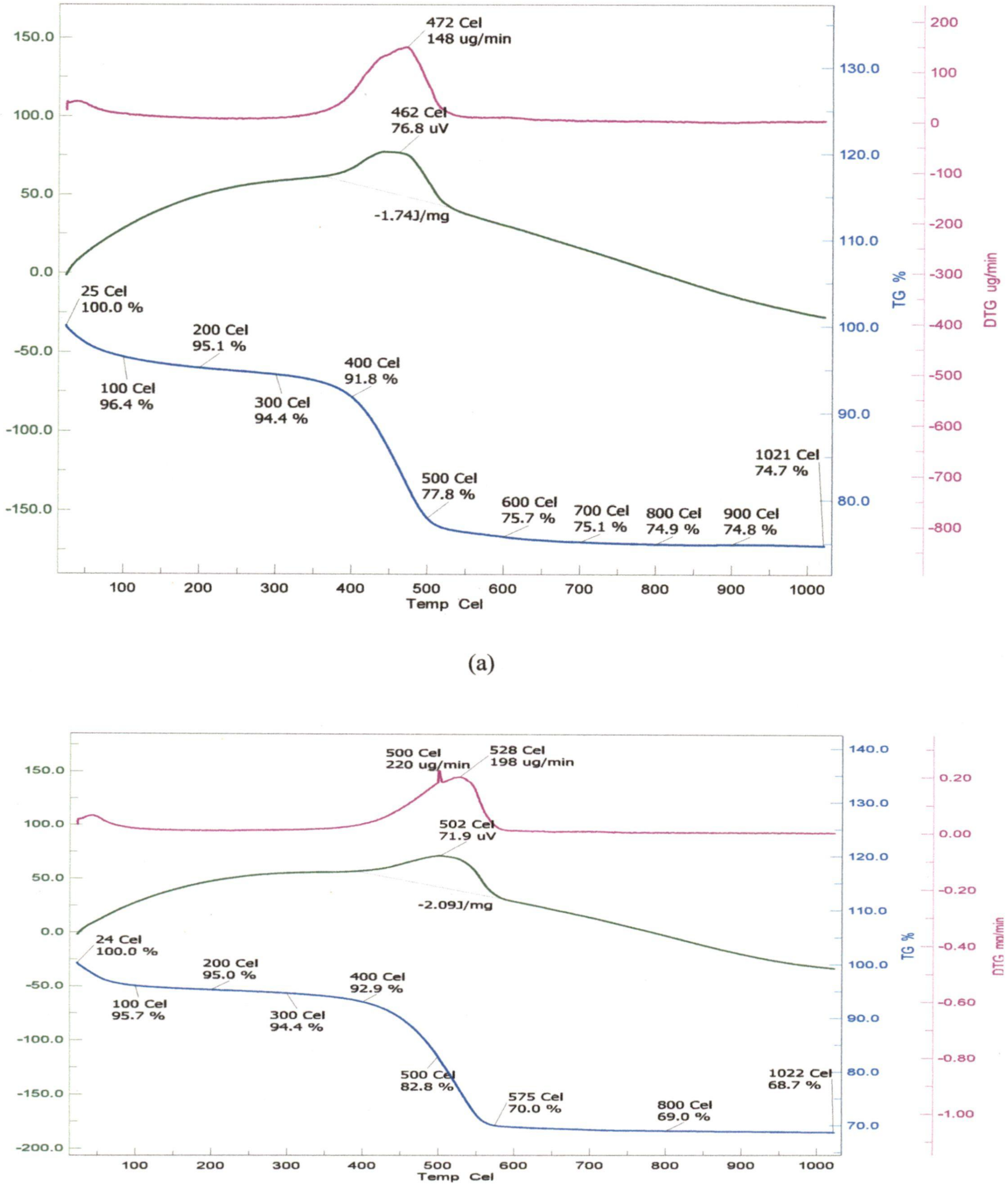


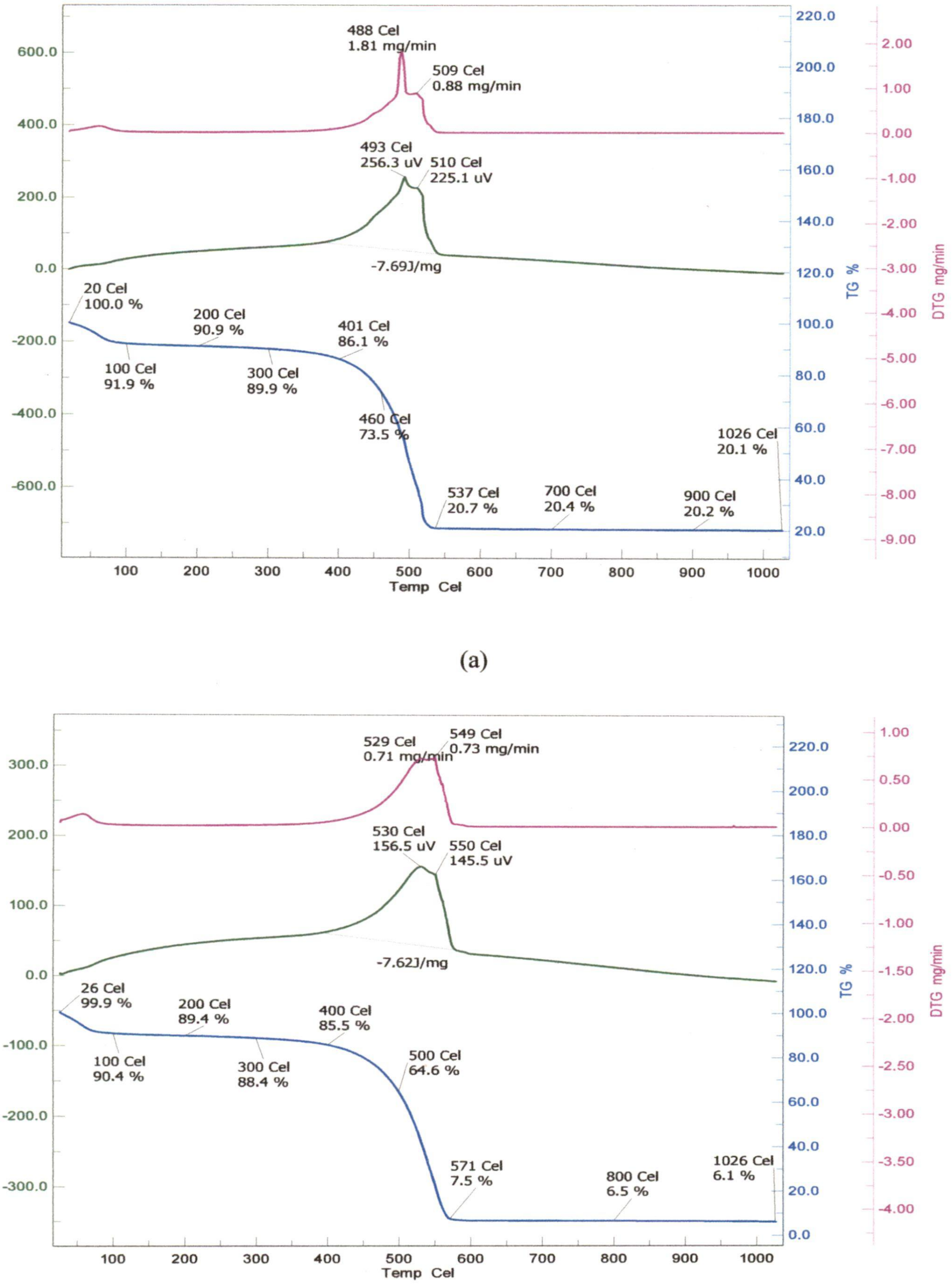
Figure 5.4 FTIR spectra of RHA after adsorption of azophloxine dye.



(a)

(b)

Figure 5.5 TGA-DTA graphs for blank (a) and loaded RHA (b).



(a)

(b)

Figure 5.6 TGA-DTA graphs for blank (a) and loaded BFA (b).

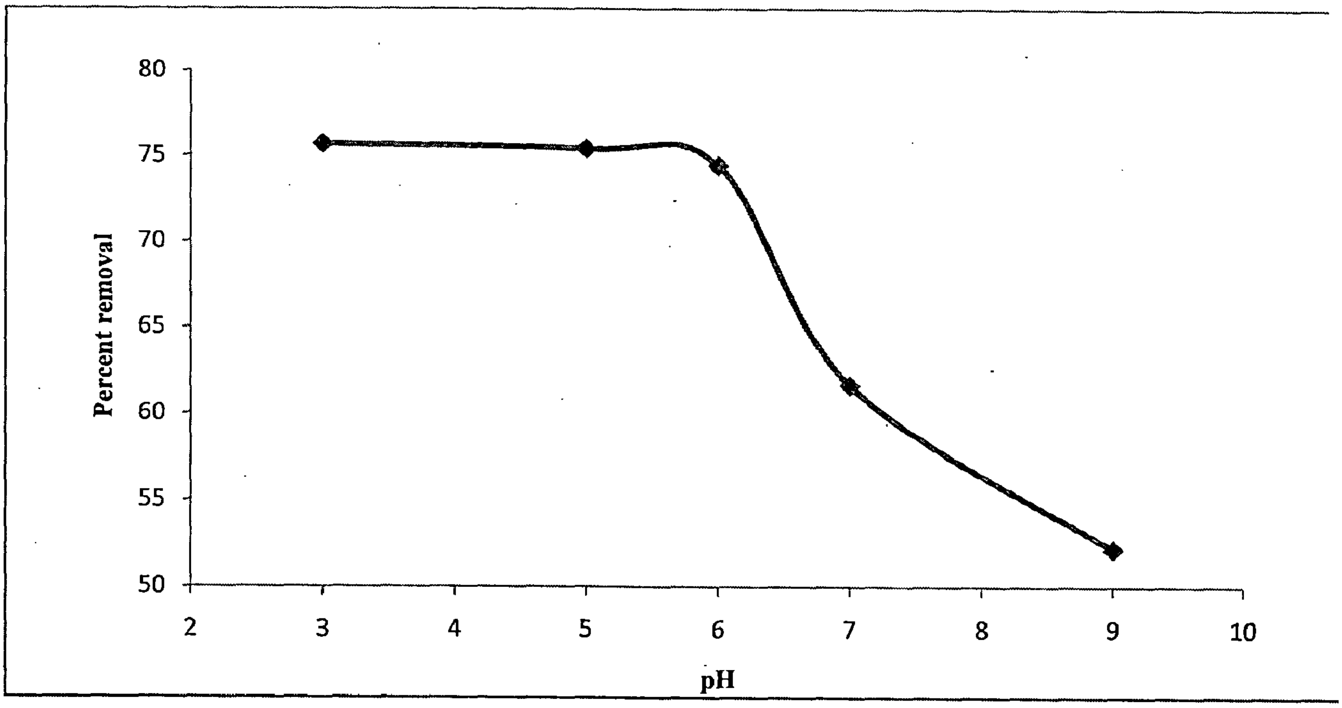


Figure 5.7 Effect of initial pH on adsorption of azophloxine dye by BFA (C_0=100mg/l, m=20g/l, T=30°C).

