

**USE OF ACTIVATED CARBON FROM DATE SEEDS TO TREAT
TEXTILE EFFLUENT**

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TEXTILE EFFLUENT**

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It is hereby declared that this thesis or any part of it has not been submitted elsewhere for the award of any degree or diploma (except for publication).

Md. Azizur Rahman

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ABSTRACT

Treatment of wastewater is one of the major problems faced by textile manufacturers because of involvement of many complicated process and chemicals used throughout the production. The possible utilization of Date seeds activated carbon as an adsorbent for the removal of color and COD from aqueous solution has been investigated. In this study, activated carbon prepared from Date seeds has been activated using zinc chloride solution. Systematic batch mode studies of removal of color and COD on Date seeds activated carbon were carried out as a function of process parameters including initial concentration, dose of adsorbent, contact time, agitation speed, temperature, particle size and pH.

Freundlich and Langmuir adsorption isotherm models were used to explain obtained data. Both the isotherms were found to be fitted well; but Freundlich isotherm fitted better. The linear regression coefficient R^2 was used to reveal the best fitting of Freundlich isotherm model ($R^2 \approx 0.999$). The monolayer (maximum) adsorption capacity (q_m) for color was found 500 Pt-Co (per gram of adsorbent per litre) and for Date seeds activated carbon. The dimensionless separation factor (R_L) indicating favorability of adsorption that lies between 0.284 to 0.581 denotes a favorable adsorption for Date seeds activated carbon.

Lagergren pseudo first order and second order model were used to explain the kinetics of adsorption. Lagergren pseudo second order model fitted better the kinetics of adsorption ($R^2 = 0.999$, $q_{e(theoretical)} \approx q_{e(experimental)}$). Intra particle diffusion model showed both external film and intra-particle pore diffusion mechanism were involved in the adsorption of color onto Date seeds activated carbon; either of the two (i.e., film diffusion or pore diffusion) or both might be the rate controlling.

Adsorption was found to be increased with increasing temperature, contact time, dosage of adsorbent, agitation speed, pH and decreasing particle sizes. Thermodynamic analysis showed negative value of ΔG indicating favorable and spontaneous adsorption, positive value of ΔH indicating endothermic physical adsorption and positive value of ΔS indicating increased disorder as randomness at the solid-liquid interface of adsorbate with Date seeds activated carbon adsorbent.

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LIST OF SYMBOLS

R^2	Correlation coefficient
q_e	Equilibrium adsorption
C_o	Initial concentration of adsorbate
C_e	Equilibrium concentration of adsorbate
m	Mass of adsorbent
V	Volume of wastewater
K_f	measure of adsorption capacity
n	adsorption intensity
q_m	Monolayer (maximum) adsorption capacity
b	Langmuir constant related to energy of adsorption
R_l	Separation factor
k_1	Pseudo first order rate constant
k_2	Pseudo second order rate constant
k_i	Intra-particle diffusion rate constant
I	Boundary layer thickness
r_o	Radius of the adsorbent
D_f	Film diffusion coefficient
D_p	Pore diffusion coefficient
δ	Film thickness
$t_{1/2}$	Time necessary to obtain half the initial concentration
ΔG	Change in free energy
ΔH	Enthalpy
ΔS	Entropy
C_{solid}	Solid phase equilibrium concentration
C_{liquid}	Liquid phase equilibrium concentration
T	Absolute temperature
R	Gas constant
$ZnCl_2$	Zinc Chloride
M	Molarity
μm	Micro meter

ABBREVIATIONS AND ACRONYMS

ASTM	American Society for Testing and Materials
BOD	Biochemical Oxygen Demand
BTMA	Bangladesh Textile Mills Associations
BUET	Bangladesh University of Engineering and Technology
COD	Chemical Oxygen Demand
DoE	Department of Environment of Peoples Republic of Bangladesh
EC	Electrical Conductivity
ECR	Environment Conservation Rules
ETP	Effluent Treatment Plant
F/M	Food to Microorganism
GAC	Granular Activated Carbon
GDP	Gross Domestic Product
KJ	Kilojoules
MLSS	Mixed Liquor Suspended Solids
PAC	Powdered Activated Carbon
ppm	Parts Per Million
TCU	True Color Units
TDS	Total Dissolved Solids
TSS	Total Suspended Solid
UNEP	United Nations Environment Programme
USEPA	United States Environmental Protection Agency

CHAPTER 1

INTRODUCTION

1.1 General

Though Bangladesh is an agricultural country, rapid growth in the industrial sector at present is playing a vital role in the development of the country. To ensure rapid development of the nation, obviously there is no alternative to massive industrialization. In Bangladesh, seventy eight percent of the total export earning comes from textile and textile related goods. The textile and clothing industry is the major sector for economic growth of Bangladesh. The number of textile industry in 1983 was only 24 (BTMA, 2004). Within next 10 year this number reached 700 showing sharp growth of this industry. This sector provides 4.5 million jobs and contributes 13% to GDP (BTMA, 2007).

The textile industry is one of the most complicated among manufacturing industries. Wastewater treatment is one of the major problems faced by textile manufacturers. A detailed study of the textile processes will reveal that there are many complicated process and chemicals used throughout the production. In the case of manufacturing of woven polyester and cotton blended fabric, the textile main processes starts from fiber production in the case of synthetic fiber followed by spinning to convert the fiber to yarns. Yarns are then strengthened with sizing chemicals like starch, polyvinyl alcohol and wax so that they can withstand vigorous movement when the yarns are weaved into fabric in high speed weaving looms. After weaving, weaved fabric must be pretreated before they can be dyed, printed and finished. During pretreatment there are various chemicals being used. Fabric is desized either with enzyme or oxidative chemicals and scoured using sodium hydroxide and detergent. Bleaching is done normally by using hydrogen peroxide to remove the natural color of the fabric white. Fabric is then mercerized using high concentration sodium hydroxide to stabilize the fabric. During dyeing and printing, many types of dyes are used e.g. disperse, reactive, vat etc. together with dyeing auxiliaries and chemicals. Fabric is finally finished to give the last touch and intended properties by using resins, softeners and other finishing agents.

The combination of the processes and products make the wastewater from textile plant contain many type of pollutants. The dyeing and finishing operations are such that the dyestuffs, chemicals and textile auxiliaries used can vary from day to day and sometimes even within several times a day (Lin and Chen, 1997). It contains various waste chemical pollutants such as sizing, agents, wetting agents, complexing agents, dyes, pigments, softening agents, fluorocarbon, surfactants, oils, wax and many other additives which are used throughout the processes. These pollutants contribute to high suspended solids (SS), chemical oxygen demand (COD), biochemical oxygen demand (BOD), heat, color, acidity, basicity and other soluble substances (Gonçalves et al., 2000).

1.2 Statement of the problem

Dyes are extensively used in many industries including printing processes, textile, plastics, cosmetics, etc. to add color for their final products. Most of the unspent dyes generate undesirable effluents and usually will be discharged to the environment with or without treatment. There are over 100,000 available dyes with more than 7×10^5 tones of dyestuff produced annually (Ping et al., 2008). Approximately 2% of dyes produced are discharged in effluent from manufacturing operations while 10% are discharged in effluent from textile and associated industries (Ping et al., 2008).

Textile dyeing process is an environmentally unfriendly process because they produce colored wastewater that is heavily polluted with dyes, textile auxiliaries and chemicals (Roussy et al., 2005). Color of textile effluents escalates environmental problem mainly because of its non-biodegradable characteristics. Color in the effluent is one of the most important indicators of water pollution and discharge of effluents highly colored are aesthetically displeasing and can damage the receiving water bodies by impeding penetration of light (Khehra et al., 2005). The treatment of textile wastewater is complicated because of significant BOD, COD and TDS content plus non-biodegradable nature of organic dyestuffs (Quader, 2010).

There have been a number of treatment options available for the treatment of textile wastewater. However most of them are expensive and therefore the industry owners are reluctant to install any of the treatment options. It is expected that, by developing a comparatively cost effective treatment method it is possible to encourage the

industry owners to treat the effluent of their industries and thus help improving the quality of water bodies in Bangladesh.

Various methods of dye/color removal, such as aerobic and anaerobic microbial degradation, coagulation, and chemical oxidation, membrane filtration, electrochemical have been proposed from time to time (Churchley, 1994). However all of these methods suffered with one or another limitation and none of these were successful in removing color from the wastewater completely. Treatment technologies can generally be divided into physico-chemical (coagulation, electrochemical, filtration, ion exchange, adsorption, membrane and photolysis) and biological methods. Although biological treatment processes remove biochemical oxygen demand, chemical oxygen demand, and suspended solids to some extent, they are largely ineffective in removing color from wastewater because most of them are toxic to the organisms used in the process. The coagulation process effectively decolorizes insoluble dyes but fails to work well with soluble dyes.

Adsorption is a more efficient and economically feasible process for treatment of wastewater containing chemically stable pollutants (Guendy, 2006 and El-Nemr et al., 2009). It proves superior to the other processes by being sludge free and can completely remove even very minute amounts of dyes in wastewater (Nigam et al., 1996).

In this light, activated carbon has long been considered the best adsorbent for the removal of organic matter in wastewater (Kadirvel et al., 2003). They contain extended surface area, a lot of internal voids, high adsorption capacity and a high degree of surface activity (Malik, 2003). Reduction of COD by adsorption on activated carbon has been reported (Das and Patnaik, 2001; Rao and Bhole, 2001). Commercially produced activated carbons, zeolites are however, very expensive. Despite the prolific use of activated carbon for the wastewater treatment, carbon adsorption remains an expensive process, and in this fact over recent years has prompted a growing research interest in the production of low cost, efficient indigenous technology capable of removing various dyes/coloring materials from industrial effluents. Present study is an attempt for removal of color and COD from textile wastewater using activated carbon prepared from Date seeds.

1.3 Objectives of the study

The main objective of this study is to reduce color and COD from the selected textile wastewater using Date seeds activated carbon. Specific objectives of this study include:

- a) To evaluate the efficiency of Date seeds activated carbon as an adsorbent for the removal of color and COD from the textile effluent.
- b) To determine the equilibrium contact time and optimum dosage for maximum color and COD reduction.
- c) To determine the removal performance at different experimental conditions i.e. effect of adsorbent dosage, temperature, particle size, agitation speed, pH and initial concentration.
- d) To establish the adsorption isotherm, kinetic models and thermodynamic data to understand the process of adsorption.

1.4 Approach and methodology

The approach and methodology followed and major specific activities carried out under the study are summarized below:

1.4.1 Literature review

For this study various relevant M.Sc. Engg. thesis papers on textile wastewater treatment from the library of Department of Civil Engineering, BUET have been studied. A lot of published journals on textile wastewater treatment by adsorption process using activated carbon were reviewed. Efforts have been made to collect and compile available information.

1.4.2 Laboratory scale activated carbon preparation from Date seeds

Activated carbon prepared from Date seeds was used as adsorbent in this adsorption process. Collected Date seeds were burned, prepared carbon were activated using $ZnCl_2$ in a standard procedure. Details of carbon preparation and activation process are given in Chapter 3. The physical properties of Date seeds activated carbon were

calculated in Environmental Engg., Geotechnical Engg and Concrete Laboratory of Department of Civil Engg, BUET.

1.4.3 Laboratory experiment of collected sample

The textile wastewater sample was collected from a textile industry located at Gazipur and different required laboratory scale experiment was done for this study. Batch adsorption process using a shaker was done in the laboratory. Detail laboratory experimental process has been discussed in Chapter 3.

1.4.4 Data analysis and interpretation

The primary data generated under the study were analyzed with a view to assess the adsorption capacity of Date seeds activated carbon for the treatment of color and COD.

1.5 Organization of the thesis

This thesis has been presented in five chapters. Chapter 1 describes the introduction of the study, present status of the problem and the major objectives of the study. Chapter 2 describes the literature review of the study. Chapter 3 presents the methodology followed to carry out in laboratory. Chapter 4 describes the results obtained from laboratory and summarizes the major findings drawn from the study. Finally chapter 5 presents the major conclusions of the study and recommendations for future studies.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Untreated and poorly treated textile liquid waste is a threat to the ecosystem and livelihood systems due to discharge into the water courses and degrade the water resources. Thus the treatment of textile effluents is of interest because of their toxic and aesthetic impacts on receiving water bodies and surrounding lands. Human health and environmental pollution concerns have become punctual the government to set a hardly achievable discharge quality standard for textile effluent.

As the quality and composition of textile industry effluent varies with the type of fiber, the involved operated processes and the classification of textile industries will help understanding the variations. Various techniques can help to reduce the strength and amount of wastewater but end pipe treatment is necessary to achieve the discharge standard set by the government. There are a number of treatment technologies available to treat textile effluent but no single solution has been satisfactory for remediation the broad diversified textile wastes.

2.2 Previous works on treatment of wastewater using activated carbon

The most important parameters in wastewater from textile industry are COD, BOD₅, TDS, TSS and color (Tufekci et al., 1998). Adsorption process has been reported as an effective treatment option for removing chemically stable color and COD constituents from wastewater.

Farhan et al., (2013) prepared activated carbon from saw dust of *Dalbergia sissoo*, *Cedrus deodara* and *Eucalyptus* spp., using H₃PO₄, H₂SO₄ and BaCl₂ as activating agents. The activated carbons were evaluated for reduction in color and COD of a real paper industry effluents using batch mode method. *Cedrus deodara* based activated carbon was most efficient; showed 93% COD reduction with 100% color removal and brought other physico-chemical parameters of wastewater within the permissible limit of discharge. The maximum percentage reduction of COD and color with *Dalbergia sissoo* activated carbon was 80% and 91% respectively, whereas with *Eucalyptus* spp. Activated carbon was 74% and 85% respectively. Effects of

operating parameters (contact time, amount of activated carbon, wastewater concentration, solution pH etc.) were evaluated for the reduction of color and COD.

