ADSORPTION STUDIES FOR THE REMOVAL OF COLOUR FROM TEXTILE WASTE WATER

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بسم الله الرحمن الرحيم

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Dedicated to:

ALMIGHTY ALLAH

HAZRAT MUHAMMAD (S.A.W)

My loving family and my parents for their love, protection, prays, faith and much more.....................

DECLARATION

I hereby declare that the work present in the following thesis is my own effort, except where otherwise acknowledged and that the thesis is my own composition. No part of the thesis has been previously presented for any other degree.

Date 29-09-11

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FORWARDING SHEET

The thesis entitled Adsorption Studies for the Removal of Color from Textile Waste Water submitted by Noreen Khalid in partial fulfillment of MS in Environmental Science has been completed under my guidance and supervision. I am satisfied with the quality of student's research work and allow her to submit this thesis, for further processes per IIU rules and regulations.

Maria 14/12/11

Dr. Syeda Maria Ali

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LIST OF ABBREVIATIONS

APHA	American Public Health Association
ASTMD	American Society for Testing and Materials
Å	Angstrom
$BaCl_2$	Barium Chloride
BOD	Biological Oxygen Demand
Ca^{2+}	Calcium
COD	Chemical Oxygen Demand
Cl^-	Chlorides
°C	Centigrade
cm	Centimeter
Conc.	Concentration
CR	Congo Red
DO	Dissolved Oxygen
EC	Electrical Conductivity
EDTA	Ethylenediaminetetraacetic acid
ΔH^o	Enthalpy change
ΔS^o	Entropy change
C_e	Equilibrium concentration
ΔG^o	Gibb's free energy
g	Gram
H_2SO_4	Sulphuric acid
C_o	Initial concentration
K	Kelvin
Kgs	Kilograms
KJ	Kilo joule
L	Litre
µm	Micrometer
M	Molar
mg	Milligram
Mg^{2+}	Magnesium
ml	Milliliter
min	Minute
N	Nitrogen
NO_3^-	Nitrates
nm	Nanometer
NEQS	National Environmental Quality Standards
HNO_3	Nitric Acid
PO_4^{2-}	Phosphates
H_3PO_4	Phosphoric acid

K^{1+}	Potassium
KCl	Potassium Chloride
%	Percent
R^2	Regression coefficient
$AgNO_3$	Silver Nitrate
Na^{1+}	Sodium
SO_4^{2-}	Sulphates
SS	Suspended Solids
NaOH	Sodium hydroxide
m^2	Square meter
TDS	Total Dissolved Solids
TSS	Total Suspended Solids
TWWS	Textile Wastewater Sample
USA	United States of America
UV	Ultraviolet
Vis	Visible
WHO	World Health Organization

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ABSTRACT

Pakistan is a country with a population of over 140 million and there are numerous problems due to rapidly growing population. Water scarcity is one of those acute problems at present times. Factors like ground water salinity, poorly performing irrigation distribution system, and recurrent droughts lead to the use of untreated urban wastewater for agriculture practice. Rapid industrialization especially textile industry in Pakistan has posed serious environmental problems causing adverse health effects, thus making it a social obligation for industries to minimize water pollution. Technologists are facinggreat challenge to develop and provide feasible and economically viable equipments and techniques for control ofindustrial pollution which includes suitable physico-chemical or biological treatment of industrial wastes/effluents. Different treatment processes are adopted for the removal of toxic metals and dyes from industrial effluents.Adsorption is one of the efficient and feasible methods in practice for the removal of toxic metals and dyes at ppm level.In the present study adsorption of colour from effluents has been investigated that include color estimation present in the wastewater samples of different textile industries.Samples were subjected to various physico-chemical parameters such as pH, Total Suspended Solids(TSS),Total Dissolved Solids(TDS),Calcium(Ca^{2+}),Magnesium(Mg^{2+}),Sodium(Na^{1+}),Potassium(K^{1+}),Phosphates (PO_4^{2-}), Sulphates (SO_4^{2-}), Nitrates (NO_3^{-}), Chlorides (Cl^{-}) and Chemical Oxygen Demand (COD). Activated charcoal was characterized for colour. The adsorption capacity of activated charcoal for colorwas studied by optimization of different adsorption parameters, i.e. amount of adsorbent, shaking time, pH, concentration of adsorbate and temperature.The present study revealed the use of activated charcoal successfully for the removal of color present in effluent in ppm levels. The adsorption experiments were performed using the batch and column technique for the adsorption of colour from effluent samples. Adsorption isotherms successfully described the experimental data. Thermodynamic parameter indicates that adsorption process was spontaneous and endothermic.

CHAPTER #1

INTRODUCTION

1.0 INTRODUCTION

Pakistan is an agricultural based country with16 million hectares of land situated in the arid and semi-arid regions (Tahir and Rauf, 2007). Continuous water shortages in the country are reasons attributed to rapid growth in population, salinity of ground water, poorly irrigation distribution system, and recurrent droughts. All of these lead to the use of untreated urban wastewater for agricultural practice (Ensink *et al.,* 2002).

Wastewater is a complex resource, along with hazardous concentration of soluble salts and heavy metals (Ghafoor *et al.,* 1995). The term wastewater is used to refer to water which has its composition and character changed by intensive human usage. Wastewater being generated by a community put negative impacts on the quality of water. It is utilized in agricultural sector and is no longer considered useful for human consumption (Ensink *et al.,* 2002).

Either raw or partially treated wastewater is reported to be used in almost 50 countries for irrigating almost 20 million hectors (Mahmood, 2006). For irrigation purposesapproximately 80% of urban wastewater is used in developing countries(Mara and Cairncross, 1989).Wastewater provides significant benefits to the farming communities due to its nutrient contents that can be used for crop production(Cooper, 1991). Farmers using sewage water for irrigation save a lot of fertilizer expenditure (Ibrahim and Salmon, 1992). At the same time negative impacts of wastewater on ecosystems is mainly due to its toxic substances that lead to water borne diseases and rapid degradation of the environment (Rose, 1999). The harmful effects of saline and metals contaminated effluent persist for several years by prolonged and intensive irrigations. As a result salts leach down and contribute to the already present salt concentration and affect groundwater quality (Feenstra *et al.,* 2000).

Industrial sectors in Pakistan especially textile industries consumes large amount of water in different process and generates wastewater with toxic pollutants (Wood, 1992).The wastewater is discharged directly into the local environment without any treatment. As a result the stagnant pools of colored and foul water in the industrial areas deteriorate the water and soil quality (Kim *et al.,* 2002).

In Pakistan textile productsconstitutealmost 55% of the total exports(Faheem and Khan,2010).Textile processes include many complicated processes likeginning, spinning, weaving, processing and stitching and use of chemicals throughout production (Schrag and Gullett, 1970). The process of woven polyester and cotton blended manufacturer involving fiber production followed by spinning for the conversion of fiber into yarns (Ahmad*et al.,* 2009).Starch, polyvinyl alcohol and wax are used as sizing chemicals for strengthening the yarn during weaving(Jenkins and David, 2003). After the process of weaving, the sizing chemicals removed with acids, alkalis or oxidizing agents i.e. desizing(Collier, 1970).Fabric is desized to prepare it for dyeing and finishing. Detergents are used for scouring of fabric (Collier, 1970)while hydrogen proxide is used tobleach the fabric(Odabasi, 2008). Concentrated solution of sodium hydroxide (NaOH) is used during the process of mercerization which provides stabilization to fabric.During finishing resins, softeners, fluorocarbon, silicones are used (Modak, 1991).

In the textile industries wet processing such as washing, scouring, bleaching, mercerizing, dyeing, finishing require the use of various toxic chemicals (Correia *et al.*, 1994),which includes complexing, sizing, wetting, softening, and finishing agents,surfactants,biocides, halogenated benzene, phenols, pesticides dyes, pigments, oils and wax, which becomes the part of wastewater as chemical pollutants (Ahn *et al.*, 1999).The amount of wastewater generated varies with the type of process operated at different industries (Selcuk, 2005). However, the excessive amounts of Alkalinity, BOD, COD, Heavy metals, Nitrogen, oils, pH, PO_4^{2-}, SS, sulphides and temperature are harmful (EPA, 1974). Metals and other dye compounds that are present in wastewater retard the natural microbial activity and leads to the failure of biological treatment system (Villegas *et al.,* 2001).

Dyes which are used in textile industries are highly colored and visible in water at concentrations as low as 1mg/L. Dye content in the range 10-200mg/L in textile processing wastewaters (O'Neill *et al.,* 1999), is usually highly colored and creates an aesthetic problem on discharge. These are highly persistent,chemically and photolytically stable in natural environments so, they create health problems to all forms of life (Prakash and Solank, 1993). They have carcinogenic properties and have the ability to absorb light that enter the water, which retards the bacterial growth and their metabolic activity (Zee, 2002). These bring about chemical and biological change and destroy the aquatic life by consuming the dissolved oxygen. It is reported that almost 10,000 different dyes and pigmentsused in industriesmost of which are synthetic (Rafi *et al.*, 1990). Textile dyes which includes aromatic amines are mutagens and carcinogenic which are formed by the reduction of azo dyes(Zee, 2002).Dyes cause severe skin problems such as allergic reactions, skin dermatoses, eczema (Su and Horton, 1998) and affect liver (Jaskot and Costa, 1994), lungs, circulatory system, immune system and reproductive system of humans(Nikulina*et al.*, 1995). Industrially important dyes are the acid, basic, direct and reactive azo dyes are ionic dyes (Anliker*et al.*,1981).

Over the last few decades, concern about the potential adverse effects of the chemical industries to the environment has increased (Pignon *et al.*, 2003). The preventive measures that should be taken towards the protection of environment are different in different parts of the world. The Government legislation in most developed countries is strict for the removal of dyes from industrial effluent (Netpradit *et al.*, 2004). For the protection of environment from pollution Europe is promoting to treat effluent before discharge (Banat *et al.*, 1996).

There are various methods for the removal of dyes that includesozonation, coagulation, flocculation, membrane separation andoxidation(Baclioglu and Arslan 2001). These methods are not economically viable so, these are not widely used (Garg *etal.*, 2003). For the removal of trace levels of pollutants methods like chemical or biological oxidation, ion exchange and solvent extraction have shown low efficiency (Goto*et al.*, 1984). After the treatment process such as filtration, coagulation and sedimentation, soluble organic materials that are resistant to biological breakdown are called refractory organics persists in the effluent. These refractory organics can be detected in the effluent as soluble COD (Davis and Cornwell, 1998). Ozonation is an effective method for color removal but it does not minimize COD(Sinder and Porter,1974). Out of these adsorption is the most economically, simple,feasible, easy and widely used technique for the control, removal and minimization of water pollution (Faust and Aly, 1987). The process of adsorption has been used for the removal of solutes from multiple sources like solutions and gasses by charcoal and clays (Mantell, 1713). Also it is one of the advanced wastewater treatment processes, which is used for the removal of refractory toxic substances and dissolved, organic from wastes and polluted waters (Weber, 1972).