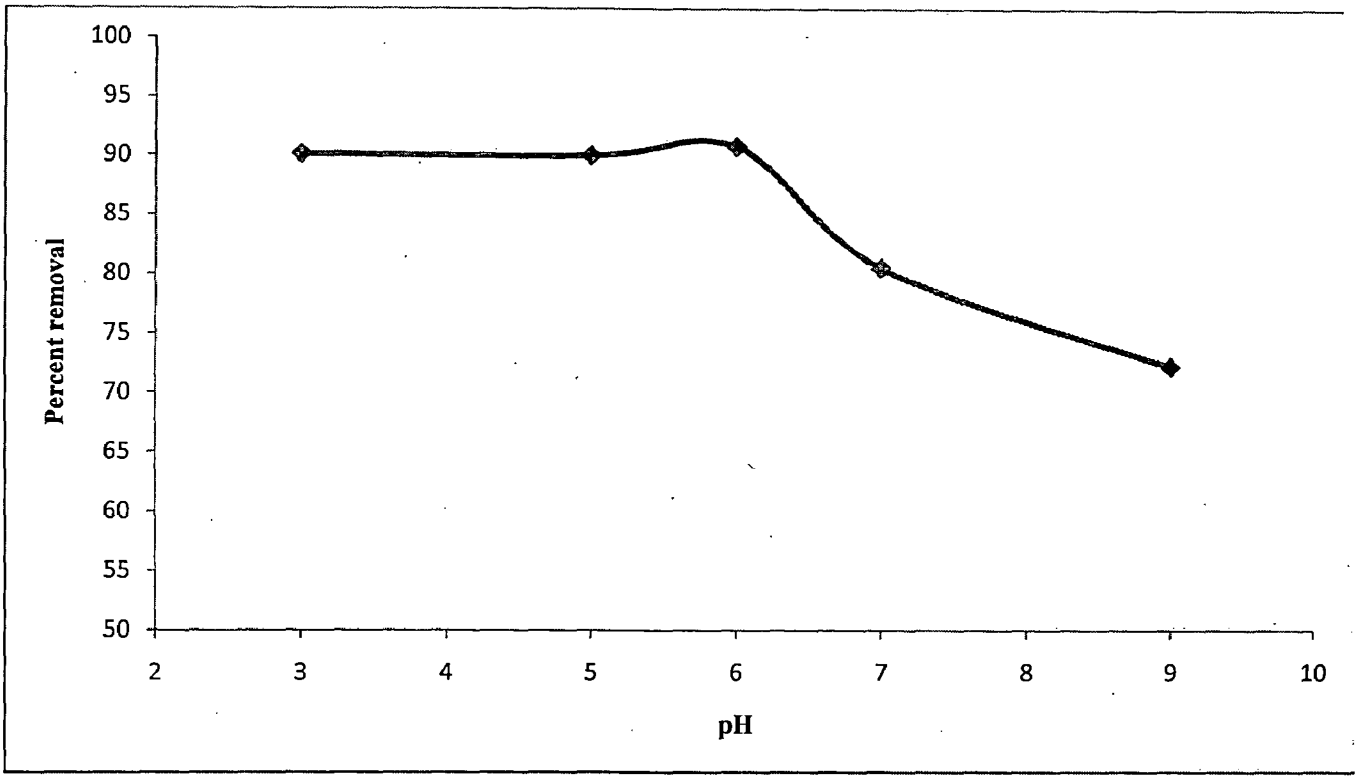


Figure 5.8 Effect of initial pH on adsorption of azophloxine dye by RHA (C_0=100mg/l, m=20g/l, T=30°C).

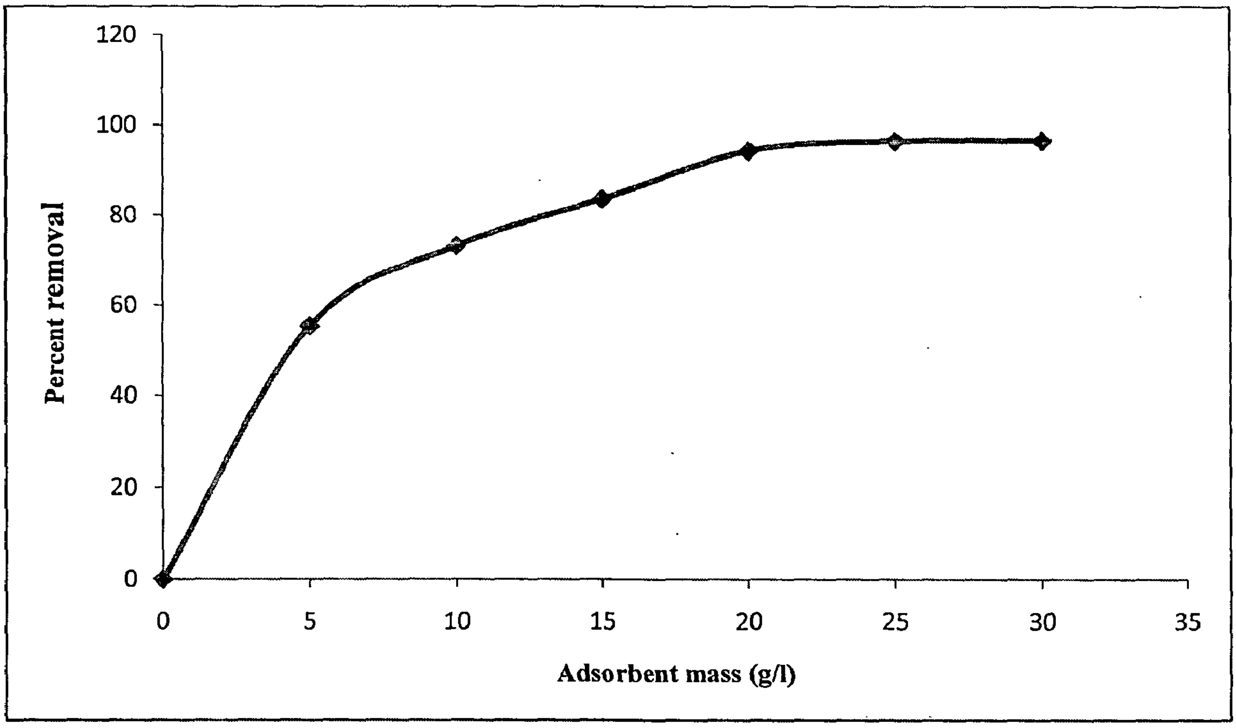


Figure 5.9 Effect of adsorbent dose on adsorption of azophloxine dye by BFA (pH_0=6, C_0=100 mg/l, T=30°C).

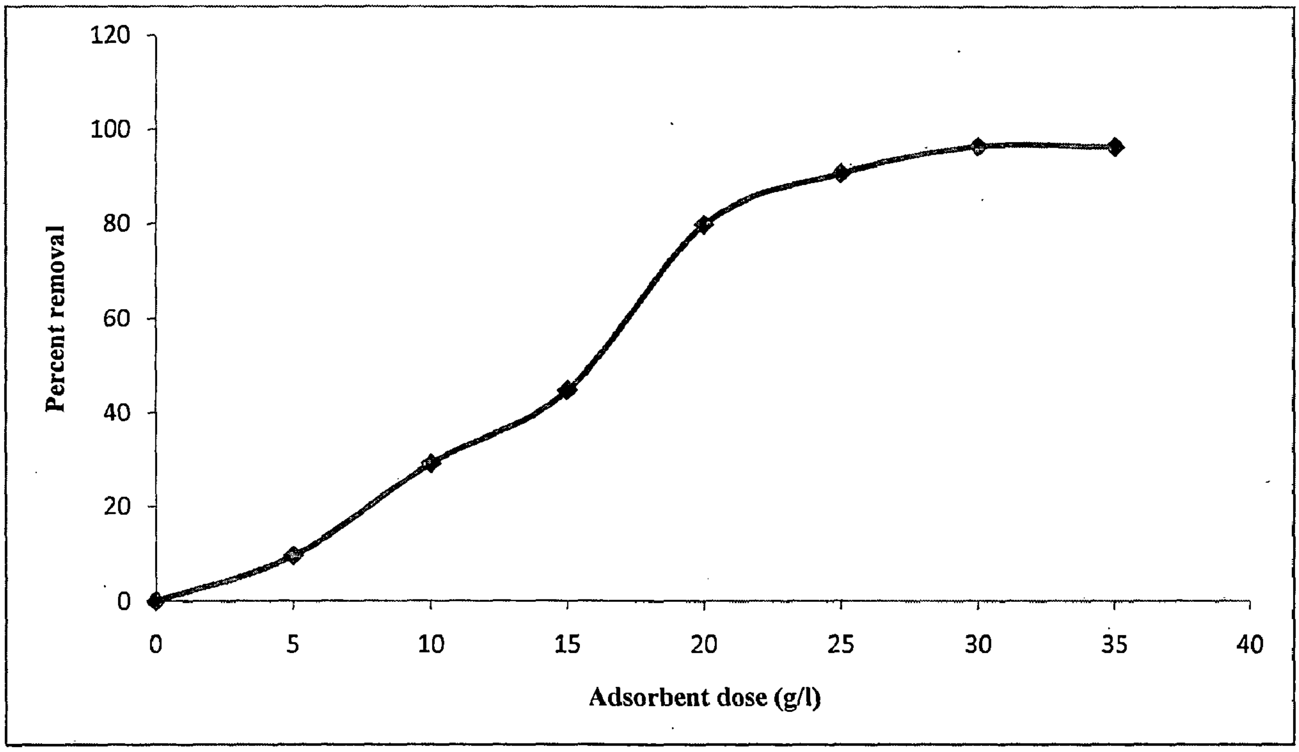


Figure 5.10 Effect of adsorbent dose on adsorption of azophloxine dye by RHA (pH_0=6, C_0=100 mg/l, T=30°C).