Alam et al., (2012) prepared activated carbon from *Rice Husk* activated by sulfuric acid and zinc chloride for removal of Methylene blue from wastewater. The maximum uptake of methylene blue by *Rice Husk* activated carbon at optimum conditions was found 97%.

Velmurugan et al., (2011) investigated the potentiality for use of cheap and eco-friendly adsorbents from *Orange peel*, *Banana peel* and *Neem leaves* for removal of Methylene blue from aqueous solution, and compared the removal efficiency with commercially available powder activated carbon. Removal efficiency of all the adsorbents was quite effective, but orange peel found to be very effective compared to other low cost adsorbent within the short period of time. Although activated carbon was the most effective adsorbent. The maximum color removal efficiency of orange peel at dosage 1.0g for time duration of 45 minutes was found to be 99% of the dye from aqueous solution.

Yakubu et al., (2008) in his study used *Date seeds* activated carbon for the reduction zinc, nickel, COD and color from tannery and textile effluents. Carbon obtained from *Date seeds* was activated with only zinc chloride and zinc chloride/steam. The carbon activated by zinc chloride/steam recorded better wastewater removal than only zinc chloride activated carbon. The only zinc chloride activated carbon removed zinc (90%), nickel (88%) and COD (91%) whereas the zinc chloride/steam activated carbon removed zinc (99%), nickel (91%) and COD (99%). Decolorization of between 85-97% was recorded for the textile effluent, and 75-90% for the tannery effluent, in all cases decreasing with temperature increase. The zinc chloride/steam activated carbon treatment was better for the textile effluent and the zinc chloride activation was better for the tannery effluent.

Singh et al., (2003) used activated carbon developed from coconut shell fibers for removal of methylene blue and methyl orange dyes in his study on *color removal from wastewater using low-cost activated carbon derived from agricultural waste material*. The study findings revealed that the adsorption of the two dyes increased

with an increase in temperature. The removal of both of the dyes was 100% at low concentration and decreased with increase in concentration.

Barduzzaman, (1987) used four low-cost materials to remove color and turbidity along with other impurities present in the textile dyeing waste. Low-cost chosen as the filter material were (i) rice husk, (ii) saw dust, (iii) charcoal and (iv) burnt rice husk or ashes of rice husk.

Fixed bed, down flow column studies were carried out to evaluate the practical usefulness of the low-cost materials. Filter column studies of these four low-cost material showed that burnt rice husk and charcoal had the highest adsorption capacity. The percentage removal of color and turbidity were 85.61% and 76.58% for charcoal filter column and 92.27% and 84.23% were for filter column formed with burnt rice husk. Also the removal percentages of different solids were significant for these two low-cost materials.

2.3 Standards for discharge of textile effluents

The Department of Environment (D_OE), Bangladesh as per Environmental Conservation Rules (ECR), 1997 set the following standards for the effluents to be discharged from composite textile mills and large processing units, Table 2.1. D_OE has not yet established methods/procedures for measuring these parameters.

Table 2.1: Standards for textile effluents as per ECR-1997(Schedule 12-B)

Parameters	Standard
pH	6.5-9.0
Suspended Solids (mg/l)	100
BOD ₅ *, 20°C (mg/l)	150
Oil and Grease (mg/l)	10
Total Dissolved Solids (mg/l)	2100
Wastewater flow (l/kg fabric processed)	100
Total Chromium as Cr (mg/l)	2 **
Sulfide as S(mg/l)	2 **
Phenolic Compounds as C ₆ H ₅ OH (mg/l)	5**

* BOD limit of 150 mg/l implies only with physico-chemical processing ** Special parameters based on type of dye used

The textile wastewater as already mentioned containing suspended solids, dissolved solids, unreacted dyestuffs and other chemicals. The color fixation efficiency being sometimes less than 60% a significant amount of dyes along with fixing chemicals are lost in the wastewater. The treatment of textile wastewater is complicated because of significant BOD (Biological Oxygen Demand), COD (Chemical Oxygen Demand) and TDS (Total Dissolved Solids) content plus non-biodegradable nature of organic dyestuffs. Though the standards for the treated textile wastewater effluents have not been set any limit for color, for aesthetical reasons it is desirable that the effluents would be colorless and clear and when discharged to water bodies the colored water cannot be used without removing colors in many applications (Quader, 2010).

2.4 Treatment of textile wastewater

Generally, it is rather difficult to treat textile effluent because the industry produces multi-component wastewater. The dye contained in the effluent can vary daily and even hourly. The hot and strongly colored wastewater contains large amount of suspended solids, high chemical oxygen demand concentration and greatly fluctuating pH which can be difficult to treat. Hundreds of small scale dyeing industries is facing closure since they are not treating their effluent as it is not economical (Rao and Rao, 2006).

There are many ways for treating the textile effluent. The best combination of methods differs from plant to plant depending on the size, type of waste and degree of treatment needed. Generally the treatment options can be divided into three main categories namely biological, chemical and physical methods.

2.4.1 Biological method

There are many types of biological treatment methods. Among them include trickling filters, activated sludge process, anaerobic process, oxidation ponding etc. To date the commonest treatment of textile wastewater has been based on mainly aerobic biological process, consisting mainly conventional and extended activated sludge system. The trickling filters simulate stream flow by spraying wastewater over a

broken, medium such as stone or plastic. The medium serves as a base for biological growth, which attacks the organic matter of wastewater, and uses it as food.

In activated sludge process, the wastewater flows into a tank after primary settling. The microorganism in activated sludge is suspended in the wastewater as aggregates. The sludge and wastewater is kept in suspension by compressed air, which also supplies the oxygen, necessary for biological activities. The aerated waste is continuously withdrawn and settled and a portion of the sludge is returned to the influent (Metcalf and Eddy, 1991).

Biological treatment can be applied to textile wastewaters as aerobic, anaerobic and combined aerobic-anaerobic. In most cases, activated sludge systems (aerobic treatment) are applied. In all activated sludge systems, easily biodegradable compounds are mineralized whereas heavily biodegradable compounds need certain conditions, such as slow food-to-mass-ratios (F/M) ($<0.15 \text{ kg BOD}_5/\text{kg MLSS.d}$), adaptation (which is there if the concerned compounds are discharged very regularly) and temperature higher than 15°C (normally the case for textile wastewater) (Lacasse and Baumann, 2004).

Ineffectiveness of aerobic biological treatment in reducing color caused by heavily biodegradable organics causes aesthetic problems in the receiving waters and encourages researchers to investigate alternatives. Dyes themselves are generally resistant to oxidative biodegradation, and a difficulty occurs in acclimation the organisms to this substrate. Acclimation presents a problem with textile wastewater due to constant product changes and batch dyeing operations (Freeman and Reife, 1996).

Depending on the dyeing process; many chemicals like metals, salts, surfactants, organic processing assistants, sulphide and formaldehyde may be added to improve dye adsorption onto the fibers (Dos Santos et al., 2007). These chemicals are mainly in toxic nature and decrease the efficiency of biological treatment in color removal regarding textile wastewater.

The treatment and safe disposal of hazardous organic waste material in an environmentally acceptable manner and at a reasonable cost is a topic of great

universal importance. There is little doubt that biological processes will continue to be employed as a baseline treatment process for most organic wastewaters, since they seem to fulfill the above two requirements. However, biological processes do not always give satisfactory results, especially applied to the treatment of industrial wastewaters, because many organic substances produced by the chemical and related industries are inhibitory, toxic or resistant to biological treatment.

Due to insufficiency of biological treatment in the removal of the dyes from textile and dyestuff manufacturing, this process requires the involvement of other physical, chemical, and physicochemical operations (Rai, 2005 and Banat et al., 1997). Physical and chemical treatment techniques are effective for color removal but use more energy and chemicals than biological processes. Therefore, the tendency in recent years is towards using alternative technologies, especially advanced oxidation processes for the removal of color caused by hardly biodegradable organics (Sevimli and Sarikaya, 2002; Birgül and Solmaz, 2007).

2.4.2 Chemical method

Chemical method includes coagulation or flocculation and oxidation. The main advantage of the conventional coagulation and flocculation is removal of the wastewater due to the removal of dye molecules from the dye bath effluent and not due to partial decomposition of dyes which can lead to an even more potentially harmful and toxic aromatic compound (Metcalf and Eddy, 1991). It was also documented that in treatment of textile wastewaters, chemical treatment methods are known to be much more effective than others in breaking down the straight, unsaturated bonds in the dye molecules (Ciardelli et al., 2001).

Chemical oxidation uses strong oxidizing agents such as hydrogen peroxides, chlorine and others to force degradation of resistant organic pollutant. Chemical oxidation is the most commonly used method of decolorization by chemical owing to its simplicity and the main oxidizing agent is hydrogen peroxide (Metcalf and Eddy, 2003).

Chemical oxidation typically involves the use of an oxidizing agent such as ozone (O_3), hydrogen peroxide (H_2O_2), Fenton's reagent, permanganate (MnO_4) etc.

to change the chemical composition of a compound or a group of compounds, e.g. dyes (Metcalf and Eddy, 2003).

Oxidation by ozone is capable of degrading chlorinated hydrocarbons, phenol, pesticides and aromatic hydrocarbon. One of the major advantage of ozonation it does not increase the volume of wastewater and sludge. A major disadvantage of this process is its short-half life typically being 20 minutes (Robinson et al., 2001).

Fenton oxidation operates at a acidic pH in the presence of H_2O_2 and excess ferrous ions yielding hydroxyl radicals which oxidize organic matter. Fenton's reagent is effective in reducing COD, color and toxicity of textile wastewaters, but has the disadvantages shifting problems from water into the solid phase. (Meriç et al., 2005 and Eckenfelder et al., 1994).

Chemical oxidation uses strong oxidizing agents such as hydrogen peroxides, chlorine and others to force degradation of resistant organic pollutant. Chemical oxidation is the most commonly used method of decolorization by chemical owing to its simplicity and the main oxidizing agent is hydrogen peroxide (Robinson et al., 2001).

2.4.3 Physical method

The common physical treatment methods used for the treatment of colored textile effluents include membrane filtration, ion exchange, adsorption with activated carbon, irradiation and coagulation and flocculation (Doble and Kumar, 2005; Metcalf and Eddy, 1991)

Membrane based separation processes have gradually become an alternative method in the treatment of textile wastewaters. Application of membrane processes allows reuse of water besides high removal efficiencies. "Ultrafiltration has been successfully applied for recycling high molecular weight and insoluble dyes (e.g. indigo, disperse), auxiliary chemicals (polyvinyl alcohol) and water. However, ultrafiltration does not remove low molecular weight and soluble dyes (acid, reactive, basic, etc.), but efficient color removal has been achieved by nanofiltration and reverse osmosis" (Fersi et al., 2005).

Related to ion exchange, Mock and Hamouda (1998) reported that an ion exchange system would decolorize a dilute mixture of a colored wastewater sample. However, because the colorant was irreversibly adsorbed onto the resin and regeneration was not possible this technology does not seem effective. They claimed that, further testing with ion exchange-macroporous polymer systems might have been successful but initial cost estimates, requirement for off-site resin regeneration, and secondary waste disposal requirements resulted in removal of this technology from consideration for color destruction. Ion exchange can not be used for the treatment of dye-containing effluents mainly due to cost disadvantage and its ineffectiveness in disperse dyes (Robinson et al., 2001).

The coagulation and flocculation process is a versatile method used either alone or combined with biological treatment, in order to remove suspended solids and organic matter as well as providing high color removal in textile industry wastewater (Meriç et al., 2005). Many coagulants are widely used in the conventional wastewater treatment processes such as aluminum, ferrous sulphate, sulphate and ferric chloride (Anouzla et al., 2009).

The adsorption is one of the effective methods and the main adsorbent used in dye removal is activated carbon. Activated carbon has been generally used to remove composite reactive dye from dyeing unit effluent. (Demirbaş, 2009). Adsorption is an efficient and economically feasible process for treatment of wastewater containing chemically stable pollutants when its dissolved or too small and cannot removed by mechanical filtration because it can remove very tiny particles or dissolved contaminants from water such as lead, PCBs, some pesticides, viruses and asbestos fibers (Guendy, 2006 and El-Nemr et al., 2009)

It proves superior to the other processes by being sludge free and can completely remove even very minute amounts of dyes in wastewater (Nigam, et al., 1996). In this light, activated carbons have long been considered the best adsorbent for the removal of organic matter in wastewater (Kadirvel et al., 2003). They contain extended surface area, a lot of internal voids, high adsorption capacity and a high degree of surface activity (Malik, 2003).

2.5 Adsorption process

Adsorption is the process of accumulating substances that are in solution on to a suitable interface. Adsorption is a mass transfer operation in that, a constituent in the liquid phase is transferred to the solid phase.

The adsorbate is the substance that is being removed from the liquid phase at the interface. The adsorbent is the solid, liquid, or gas phase onto which the adsorbate accumulates.

2.5.1 Fundamentals of adsorption

All activated carbons act on a principle called adsorption, which is an adherence of substances to the surface of activated carbon. The attraction of a substance in a solution (adsorbate) to an activated carbon particle (adsorbent) occurs in three distinct steps:

- i) The adsorbed molecule must be transferred from a bulk phase of the solution to the surface of the adsorbent particle. In doing so, it must pass through a film of solvent that surrounds the adsorbent particle. This is called film diffusion.
- ii) The adsorbed molecule must be transferred to an adsorption site on the inside of the pore. This process is referred to as pore diffusion.
- iii) The adsorbate must become attached to the surface of adsorbent. This is the actual adsorption step (Hung et al., 2006).