The Adsorption process involves the accumulation of solute molecules that are adsorbate on the solid material that is known as the adsorbent(Cussler, 1997).Adsorption is of two type's i.e. physical adsorption and chemisorptions depending upon the forces of attraction between the adsorbate and adsorbent molecules (Henderson *et al.*, 2009). Physical adsorption is reversible while the chemisorptions is irreversible and involves the formation of chemical bonds between the adsorbent and adsorbate (Perry and Green, 1997).

The efficiency of adsorption depends on the nature of adsorbent. A good adsorbent has high porosity and large surface area, for which less time is required for adsorption equilibrium(Karcher*et al.*, 1999). Alumina, zeolites, silica, metal hydroxides and activated carbon are the most commonly used adsorbent materials (Jaung *et al.*, 1996). Among all of them activated carbon is economically favorable and widely used adsorbent in waste water treatment (Al-degas *et al.*, 2000). It is a microcrystalline material made by thermal decomposition of wood, vegetable shells, coal and has surface area of 300 m^2 to 1200 m^2/g with average pore diameter of 10 to 60 Å (Geankoplis, 1993). The activated charcoal is selected for adsorption on the basis ofsurface area and internal porous structure (Ahmedna *et al.*, 2000).

Activated charcoal is widely used adsorbent for the removal of color from textile effluents because it has a high capacity for organic matter (Jaung *at al.*, 1996). Raw charcoal from organic based materials is carbonized and activated to produce the highly porous product. The activated charcoalfor adsorption has two types of pores, i.e. macropores (>5000 A°) and the micropores (<40 A°) (Abood, 2004).The micropores are responsible for adsorption because they provide large surface area of activated charcoal while macropores provide a passageway to the particle's interior and to the micropores (Cheremisinoff and Ellerbusch, 1978). Different types of activated carbon are used for the removal of different types of dyes which are cationic and anionic. The studies on activated charcoal reported that adsorption of dyes is higher on activated charcoals due to higher surface area (Al Degs *et al.*, 2001).

Through activated carbon, the percent dye removal is about 96.7% for direct blue, 98.7% for sulphur black and 98.4% for vat yellow respectively (Shakir, 2002). The activated carbon used in wastewater treatment is prepared from coconut shells, peat, sawdust (Faust and Aly, 1987). The effect of activated charcoal on thewater soluble organic dye showed that the maximum adsorption capacities ranged between 132.5- 265 mg of dyes per one gram of the adsorbent (Safarik *etal.*, 1997).

The Adsorption capacity of activated carbon increases with increasing mesopore volume and mesopore contribution to their porous texture is 52 to 83% (Bagreev *et al.*, 2001).There are various chemicals which are used for the activation of raw carbon such as potassium hydroxide(KOH), sodium hydroxide(NaOH), zinc chloride($ZnCl_2$) and phosphoric acid (H_3PO_4)(Guo and Rockstraw, 2007). For chemical activation H_3PO_4 is mostly used because it is economic and environmental friendly. It also needs low temperature for activation which lies in the range of 400-450°C(Hsisiheng *et al.*, 1998).

Under static conditions the adsorption was preferred at 7.8-8.3 pH(Sabio*et al.*, 2004). The Langmuir equation better described the adsorption of congo red (CR) (Ewa and Grazyna,2006). Langmuir adsorption isotherms have been used to interpret the adsorption behavior on these activated carbons (Sirichote, 2002).

Amongst the low cost adsorbents, such as coconut and coffee husks act as potential efficient biosorbents for hazardous dye (Walker *et al.*, 2003). Batch experiments showed that the process is exothermic because adsorption decreased with increasing temperature. The results successfully explained by the pseudo-first-order kinetics and Langmuir and Freundlich isotherms (Mital*et al.*, 2010).

Faisalabad is the third largest city of Pakistan that has made rapid strides in the field of industry. In Punjab there are total of 1395 textile units, out of which 691 are woven textile processing units and rest are knitwear processing units (ICTP, 2008). It is reported that the textile industry of Pakistan has spinning and weaving capacity of 1550 million kgs of yarn and 4368 million square metres of fabric respectively.The industry has 4000 million square meters of finishing capacity and production capacity includes 670 million units of garments, 400 million units of knitwear and 53 million kgs of towels. In Faisalabad, total 561 textile industries are working. There are 105 large, 248 medium and 208 are small textile industries (ICTP, 2008) most of which do not possess proper discharge system (Ara, 1999).

Keeping in view the adsorption technique and its significance for the removal of dyes from textile waste, following aims of study was outlined to obtain the desired results:

i. To assess the physiochemical properties and pollution load due to textile wastewater

ii. Treatment of textile waste water by using adsorption technique

CHAPTER #2

MATERIALS AND METHODS

2.0 MATERIALS AND METHODS

2.1 CHARACTERIZATION OF TEXTILE WASTEWATER

2.1.1 Sampling Methodology and Sampling Locations

Nineteen samples were collected from different textile industries located in the vicinity of Faisalabad(Table 2.1). Samples were collected from each textile industry on day to day basis.

Table: 2.1 Codes, Location and Industries of Textile Wastewater Samples

Sample Code	Textile Industries and their Location
TWWS-1	Saddique Processing Industry Faisalabad
TWWS-2	Orient Coating And Finishing Mill Faisalabad
TWWS-3	Dawood Textile Printing Industry Faisalabad
TWWS-4	Magma Printing Press
TWWS-5	Saddaqat Textile Mill Faisalabad
TWWS-6	Saddaqat Textile Mill Faisalabad
TWWS-7	Magma Printing Press Faisalabad
TWWS-8	Bismilla Textile Industry And Printing Press Faisalabad
TWWS-9	Dawood Textile Printing Industry Faisalabad
TWWS-10	J.S Printing Press Faisalabad
TWWS-11	Orient Coating And Finishing Mill Faisalabad
TWWS-12	Khalid Printing Press Faisalabad
TWWS-13	Orient Coating And Finishing Mill Faisalabad
TWWS-14	Khalid Printing Press Faisalabad
TWWS-15	Saddaqat Textile Mill Faisalabad
TWWS-16	Khalid Printing Press Faisalabad
TWWS-17	J.S Printing Press Faisalabad
TWWS-18	Dawood Textile Printing Industry Faisalabad
TWWS-19	K.S Printing Press Faisalabad

2.1.2 Sample Containers, Preservation and Storage

Polyethylene bottles were used for the collection of samples. The bottles were first cleaned with nonionic detergent and then tap water was used. These were dipped for 24 hours at70°C in nitric acid(HNO_3) solution. After 24 hours deionized water was used to rinsed the bottles(Rosin, 1967). After acidification with 5ml concentrated HNO_3/L, the samples were preserved and stored at 4°C in a refrigerator. It is ensured that the pH of the stored samples less than 2.Under these conditions the samples were found to be stable for up to six months (Wendlant, 1986).

2.1.3 Reagents and Standards

Analytical grade chemicals were used (Subramanian*et al.,* 1978). High purity (99.9%)Merck salts and standards of powdered dyes were used. The standard solutions of thedyes Direct red 80 and Direct blue 15 wereprepared by weighing out 0.1 g of each dye and raising its volume to 1000ml.The results were recorded using UV-Vis spectrophotometer (analytikjena specord 200).

2.1.4 Physico-Chemical Analysis

- The colour was detected by using a UV-Vis Spectrophotometer, analytikjena specord 200(Method 2120 C APHA, 1998). The initial value of color for Direct blue 15 and Direct red 80 weremeasured at λmaxof 607nm and 527nm respectively.
- The pH was measured by standard test method ASTMD 3838-80 with microprocessor pH meter (HANNA-pH 210). For measurement each time the pH meter was adjusted to neutral pH by using the buffers of pH 4.0, 9.0 and 10.0 respectively.
- Microprocessor conductivity meter (HANNA-HI 9932) was used to measure the EC. ElectricConductivity meter was calibrated with 0.01M potassium chloride(KCl) solution (Method 2510 B APHA, 1998).
- For the measurement of TDS, filtered wastewater samples were evaporated in a drying oven for one hour at 180±2°C, cool down in a desiccators and TDS was recorded after repeated cycles of drying, cooling, desiccating andwashing till constant weight (Method 2540c APHA,1998).
- TSS was also measured by following method 2540D (APHA, 1998). Electric oven was used to dry the filter papers at 90°C for one hour and their weight was recorded. Then, filtered waste water samples through dried filter papers and residue was dried till constant weight at 100°C for one hour. The weight of filter paper and dried residue was recorded. The increased in weight of the filter paper represents the TSS.
- EDTA Titrimetric method(Method 3500-Ca B APHA, 1998)was used to determine the concentration of Ca^{2+}.The pH of 1ml sample was adjusted to the acid range.Addedto it 2ml of 0.1N NaOH solution and 0.2g murexide

indicatorand was titrated against EDTA till the achievement of an end point i.e. light pink to purpleEDTA Titrimetric method was also used to determine the concentration ofMg^{2+}. Buffer(2ml) solutionwas added with pH 10 and 3 drops of erichrome black T in 1ml sample and titrated against EDTA till the achievement of an end point i.e. light red to blue. The value which was obtained is a combined concentration of $Ca^{2+}$and Mg^{2+} i.e. total hardness. The concentration of magnesium was obtained by subtracting the result of measurement for total Hardness from that of measurement for Ca^{2+}(Method 3500-Mg B APHA, 1998).

- The samples were analyzed for$Na^{1+}$and $K^{1+}$by using flame photometer(Method 3500-Na B and 3500-K B APHA,1998).
- The concentration of Cl^- was determined by Argentometric method(Method 4500-Cl^-B APHA, 1998).The pH of 1ml was adjusted to 7 to 10 with sulphuric acid or sodium hydroxide. In the sample 1ml potassium chromate indicator solution was added and titrated against standard silver nitrate solution ($AgNO_3$) titrant till the achievement of an end point i.e. greenish yellow to reddish brown
- The concentration ofSO_4^{2-} was determined by turbidimetric method(Method 4500-SO_4^{2-} APHA, 1998).A standard solution with SO_4^{2-} concentrations was prepared in the range of 0 to 50mg/L. Solid 0.3mg Barium Chloride ($BaCl_2$)was added during stirring and the stirring. Afterwards, the solution was transferred to a cuvette and the absorption at 420nm was measured repeatedly over a period of two minutes. The highest measured value was noted.
- In 40ml sample,8 ml reaction mixture was added and the volume was raised upto 50ml. After mixing, the solutions were left for 10 min and PO_4^{2-}concentration was measured at 880nm in the spectrophotometer analytikjena specord 200(Method 4500-P E APHA, 1998).
- The concentration of $NO_3^-$was determined by using ion analyzer(Method 4500-NO_3^- D APHA, 1998).
- COD for waste water samples was determined by closed reflux method (Method 5220 B APHA, 1998). Wastewater samples (20ml) and concentrated dichromate solution (10ml) were placed in the flask with anti-bump granules. Then 30 ml of the silver containing sulphuric acid solution werecarefully added. Mercurous

sulphate solution (2ml) was also added. The mixture is then carefully boiled under reflux for 2 hours. After cooling the volume of the mixture was raised to 150ml. The excess of dichromate was back titrated with the ferrous ammonium sulphate solution. The indicator changes colour from blue-green to red-brown at the end point. A control sample consisting of 20ml distilled water was measured at the same time

2.2 Preparation of Activated Carbon from Coconut Shells

Coconut shells were burned in an electric furnace (Carbolite CWF-1200) at 450°C for 45 minutes. After cooling, the burned shells were crushed into powdered form to get a uniform particle size, these crushed coconut shells were sieved (Tahir and Rauf, 2004). The powdered charcoal was chemically activated by using phosphoric acid (H_3PO_4) in 1:1(Suhas *et al.,* 2007).H_3PO_4 impregnated at 150°C for 48 hours(Diao *et al.,* 2002). After impregnation, the samples were washed with distilled water till there was no change in its pH (Marsh *et al.,* 1975). The washed charcoal was dried at100°C for 2 hours in an electric oven(Manohar*et al.,* 2006).