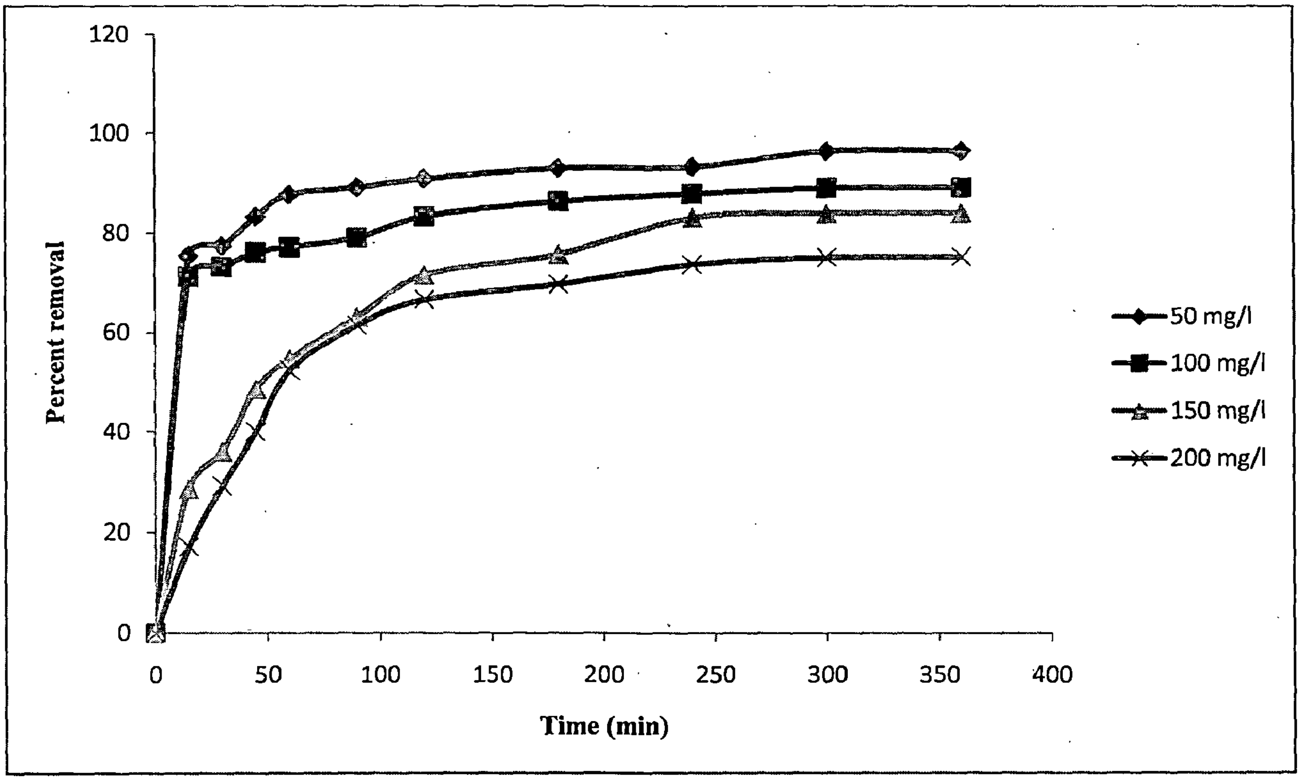


Figure 5.11 Effect of initial dye concentration on adsorption of azophloxine dye by BFA (pH_0=6, m=20 g/l, T=30°C).

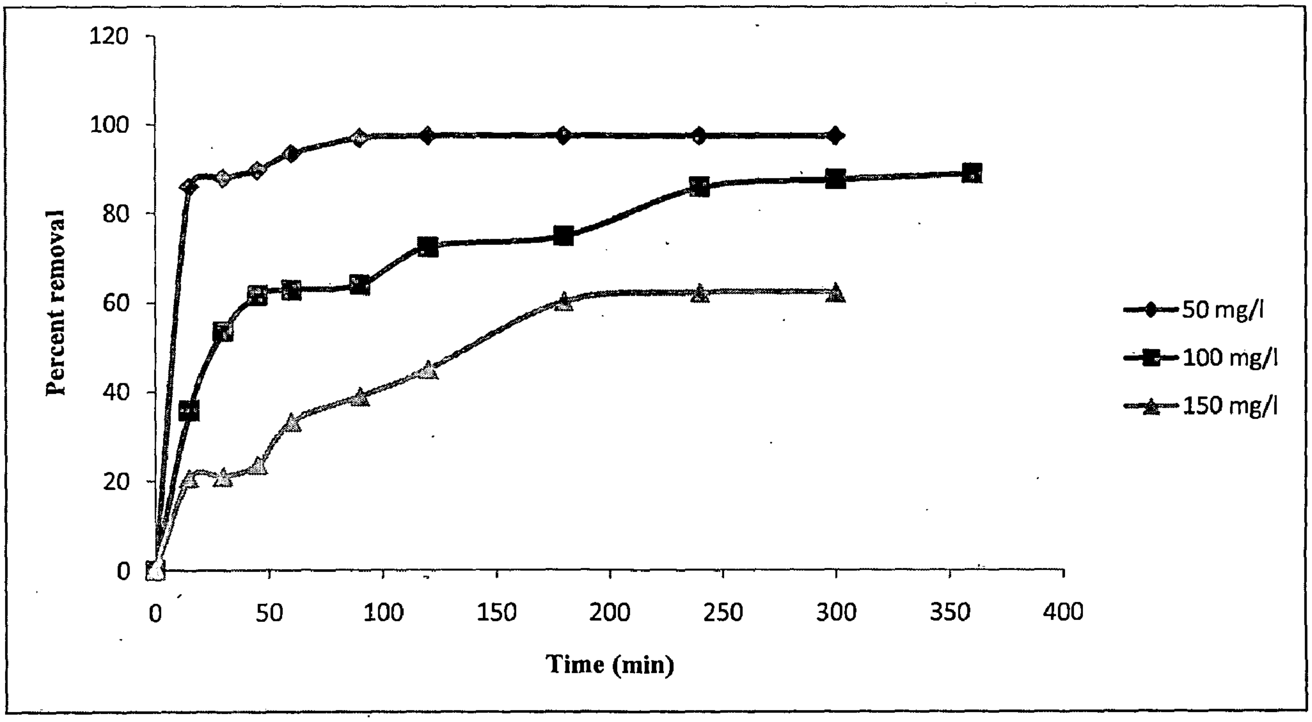


Figure 5.12 Effect of initial dye concentration on adsorption of azophloxine dye by RHA (pH_0=6, m=25 g/l, T=30°C).

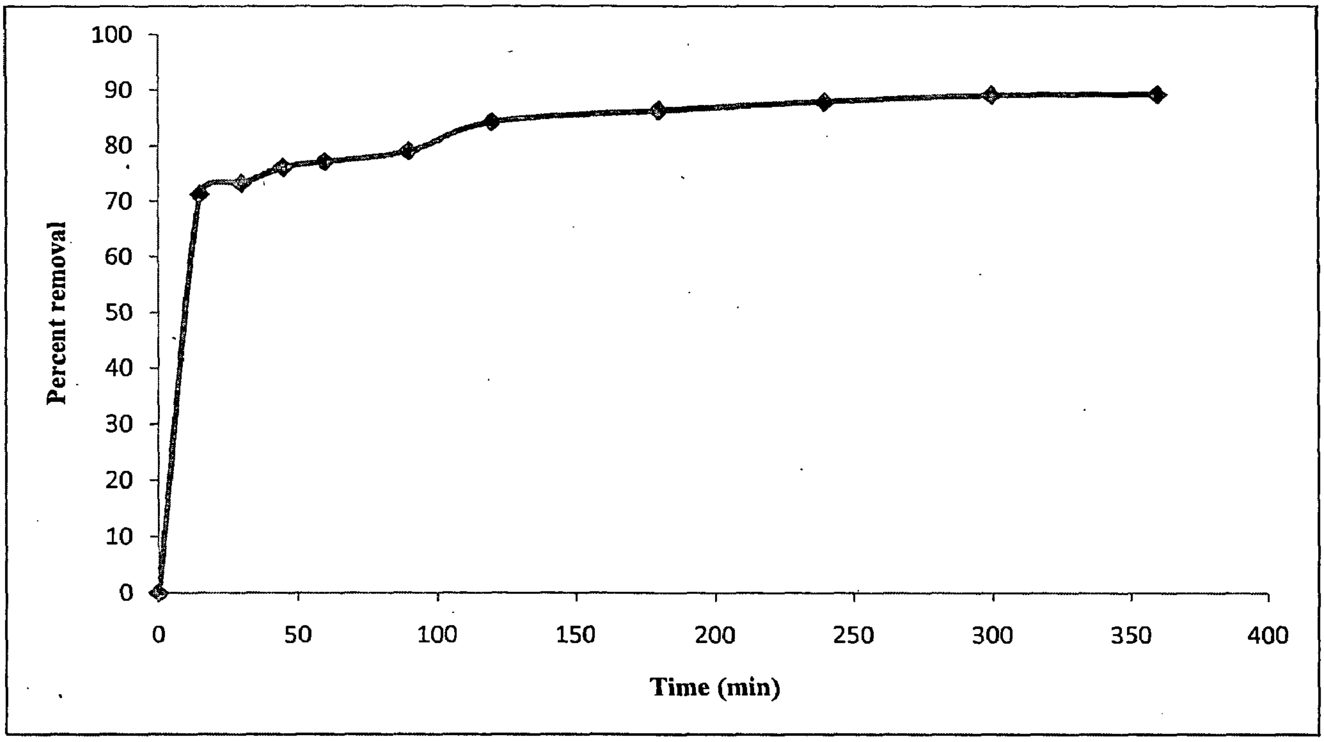


Figure 5.13 Effect of contact time on adsorption of azophloxine dye by BFA (pH_0=6, C_0= 100 mg/l, m=20 g/l, T=30°C).