Adsorption can occur on the outer surface of the adsorbent and in the macropores, mesopores, micropores, and sub-micropores, but the surface area of the macro- and mesopores is small compared with the surface area of the micropores and sub-micropores and the amount of materials adsorbed, these are usually considered negligible. Adsorption forces include (Crittenden, 1999):

- Columbic-unlike charges
- Point charge and a dipole
- Dipole-dipole interactions
- Point charge neutral species
- London or Van der Waal's forces

- Covalent bonding with reaction
- Hydrogen bonding

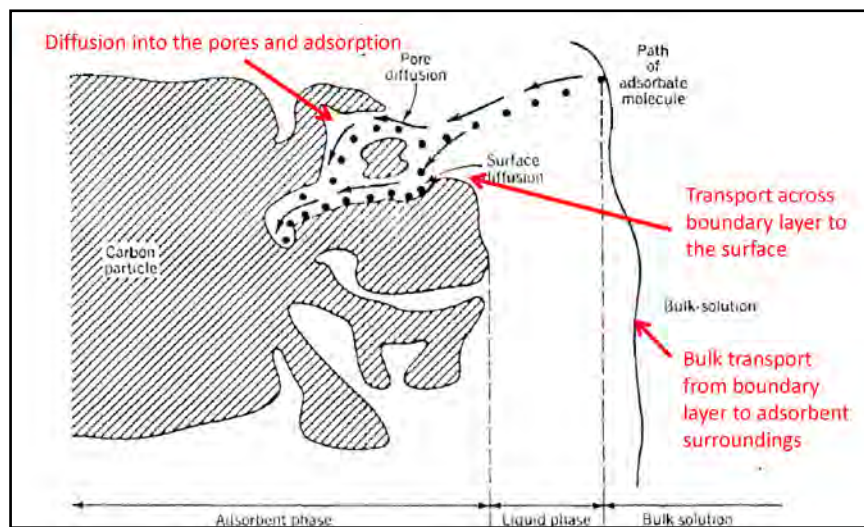


Figure 2.1: Diffusion between adsorbate and adsorbent (Montgomery, 1985)

2.5.2 Types of adsorption

Adsorption may be characterized either physical or chemical. Physical adsorption consists mainly of Van der Waals' forces and is reversible. This occurs when the molecular forces of attraction between the adsorbent and the solute is greater than the forces of attraction between solute and solvent. Chemical adsorption, as the name implies, involves a chemical reaction between the adsorbent and the adsorbate. Physical adsorption is much stronger type of adsorption and is often times irreversible.

2.5.3 Factors affecting adsorption process

Activated carbon adsorption is not a unique homogeneous process, but is rather dependent on the various factors outlined below:

- Agitation;
- Physical and chemical characteristics of the adsorbent;
- Physical and chemical characteristics of the adsorbate;
- pH and
- Temperature.

2.5.3.1 Agitation

In a bulk solution of wastewater and activated carbon in batch reactor, diffusion in the surface of carbon particle and adsorbate will be lower in highly agitated system and pore diffusion between the carbon particles will be higher in highly agitated system.

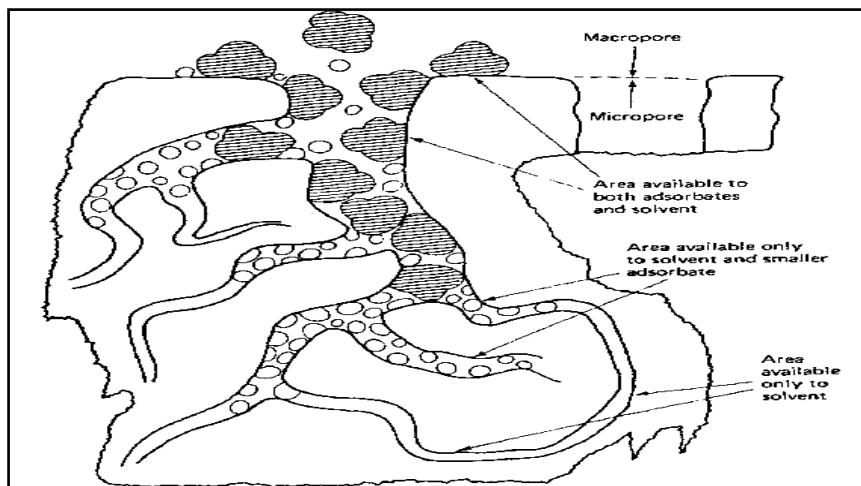


Figure 2.2: Voids and area available in the adsorbent (Montgomery, 1985)

2.5.3.2 Physical and chemical characteristics of the adsorbent

The adsorption performance is dependent on the condition of internal surface accessibility. A very important and decisive property of the adsorbent is the internal pore structure. The total number of pores, size and shape determines the adsorption capacity and even rate of adsorption. The significance of pore in adsorption processes largely depends on their size (Snoeyink and Summers, 1999). If the particle size of activated carbon is powder than the surface area of the adsorbent will be more to adsorb the adsorbate and rate of adsorption will be more. The extent of adsorption is generally to be considered to be proportional to the specific surface area. Specific surface area is that proportion of the total surface area which is available for adsorption. The more finely divided and more porous adsorbent would be expected to yield more adsorption per unit weight of adsorbent. The surface can be characterized either as external when it involves bulges or cavities with width greater than depth or internal when it involves pores and cavities that have depth greater than width.

2.5.3.3 Physical and chemical characteristics of adsorbate

In general, the adsorbability of a compound increases with increasing the molecular weight and increasing number of functional groups such as double bonds or halogens.

Larger molecules are adsorbed onto activated carbon better than the smaller molecules. The degree of solubility of a solute is also of primary concern for adsorption. There is an inverse relationship between the extent of adsorption of a particular solute and its solubility in the solvent from which the adsorption occurs. High solubility means the bond between the solute and the solvent is stronger than the attractive force between the solute and the adsorbent.

Polarity of the adsorbate is another important factor. A polar solute is preferably adsorbed by a polar adsorbent whereas a nonpolar solute is more easily adsorbed by a nonpolar adsorbent. Activated carbon adsorbs nonpolar molecules better than polar molecules. An increase in solubility reflects greater affinity between the solute and the solvent and acts to oppose the attraction exerted by the carbon. Consequently, any change that increases the solubility may be associated with reduced adsorbability. Thus, polar groups (characterized by an affinity of water) usually diminish adsorption from aqueous solutions.

Dissociation constants of weak acids and bases also influence the extent of their adsorption. The reason is that the extent of ionization is determined by the dissociation constant. The adsorption of ionic and molecular forms differ such that the latter is much better adsorbed compared to the former. Greater dissociation constant results in higher amount of the ionic form which is usually not adsorbable on activated carbon.

The presence of substituent groups also affects the adsorbability of organic chemicals. The influence of substituent groups depends on the position occupied, for example, ortho, meta and para (Velmurugan et al., 2011). Branched chains are usually more adsorbable than straight chains. On the other hand, an increasing length of chain results in an increase in adsorption capacity (Hoehn, 1996). Aromatic compounds are in general more adsorbable than aliphatic compounds of similar molecular size.

2.5.3.4 pH

Organic molecules form negative ions at high pH values, positive ions at low pH values and neutral molecules at intermediate pH values. Adsorption of most organic materials is higher at neutral conditions. In general, liquid phase adsorption of organic pollutants by activated carbon is increased with decreasing pH. This results from the

neutralization of the negative charges at the surface of the carbon at low pH values. Neutralization of the negative charges reduces to diffusion and more active adsorption sites. The extent of this varies with the type and activation technique of activated carbon. The differences in pH values may also arise due to acidic and basic surface functional groups on activated carbon. These groups could be freed by simple contact with distilled water rather than the fixed surface functional groups (Das, 2000).

pH affects dissociation of electrolytes and non electrolytes not affected. As the pH of the solution increases, adsorption rate decreases. This is because of the electrostatic repulsion between the negatively charged activated carbon and the deprotonated adsorbate molecules.

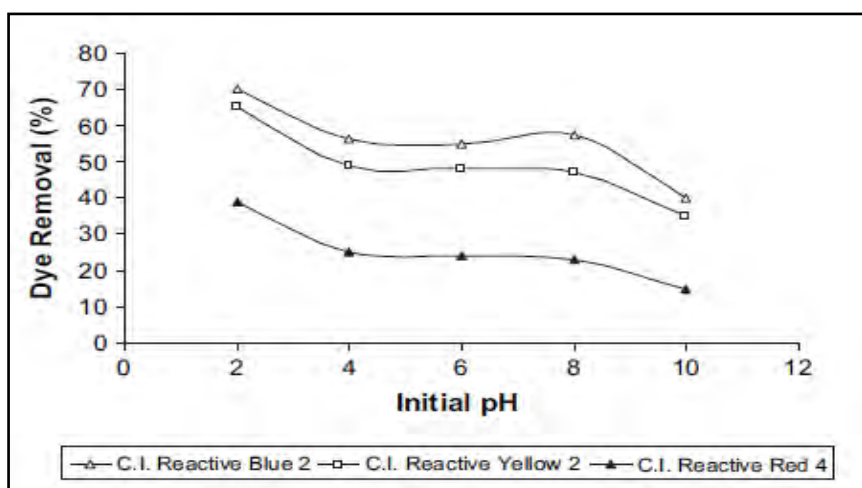


Figure 2.3: Effect of pH on adsorption (Walker et al., 2007)

2.5.3.5 Temperature

With the increase of temperature, the adsorption rate increases because the surface coverage is increased at higher temperatures, this may be attributed to increased penetration of reactive dyes inside micro-pores at higher temperatures or the creation of new active sites.

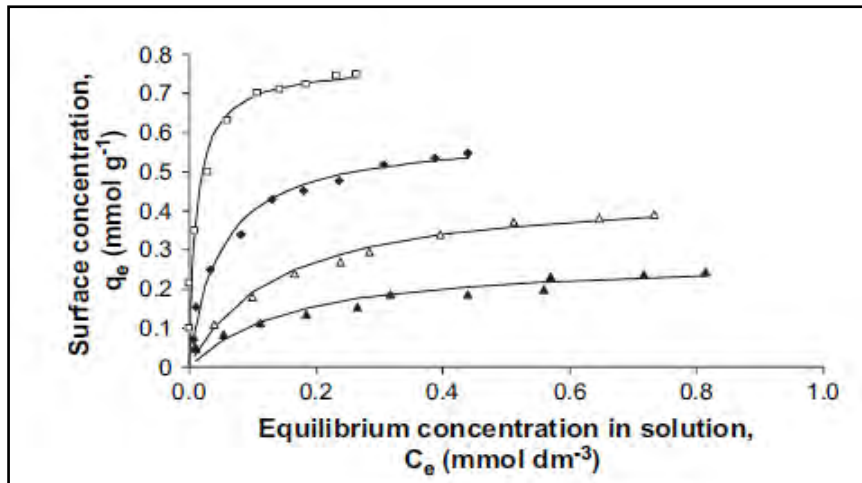


Figure 2.4: Effect of temperature on adsorption (Walker et al., 2007)

2.6 Activated carbon adsorption

Throughout history, people have used carbon (charcoal) as an effective adsorbent, in such processes as water and wastewater treatment, sugar purification and color removal from liquids. Activated carbons have long been considered the best adsorbent for the removal of organic matter in wastewater. They contain extended surface area, a lot of internal voids, high adsorption capacity and a high degree of surface activity.

2.6.1 Materials used for activated carbon preparation

Materials with high carbon content and low inorganic components materials, such as petroleum coke, sawdust, lignite, coal, peat, wood, charcoal, nutshell, and fruit pits, may be used for the manufacture of activated carbon. Also, more unconventional materials like straw and automobile tires can also be used. The main criteria for these materials are (Dabrowski et al., 2005 and Moreno-Castilla et al., 1995):

- low inorganic matter (ash content)
- high carbon content
- ease of activation
- availability and low cost
- low degradation

But the properties of the finished material are governed not only by the raw material, but also by the method of activation used. The choices of raw material are based upon

the end use of the activated carbon, availability, cost of the raw material, and national and international economic and political considerations (Rao et al., 2004).

2.6.2 Activated carbon preparation

Activated carbon is prepared by first making a char from organic matter. The char is produced by heating the base material to a red heat (less than about 700⁰ C) in a retort to drive off the hydrocarbons, but with an insufficient supply of oxygen to sustain combustion. The char particle is then activated by exposing oxidizing agent to develop porous structures thus creates a large internal surface area. The resulting pore sizes are defined as follows:

Macropores >25 nm

Mesopores > 1 nm and < 25 nm

Micropores >1 nm

After activation, the carbon can be separated into, or prepared in, different sizes with different adsorption capacity.

2.6.3 Framework of activated carbon

Activated carbon is highly heterogeneous, both in morphology and in surface characteristics. An elemental analysis indicated that the main elements in the activated carbon framework are carbon (92 % w/w) and oxygen (7% w/w). For commercial activated carbons, the amount of oxygen can vary between <1 % to up to 16%. On an atomic level, activated carbon is considered to consist of graphene layers – layers of interlocking aromatic rings, which are also referred to as “basal planes” (Brennan et al., 2001). At the edges of a basal plane, various oxygen- or nitrogen-containing functional groups are presented.