2.3 Physico-Chemical Characterization of Activated Carbon

The principal methods of characterization of activated charcoal to be suitable as an adsorbent are described here:

- For pH determination 1.0 g of activated charcoal sample was weighed and raised the volume up to 100ml with distilled water into a beaker. After stabilization pH was measured with microprocessor pH meter (HANNA-pH 210). Activated carbon samples were run in triplicates(standard method ASTMD3838-80).
- For the determination of moisture content of activated charcoal a small beaker was weighed then 5g of activated charcoal was added to the beaker and again weighed. The activated charcoal sample was dried at 110°C till constant weight for 48hours and weighed again (Mckeague, 1976).
- For the bulk density weighed an empty cylinder of known volume and then weighed again when it was filled with activated charcoal sample. For tap density measurement, mechanically tapped the cylinder, while being filled and the

values of bulk and tap densities were obtained by dividing weight by volume of the cylinder (Tahir and Rauf, 2004).

- The empty relative density bottles were cleaned, dried and weighed for the measurement of density. The activated charcoal samples (1/3) were put into it and weighed again. The relative density bottles were filled with water and weighed again. Then the bottles were emptied, cleaned of the activated carbon particles and filled with water alone and weighed. The specific gravity of the activated charcoal was calculated in duplicate(Tahir and Rauf, 2004).
- Surface area of activated charcoal samples were measured using the Quantasorb sorption system (M/s Quantachrome Corporation, New York (USA) by continuous flow method (Van, 1970).
- For ash content determinationcrucible was pre-heated in a furnace to about 500°C, cooled in a dessicator and weighed. Activated charcoal samples (1.0g) were transferred into the crucibles and weighed again. The crucibles containing samples at 500°C were placed in a furnace. It was removed and cooled down in desiccators to room temperature and weighed again(Standard test method for ash content -ASTMD2866-94).

2.4 Analytical Procedure for the Removal of Direct Blue 15 and Direct Red 80 from Textile Wastewater

In the present study batch and column adsorption techniques have been applied under optimal conditions of temperature, shaking time, amount of adsorbent and adsorbate for the removal of Direct blue 15 and Direct red 80 from textile wastewater in an orbital shaker at 120 rpm (Kubilay *et al.*, 2007).For optimizing the contact time 1.0g of activated charcoal was used with initial concentration of 110 mg/L and 89.98 mg/L for Direct blue and Direct red 80 dye, respectively.After optimizing the time, the amount of adsorbent was optimized by using 0.1g-6.0g activated charcoal with same initial concentration as mentioned above(Manohar*et al.*, 2006).Samples solutions were withdrawn at predetermined time intervals filtered with whatmann filter paper No.42 and analyzed for the colour removal with UV-visible spectrophotometer (analytikjena specord 200) atlambda maximum of 607nm and 527nmfor Direct blue 15 and Direct red 80 respectively (Safa and Adnan, 2005). After optimizing the time and amount of adsorbent, adsorption was applied for the removal of color from wastewater sample solutions under optimal conditions of pH, concentration and temperature(Tahir and Rauf, 2003).

For Column studies, a column with 2 cm internal diameter and 15 cm total length made of Pyrex glass was used (Gong*et al.,* 2005). Glass wool was used to safe guarded the column then was filled with 10 g of dried activated charcoal (Bautista *et al.,* 2003). It was tapped so that maximum amount of adsorbent was packed. The dyesolutions of known initial concentration and pH were introduced from the funnel into the column (Sumanjit and Tejinder, 2008). pH meter (HANNA pH 210 microprocessor) was used to determin the pH value of the solutions. The dye solutions passed through the activated charcoal bed at constant down flow rate of 5 ml/min with the help of a fine metering valve (Siva*etal.,* 2009).After definite time intervals effluents were collected from the column. Thesolutions dye concentrations before and after adsorptions were determined with the help of UV-visible spectrophotometer (analytikjena specord 200)(Liao and Shiau, 2000). The percentage adsorption was measured by using the following equation (Tahir and Rauf, 2004):

$$\text{Percentage adsorption} = \frac{\text{Co} - \text{Ce}}{\text{Co}} \times 100$$

Where C_o and C_e are the initial and the equilibrium concentrations, respectively. The thermodynamics values ofenthalpy change (ΔH^o), entropy (ΔS^o) and Gibb's free energy(ΔG^o) of adsorption was also calculated (Tahir and Rauf, 2004).

CHAPTER #3

RESULTS

3.0 RESULTS

3.1 Physico-Chemical Characterization of Textile Wastewater

The textile industries consume large quantities of water and generate large volumes of wastewater with toxic chemicals, high concentration of salts and dyes(Liang,1991). These chemicals, dyes and salts have an adverse effecton environment. The wastewater characterization is necessary for the effective treatment of effluents before their discharge into the environment(Pagga and Jaeger, 1994). Nineteen industries in the vicinity of Faisalabad were targeted to check the pollution load from wastewater. For this purpose, the samples were subjected to various physico-chemical analyses for design the wastewater treatment plan. Physicochemical parameters were pH, EC, TDS, TSS, COD, Ca^{2+}, Mg^{2+}, Na^{+1}, K^{+}, PO_4^{2-} ,NO_3^-, $SO_4^{2-}$and Cl^-. Table 3.1 shows the basic statistics of analyzed parameters.

Wastewater samples pH lies between the ranges of (0.84 to 12.34). Wastewater samples of six industries (TWWS-1, TWWS-2, TWWS-3, TWWS-5, TWWS-18 and TWWS-19) were found acidic pH while two of them showed basic pH (Table 3.1). These are not according to permissible limits of NEQS (Table 3.1) which shows that optimum pH shall remain neutral to slightly basic i.e. 6-9. High concentrations of TSS, TDS, Ca^{2+} and Mg^{2+} were found in samples collected from different industries (Table 3.1). TSS and TDS value was found above the standard limits prescribed by NEQS (Table 3.1).Ca^{2+} and Mg^{2+} does not lie within the safe limit(Table 3.3) in the samples collected from different textile industries located in Faisalabad(Table 3.1).The wastewater samples from all textile mills have high levels of Na^{2+} ,$SO_4^{2-}$and Cl^- (Table 3.1) then the prescribe limit (Table 3.1).The concentration of NO_3^- alsoin the wastewater samples does not lie within the safe limit, as prescribed by the WHO (Table 3.1).The values for COD in the waste water samples lie in the range of 9.704 mg/L to 542.56 mg/L. The values of COD for textile wastewater samples TWWS-7, 9, 11, 12 , 14,16,17, 18 and 19 does not lies within the standard permissible limit given by NEQS (Table 3.1).

Table 3.1. Physicochemical Characterization of Wastewater from Textile Industries Located In the Vicinity of Faisalabad

Sample Code	pH	EC (m□)	TDS (mg/l)	TSS (mg/l)	COD (mg/l)	Ca^{2+} (mg/l)	Mg^{2+} (mg/l)	Na^{1+} (mg/l)	K^{1+} (mg/l)	PO_4^{2-} (mg/l)	NO^{3-} (mg/l)	SO_4^{2-} (mg/l)	Cl^- (mg/l)
	Mean ±SD	Mean ±SD	Mean ±SD	Mean ±SD	Mean ±SD	Mean ±SD	Mean ±SD	Mean ±SD	Mean ±SD	Mean ±SD	Mean ±SD	Mean ±SD	Mean ±SD
TWWS -1	1.85 ±0.05	16.23 ±0.25	7946.6 ±0.28	1340 ±10	155.91 ±4.407	499.5 ±23.3	397.55 ±37.1	3250 ±25	80±5	3.13 ±0.05	69.04 ±0.85	1087.56±12.4	8262.12 ±82.38
TWWS -2	1.16 ±0.04	51.8 ±0.20	25500 ±1.3	560 ±10	197.08 ±0	391.5 ±23.3	365.1 ±24.3	2650 ±25	70±5	2.86 ±0.02	58.96 ±0.01	953.41 ±12.03	6701.46 ±49.27
TWWS -3	0.84 ±0.03	60.03 ±0.70	29233.33±0.5	980 ±0	156.78 ±3.58	607.5 ±40.5	156.04 ±24.3	8250 ±0	210±5	2.3±0	204 ±36.8	1404.06±18.2	7539.15 ±1.11
TWWS -4	8.2 ±0.5	9.32 ±0.24	4396.66±1.0	1940 ±5	167.84 ±0.11	243 ±40.5	486.8 ±73.02	5300 ±50	160±5	2.2±0	56.51 ±0.41	1428.71±3.52	2463.77 ±197.10
TWWS -5	1.45 ±0.1	22.45 ±0.84	11023.33±0.9	890 ±0	167.95 ±0	175.5 ±23.3	916.80 ±37.17	3950 ±25	145±5	1.38 ±0.02	116.6 ±1.56	625.51 ±4.86	16507.29 ±1098
TWWS -6	9.49 ±0.1	6.22 ±0.59	3556.66±0.1	470 ±10	190.70 ±0.20	202.5 ±0	227.17 ±14.05	1300 ±25	20±5	1.05 ±0	52.26 ±0.30	993.41 ±3.97	1971.01 ±49.27
TWWS -7	6.61 ±0.01	7.78 ±0.13	3723.33±0.1	1165 ±10	165.05 ±10.06	513 ±27	197.36 ±73.02	2150 ±20	50±5	2.7 ±5.44	49.2 ±1.4	965.88 ±1.54	3038.65 ±0
TWWS -8	7.13 ±0.02	6.12 ±0.12	3590 ±0	242±6	158.24 ±0	270 ±46.7	527.36 ±14.05	1300 ±50	35±0	2.3±0	48.73 ±1.15	607.26 ±2.67	1658.94 ±16.42
TWWS -9	6.5 ±0.2	6.93 ±0.08	14420 ±1.1	486±8	223.28 ±11.26	972 ±40.5	152.45 ±14.05	4300 ±50	90±5	2±0	46.2 ±4.50	606.95 ±3.80	2381.64 ±32.85
TWWS -10	6.26 ±0.02	5.51 ±0.16	3580 ±0.9	162±8	160.78 ±0	310.5 ±23.3	151.7 ±84.31	2400 ±25	110±5	3.88 ±0.02	118.86 ±0.9	1456 ±3.32	2266.67 ±49.27
TWWS -11	12.07 ±0.02	132.1 ±3.08	66466.67±0.2	5691 ±0	253.06 ±11.79	324±0	494.91 ±14.05	2750 ±50	110 ±20	7.5±0	57.4 ±5.29	4570.86±227	2414.49 ±0
TWWS -12	12.34 ±0.02	130 ±0	67333.33±0.9	7767 ±0	542.56 ±8.59	634.5 ±61.8	551.70 ±37.17	2200 ±50	90±10	2.1±0	128.6 ±1.73	1882.48±9.30	2463.77 ±98.55
TWWS -13	7.73 ±0.01	19.4 ±0.34	9330 ±0.96	620±5	159.72 ±1.27	175.5 ±23.3	173.02 ±0	1350 ±50	50±20	0.88 ±0.02	66.46 ±1.52	1626.73±1.69	7539.15 ±49.28
TWWS -14	7.88 ±0.01	13.08 ±0.01	6340 ±0.22	1620 ±10	184.45 ±0	310.5 ±23.3	324.53 ±14.05	550 ±10	20±0	1.9 ±2.72	62.13 ±3.10	1718.3 ±1.25	5748.8 ±82.12
TWWS -15	8±0.1	15.21 ±0.11	7443.33±0.1	570 ±20	187.37 ±0	391.5 ±23.3	770.76 ±14.05	600 ±50	20±0	2.23 ±0.05	237.33 ±1.1	1458.88±1.75	6389.38 ±82.11
TWWS -16	7.62 ±0.01	18.27 ±0	9666.66±0.6	509±6	248.94 ±22.75	202.5 ±0	186.60 ±14.05	5200 ±50	45±5	0.78 ±0.02	53.2 ±0.34	1271.71±7.22	8968.14 ±0
TWWS -17	8.45 ±0.01	27.78 ±0.57	14143.33±0	420±0	300.94 ±0	297 ±27	397.55 ±40.57	8300 ±50	65±5	2.2±0	258±2	3490.83±16.6	8064.75 ±32.85
TWWS -18	2.52 ±0.01	19.53 ±0.35	19200 ±0.6	170.56 ±0	300.94 ±0	810 ±110	243.4 ±97.36	8300 ±0	65±5	0.85 ±0	99.33 ±2.51	3490.83±600	8081.18 ±0
TWWS -19	2.66 ±0.01	22.3 ±0	16300 ±1.3	510 ±10	297.91 ±17.81	706 ±139	223.6 ±90.18	8200 ±25	55±5	2.2 ±0.2	99.33 ±8.38	3086 ±1	7568.36 ±512.82
NEQs	6-10	-	3500	150	150	-	-	-	-	-	-	600	1000
WHO	-	-	500	05	10	100	150	200	12	-	45	300	200-500