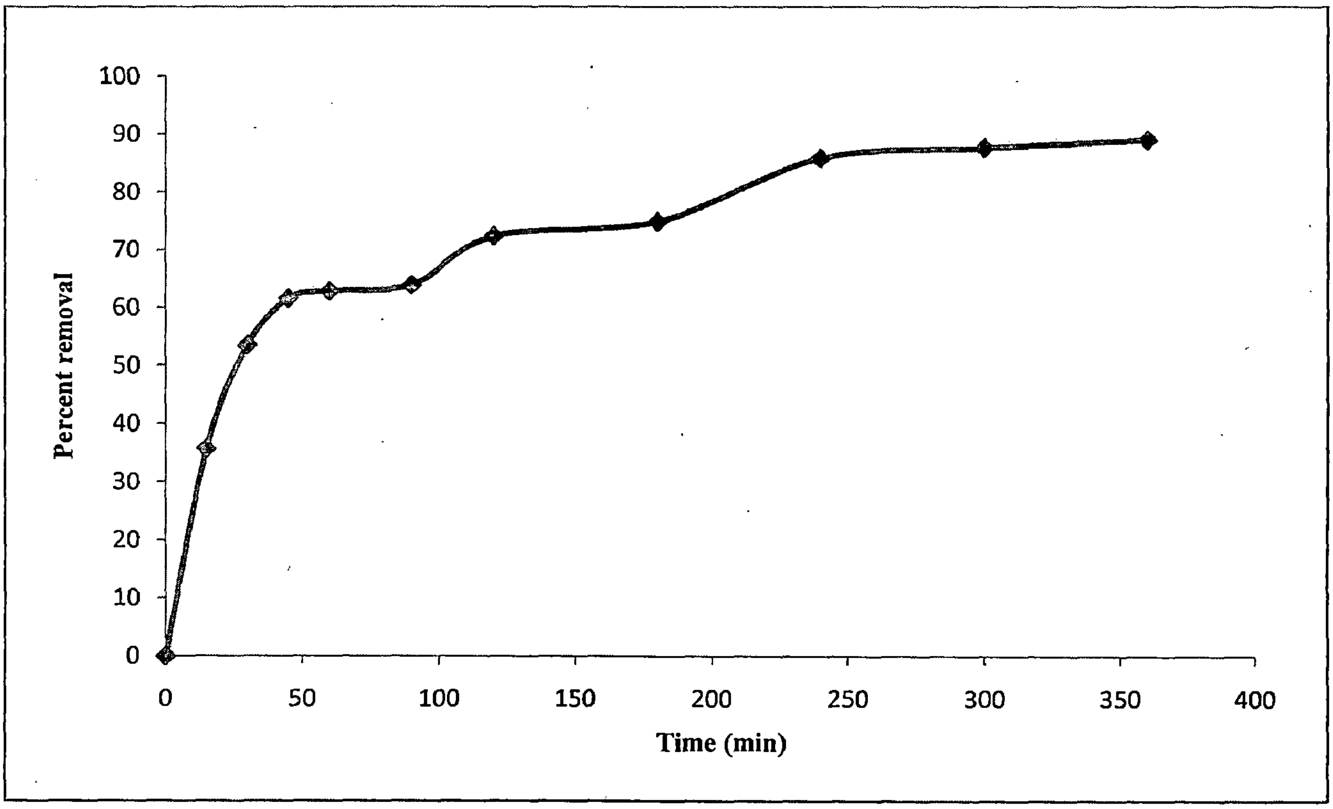


Figure 5.14 Effect of contact time on adsorption of azophloxine dye by RHA (pH_0=6, C_0= 100 mg/l, m=25 g/l, T=30°C).

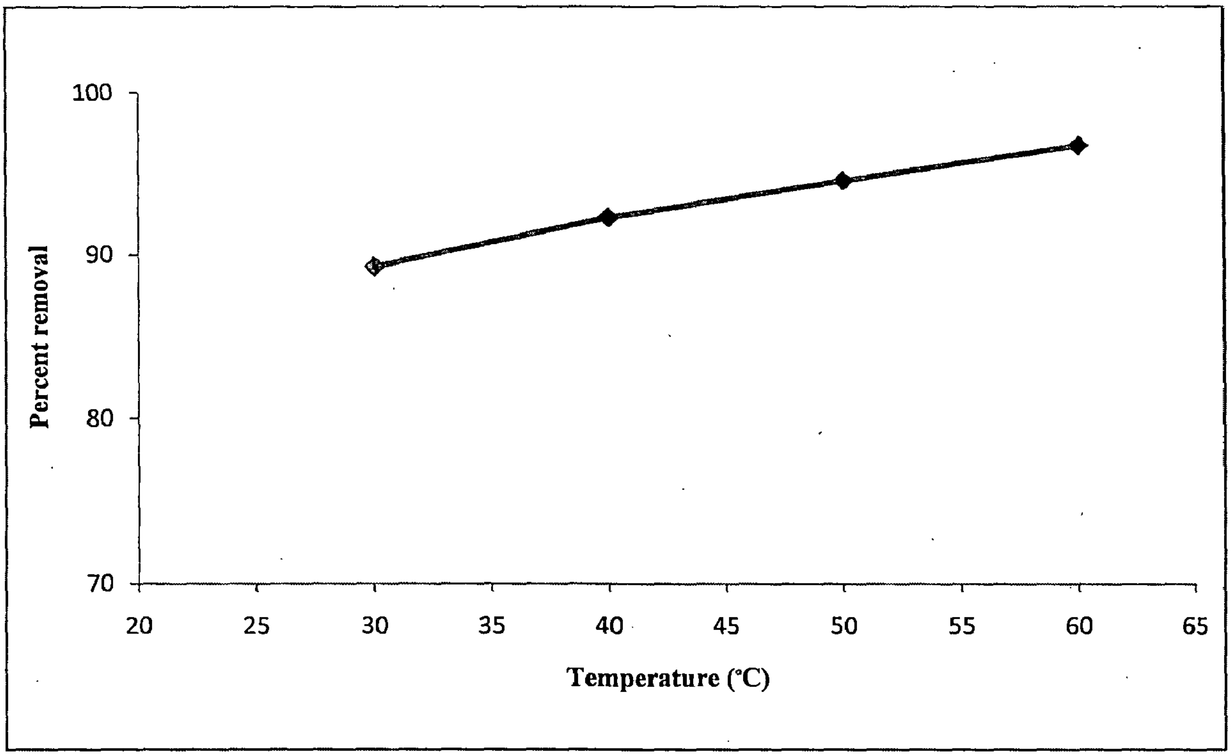


Figure 5.15 Effect of temperature on adsorption of azophloxine dye by BFA (pH_0=6, C_0= 100 mg/l, m=20 g/l, t=300 min).

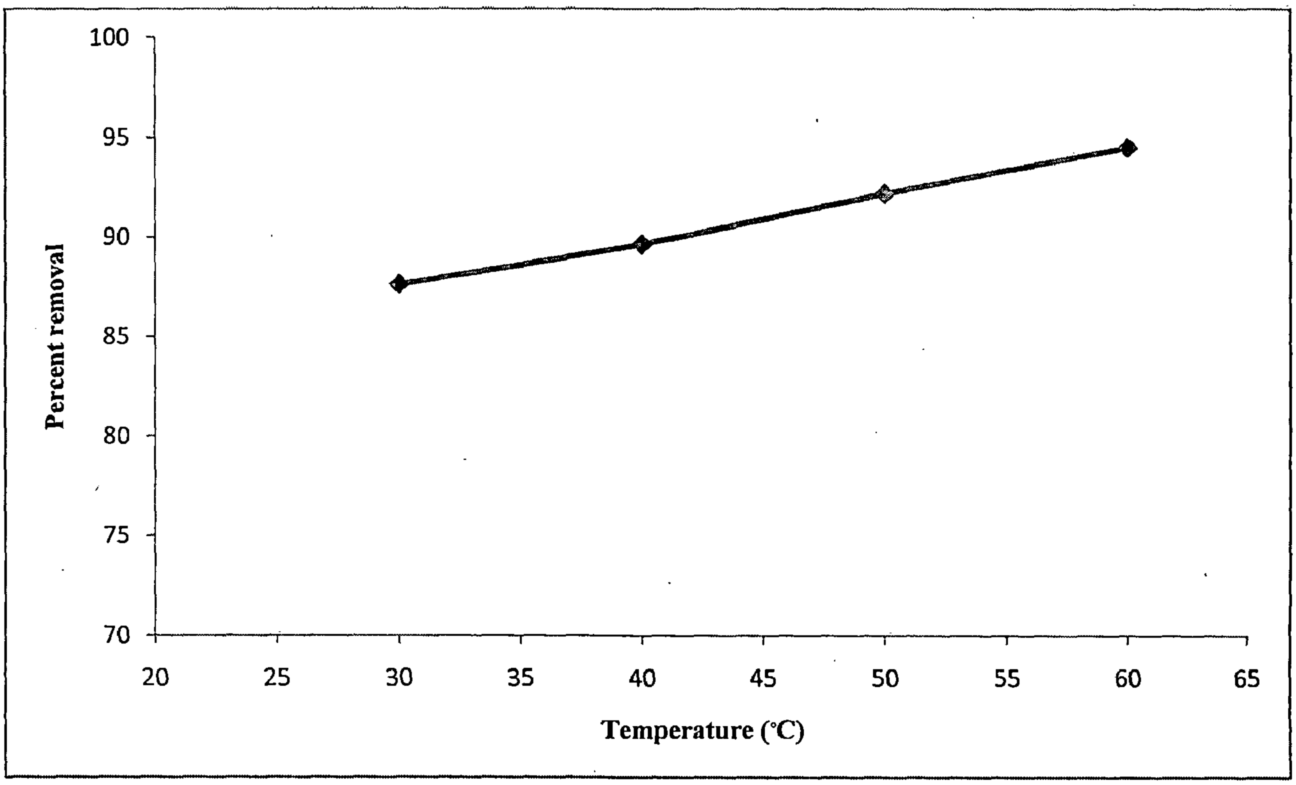


Figure 5.16 Effect of temperature on adsorption of azophloxine dye by RHA (pH_0=6, C_0= 100 mg/l, m=25 g/l, t=300 min).