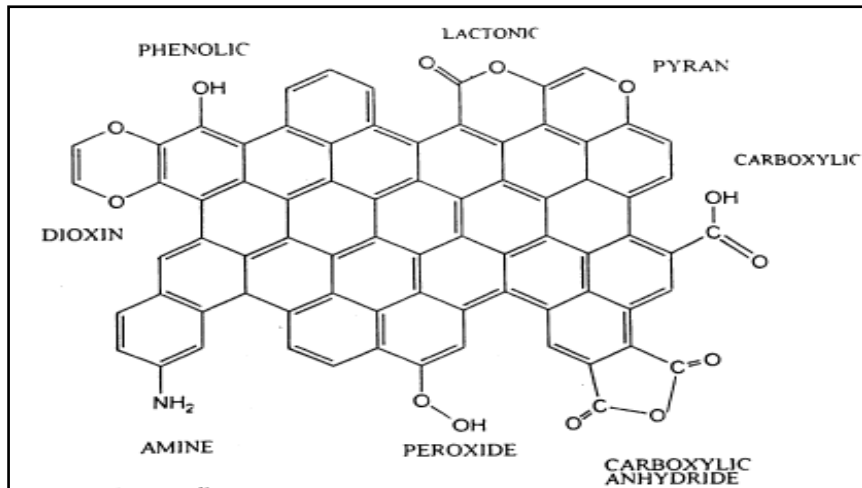


Figure 2.5: Activated carbon basal plan with functional groups (Brennan et al., 2001)

2.6.4 Surface charge of activated carbon

Solute adsorption can be influenced by electrostatic repulsion or attraction when both solute and carbon have a certain electrostatic charge. The charge of activated carbon is dependent on pH as is illustrated in Figure below. Functional groups with an acid character, such as phenol (-OH) and carboxyl (-COOH), may dissociate at higher pH, releasing their proton (H⁺) and obtaining a negative charge. A positive surface charge can be attributed to basic functional groups, such as amine (-NH₂), chromene and pyrene (both O-containing) as these functional groups protonate at lower pH, taking up H⁺ and obtaining a positive charge. Electron-rich areas on the graphene plates also increase activated carbon basicity (Moreno-Castilla, 2004).

Acidic, basic, and neutral functional groups can bind to water molecules through hydrogen bond formation. Activated carbons with higher quantities of O-containing or N-containing functional groups have a higher affinity for water, and are considered *hydrophilic* (Li et al., 2002). As hydrophilic carbons promote bonding with water, the number of available adsorption sites for the solute is reduced. Also water clusters can be formed, which can block the entrance of micro-pores (Franz et al., 2000).

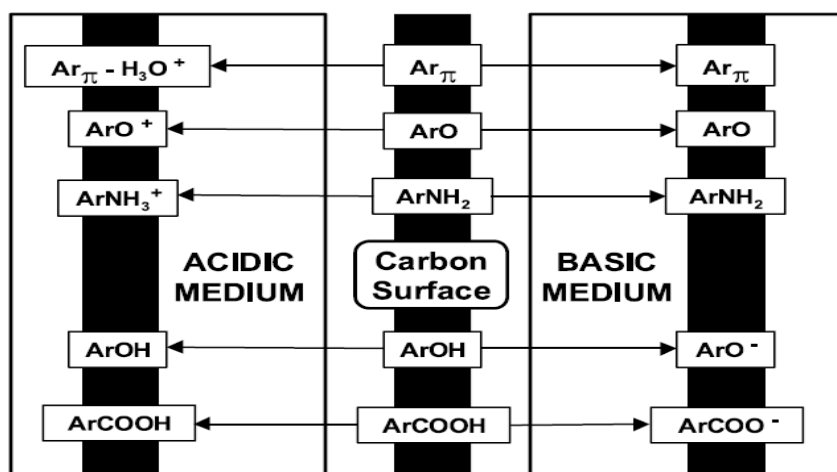


Figure 2.6: pH effects on the activated carbon surface charge (Moreno-Castilla, 2004)

Li et al., (2002) found that the removal of solutes was lower with more hydrophilic activated carbons, even when the solutes were also able to form hydrogen bonds with the functional groups. These solutes did, however, show higher removal on hydrophilic activated carbons when they were dissolved in cyclohexane, which is a solvent that cannot form H-bonds (Franz et al., 2000).

2.6.5 Types of activated carbon

The activated carbon is mainly classified into two size classifications are powdered activated carbon (PAC), which typically has a diameter of less than 0.074 mm (200 sieve), and granular activated carbon (GAC), which has a diameter greater than 0.1 mm (~140 sieve). Comparison of different parameters of powder and granular activated carbon is shown in Table 2.5. Depending on the desired results, activated carbon may be used in powdered or granular form.

Table 2.2: Characteristics of activated carbon (Metcalf and Eddy, 2003)

Parameter	Unit	Type of activated carbon	
		GAC	PAC
Total surface area	m ² /g	700-1300	800-1800
Bulk density	kg/m ³	400-500	360-740
Particle density (wetted)	kg/L	1.0-1.5	1.3-1.4
Particle size range	mm	0.1-2.36	5-50
Mean pore radius	Å	16-30	20-40
Ash	%	≤ 8	≤ 6
Moisture as packed	%	2-8	3-10

Granular activated carbon is commonly used in water treatment facilities where the water is passed through a granular carbon bed to remove tastes, colors, odors, and dissolved organics. Powdered carbon also is used in treatment facilities at various points for its quicker rate in removing various contaminants. Powdered carbon is the preferred choice in point-of-use water filtration systems because it is faster and is a better mechanical filter than granular activated carbon. It also takes up a minimum of space given its large surface area-to-volume ratio.

2.7 Adsorption isotherm study

Adsorption isotherm indicates the relationship between the adsorbate in the liquid phase and the adsorbate adsorbed on the surface of the adsorbent under equilibrium at constant temperature (Nwabanne and Mordi, 2009). Adsorption efficiency decreases over time. Adsorption isotherms are important to describe the interaction of adsorbate molecules with adsorbent surface. Isotherms are empirical relations which are used to predict how much solute can be adsorbed by adsorbent. The study of the isotherm is essential in assessing the adsorption efficiency of the adsorbent. This study is also useful in optimizing the operating conditions for effective adsorption (Velmurugan et al., 2011). Generally, the amount of material adsorbed is determined as a function of the concentration at a constant temperature, and the resulting function is called an adsorption isotherm. The applicability of the isotherm equation is compared by judging the correlation coefficient, R^2 .

Adsorption isotherms are developed by exposing a given amount of adsorbate in a fixed volume of liquid to varying amounts of adsorbent. Typically in a container, a known amount of adsorbent was added to each container and agitated intermittently for the desired time periods. At the end of the test period, the amount of adsorbate remaining in solution is measured. The adsorbent phase concentration after equilibrium is computed using the equation:

$$q_e = (C_o - C_e) \frac{V}{m} \dots \dots \dots (1)$$

Where, q_e = equilibrium adsorption, mg/g; C_o = initial concentration of adsorbate, mg/L; C_e = final equilibrium concentration of adsorbate after adsorption, mg/L; m = mass of adsorbent, g; and V = volume of wastewater, L.

The study of isotherm data is important to find out the adsorption capacity of various adsorbents. In this study Freundlich and Langmuir adsorption isotherm model is used.

2.7.1 Freundlich isotherm

The Freundlich equation is an empirical relationship describing the sorption of solutes from a liquid to solid interface. Freundlich model is expressed as

$$q_e = K_f C_e^{\frac{1}{n}} \dots \dots \dots (2)$$

Where, q_e is the amount adsorbed at equilibrium (mg/g); C_e is the equilibrium concentration of adsorbate (mg/L); K_f is the measure of adsorption capacity and n is the adsorption intensity. Linear form of Freundlich equation is

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \dots \dots \dots (3)$$

A plot of $\log q_e$ against $\log C_e$ gives a linear line with a slope of $1/n$ and intercept of $\log K_f$. From the experimental data, K_f values increase with increasing temperature. Values $n > 1$ represent a favorable adsorption condition (Baseri et al., 2012)

2.7.2 Langmuir isotherm

The Langmuir model was developed based on the assumption of the formation of a monolayer of the adsorbate species onto the surface of the adsorbent. It has also been assumed that the surface sites are completely energetically homogeneous. But in the true sense, the adsorbent surface is energetically homogeneous. The Langmuir adsorption isotherm is defined as:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \dots \dots \dots (4)$$

Where, q_e is the amount adsorbed at equilibrium (mg/g); C_e is the equilibrium concentration of adsorbate (mg/L); q_m is monolayer (maximum) adsorption capacity (mg/g) and b is Langmuir constant related to energy of adsorption. A linear plot of

C_e/q_e against C_e suggests the applicability of the Langmuir isotherms. The values of q_m and b were determined from the slope and intercepts of the plots.

The essential features of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor, R_l which is defined by the following relation given by Hall et al., (1966).

$$R_l = \frac{1}{1 + bC_o} \dots \dots \dots (5)$$

Where C_o is initial adsorbate concentration (mg/L), the nature of adsorption if, $R_l > 1$ = Unfavorable; Linear, if $R_l = 1$; Irreversible, if $R_l = 0$ and $0 < R_l < 1$, then Favorable.

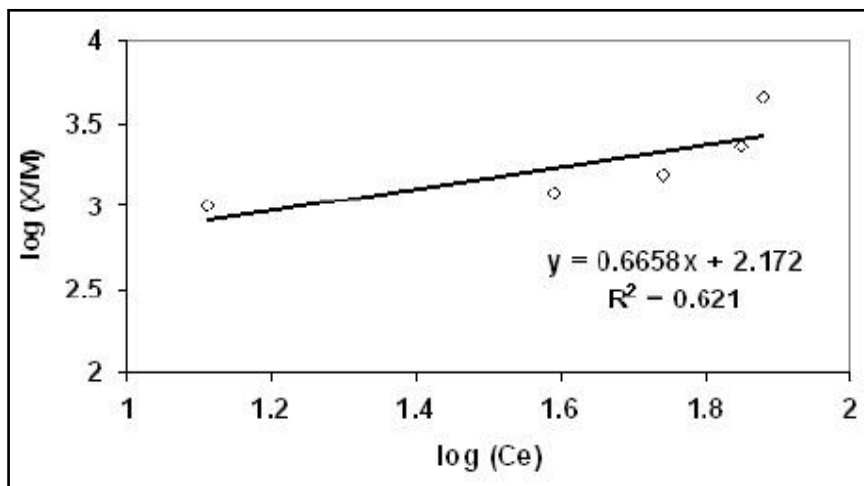


Figure 2.7: Typical Freundlich isotherm curve (Velmurugan et al., 2011)

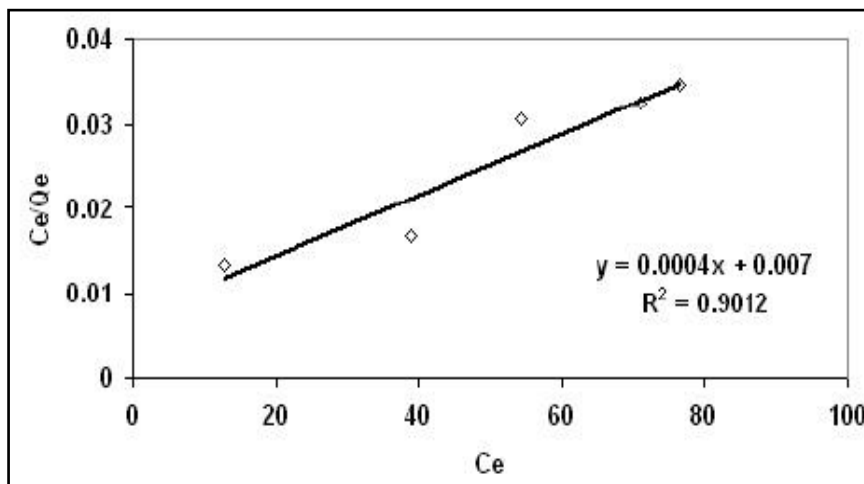


Figure 2.8: Typical Langmuir isotherm curve (Velmurugan et al., 2011)

2.8 Adsorption kinetics study

Adsorption kinetics is used to investigate the mechanism and the rate controlling steps of a dsorption. The mechanism of a dsorption involves the chemical reaction of functional groups present on the surface of the adsorbent and the adsorbate, temperature and pH (Baseri et al., 2012). In the literature, several models have been applied to know the order of adsorbent-adsorbate interactions and the rate of adsorption of color and COD. In this present study the following three kinetic models are applied for the experimental data.

2.8.1 Pseudo first order kinetic model

This model assumes that the rate of change of solute uptake with time is directly proportional to difference in saturation concentration and the amount of solid uptake with time. The Langergen pseudo- first order rate expression as shown below:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \dots \dots \dots (6)$$

Where q_t and q_e are the amount of adsorbate adsorbed (mg/g) at contact time t and at equilibrium, and k_1 , the Pseudo first order rate constant (min^{-1}). After integrating with the boundary conditions at initial time ($t = 0$), $q_t = 0$ and at any time ($t > 0$), amount of adsorbate adsorbed is q_t and by rearranging Eq. (6), the rate law for a pseudo first order reaction becomes:

$$\log (q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right) t \dots \dots \dots (7)$$

The plot of $\log (q_e - q_t)$ versus t should give a straight line with slope of $-k_1/2.303$ and intercept $\log q_e$ which allows calculation of adsorption rate constant k_1 and equilibrium adsorption capacity q_e .

2.8.2 Pseudo second order kinetic model

The Langergen pseudo second kinetic model (Ho and McKay, 1998) is based on the assumption that the adsorption of adsorbate onto adsorbent supports second order chemisorptions.