3.2 Physico-Chemical Characterization of Activated Charcoal

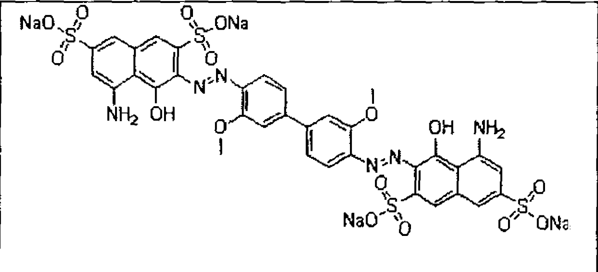
The raw charcoal was activated by using H_3PO_4 and characterized in terms of different parameters summarized in Table 3.4. pH of activated carbon lies in acidic range,while the moisture content is 5.5%. Activated carbon has large surface area and porosity which makes it an efficient adsorbent (Jason, 1999).

Table: 3.2 Physico-Chemical parameters of Activated Charcoal

S.No.	Parameters	Activated Charcoal With H_3PO_4
1.	pH	3.5
2.	Moisture content (%)	5.5
3.	Ash Content (%)	4.8
4.	Bulk Density (g/cm^3)	0.51
5.	Tap Density (g/cm^3)	0.62
6.	True Density (g/cm^3)	2.65
7.	Specific Surface Area (m^2/g)	101.19
8.	Pore Volume (cc/g)	1.05
9.	Pore Diameter (nm)	9.863

3.3 Removal of Direct blue 15 from Textile Wastewater by Adsorption onto Activated Charcoal

Various adsorption parameters for the removal of Direct blue 15 from textile wastewater onto activated charcoal have been studied and optimized, which are as follows:



MolecularFormula: $C_{34}H_{28}N_6O_{16}S_4{}^{\cdot}{}_4Na$

Molecular weight: 992.80

Figure.3.1. Molecular Structure of Direct blue 15

3.3.1 Effect of Shaking Time

The Direct blue 15 adsorption behavior was studied with the initial concentration of 110.30 mg/land 1.0g of activated charcoal within the time interval of 5-240 minutes. The percentage adsorption of Direct blue 15 as a function of contact time indicates that the equilibrium between Direct blue 15 and the activated charcoal was attained within 60 minutes (figure 3.2), therefore it was followed in all further experiments.

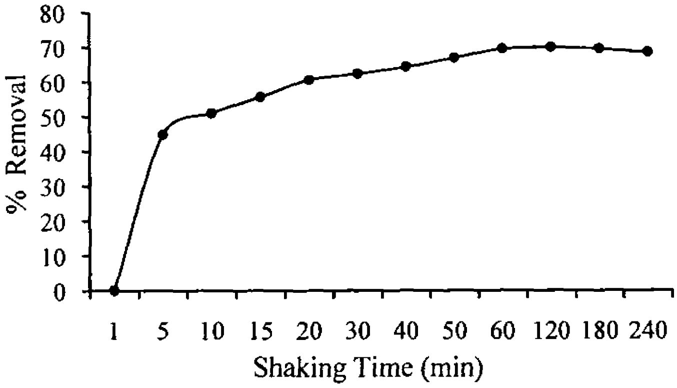


Figure: 3.2. Effect of shaking time on the adsorption of Direct blue 15 onto activated charcoal.
*Experimental conditions: Conc. of Direct blue 15 = 110.3 mg/l; Amount of adsorbent= 1.0g; Temperature= 27°C ± 2 °C; Medium= wastewater

3.3.2 Effect of Adsorbent Amount

The dependence of Direct Blue 15 dye adsorption on the amount of activated charcoal is shown in figure.3.3. The amount of activated charcoal was varied which ranged between 0.1--8.0g with the110mg/L initial concentration of Direct blue 15 and 60 minutes shaking time, respectively. The results showed that with the increased concentration of adsorbent the % removal of Direct blue 15 also increased and up to 5.0g the % adsorption remains constant. Therefore, 5.0g of adsorbent used in all the further experiments. The activated sites for the dye adsorption increased by increasing the amount of adsorbent it would leads to the increase in color removal percentage(Namasivayam and Yamuna, 1994; Sarioglu and Atay, 2006).

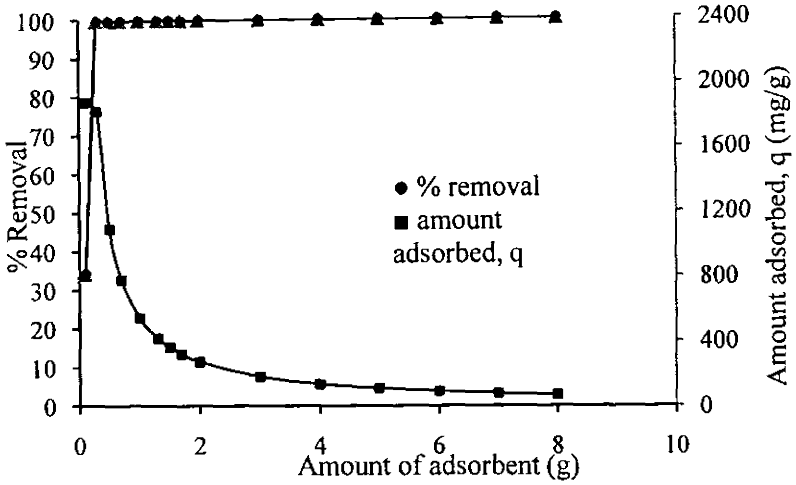


Figure: 3.3. Effect of amount of activated charcoal on the adsorption of Direct blue 15.

*Experimental conditions:Conc. of Direct blue 15 = 110.3 mg/l; Shaking time= 60 min; Temperature= 27°C ± 2 °C; Medium= wastewater

3.3.3 Effect of pH

The adsorption of Direct blue 15 on different pH is shown in figure.3.4.

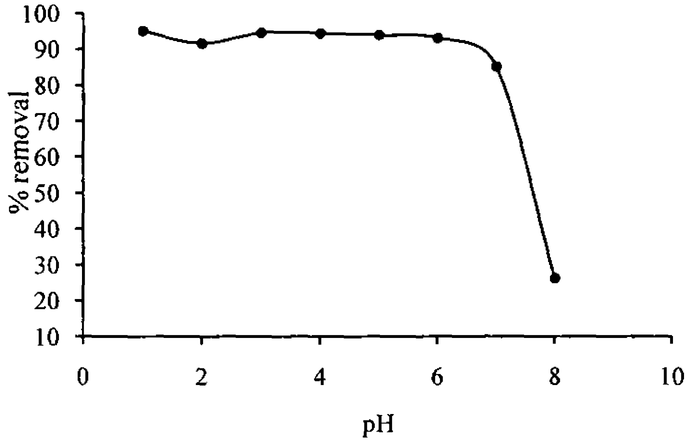


Figure: 3.4. Effect of pH on the adsorption of Direct blue 15shaking time onto activated charcoal.

*Experimental conditions: Conc. of Direct blue 15 = 110.3 mg/l; Amount of adsorbent= 5.0g; Temperature= 27°C ± 2 °C; Medium= wastewater

The pH of the solutions was varied from highly acidic to basic with the initial concentration of Direct blue 15, shaking time and amount of adsorbent were 110.3 mg/L, 60 minutes and 5 g, respectively. The results showed that, the adsorption behavior did not vary considerably from pH 1-6 while there was not effective adsorption at basic pH(Colak *etal.*, 2009).

3.3.4 Effect of Adsorbate Concentration

The Direct blue 15 adsorption over the range from 110mg/L – 800mg/L on the fixed amount of adsorbent 5.0g in wastewater medium is shown in figure.3.5.