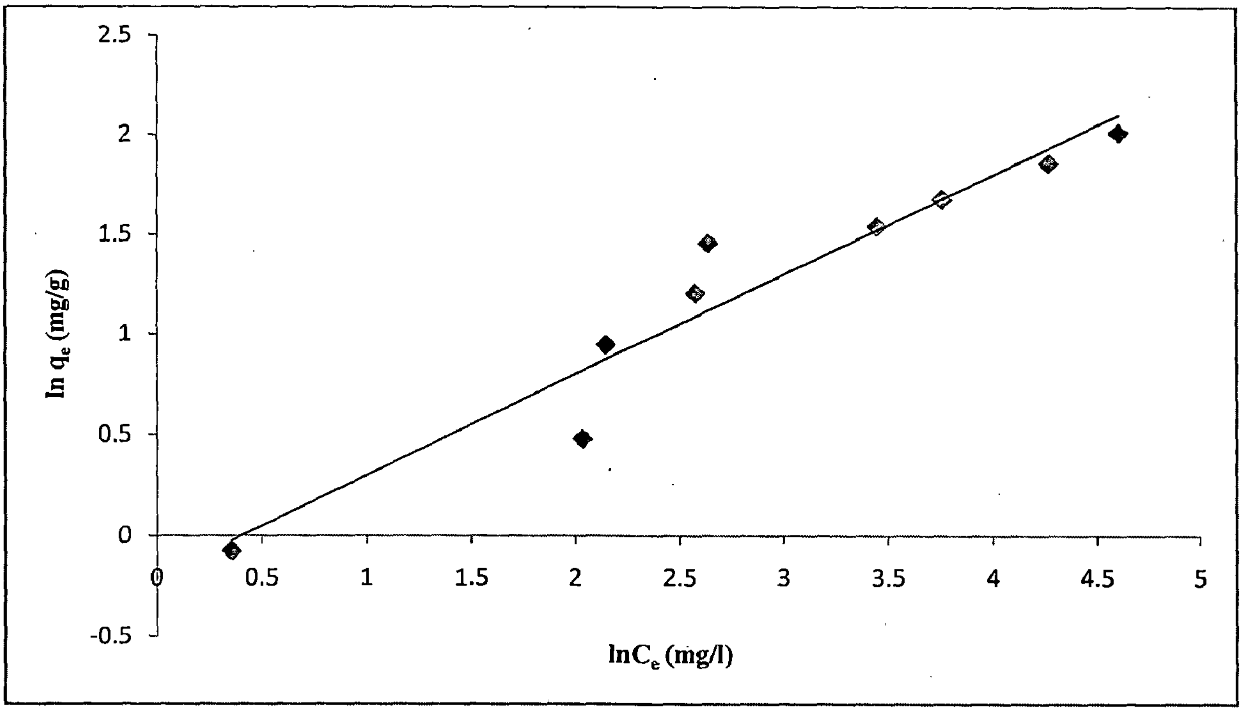


Figure 5.17 Freundlich isotherm for adsorption of azophloxine dye by BFA (pH_0=6, T=30°C, m=20 g/l, t=300 min).

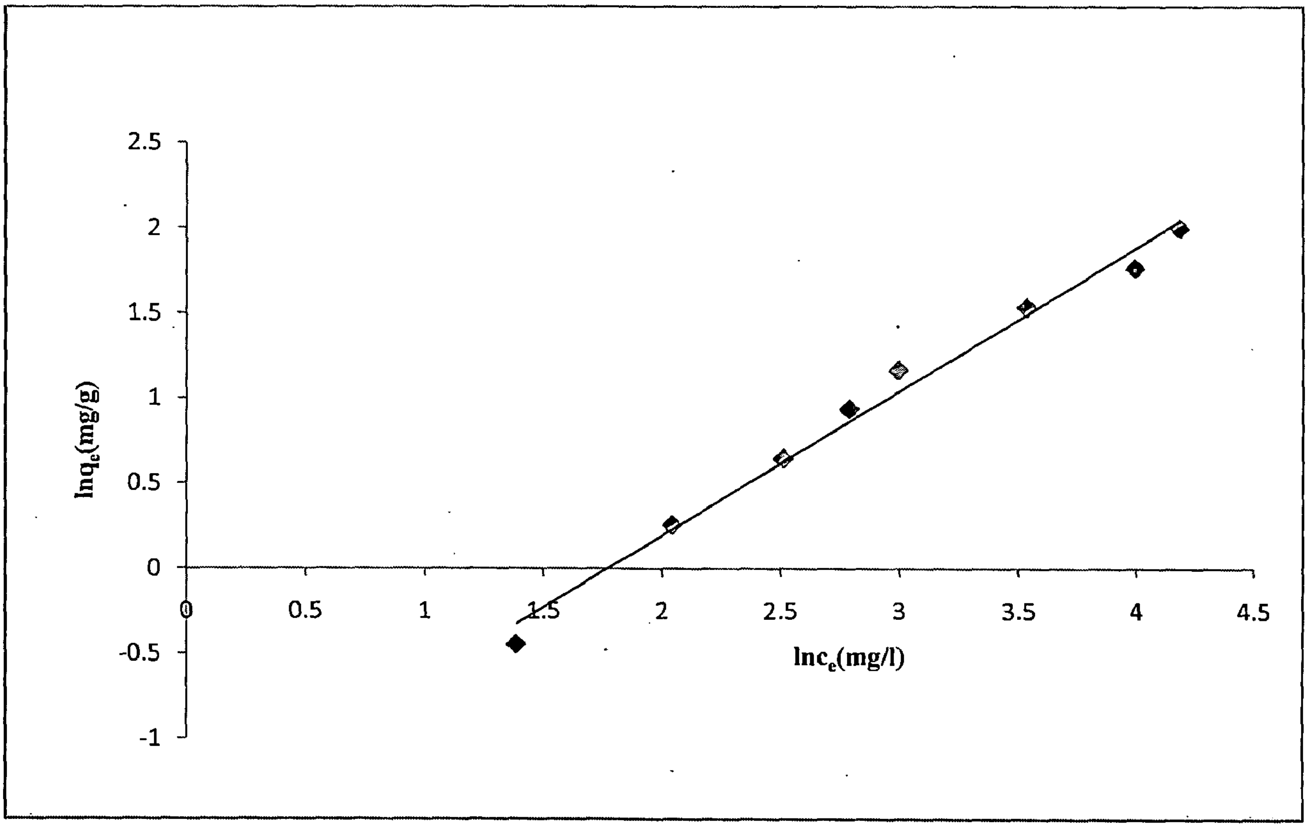


Figure 5.18 Freundlich isotherm for adsorption of azophloxine dye by RHA (pH_0=6, T=30°C, m=2.5g/l, t=300 min).

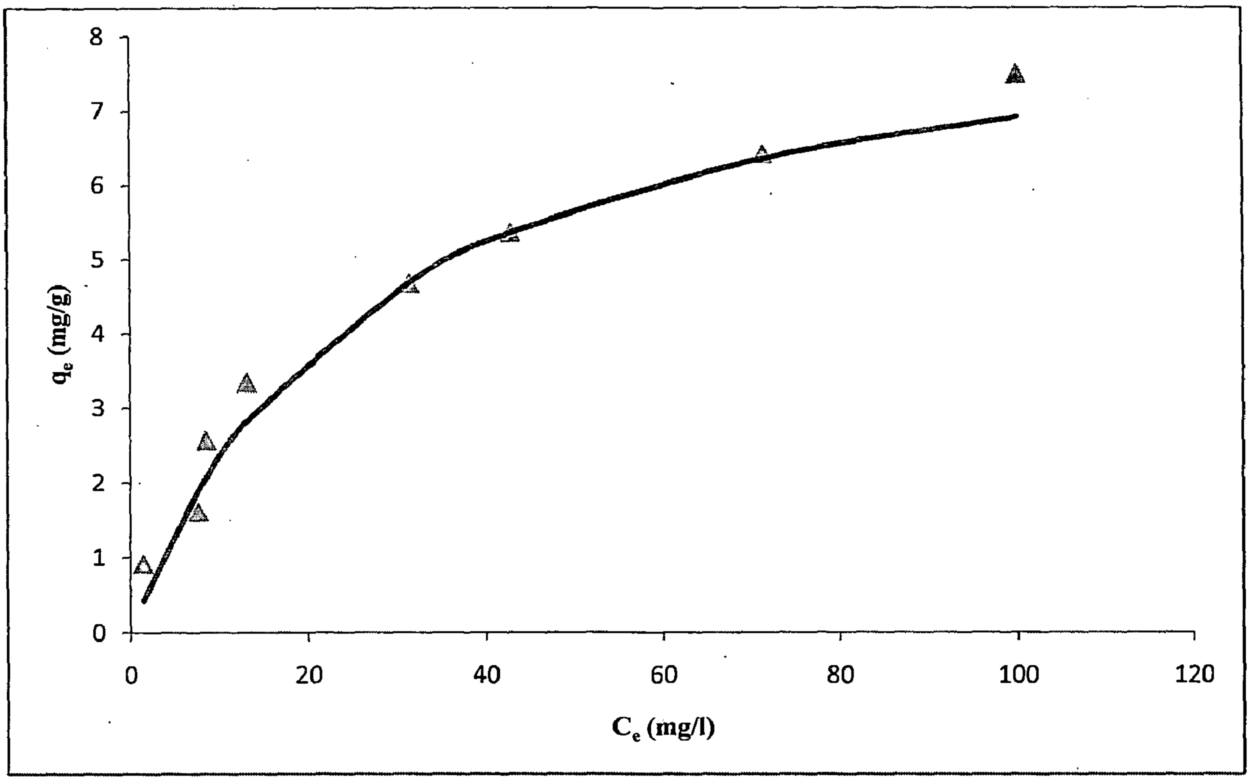


Figure 5.19 Langmuir isotherm for adsorption of azophloxine dye by BFA (pH_0=6, T=30°C, m=20 g/l, time=300 min).