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$$

Where q_t and q_e are the amount of adsorbate adsorbed (mg/g) at contact time t and at equilibrium, and k_2 , the pseudo second order rate constant (min^{-1}). After integrating

with the boundary conditions at initial time ($t = 0$), $q_t = 0$ and at any time ($t > 0$), amount of adsorbate adsorbed is q_t and by rearranging the above equation, the rate law for a pseudo first order reaction becomes:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \dots \dots \dots (8)$$

The initial adsorption rate h (mg/g/min) is also related as (Ho, 2003)

$$h = k_2 q_e^2 \dots \dots \dots (9)$$

When the pseudo second order kinetic is applicable, the plot of t/q_t against t should give a linear relationship from which k_2 and q_e can be determined respectively from the intercept and slope of the plot. The correlation coefficient values are higher than the values of pseudo first order model. Further the rate constant, k_2 decreases with the increase in initial adsorbate concentration.

2.8.3 Intra particle diffusion model

Since the pseudo first order and second order models could not identify the diffusion mechanism through the pores present in the surface of the adsorbent, the kinetic results are further analyzed by using the inter particle diffusion model. Adsorption is a multi-step process involving transport of solute from aqueous to surface of solid and diffusion of solute into the interior of pores, which is generally a slow rate determining process.

During the adsorption of adsorbate over a porous adsorbent material, the following three consecutive steps were taken place: (i) transport of the ingoing adsorbate ions to external surface of the adsorbent (film diffusion), (ii) transport of the adsorbate ions within the pores of the adsorbent except for a small amount of adsorption, which occurs on the external surface (particle diffusion) and (iii) adsorption of the ingoing adsorbate ions on the interior surface of the adsorbent (Weber and Morris, 1963). Out of these three processes, the third process is considered to be very fast and is not the rate limiting step in the uptake of the organic compounds. The remaining two steps impart the following three possibilities:

Case1: External transport > internal transport, where rate is governed by particle diffusion, Case 2: External transport < internal transport, where rate is governed by

film diffusion and Case 3: External transport \approx internal transport, which accounts for the transport of the adsorbate ions to the boundary and may not be possible within a significant rate, which later on gives rise to the formation of a liquid film surrounded by the adsorbent particles with a proper concentration gradient. In the batch mode contact time adsorption experiments, rapid stirring was maintained. Hence, the transportation of the adsorbed species is happened from the solution to the pores of the adsorbent material and this step may control the rate of the adsorption process.

Assuming that the rate is controlled by pore and intra-particle diffusion (Baseri et al., 2012). According to Weber and Morris (1963), the intra particle diffusion rate constant (k_i) is given by the following equation

$$q_t = k_i t^{1/2} + I \dots \dots \dots (10)$$

Where, k_i is the intra-particle diffusion rate constant, and I is a constant that gives ideas about the boundary layer thickness. The intra particle diffusion rate constant (k_i) and I are obtained from the slope and intercept of the plot q_t against $t^{1/2}$

If, this model shows a linear relationship after certain time but they do not pass through origin. This is due to boundary layer effect. The larger the intercept, the greater the contribution of surface sorption in rate determining step. The intercepts and k_i values of plot against $t^{1/2}$ increases with increase the initial concentration of adsorbate.

According to this model, if the plot of q_t against $t^{1/2}$ gives a straight line, then the adsorption process is controlled by only intra-particle diffusion and if the data exhibit multi-linear plots, then two or more steps control the adsorption process (Saha, 2010). Initial portion is attributed to the liquid film mass transfer and linear portion to the intra particle diffusion.

Assuming spherical geometry of the adsorbents, the overall rate constant of the process can be correlated to the pore and film diffusion coefficient in accordance with the expression (Helfferich, 1962),

$$t_{1/2} = 0.03 \frac{r_o^2}{D_p} \dots\dots\dots (11)$$

$$t_{1/2} = 0.23r \left(\frac{\delta}{D_f} \right) \left(\frac{C}{C_e} \right) \dots\dots\dots (12)$$

Where r_o is radius of the adsorbent (cm), D_f and D_p are film and pore diffusion coefficient (cm²/sec), $\frac{C}{C_e}$ is equilibrium loading of the adsorbent, δ is the film thickness (cm) and $t_{1/2}$ is the time necessary to obtain half the initial concentration (sec) is obtained by the following relation (You et al., 2006).

$$t_{1/2} = \frac{1}{k_2 q_e} \dots\dots\dots (13)$$

Michelson et al., (1975) suggested if the diffusion coefficient lies between 10⁻⁶ – 10⁻⁸ cm²/sec, the film diffusion will be rate limiting while if pore diffusion coefficient is in the range of 10⁻¹¹ – 10⁻¹³ cm²/sec, the pore diffusion will be the rate limiting.

2.9 Thermodynamics of adsorption

Thermodynamic parameters provide in-depth information of inherent energetic changes associated with adsorption; therefore, these parameters should be accurately evaluated. Thermodynamic parameters such as change in free energy, ΔG (J/mole), enthalpy, ΔH (J/mole) and entropy, ΔS (J/K/mole) were determined using following equations

$$K_o = \frac{C_{solid}}{C_{liquid}} \dots\dots\dots (14)$$

$$\Delta G = \Delta H - T\Delta S \dots\dots\dots (15)$$

$$\Delta G = -RT \ln K_o \dots\dots\dots (16)$$

$$\ln K_o = -\frac{\Delta G}{RT} \dots\dots\dots (17)$$

$$\ln K_o = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \dots\dots\dots (18)$$

Where, K_o is equilibrium constant, C_{solid} is solid phase concentration at equilibrium (mg/L), C_{liquid} is liquid phase concentration at equilibrium (mg/L), T is absolute temperature in Kelvin and R is gas constant. $R = 8.314$ J/K/mole. At equilibrium, K_o

is the ratio of the concentration of adsorbate in adsorbent and concentration of adsorbate in aqueous solution.

ΔG values is obtained from Equation (16), ΔH and ΔS values are obtained from the Equation (18). The negative value of ΔG indicates the adsorption is favorable and spontaneous. ΔG values increases with increase in temperature and decreases with increase in initial concentration. The slope and intercept of plot $\ln K_o$ against $1/T$ give the values of ΔH and ΔS . The positive value of ΔH indicates endothermic nature of adsorption, which is supported by the increase on adsorption with the increase in temperature and values of $\Delta H > 30$ kJ/mole indicates chemisorptions and $\Delta H < 30$ kJ/mole denote physisorption (Arivoli, 2007 and Renmin et al., 2005). The positive values of ΔS indicate the increased disorder and randomness at the solid liquid interface of adsorbate with the adsorbent.

CHAPTER 3

METHODOLOGY

3.1 Introduction

The following chapter details the materials and method used during this study. This chapter deals with the adsorbent materials used for adsorption, activation process and determination of physical properties of adsorbent, location of sampling point and treatment process adopted in this study. Both commercial powder activated carbon and Date seed activated carbon were used for the treatment of color and COD from the textile effluent. Batch adsorption process is used in this study. A detail methodological step for achieving the study objectives is shown in Figure 3.1.

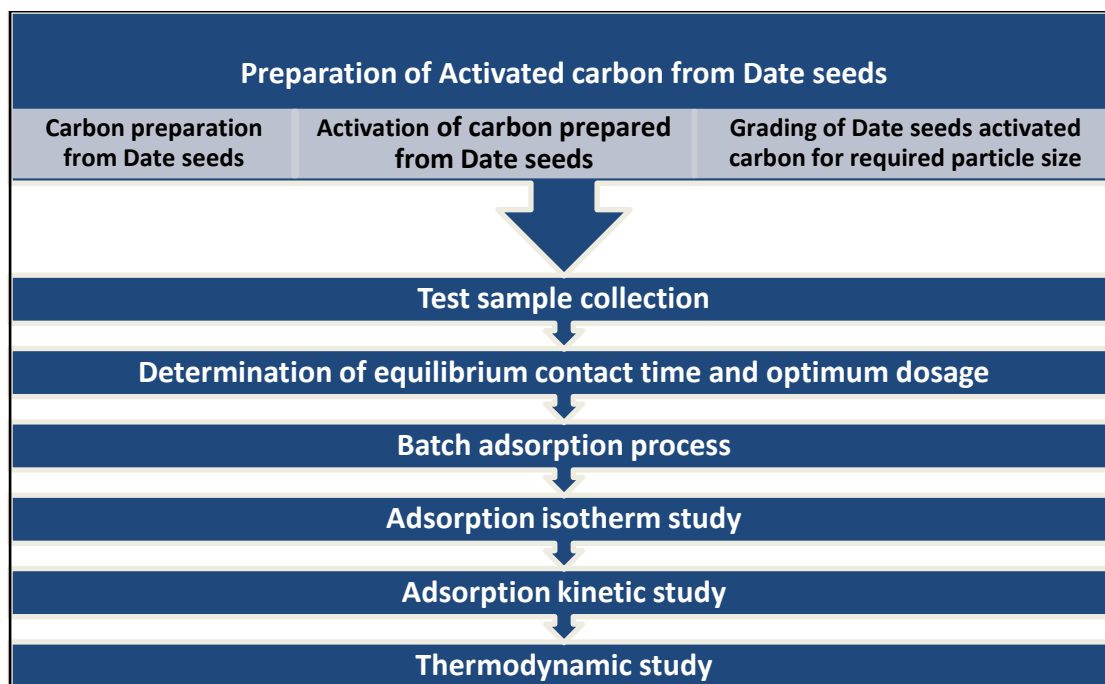


Figure 3.1: Methodological steps of the study

3.2 Activated carbon preparation

Adsorbent is the material onto which the pollutants are attached into the voids and surface of the materials. Activated carbon is used as the adsorbent in this study. Two types of activated carbon are used as adsorbent. Between these two types commercial powder activated carbon is purchased from the market and Date seed activated carbon prepared in the laboratory.

3.2.1 Carbon preparation from Date seeds

The activated carbon preparation process is divided into two steps: first one is carbon preparation from Date seeds (shown in Figure 3.2) and the other is activation process of prepared carbon using activating agent.

For this study, Date seeds were collected from Rajshahi and Jessore. Seeds were recovered from Dates and washed several times under tap water until the seeds become completely free from dirt. The seeds were then dried, cut down into small pieces by cutter and filled into the Crucibles in moderately dense manner so that the seeds could be completely burnt during burning; seeds were placed into the Muffle Furnace burner. Temperature of Furnace was 500°C and Date seeds were burned for one hour. After one hour, when the Furnace temperature became 0 °C, then the exit

tray kept open for half an hour for complete cooling of Furnace. After complete cooling, Date seed were taken out from the Furnace and were made powder using the *Hamandista* and grinder.



Figure 3.2: Process steps of carbon preparation from Date seeds

3.2.2 Activation of carbon prepared from Date seeds

In most of the carbonaceous materials, there are a certain degree of porosity and internal surface area. After activation, these internal surface areas become extended and increase the adsorption capacity of activated carbon. In this study, carbon derived from date seeds were activated using $ZnCl_2$ solution. Equal mass of carbonized Date seed powder was soaked in 1:1 (ratio of mass of the Date seed to mass of the $ZnCl_2$) equal mass of 1M, $ZnCl_2$ solution overnight. For the preparation of 1M $ZnCl_2$ solution, 100 gm $ZnCl_2$ is mixed into distilled water to make 743 ml $ZnCl_2$ solution. After overnight soaking Date seed activated carbon were filtered, washed several times and dried in an oven at 100 °C for four hours. By this process, Date seed activated carbon was prepared for this study.

3.2.3 Grading of Date seeds activated carbon for required particle size

This test is performed to determine the percentage of different particle sizes contained within Date seeds activated carbon. The mechanical sieve analysis is performed by

Test Sieve Shaker (shown in Figure 3.3) using USA Standard Testing Sieve (#100, #50, #40 and #30) at geotechnical engineering laboratory of Department of Civil Engineering, BUET, Dhaka, Bangladesh. Test is performed followed by ASTM D 422 - Standard Test Method for Particle-Size Analysis of Soils.



Figure 3.3: Test Sieve Shaker

Test procedure for sieve analysis was as follows: at first the weight of each sieve as well as the bottom pan used in the analysis was wrote down. Mass of dry Date seeds sample was weighted. All the sieves (sieve #30, #40, #50 and #100) were cleaned, assembled them in the ascending order of sieve numbers (sieve #30 at top and #100 sieve at bottom) and placed the pan below #100 sieve. The Date seeds sample was poured carefully into the top sieve and placed the cap over it. Placed the sieve stacks in the Test Sieve Shaker and shaken for 10 minutes. After 10 minutes, switched off the Test Sieve Shaker; removed the stacks from the shaker and carefully weighted and recorded the weight of each sieve and bottom pan with its retained sample.

The mass of Date seeds activated carbon retained on each sieve was obtained by subtracting the weight of the empty sieve from the total mass of the sieve and retained sample, and record this mass on the data sheet as the weight retained in each sieve. The percent retained on each sieve was calculated by dividing the weight retained on each sieve by the original sample mass. The percent passing (or percent finer) was calculated by starting with 100 percent and subtracting the percent retained on each sieve as a cumulative procedure.

3.3 Wastewater sample collection

The textile industrial effluent consists of a variety of residue materials used in the production process. It was very difficult to prepare a representative sample in the laboratory. Therefore, collection of real effluent was necessary to determine the efficiencies of treatment. Very few industries have Effluent Treatment Plant (ETP). Out of them, only few industries actually operate their ETP. The textile industries are very sensitive about their effluent. For this study, wastewater sample collected from Echotex Limited at Pollibiddut, Chandra, Gazipur, hundred percent export oriented composite textile industry.