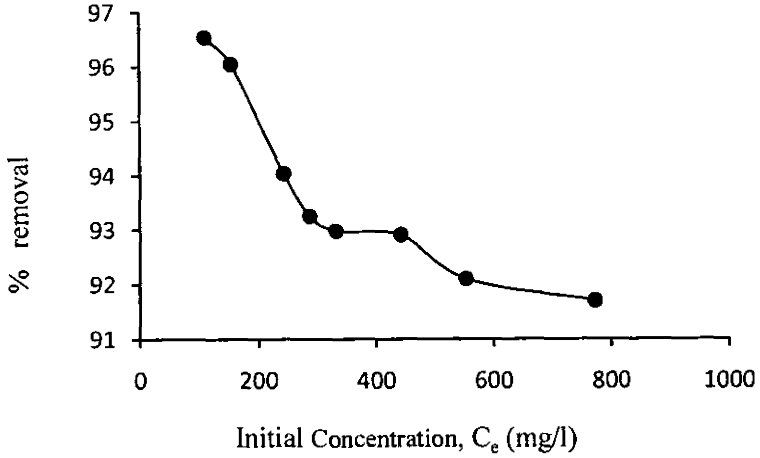


Figure: 3.5. Effect of different concentrations of Direct blue 15 on its adsorption onto activated charcoal.
*Experimental conditions: Amount of adsorbent= 5.0g; Temperature= 27°C ± 2 °C; Shaking time=60min; Medium= wastewater;

From the figure it is clear that the adsorption remains maximum 96% for 110mg/L concentration and decreases as the Direct blue 15 concentration increases due to the formation of monolayer on the adsorbent(Khattri and Singh, 2009).The results showed that adsorption process depends on the concentration of the solution (Verma and Mishra, 2005).

3.3.4 Effect of Different Temperature

The effect of different temperature (27°C, 37°C and 47°C) with different concentrations (110.30mg/L to 772.10mg/L)of Direct blue 15 was investigated with the shaking time of 60 minutes and 5.0 g activated charcoal respectively.The adsorption capacity of the activated charcoal increased with increase in the temperature from 27°C-47°C.

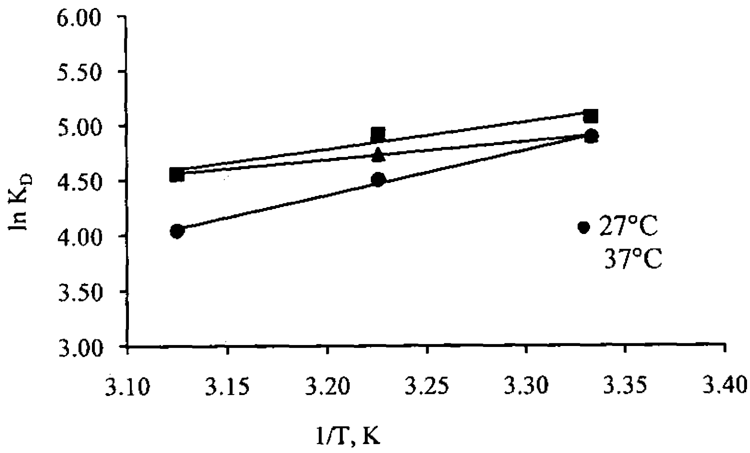


Figure: 3.6. Van't Hoff plot for the adsorption of Direct blue 15 onto activated charcoal.

*Experimental conditions: Temperature= 27°C, 37 °C and 47°C ± 2 °C; Shakingtime= 60 min; Amount of adsorbent= 5.0 g; Medium= wastewater.

Thermodynamic parameters such as change in Gibb's free energy (ΔG^{o}) kJ/mol, enthalpy (ΔH^{o}) kJ/mol and entropy (ΔS^{o}) J/mol were determined by using the following equations (Kocke and Hemphill., 1981)

$$\ln K_D = \Delta S^{o}/R - \Delta H^{o}/RT$$

The free energy of specific adsorption ΔG^{o} is calculated from the relation:

$$\Delta G^{o} = \Delta H^{o} - T\Delta S^{o}$$

The values of ΔH^{o} and ΔS^{o} were calculated from the slopes and intercepts of Van't Hoff plots (Berrueta *et al*, 1990) as shown in Table 3.3.

Table: 3.3. Thermodynamic parameters for the adsorption of Direct blue 15 onto activated carbon

S.No.	Concentration of Direct blue 15 (mg/l)	ΔH° (kJ/mol)	ΔS° (kJ/K.mol)	-ΔG° (kJ/mol)		
				300K	310K	320K
1.	242.66	13.029	2.794	13.867	13.895	13.922
2.	330.99	19.821	23.729	26.940	27.177	27.415
3.	441.2	33.099	69.699	54.009	54.706	55.403

3.3.5 Adsorption Isotherms

Results were analyzed by using Langmuir and Freundlich isotherms. Langmuir plot for the adsorption of Direct blue 15 at different temperatures (27°C, 37°C and 47°C) is shown in figure.3.7- 3.9. The Langmuir isotherm shows the saturation monolayer is represented by the followingequation (Langmuir, 1918).

$$C_e / q = 1/Q_o b + Ce / Q_o$$

WhereC_e is equilibrium concentration in mg/L, at equilibrium q is the amount adsorbed in mg, Q_o and b are Langmuir constants related to adsorption capacity and energy of adsorption respectively. The linear plot of specific adsorption (C_e/q) against the equilibrium concentration (C_e) showed that the adsorption obeys the Langmuir model in figure 3.7-3.9.The values of regression correlation (R^2)of Langmuir isotherm were 0.640-0.940 at 27°C, 37°C and 47°C respectively. These values showed the applicabilityof the isotherm (Krishna and Bhattacharrya, 2002).

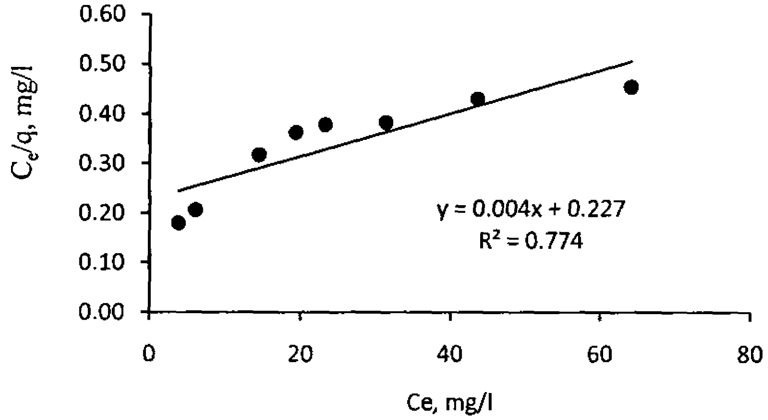


Figure: 3.7. Langmuir plot for the adsorption of Direct blue 15 onto activated charcoal.

*Experimental conditions: Amount of adsorbent= 5.0g; Temperature= 27°C ± 2 °C;
Shaking time=60min; Medium= wastewater

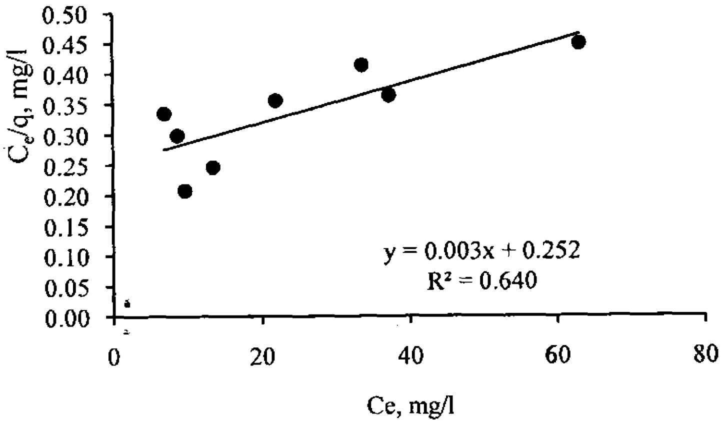


Figure: 3.8. Langmuir plot for the adsorption of Direct blue 15 onto activated charcoal.

*Experimental conditions: Amount of adsorbent= 5.0g; Temperature= 37°C ± 2 °C;
Shaking time=60min; Medium= wastewater

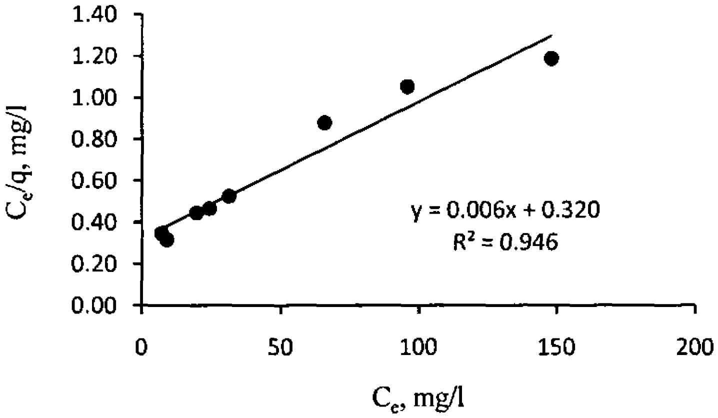


Figure: 3.9. Langmuir plot for the adsorption of Direct blue 15 onto activated charcoal.

*Experimental conditions: Amount of adsorbent= 5.0g; Temperature= 47°C ± 2 °C;
Shaking time= 60min; Medium= wastewater

The Freundlich isotherm (Freundlich, 1906) is represented as:

$$\text{Log } q = \log K + (1/n) \log C_e$$

Where C_e is the equilibrium concentration of Direct blue 15 in mg/l and q is the amount adsorbed. The value of K indicates the adsorption capacity while 1/n indicates the intensity of reaction (Namasivayan and Ranganthan, 1999). The dominace of adsorption capacity showed by the logarithmic plot of Freundlich expression for the amount of

Direct blue 15 adsorbed per unit mass of adsorbent and the concentration of Direct blue 15 at equilibrium in figure 3.10-3.12.

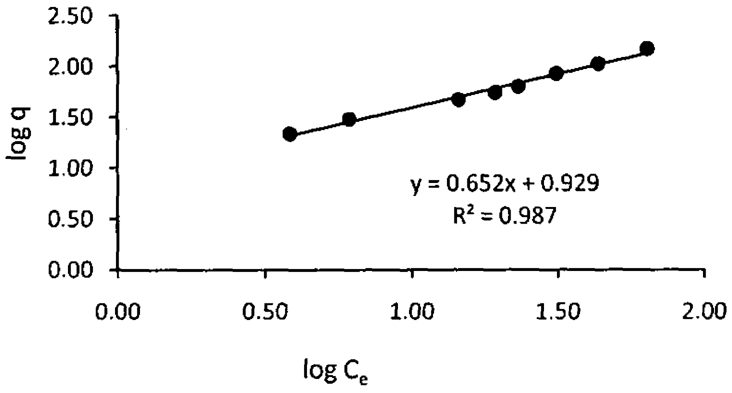


Figure: 3.10. Freunlich plot for the adsorption of Direct blue 15 onto activated charcoal.