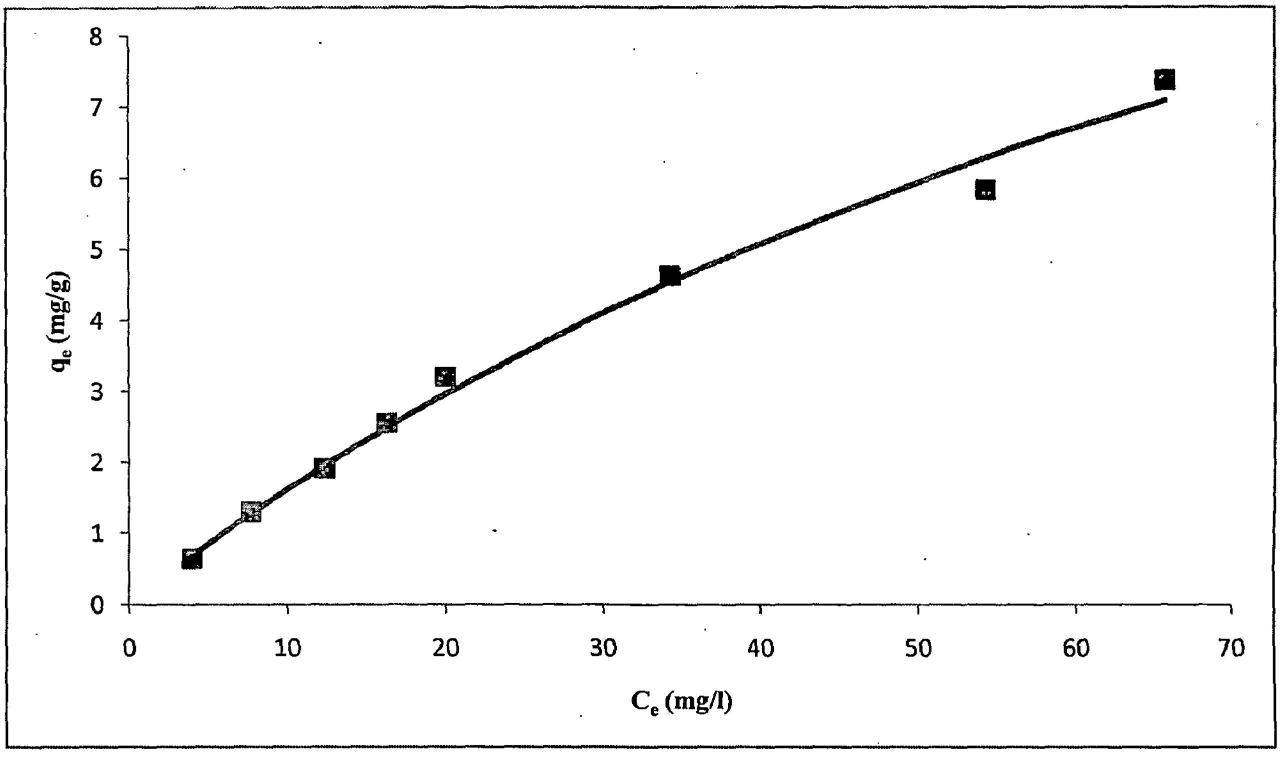


Figure 5.20 Langmuir isotherm for adsorption of azophloxine dye by RHA (pH_0=6, T=30°C, m=25g/l, time=300 min).

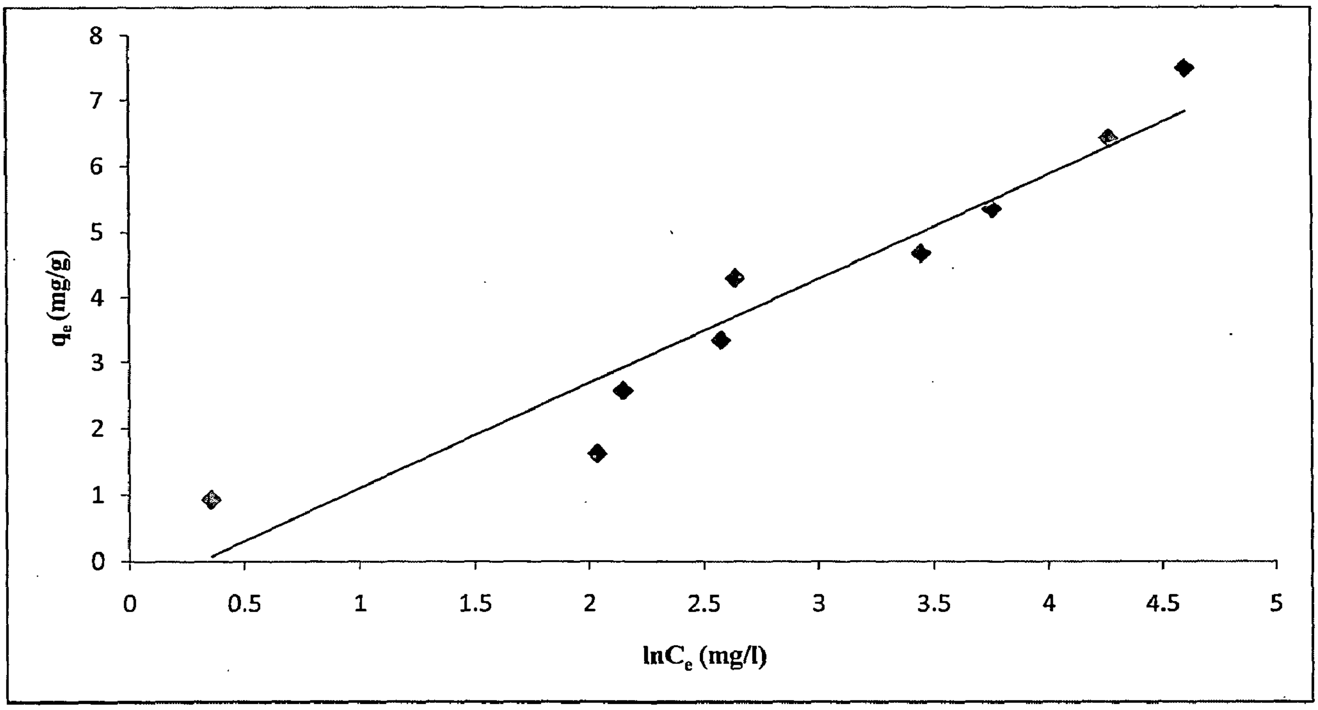


Figure 5.21 Temkin isotherm for adsorption of azophloxine dye by BFA (pH_0=6, T=30°C, m=20 g/l, Time=300 min).

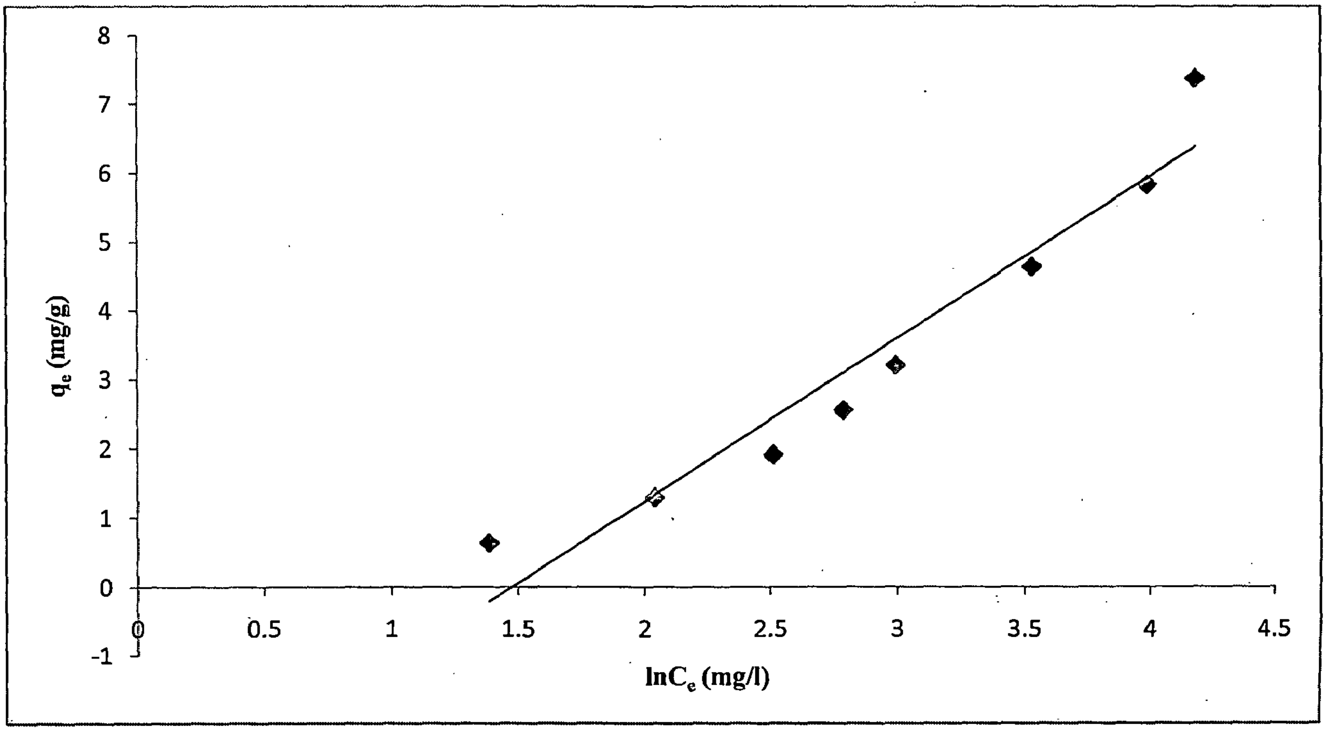


Figure 5.22 Temkin isotherm for adsorption of azophloxine dye by RHA(pH_0=6, T=30°C, m=25 g/l, time=300 min)