Wastewater is discharged from different machines and stages of process. The quality of wastewater varies with stages. Hence, wastewater samples were collected from the equalization tank of the ETP. Collected wastewater sample was stored in refrigerator in the laboratory. Sample was taken out from the refrigerator 2-3 hours prior of starting the test so that the temperature of the sample obtains room temperature. This study was conducted in the environmental engineering laboratory in department of Civil Engineering, BUET, Dhaka, Bangladesh.

3.4 Determination of equilibrium contact time and optimum dosage

A series of 250 mL conical flask was filled with 100 mL of wastewater sample and adjusted to desired pH (8.0). 0.5 g adsorbent (activated carbon) was added to each flask, placed in rotator shaker and agitated intermittently for the different time periods (5, 10, 15, 20, 30 and 60 minutes) with all other selected conditions. After desired time period respective conical flask was taken out from the shaker, kept for few minutes to be stable and the fresh supernatant sample was taken out by pipette. Filtered the supernatant using Whatmann No. 44 filter paper and residual color concentration of the filtrate were measured using a Spectrophotometer. Color adsorption is calculated for different contact time that is shown in Figure 3.4. From this, equilibrium contact time was selected for a contact time after that no significant adsorption takes place.

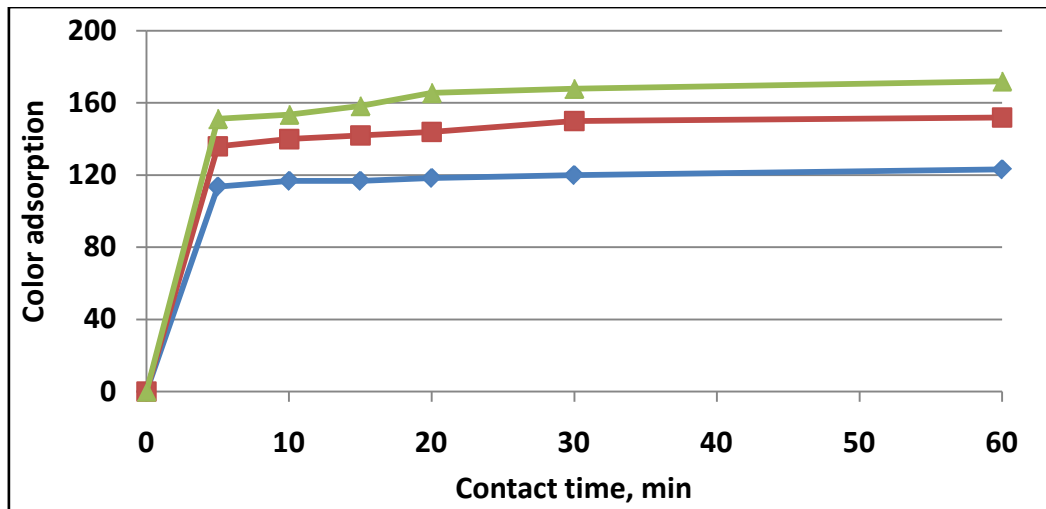


Figure 3.4: Determination of equilibrium contact time for batch adsorption process

Different amount of adsorbent (0.4, 0.6, 0.8, 1.0, 1.2 and 1.4 g) is added to each conical flask containing 100 ml sample and shaken for equilibrium time. After equilibrium time period respective conical flask was taken out from the shaker, kept for few minutes to be stable and the fresh supernatant sample was taken out by pipette. Filtered the supernatant using Whatmann No. 44 filter paper and residual color concentration of the filtrate were measured using a Spectrophotometer. From this, adsorption loading is calculated for different dosage.

Adsorption loading is plotted against residual concentration as shown in Figure 3.5. From this plot, for a certain residual concentration, a adsorption loading (eventually dose) is calculated. By this process optimum dosage is calculated and used for further studies.

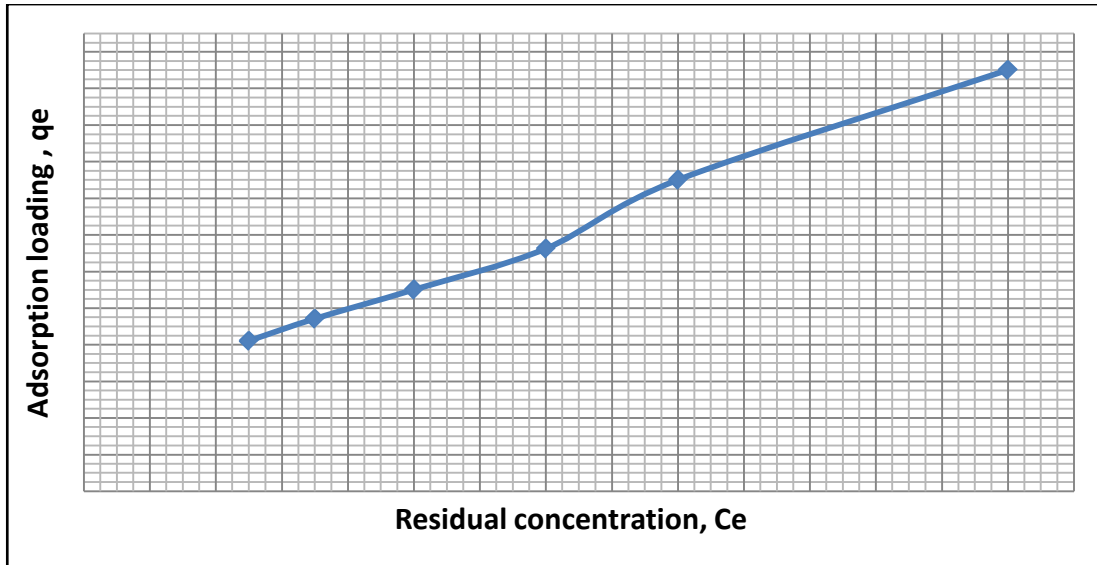


Figure 3.5: Determination of optimum dosage for batch adsorption process

3.5 Batch adsorption process

Adsorption of color and COD on Date seeds activated carbon was carried out in batch adsorption process as shown in Figure 3.6. The batch technique was selected because of its simplicity. For isotherm studies, a series of 250 mL conical flasks were employed. Each conical flask was filled with 100 mL of wastewater sample of varying concentrations and adjusted to desired pH.



Figure 3.6: Batch adsorption process

Using predetermined equilibrium contact time and optimum dosage, adsorption is carried out at different temperatures, agitation speeds, particle sizes, pH and initial concentrations to find the effect of these parameters. After equilibrium contact time

respective conical flask was taken out from the shaker, kept for few minutes to be stable and the fresh supernatant sample was taken out by pipette. Filtered the supernatant using Whatmann No. 44 filter paper and residual color and COD concentration of the filtrate were measured using Spectrophotometer.

The residual concentration is compared with initial concentration and calculated color and COD removal efficiency in percentage for different experimental conditions (e.g., temperatures, agitation speeds, particle sizes, pH and initial concentrations).

3.5.1 Effect of contact time with initial wastewater concentration

Batch adsorption experiment is done at different contact times such as 5, 10, 15, 20, 30 and 60 minutes for initial color concentration of 800, 1000 and 1200 Pt-Co. Dosage of Date seeds activated carbon of particle size 150 μm was 0.5 gm and 100 mL wastewater solution was kept constant. The experiment was carried out at 30°C temperature using agitation speed of 200 rpm and pH = 8.0. Impurity uptake per unit mass of adsorbent is plotted against contact time to identify optimum contact time for further batch experiments.

3.5.2 Effect of adsorbent dosage

Effect of Date seeds activated carbon adsorbent dosage on color adsorption was carried out for fixing the dosage. The experiment was done at different dosage 4, 6, 8, 10, 12 and 14 gm/L with 100 mL wastewater sample of 1200 Pt-Co color and 300 mg/L COD concentration. Other experimental conditions were contact time = 30 minutes, temperature = 30°C, agitation speed = 200 rpm, particle size 150 μm and pH = 8.0 during the experiment. An adsorption isotherm is obtained by plotting impurity loading per unit mass of adsorbent against residual impurity on a logarithmic scale. From this plotting, impurity loading is obtained against a desired level of residual impurity. From this loading, adsorbent dosage was fixed for further batch experimental study.

3.5.3 Effect of temperature with initial wastewater concentration

Adsorption experiment is carried out at three distinct temperatures 30 \pm 1°C, 35 \pm 1°C and 45 \pm 1°C for three samples with 800, 1000 and 1200 Pt-Co color concentration and 185, 225 and 300 mg/L COD concentration respectively. Contact time = 30 minutes,

adsorbent dosage = 7 gm/L, agitation speed = 200 rpm, particle size = 150 μm and pH = 8.00 were kept constant.

3.5.4 Effect of agitation speed with initial wastewater concentration

Effects of agitation speed on color and COD adsorption was carried out at three different speeds 150, 200 and 250 rpm respectively. Initial color concentration of these three samples was 800, 1000 and 1200 Pt-Co and COD concentrations were 185, 225 and 300 mg/L respectively. Contact time = 30 minutes, adsorbent dosage = 7 gm/L, temperature = 30°C, particle size 150 μm and pH = 8.00 were kept constant.

3.5.5 Effect of particle size

Three different sized particles of 150 μm , 150-300 μm and 300-425 μm were used in conjunction with initial color concentration of 1200 Pt-Co and 300 mg/L COD concentration. Contact time = 30 minutes, adsorbent dosage = 7 gm/L, temperature = 30°C, agitation speed = 200 rpm, pH = 8.00 were kept constant.

3.5.6 Effect of pH

Effects of pH on color and COD removal were assessed by carrying out the experiment with samples of pH from 5 to 11. Initial color and COD concentration of this sample was 1200 Pt-Co and 300 mg/L respectively. Contact time = 30 minutes, adsorbent dosage = 7 gm/L, temperature = 30°C, agitation speed = 200 rpm and particle size 150 μm were kept constant.

3.6 Adsorption isotherm study

Freundlich and Langmuir adsorption isotherm models were studied to find out the adsorption capacity of Date seeds activated carbon. Data of effects of temperature on COD removal with initial concentration by the adsorbent were used to fit into both the models. In Freundlich isotherm model $\log C_e$ is plotted against $\log q_e$, to find out adsorption capacity K_f and adsorption intensity n . In Langmuir isotherm model C_e/q_e is plotted against C_e ; q_m is monolayer (maximum) adsorption capacity and b is Langmuir constant related to energy of adsorption is obtained from the slope and intercept of the plot. The correlation coefficient, R^2 values are obtained from both the models.

3.7 Adsorption isotherm kinetics analysis

Adsorption isotherm kinetics analysis was carried out to assess both rate and mechanism of adsorption. Three models were used: Pseudo first order kinetic model, Pseudo second order kinetic model and Intra particle diffusion model. In Pseudo first order kinetic model, $\log (q_e - q_t)$ is plotted against t and from the slope and intercept of this plot, adsorption rate constant k_1 and equilibrium adsorption capacity q_e are obtained.

Whereas in Pseudo second order kinetic model t/q_t is plotted against t and from the intercept and slope of the plot, rate constant of pseudo second order adsorption k_2 and the equilibrium adsorption capacity q_e are obtained.

For intra particle diffusion model, rate constant k_i value is obtained from the slope of the plot q_t against $t^{1/2}$.

3.8 Thermodynamic analysis

Thermodynamic parameters such as change in free energy ΔG , enthalpy ΔH and entropy ΔS were determined by using the adsorption data of effects of temperature on COD and color removal with initial concentration. At first values of K_o is calculated from the following expression:

$$K_o = \frac{C_{solid}}{C_{liquid}}$$

By using the value of K_o , gas constant $R = 8.314 \text{ J/K/mole}$ and absolute temperature T in Kelvin (303K, 308K and 318K), change in free energy ΔG are calculated from the following expression:

$$\Delta G = -RT \ln K_o$$

Enthalpy ΔH and entropy ΔS were determined from the slope and intercepts of plot $\ln K_o$ against $1/T$.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

Textile effluent liquid wastewater consists of a wide variety of residual chemicals, organic matters and pollutants. These residuals present in the wastewater are necessary to determine the characteristics of wastewater for the assessment of the treatment requirement, treatability, mode and level of treatment. This is also important for the determination of the treatment efficiencies of the treatment effluent plants.

In this chapter, characteristics of the collected textile wastewater effluents have been determined and analyzed. Some of the common parameters have been tested to determine the characteristics of the wastewater which were pH, EC, color, COD, BOD₅ and heavy metals (Pb and Cd). This study had been conducted to find out the efficiency of activated carbon in the tertiary treatment of textile effluent.

In this study, activated carbon prepared from Date seeds was used for assessing the color and COD removal efficiency under different test conditions (contact time, adsorbent dosage, temperature, agitation speed, particle size and pH). Adsorption isotherm models (both Freundlich and Langmuir) were used to fit the experimental data and for determining adsorption capacity of Date seeds activated carbon adsorbent.

4.2 Characteristics of raw textile wastewater

In this study, wastewater samples were collected from Echotex Limited at Pollibiddut, Chandra, Gazipur. The quality of wastewater varied with different stages of production; hence, representative wastewater samples were collected from the equalization tank of Effluent Treatment Plant (ETP). All possible efforts were made to minimize the time lag between collection and analysis so that no significant change may occur in the quality of the samples. The collected samples were transported to the laboratory quickly and then samples were preserved in the refrigerator in accordance with the standard methods. Finally the concentrations of BOD₅, COD, color and heavy metals (Pb and Cd) were analyzed in the Environmental Engineering laboratory, BUET according to the standard methods (APHA, 1998). Characteristic

parameters for both unfiltered and filtered samples were calculated and are shown in Table 4.1. Sample was filtered to avoid the effect of filtration on test results and to know the actual adsorption capacity of Date seeds activated carbon. Final experiments were carried out using filtered sample.