*Experimental conditions: Amount of adsorbent= 5.0g; Temperature= 27°C ± 2 °C; Shaking time=60min; Medium= wastewater

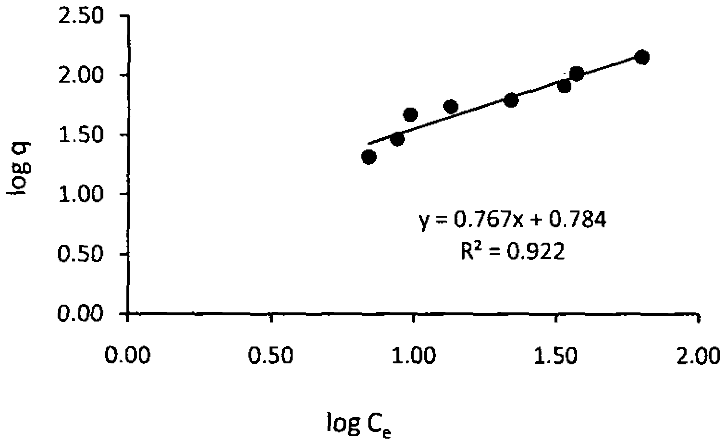


Figure: 3.11. Freundlich plot for the adsorption of Direct blue 15 onto activated charcoal.

*Experimental conditions: Amount of adsorbent= 5.0g; Temperature= 37°C ± 2 °C; Shaking time=60min; Medium= wastewater

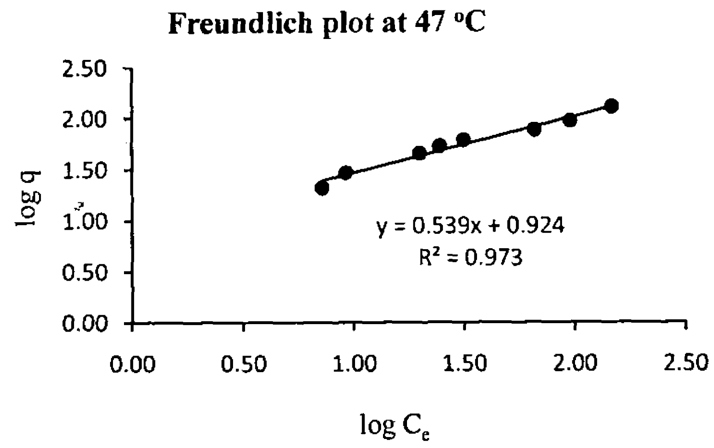


Figure: 3.12. Freundlich plot for the adsorption of Direct blue 15 onto activated charcoal.
*Experimental conditions: Amount of adsorbent= 5.0g; Temperature= 47°C ± 2 °C;
Shaking time=60min; Medium= wastewater

3.3.6 Column Studies

For column adsorption studiesat room temperature the initial concentration of Direct blue 15 was 110.30 mg/L with 10g activated charcoal respectively.By plotting a graph between the ratios of effluent concentration to initial concentration versus the volume of the effluent breakthrough curve was obtainedshown in figure 3.13.

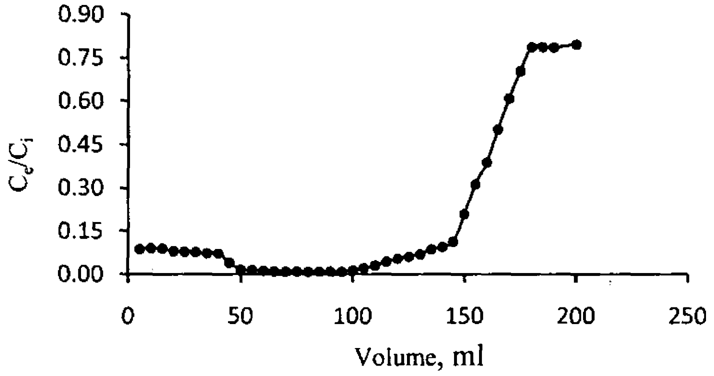
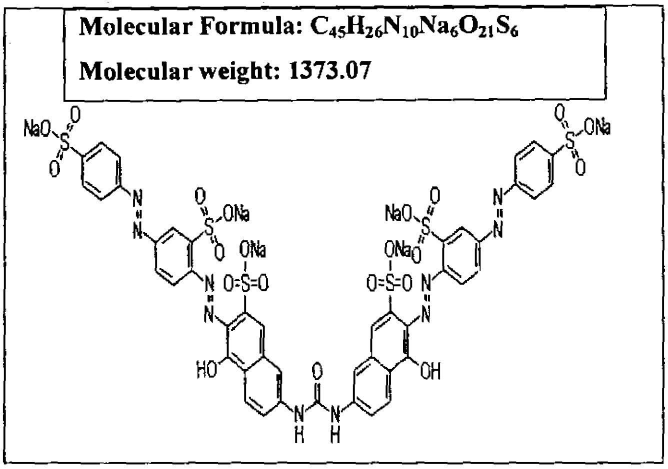


Figure: 3.13. Effect of shaking time on the adsorption of Direct blue 15 onto activated charcoal.
*Experimental conditions: Amount of adsorbent= 5.0g; Temperature= 27°C ± 2 °C;
Medium= wastewater; Volume of wastewater= 200ml

When the concentration of the solute in the effluent is equal to the influent concentrationbreakthrough curve was attained (Vijayaraghavan *et al.*, 2005).

3.4 Removal of Direct Red 80 from Textile Wastewater By Adsorption onto Activated Charcoal

Various adsorption parameters for the effective removal of Direct red 80 by using activated charcoal as an adsorbent from wastewater samples was studied and optimized.



Molecular Formula: $C_{45}H_{26}N_{10}Na_6O_{21}S_6$

Molecular weight: 1373.07

Figure:3.14 Molecular Structure of Direct Red 80

3.4.1 Effect of Shaking Time

The effect of shaking time for the adsorption of Direct red 80 is shown in figure 3.15. It is observed that adsorption of Direct red 80 with initial concentration of 82.98 mg/L increases rapidly with time then slows down and attains equilibrium after 60 minutes at room temperature (27±2^{0}C). Therefore, 60 minutes time was followed in all further experiments.

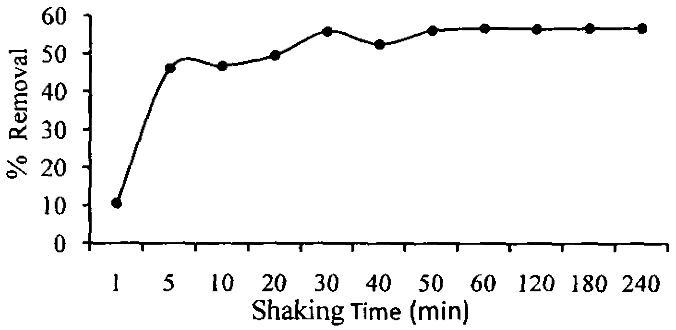


Figure: 3.15. Effect of shaking time on the adsorption of Direct red 80 onto activated charcoal.

*Experimental conditions: Cone. of Direct red 80= 82.98 mg/L;Amount of adsorbent= 1.0 g; Temperature= 27°C ± 2 °C; Medium wastewater

3.4.2 Effect of Adsorbent Amount

The dependence of Direct red 80 dye adsorption on the amount of activated charcoal is shown in figure.3.16.The amount of activated charcoal was varied from 0.1g to 8.0g with the82.98 mg/L initial concentration of Direct red 80and 60 minutes shaking time respectively. The results showed that with the increased concentration of adsorbent the % removal of Direct red 80 also increased and up to 3.0g the % adsorption remains constant. Therefore, 3.0g of adsorbent used in all the further experiments.

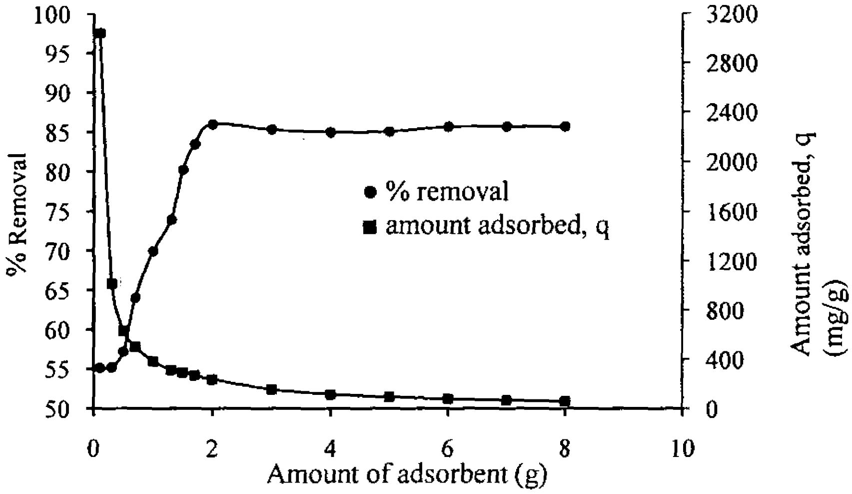


Figure: 3.16. Effect of amount of activated charcoal on the adsorption of Direct red 80.

*Experimental conditions: Conc. of Direct red 80= 82.98 mg/L;Temperature= 27°C ± 2 °C. Shaking time= 60min; Medium= wastewater.

3.4.3 Effect of Different pH

The pH of the solutions was varied from highly acidic to basic with the initial concentration of Direct red 80, shaking time and amount of adsorbent were 82.98 mg/L, 60 minutes and 3.0 g, respectively. The adsorption of Direct red 80 on different pH is shown in figure.3.17. The results showed that, the adsorption behavior did not vary considerably from pH 1-5.

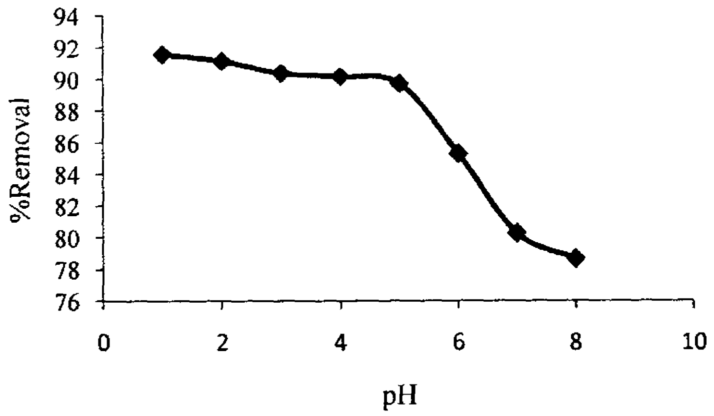


Figure: 3.17. Effect of pH on the adsorption of Direct red 80 onto activated charcoal.

*Experimental conditions: Conc. of Direct red 80= 82.98 mg/L;Amount of adsorbent= 3.0 g; Temperature= 27°C ± 2 °C; Shaking time=60min Medium=wastewater

3.4.4 Effect of Adsorbate Concentration

From the figure 3.18 it is clear that the adsorption remains maximum 94% for 82.89mg/L concentration and decreases as the Direct red 80 concentration increases due to the formation of monolayer on the adsorbent(Khattri and Singh 2009).