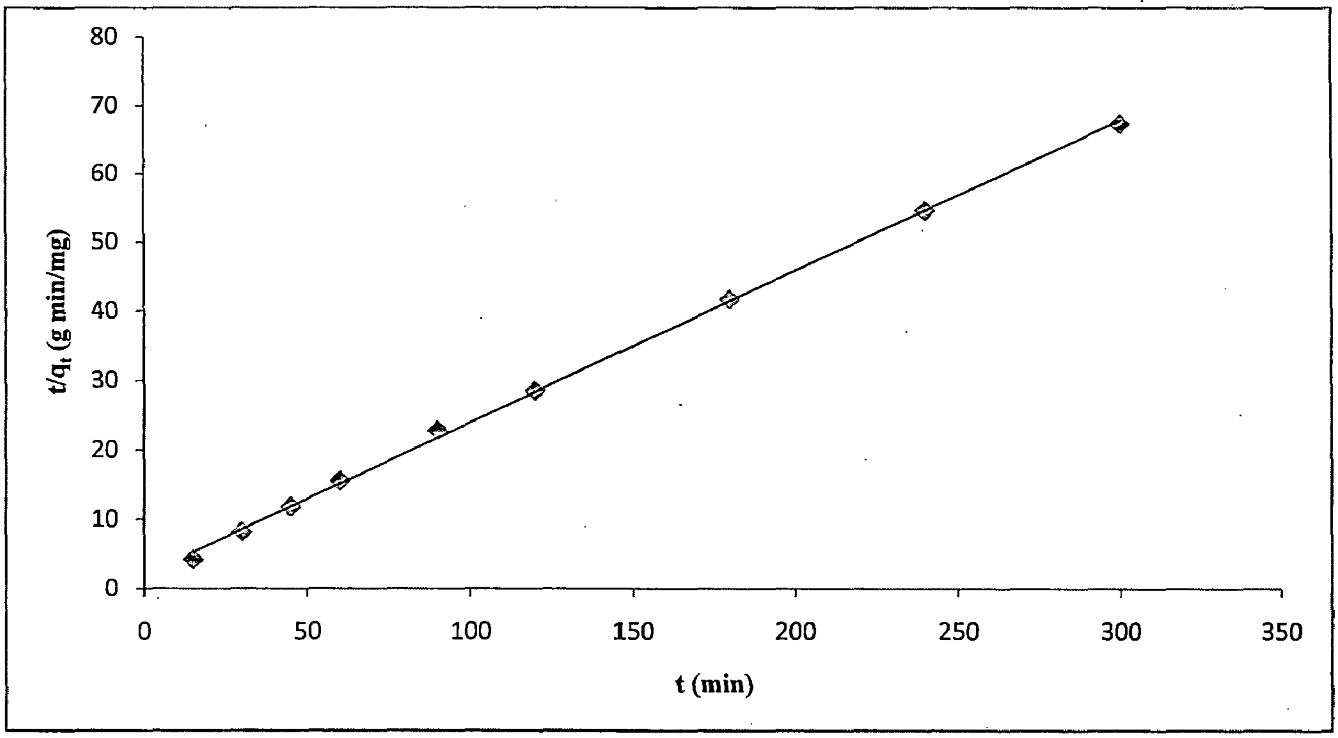


Figure 5.23 Pseudo-second-order kinetics for removal of azophloxine dye by BFA (pH_0=6, T=30°C, m=20 g/l, C_0=100 mg/l, contact time =300 min).

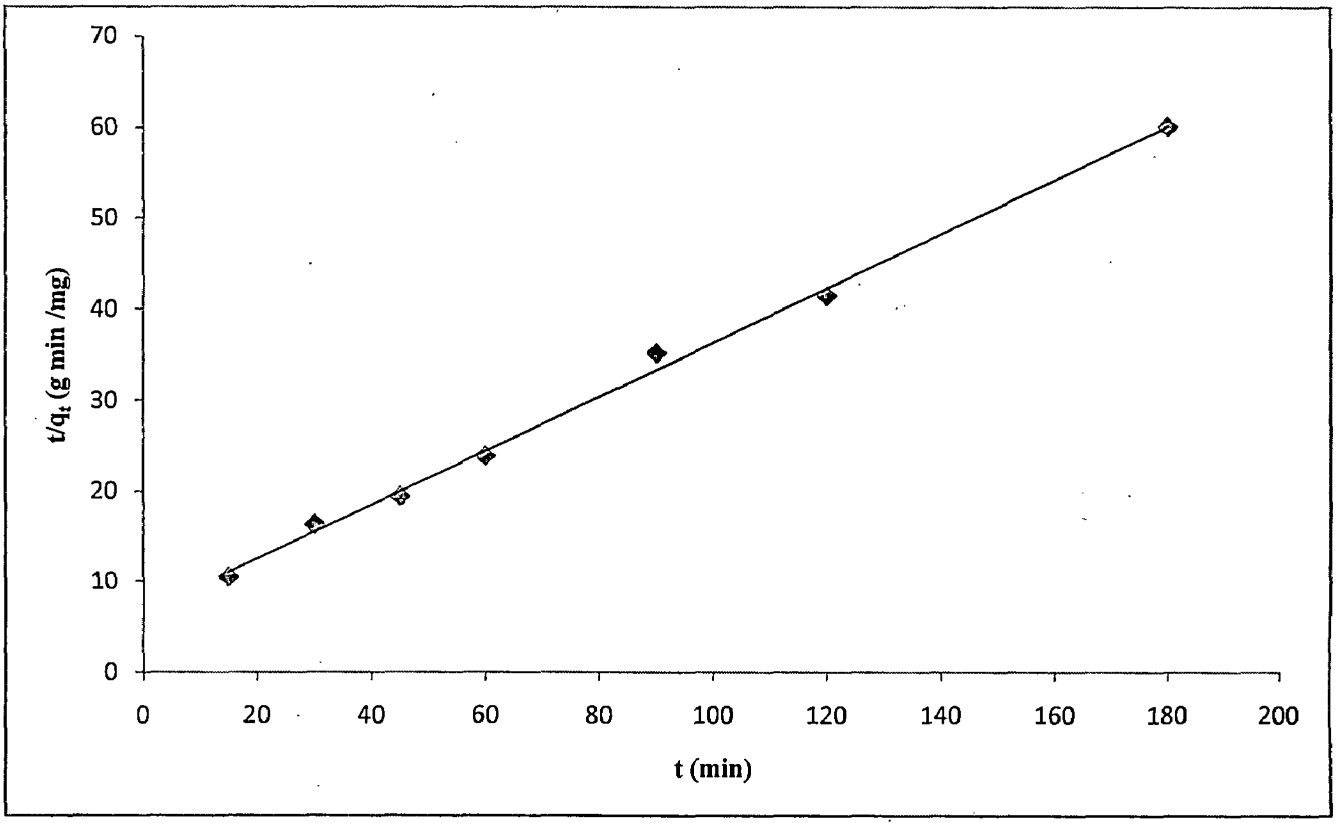


Figure 5.24 Pseudo-second order kinetics for removal of azophloxine dye by RHA (pH_0=6, T=30°C, m=25 g/l, C_0=100 mg/l, contact time =300 min).

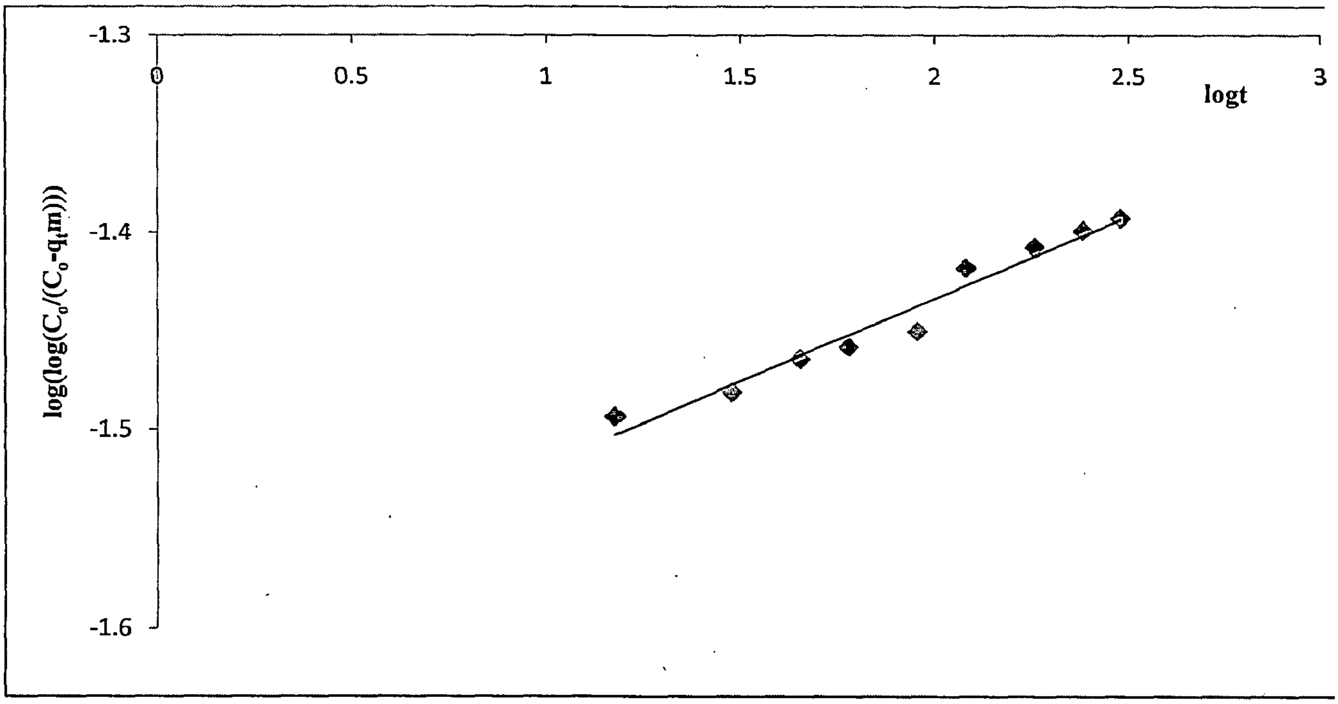


Figure 5.25 Bangham equation for removal of azophloxine dye by BFA(pH_0=6, T=30°C, m=20 g/l, C_0=100 mg/l, contact time =300 min).