Table 4.1: Characteristics of raw wastewater

Parameters	Unfiltered sample	Filtered sample
pH	8.52	8.05
EC (mS/cm)	3.82	3.70
Color (Pt-Co unit)	1410	1200
BOD ₅ (mg/L)	104	45
COD (mg/L)	611	300
Pb (ppm)	0.037	0.030
Cd (ppm)	0.00	0.00

In this study, pH of the raw sample was 8.05 indicates that the sample was basic in nature. Literature suggests that maximum pH value of textile industrial wastes in Bangladesh was 11.0 and minimum 3.9 with an average value of 8.80 (Rahman, 1997). The collected samples both filtered and unfiltered met the discharge standard of treated effluents setting out in Schedule 12-B of ECR'97.

Electrical Conductivity (EC) of the filtered sample was 3.70 mS/cm. In ECR, 97 (Schedule-10) for treated effluent discharge standard for EC is 1200 micro S/cm for discharge into inland surface, public sewer or irrigated land. Hence, EC value of this raw wastewater sample was much higher than the standard value for discharge.

The BOD₅ of this raw filtered sample was found 45 mg/L. Literature suggests that the BOD₅ of textile effluent usually be in the range of 200 mg/L to 650 mg/L. The discharge standard (included in schedule 12-B in ECR-1997) for composite textile plant and large processing unit (in which capital investment is more than thirty million Taka) is 150 mg/L.

The COD (permanganate) value of the study effluent (filtered) was found 300 mg/L whereas COD for non-filtered sample was 611 mg/L. The discharge standard of COD for treated effluent setting out in Schedule -10 of ECR' 97 were 200 mg/L, 400 mg/L

and 400 mg/L for discharge into inland surface water, public sewer at secondary treatment plant and irrigated land respectively.

Ratio of BOD_5 / COD is very important for selecting the treatment process. In this study, for raw wastewater ratio of BOD_5 / COD was $0.15 < 0.3$. This indicates more presence of non biodegradable organic matter than the biodegradable organic matter; hence physico-chemical treatment is required (Rao and Datta, 1987).

Color of the wastewater was found to be 1200 Pt-Co units. For Bangladesh, it has been found that color values vary up to 12000 TCU (Rahman, 1997). Although there is no standard limit of color in ECR-1997 for discharging treated effluent into inland surface water body. It was very difficult to make comment on result that was found for color in this study based on ECR' 97 but US (EPA) allowable limit for color is 150 Pt-Co units (Khan et al., 2014). Non-biodegradable color content from the textile effluent should be removed for the aesthetic reason. On that basis the sewage sample is needed to be treated.

In this study, concentration of lead (Pb) in sample was 0.037 and no cadmium (Cd) was present. Discharge standard of lead (Pb) into inland surface water, public sewer at secondary treatment plant and irrigated land was 0.1 mg/L. Therefore, lead (Pb) and cadmium (Cd) values of the collected sample were within the range of discharge standard and hence lead and cadmium was not a matter of concern for this sample.

4.3 Results and data analysis of batch adsorption process

The experimental data obtained from batch experiment were analyzed to find out the amount of adsorption and removal percentage of color and COD using Date seeds activated carbon. The effect of different parameters on color and COD removal were assessed. Variations of removal with initial concentrations of sample have been analyzed. Rate and mechanism of adsorption have been found by using different kinetic models. Isotherm models have been used to explain the experimental data obtained. Thermodynamic parameters have been studied also.

4.3.1 pH variation with dose of activated carbon

Variation of residual pH with the increase of dosage of Date seeds activated carbon is shown in Figure 4.1. Initial pH of the wastewater samples was 8.0. With the increase

of dosage of adsorbent the residual pH gradually decreased. Maximum residual pH was 6.8 at dosage 4 g/L and minimum was 5.25 for the dosage 14 g/L. The possible reason for this would be the formation of acidity in the solution since Date seeds activated with $ZnCl_2$. Hence with the increase of dosage of Date seeds activated carbon, more dissociation took place and pH gradually decreased.

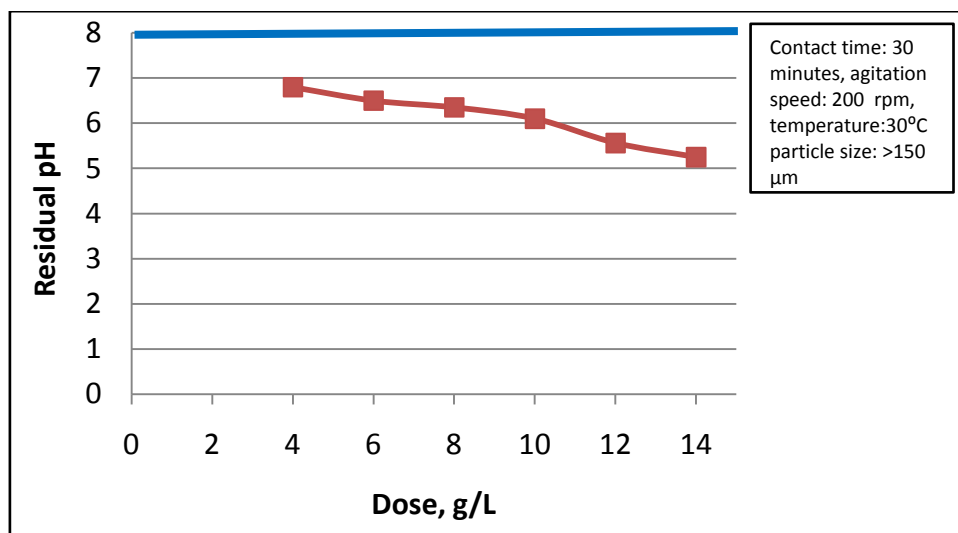


Figure 4.1: pH variation with dose of activated carbon

4.3.2 Color and COD removal variation with different parameters

In this study, for batch adsorption process, Date seeds activated carbon was used as adsorbent for removal of color and COD. Effects of different parameter such as dosage of adsorbent, contact time, pH, initial concentration and temperature on color and COD removal were studied. Initial color and COD for the filtered raw sample was 1200 Pt-Co and 300 mg/L respectively. Another two raw samples were prepared from this first raw sample by dilution process using distilled water, color of these two diluted samples were 1000 and 800 Pt-Co respectively and COD were 225 and 185 mg/L respectively. These two diluted samples were used as second and third raw sample. pH of these raw samples were adjusted using HCl/NaOH.

4.3.2.1 Effect of contact time with initial concentration on color and COD removal

Effect of contact time with initial color concentration on adsorption of color of textile wastewater using Date seeds activated carbon was assessed in batch experiments. Adsorption of color with contact time for these three initial concentrations is given in

Figure 4.2. The adsorption of color was rapid in first 5 minutes for all three initial concentrations and after 30 minutes amount of color adsorbed was insignificant with the increase of contact time. Therefore, for batch experiments 30 minutes equilibrium time was selected and used for further studies. The equilibrium contact time is independent of initial concentration of color.

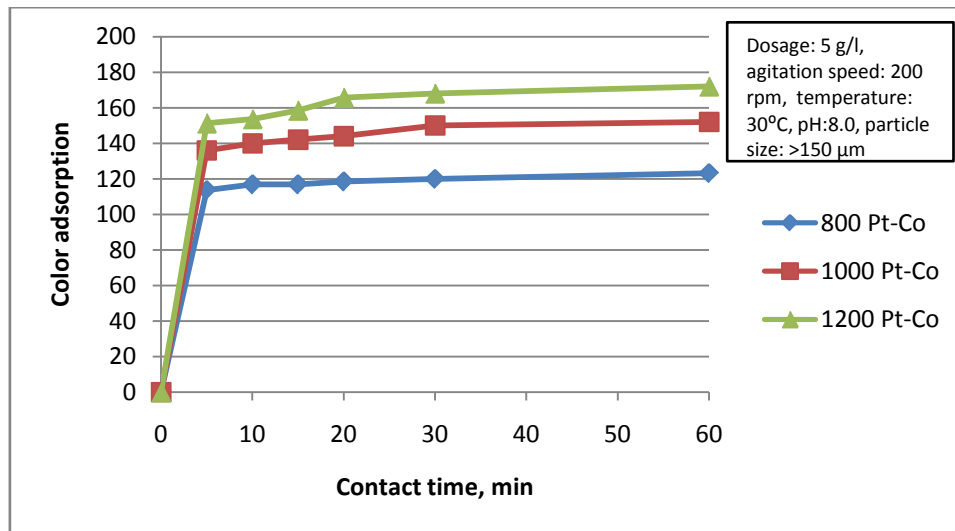


Figure 4.2: Effect of contact time with initial concentration on adsorption of color

Color adsorption on Date seeds activated carbon adsorbent for three different initial concentrations 800, 1000 and 1200 Pt-Co is shown in Figure 4.2. A amount of color adsorption per unit mass of adsorbent increased with the increase of initial concentration. For 800 Pt-Co initial color concentrations, color adsorption rate was 120 Pt-Co (per gram of adsorbent per litre), whereas adsorption rate was 150 Pt-Co (per gram of adsorbent per litre) for 1000 Pt-Co initial concentration and 168 Pt-Co (per gram of adsorbent per litre) for 1200 Pt-Co color concentration. But color removal percentage decreased with the increase of initial concentration as shown in Figure 4.3. Adsorption rate increase with the increase of initial concentration, this may be due to higher interaction between adsorbate and adsorbent. Increasing the initial color concentration would increase the mass transfer driving force and therefore the rate at which color induced molecules pass from the bulk solution to the particle surface. Hence a higher concentration of color enhances the adsorption process. This would increase the rate of adsorption process.

Color removal percentage was more for the contact time from 0 to 30 minutes than from 30 to 60 minutes. Maximum 77 percent color removed with 800 Pt-Co initial color concentration, whereas for 1000 Pt-Co initial color concentration 76 percent color removed and 74 percent removed for 1200 Pt-Co initial color concentration. At 30 minutes equilibrium contact time, color removal percentages were 75 percent for both the sample of 800 and 1000 Pt-Co initial color concentration and 70 percent for 1200 Pt-Co initial concentration. The color removal depends on the availability of active sites present in adsorbent. As the treatment time progresses, the activated carbon sites had the affinity towards saturation. At the start of experiment, the available sites present in adsorbent is more, so the adsorption rate is more. As the time progresses the availability of active site inside or outside of adsorbent gradually decreases, so the color removal gradually decreases. So after equilibrium, adsorption rate was not significant.

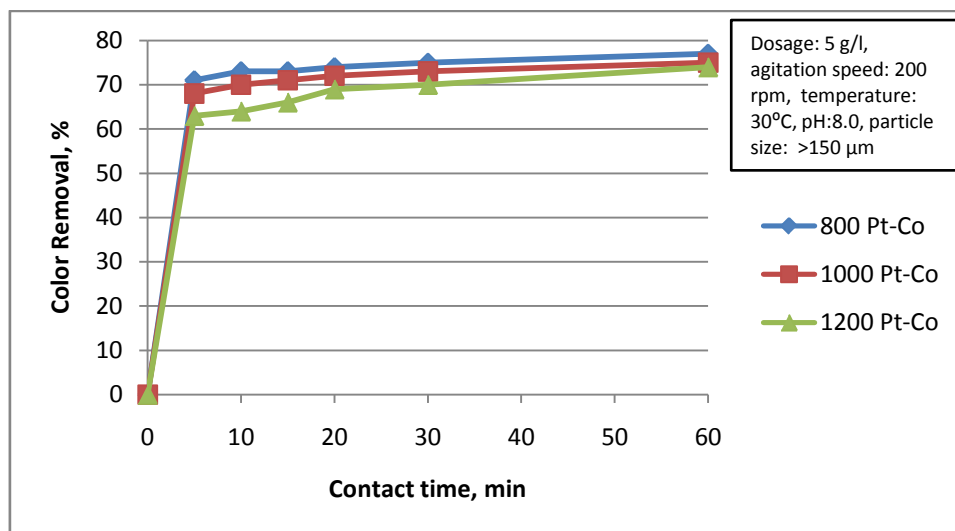


Figure 4.3: Effect of contact time with initial concentration on removal of color

Effect of contact time with initial concentration on removal of COD of textile wastewater using Date seeds activated carbon was assessed in batch experiments. Once the 30 minutes equilibrium contact time was selected for this study, further COD removal was carried out for 30 minutes contact time. COD removal percentage for three different initial COD concentrations 185, 225 and 300 mg/L is shown in Figure 4.4.

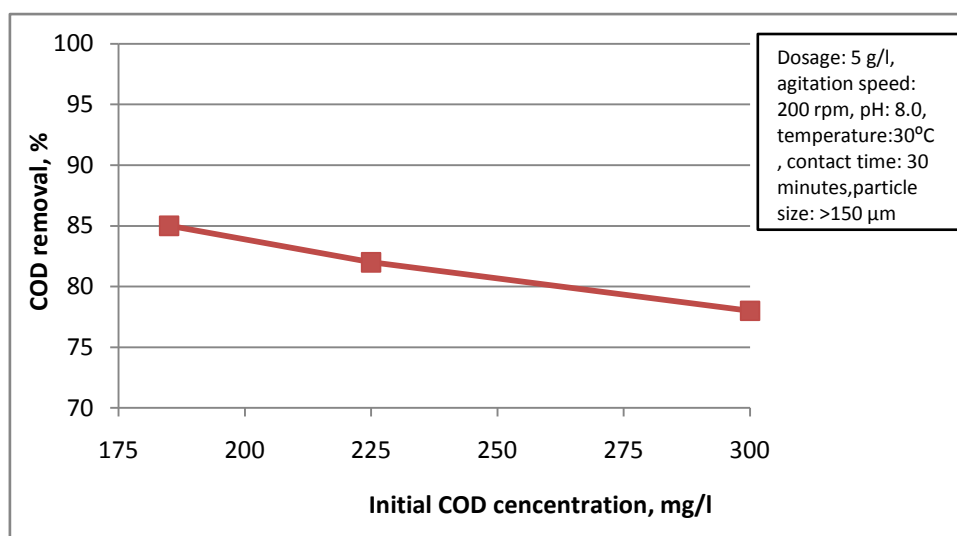


Figure 4.4: Effect of contact time with initial concentration on COD removal

COD removal percentage decreased with the increase of initial concentration. About 85 percent COD removed with 185 mg/L initial COD concentration, whereas 82 percent COD removed for 225 mg/L concentration and 78 percent removed for 300 mg/L. The COD removal percentage depends on the number of availability of active sites inside or outside of an adsorbent. For a fixed amount of adsorbent as the initial concentration increases the amount of pollutants increases and removal percentage decreases.