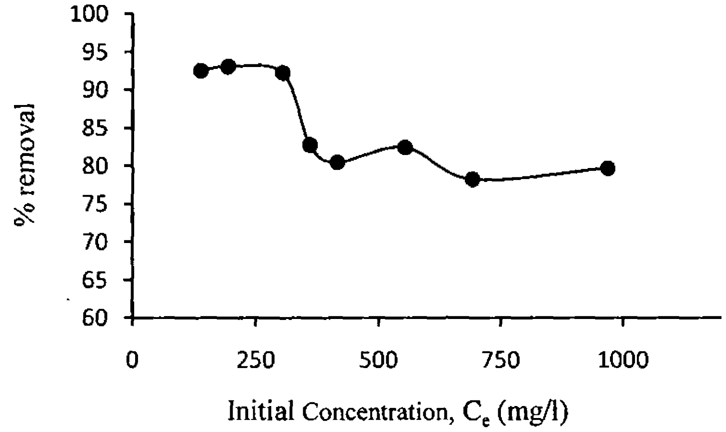


Figure: 3.18. Effect of different concentrations of Direct red 80 on its adsorption onto activated Charcoal.

*Experimental conditions: Temperature= 27°C ± 2 °C; Shaking time= 60 min; Amount of activated carbon= 3.0 g;medium= wastewater

3.4.5 Effect of Different Temperature

The effect of different temperature (27°C, 37°C and 47°C) with different concentrations (138.30mg/L to 968.10mg/L)of Direct red 80 was investigated with the shaking time of 60 minutes and 3.0 g activated charcoal respectively.The adsorption capacity of the activated charcoal increased with increase in the temperature from 27°C-47°C.

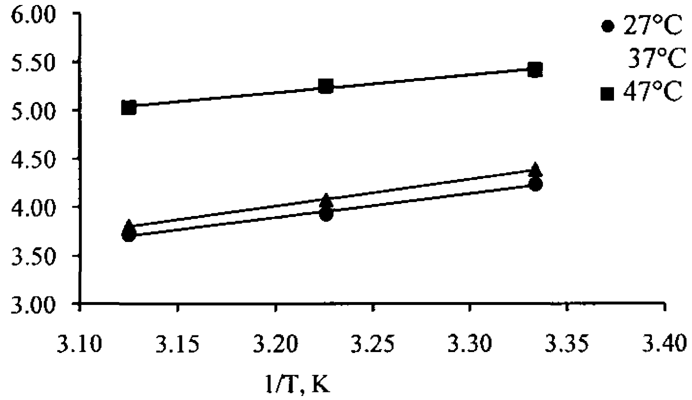


Figure: 3.19. Van't Hoff Plot for the Adsorption of Direct red 80 onto Activated Charcoal
*Experimental conditions: Temperature= 27°C, 37°C and 47°C ± 2 °C; Shaking time= 60min, Amount of adsorbent= 3.0 g;Medium= Wastewater.

Thermodynamic parameters such as change in Gibb's free energy (ΔG^o) kJ/mol, enthalpy (ΔH^o) kJ/mol and entropy (ΔS^o) J/mol were determined by using the following equations (Kocke and Hemphill., 1981)

$$\ln K_D = \Delta S^o/R - \Delta H^o/RT$$

The free energy of specific adsorption ΔG^o is calculated from the relation:

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

The values of ΔH^o and ΔS^o were calculated from the slopes and intercepts of Van't Hoff plots (Berrueta *et al,* 1990) as shown in Table 3.4.

Table 3.4. Thermodynamic Parameters for the Adsorption of Direct red 80 onto Activated Carbon

S..No	Concentration of Direct Red 80 (mg/l)	ΔH^o (kJ/mol)	ΔS^o (kJ/K.mol)	$-\Delta G^o$ (kJ/mol)		
				300K	310K	320K
1.	193.62	15.016	5.022	16.522	16.572	16.623
2.	359.58	22.906	39.984	34.901	35.301	35.701
3.	414.4	20.511	33.307	30.504	30.837	31.170

3.4.5 Adsorption Isotherms

Results were analyzed by using Langmuir and Freundlich isotherms. Langmuir plot for the adsorption of Direct red 80 at different temperatures (27°C, 37°C and 47°C) is shown in figure.3.20-3.22. The Langmuir isotherm shows the saturation monolayer is represented by the followingequation (Langmuir, 1918).

$$C_e/q = 1/Q_ob + Ce / Q_o$$

WhereC_e is equilibrium concentration in mg/L, at equilibrium q is the amount adsorbed in mg , Q_o and b are Langmuir constants related to adsorption capacity and energy of adsorption respectively. The linear plot of specific adsorption (C_e/q) against the equilibrium concentration (C_e) showed that the adsorption obeys the Langmuir model in figure 3.20-3.22.

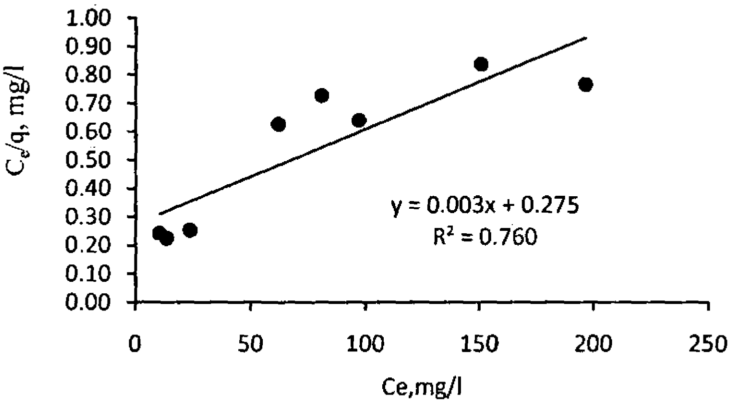


Figure: 3.20. Langmuir plot for the adsorption of Direct Red 80 onto activated charcoal
*Experimental conditions: Temperature= 27°C ± 2 °C; shaking time= 60min; Amount of activated carbon= 3.0 g;Medium= wastewater.

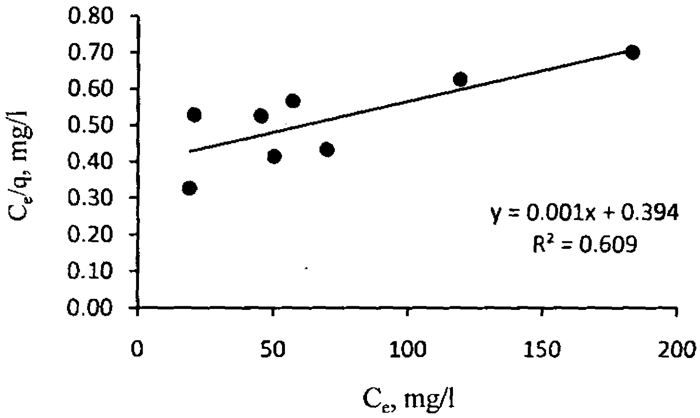


Figure: 3.21. Langmuir plot for the adsorption of Direct red 80 onto activatedcharcoal
*Experimental conditions: Temperature= 37°C ± 2 °C; shaking time= 60min; Amount of adsorbent= 3.0 g; medium= wastewater

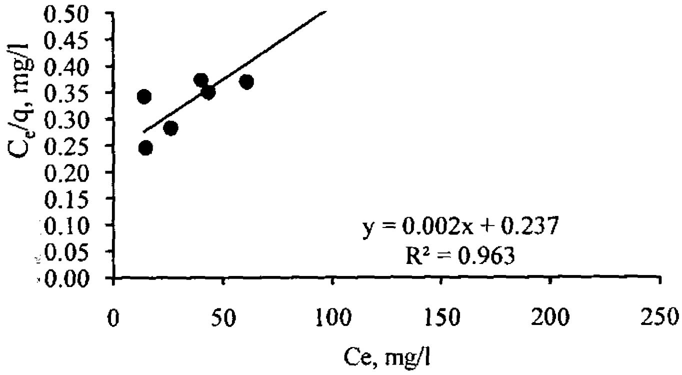


Figure: 3.22. Langmuir plot for the Adsorption of Direct red 80 onto Activated Charcoal
*Experimental conditions: Temperature= 47°C ± 2 °C; shaking time= 60min; Amount of adsorbent= 3.0 g; medium= wastewater.

The trend in the figures indicatesadsorbent binds with acidic ions and the process is endothermic (Khattri and Singh 1999). The values of regression correlation (R^2)of Langmuir isotherm were0.760 - 0.963 at 27°C, 37°C and 47°C respectively. These values showed the applicability of the isotherm (Krishna and Bhattacharrya 2002).

The Freundlich isotherm (Freundlich, 1906) is represented as:

$$\text{Log } q = \log K + (1/n) \log C_e$$

where C_e is the equilibrium concentration of Direct red 80 in mg/l and q is the amount adsorbed. The value of K indicates the adsorption capacity while 1/n indicates the intensity of reaction (Namasivayan and Ranganthan 1999). The dominace of adsorption capacity showed by the logarithmic plot of Freundlich expression for the amount of Direct blue 15 adsorbed per unit mass of adsorbent and the concentration of Direct blue 15 at equilibrium in figure 3.22--3.24

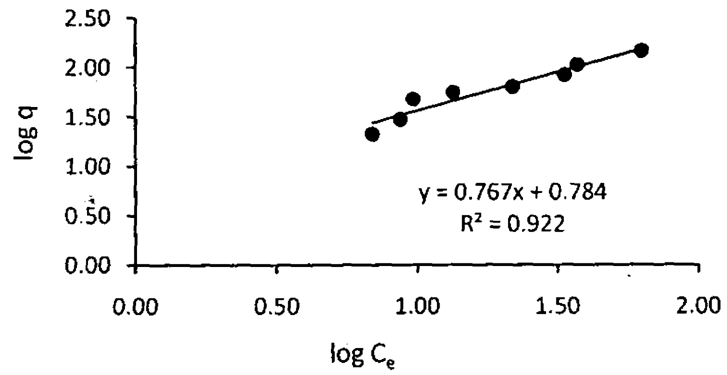


Figure: 3.23. Freundlich plot for the adsorption of Direct red 80 onto Activated Charcoal
*Experimental conditions: Temperature= 27 ± 2 °C; Shaking time= 60min; Amount of adsorbent= 3.0 g; medium= wastewater.

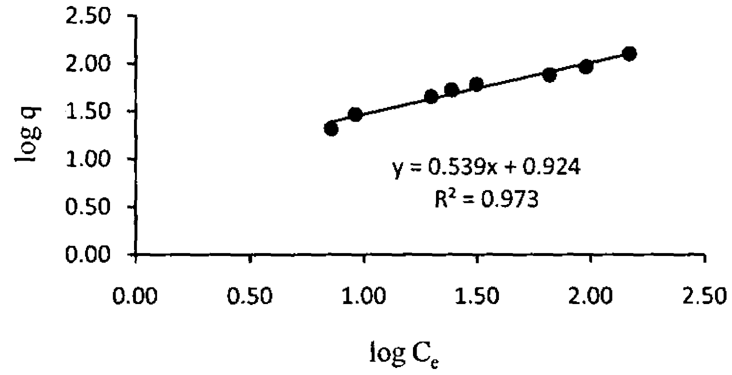


Figure: 3.24. Freundlich plot for the adsorption of Direct red 80 onto activated charcoal
*Experimental conditions: Temperature= 37°C ± 2 °C; shaking time= 60min
Amount of adsorbent= 3.0 g; medium= wastewater.