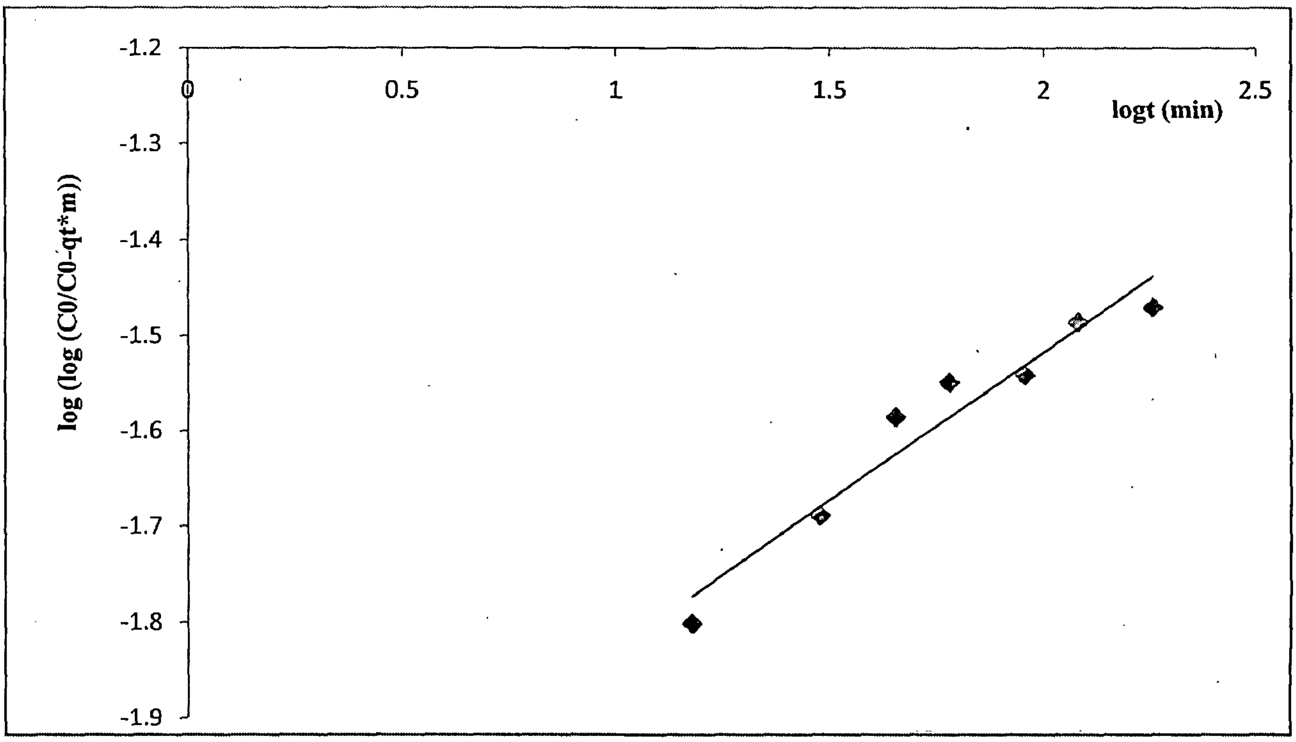


Figure 5.26 Bangham equation for removal of azophloxine dye by RHA (pH_0=6, T=30°C, m=25 g/l, C_0=100 mg/l, contact time =300 min).

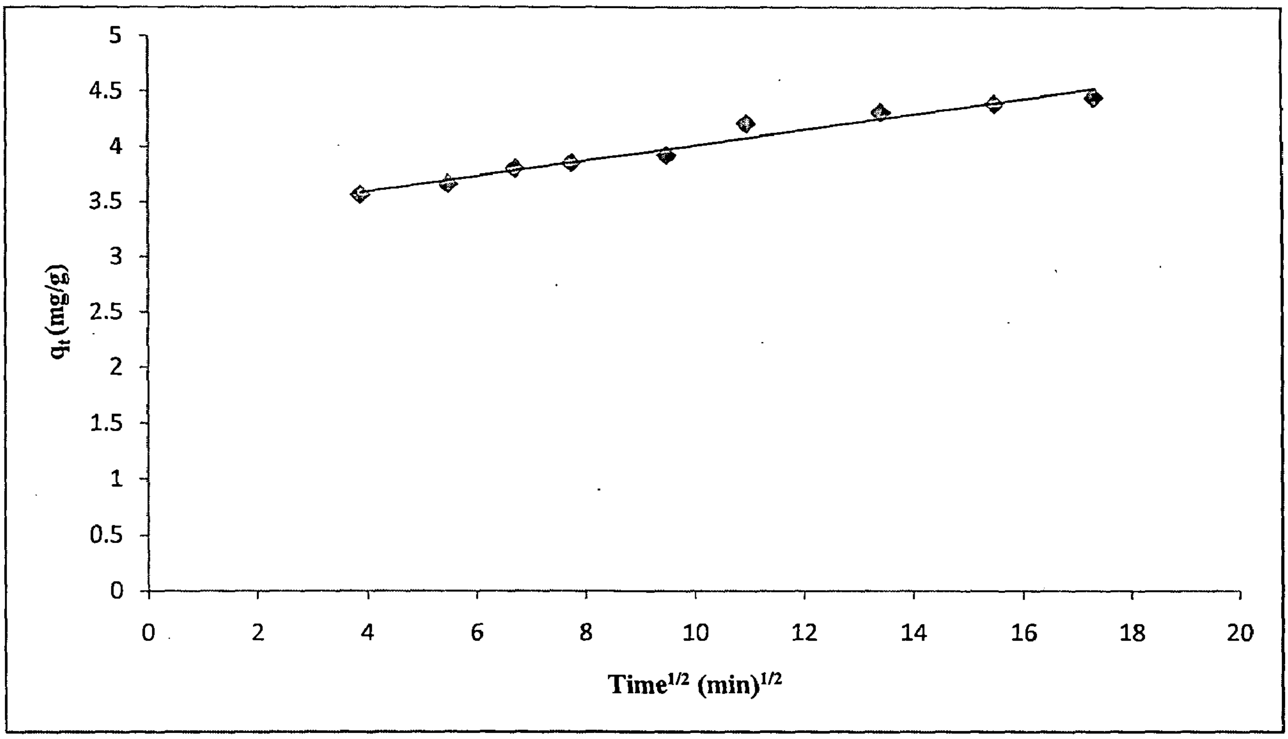


Figure 5.27 Weber and Morris intra particle diffusion for removal of Azophloxine dye by BFA (pH_0=6, T=30°C, m=20 g/l, C_0=100 mg/l, contact time =300 min).

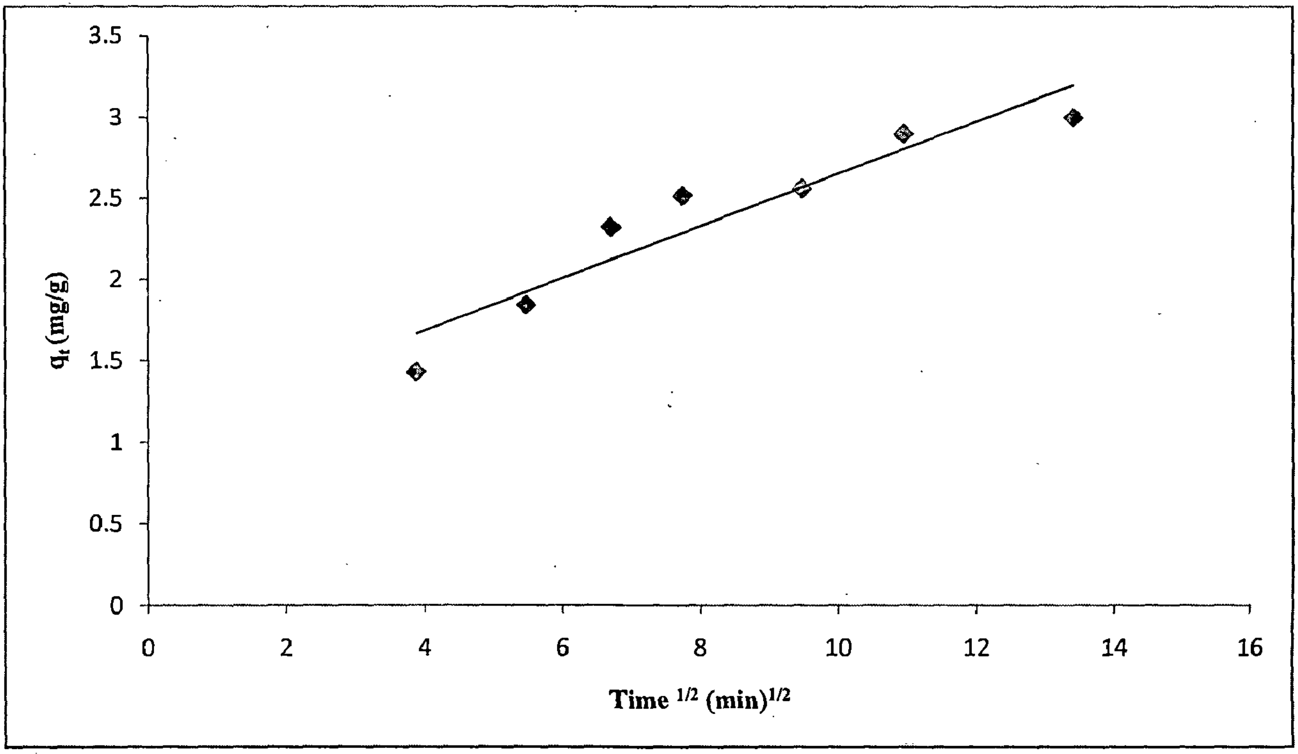


Figure 5.28 Weber and Morris intra particle diffusion for removal of Azophloxine dye by RHA (pH_0=6, T=30°C, m=25g/l, C_0=100 mg/l, contact time =300 min).

CONCLUSIONS AND RECOMMENDATIONS

COLCLUSIONS:-

1. This study shows that the rice husk ash (RHA) and bagasse fly ash (BFA) both are effective adsorbents for the removal of azophloxine dye from aqueous solution.
2. Higher percentage of azophloxine removal was possible provided that the C_0 in the solution was low. The equilibrium condition between the adsorbate and adsorbent was practically achieved in 5h. Equilibrium adsorption data for azophloxine on BFA were well represented by Langmuir isotherm and for RHA were well represented by Freundlich and Langmuir isotherms. Adsorption kinetics was found to follow Pseudo-second-order Kinetics.
3. Adsorption of azophloxine is favourably influenced by an increase in temperature.
4. Results clearly show that for the removal of azophloxine dye BFA is a better adsorbent as it gives more removal efficiency even at lower adsorbent dose in comparison to RHA for other optimised conditions of temperature, pH, dye concentration and contact time.

RECOMMENDATIONS:-

1. It is better to treat the dye bearing wastewater by RHA and BFA as they are low cost adsorbents and easily available in market in comparison to the other available adsorbents.
2. A comparative study of two adsorbents is better than the individual study as it helps in selecting the best adsorbent.
3. For removal of azophloxine dye more efficiency can even be obtained at higher temperatures as my study is limited only to 60°C.

CHAPTER 7

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