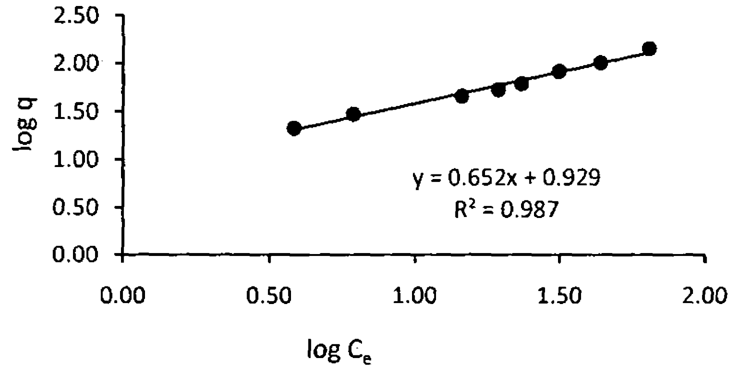


Figure: 3.25. Freundlich plot for the adsorption of Direct red 80 onto activated charcoal
*Experimental conditions: Temperature= 47°C ± 2 °C; shaking time= 60min
Amount of adsorbent= 3.0 g; medium= wastewater.

3.4.6 Column Studies

For column adsorption studiesat room temperature the initial concentration of Direct red 80 was 1138.30 mg/L with 10g activated charcoal respectively. By plotting a graph between the ratios of effluent concentration to initial concentration versus the volume of the effluent breakthrough curve was obtainedshown in figure 3.26. When the concentration of the solute in the effluent is equal to the influent concentrationbreakthrough curve was attained (Vijayaraghavan *et al.*, 2005).

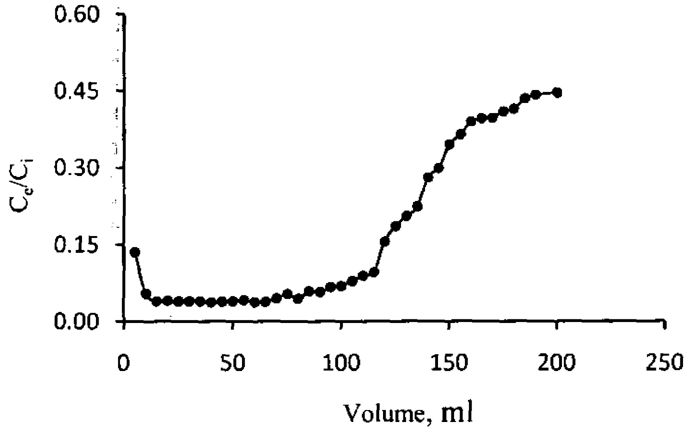


Figure: 3.26. Column breakthrough curve for the adsorption of Direct red 80 onto activated charcoal.

*Experimental conditions: Temperature= 27°C ± 2 °C; shaking time= 60min; Amount of adsorbent= 3.0 g; medium= wastewater; Volume of wastewater=200ml

CHAPTER #4

DISCUSSIONS

4.0 DISCUSSION

It is observed in this study that textile mills located in Faisalabad generates effluents which have high pollution rate along with hazardous concentration of dyes.pH is very important quality parameter for both natural and waste water because water with very high acidic or basic pH is not suitable for humans consumption(Pagga and Jaeger, 1994). At low pH most of the metals become soluble and persistent in the environment while most of the metals become insoluble at high pH and accumulates in the sludge and sediments (WHO, 1993). Textile plants use water from various sources like rivers, lakes and subterranean water from wells. According to source which may be rivers, lakes or subterranean water, natural and pre-treated water may contain variety of salts, many dissolved and suspended solids (Asia *et al.*, 2006). During the textile processing all the natural impurities, dirt, oil, grease must be removed in scouring process. The suspended solids, effects the aquatic flora and fauna, reduce the light penetration into the water, decrease the rate of photosynthesis and reduces the dissolved oxygen (DO) level (Shobana, 2008). Also these reduce the growth rate of fish or killed them by clogging its gills. High TDS level makes water unsuitable for irrigation (Goel, 1997). High level of Ca^{2+} and Mg^{2+} leads to hardness of water (Frantisek, 2003)

During the dying process large quantities of sodium chloride (NaCl) and sodium sulphates ($Na_2SO_4^-$) were used. $Na_2SO_4^-$ helps in leveling and reducing negative charges on fiber, so, that dyes can penetrate evenly within the fabric (Suresh *et al.*, 2006). SO_4^- changes the pH of water because they have the ability to form strong acids. Higher concentration of SO_4 also causes cathartic action in the bodies of living organisms and leads to long term illness. (Agarwal, 1996). High Cl^- concentration affects metallic pipes and is harmful for agricultural crops. This higher level of Cl^- also kills some microbes like which are important in food chain of aquatic life (Kumar, 1989). High concentration of NO_3^- in water leads to eutrophication and depletion of oxygen (Bartram *et al.*, 1999)

Wastewater generated from sizing, dyeing, printing and finishing processes contains high concentration of salts, COD and acids. COD is the measure of chemically decomposable organic and inorganic matter (Lenore *et al.*, 1998). High COD is attributed to different factors like unaesthetic color, endanger water supplies and decreasedrecreational value of water ways (Tayagi and Mehra, 1990). The effluents with high levels of COD are toxic for biological life (Metcelf and Eddy, 1991).

For the removal of dyes and reduce the concentration of pollutants adsorption is a feasible and economic process. Raw charcoal which was activated by using H_3PO_4, physicochemically characterized. The large surface area and pore size makes activated carbon suitable adsorbent during the adsorption process.

The adsorption process showed that the optimized time for Direct blue 15 (110.30 mg/l) and Direct red (82.98 mg/l) dye is 60 minutes.In the start the removal of dye increases with increasing time but with the passage of time it slows down and finally reaches to an equilibrium stage. During adsorption process, after 60 minutes the final concentration of dye did not vary with the initial concentration. During the adsorption process a monolayer was formed on the surface of adsorbent by adsorbate and the process becomes slows down due to the saturation of activated charcoal (Verma and Mishra, 2004; Khatri and Singh, 2000).

In the adsorption process pH of the aqueous solution is very important controlling parameter (Ajmal *et al.*, 2008; Nuhoglu and Oguz, 2003) because solution pH determines the surface properties and rate of adsorbent ionization (Gupta *et al.*, 1918).The acidic medium activates the adsorbent surface chemically and the adsorbent surface gains positive charge and reacts with accompanying SO^{-3} existing in Direct blue 15and Direct red 80 molecules and results in the electrostatic attraction between adsorbates and adsorbent and this finally leads to more adsorption while at basic pH electrostatic repulsion dominates due to the large number of negatively charged ions on the adsorbent (El-Nemr *et al.*, 2009).

The adsorption process is dye concentration dependent when the amount of activated charcoal was not varied. At lower concentration the number of dye molecules to the available adsorbent surface area was lower so, the adsorption process did not depend on the initial concentration (Garg *et al.*, 2003) but at high concentration the percentage removal of dye was dependent upon initial concentration because the number of dye molecules increased to the available adsorbent active sites (Senthilkumar *et al.*, 2005). The adsorption process becomes slowed down with increasing the initial Direct blue 15 and Direct red 80 dye concentration without increasing the adsorbent amount leads to the saturation of active sites (Gupta *et al.*, 1988).

Temperature has very strong effect on the adsorption of dyes. The kinetic energy of adsorbate molecules and pore size of adsorbent increased by increasing the temperature (Aksu *et al.,* 2008) and the large adsorbate molecules moves into the adsorbent porus structure (Mckay, 1982; Admson, 1980; Setheraman, 1973, Saker and Podar, 1994: Mall and Upadhyaya, 1995). At higher temperature there was more interaction between the adsorbent and adsorbate which leads to more removal of dyes (Pandey *et al.*, 1988). The adsorption behaviour of Direct blue 15 and Direct red 80 showed the positive values of ΔH° that the adsorption is physical and endothermic in nature (Namasivayam and Yamuna, 1995). In the case of physical adsorption the dye removal increases with increasing the temperature (Sivaraj *et al.,* 2001).The negative values of ΔG° (Table 3.2) indicates spontaneous adsorption process. The positive values of ΔS° (Table 3.2) indicate the increased disorder and randomness at the solid solution interface during the adsorption of dye on the adsorbent (Khattri and Singh, 1999).

The results showed the applicability for the both adsorption isotherms models for the Direct blue 15 and Direct red 80 dyes. According to Langmuir adsorption isotherm it is the process in which adsorbate molecules in the form of monolayer adsorbed on the surface of adsorbent (Reundlich, 1906) which leads to the saturation of active sites (Senthilkumar *et al.*, 2005).

Freundlich adsorption isotherm indicates adsorbent binds with acidic ions and the process is endothermic (Khattri and Singh, 1999). According to Freundlich isotherm, the equilibrium during the adsorption process is measured by the distribution of adsorbate between the liquid phase and adsorbent. The values for the regression correlation factor R^2 were 0.987- 0.973 showed that the adsorption is favourable with the Freundlich isotherm adsorption model (Khan *et al.*, 2004).

The results of column studies for both dyes i.e. Direct blue 15 and Direct red 80 showed that adsorption process was very fast in the start and then slowed down at the equilibrium. As the binding sites were saturated the rate of dye removal becomes decreased (Albanis *et al.,* 2000).

The present study revealved that high concentration of dyes which are present in the human environment are recognized as a risk factor for human health. These dyes alter the metabolism and are carcinogenic. The textile wastewater samples were subjected to physico-chemical analysis and the results showed the high concentration of salts, metals and some non-metals when the data was compared with the WHO and NEQS limits. The present investigations showed thatactivated charcoal prepared from coconut shells was an efficient adsorbent for the removal of Direct blue 15 and Direct red 80 from textile wastewater due to its large surface area and porosity. Acidic pH favors the adsorption process and % removal of dyes increased with the increases in temperature. The Langmuir and freundlich adsorption models successfully described the equilibrium data. The positive value of ΔH^{o} and ΔS^{o}while the negative value of ΔG^{o} showed that the adsorption process was spontaneous and endothermic.

4.1RECOMMENDATIONS AND FUTURE PROSPECTS

Adsorption is an environmental friendly process, for the removal of dyes and minimizes the pollution load within acceptable limit. Although it is a laboratory scale study but this process can be implemented on the industrial scale in small units. For further research it is recommended to identify the safe method of adsorbent regeneration and find outmore and more sources of adsorbent which are not only cheaper but could be used efficiently and quickly on large scale.

CHAPTER #5

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