4.3.2.2 Effect of adsorbent dosage on color and COD removal

To assess the effect of dosage of Date seeds powder activated carbon adsorbent on color and COD removal, optimum dosage for a certain residual concentration is calculated first. Optimum dosage for batch adsorption process was selected for a sample of 1200 Pt-Co initial color concentration and 300 mg/L initial COD concentration from the plot of adsorption loading q_e against residual concentration C_e . For color adsorption, values of residual color and adsorption loading were calculated for different adsorption dosage ranges from 4 g/L to 14 g/L. Adsorption loading q_e is plotted against residual concentration C_e for 1200 Pt-Co initial color concentration as shown in Figure 4.5. From this plot adsorption loading was calculated for residual color 150 Pt-Co. For this sample, 7.34 g/L adsorbent dosage is calculated for 150 Pt-Co residual color but 7 g/L is used for further studies because of simplicity.

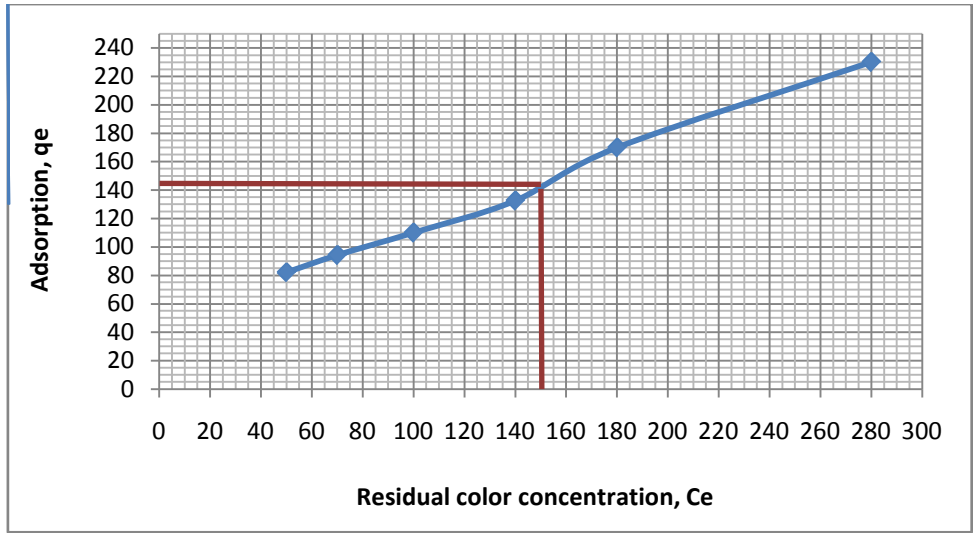


Figure 4.5: Adsorption loading for residual color

Color removal percentage increased with the increase of dosage of Date seeds activated carbon adsorbent and decreased with the increase of initial concentration of wastewater sample. This is shown in Figure 4.6. This may be due to the increase in availability of surface active sites resulting from increased dose and accumulation of the adsorbent. The amount of color removal increased from 77 to 96 percent with increase in dosage of adsorbent from 4 to 14 g/L for 1200 Pt-Co initial color concentration sample and 87 percent color removed at 7g/L equilibrium dosage.

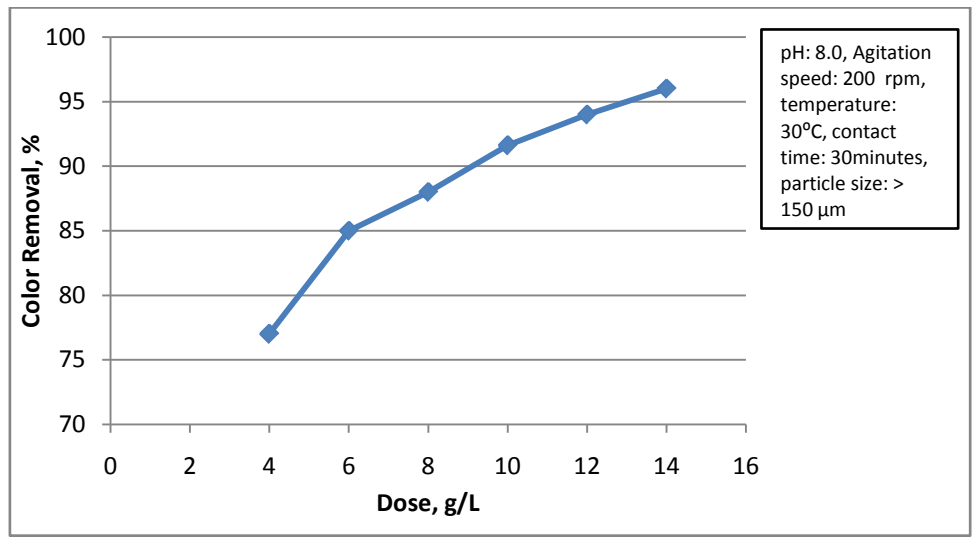


Figure 4.6: Effect of adsorbent dosage on color removal

For investigating the effect of dosage of Date seeds activated carbon on COD removal percentage, a plot of COD removal percentage against dosages from 4 to 14 g/L is

shown in Figure 4.7 for a sample of 300 mg/L initial COD concentration. With the increase of dosage of adsorbent, COD removal percentage increased. Maximum 96 percent COD removed at 14 g/L adsorbent dosage whereas for 7 g/L dosage, COD removal percentage was 83 percent.

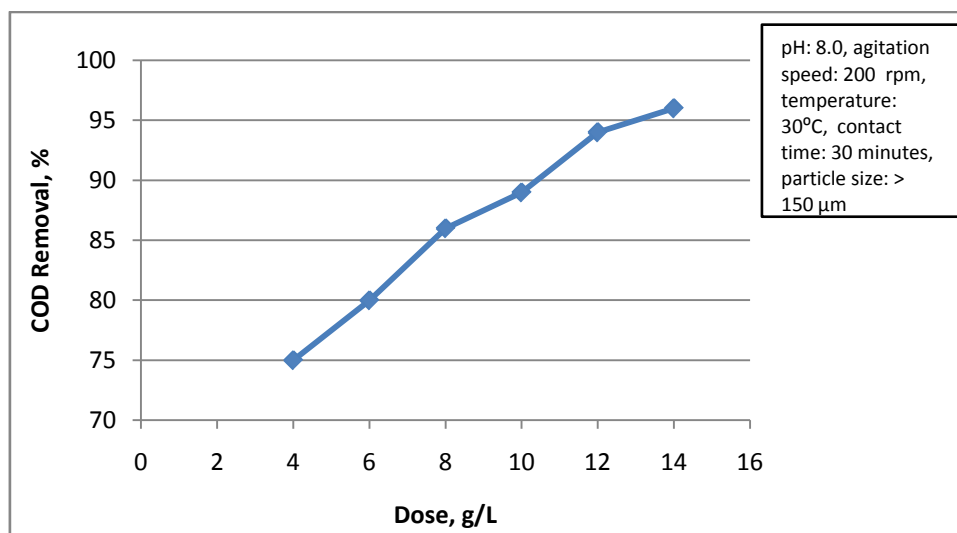


Figure 4.7: Effect of adsorbent dosage on COD removal

4.3.2.3 Effect of temperature with initial concentration on color and COD removal

Temperature has significant effects on adsorption process. Thermodynamic parameters like heat of adsorption and energy of activation play an important role in predicating the adsorption behavior and both the parameters are strongly dependent on temperature. Adsorption of color at three different temperatures (30°C, 35°C and 45°C) onto Date seeds activated carbon was studied for 800, 1000 and 1200 Pt-Co initial color concentrations. Results are shown in Figure 4.8.

It is observed that with the increase of experimental temperature and decrease of initial concentration, color removal percentage increased. For the sample of 1200 Pt-Co initial color concentration, color removal percentage increased from 67.5 to 75 percent with the increase of temperature from 30°C to 45°C, whereas for 1000 Pt-Co color concentration sample, removal percentage increased from 69 to 76 percent with increasing of temperature from 30°C to 45°C and for 800 Pt-Co initial concentration 72 to 78.33 percent color removed with increasing of temperature from 30°C to 45°C.

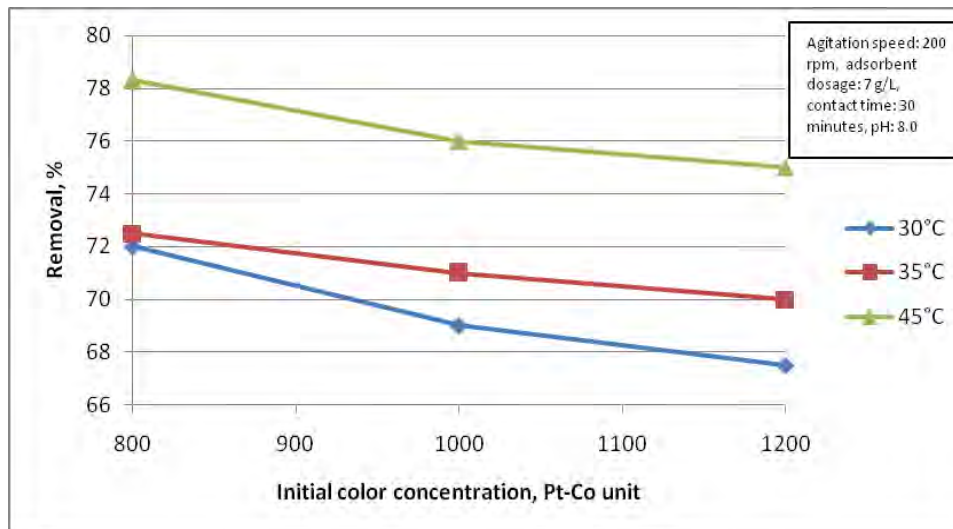


Figure 4.8: Effects of temperature with initial concentration on color removal

The increase in color removal percentage with the increasing experimental temperature may be attributed as the temperature increases, rate of diffusion of adsorbate molecules across the external boundary layer and internal pores of Date seeds activated carbon adsorbent particle increases.

For assessing the effect of temperature on COD removal batch adsorption process was also studied at three different temperatures (30°C, 35°C and 45°C) onto Date seeds activated carbon for 185, 225 and 300 mg/L initial COD concentrations. It is observed from the Figure 4.9 that with the increase of experimental temperature and decrease of initial concentration COD removal percentage also increased. For the sample of 185 mg/L initial COD concentration, COD removal percentage increased from 85 to 92 percent with the increase of temperature from 30°C to 45°C, whereas for 225 mg/L COD concentration sample, removal percentage increased from 80 to 87 percent with increasing temperature from 30°C to 45°C and for the sample of 300 mg/L COD, 78 to 85 percent COD removed with increasing temperature from 30°C to 45°C.

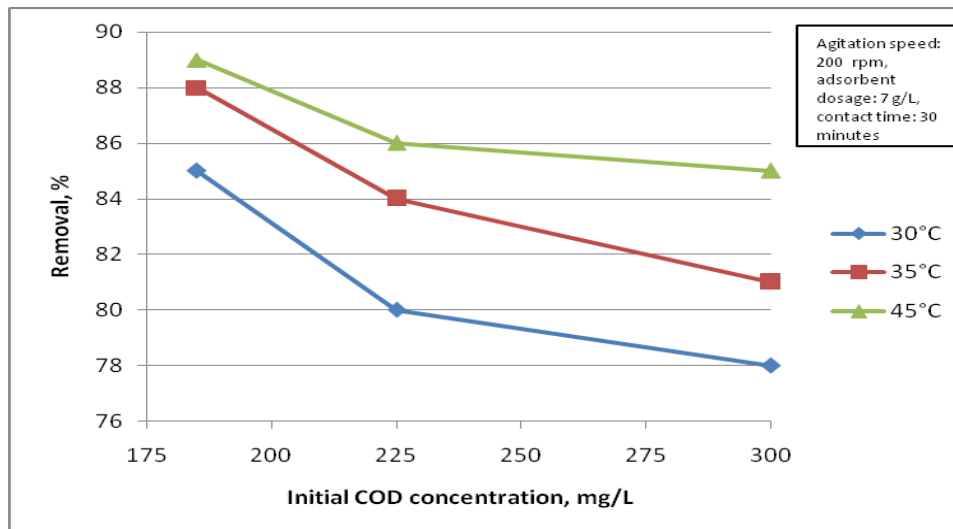


Figure 4.9: Effects of temperature with initial concentration on COD removal

4.3.2.4 Effect of agitation speed of shaker with initial concentration on color and COD removal

Adsorption is influenced by mass transfer parameters that are related to contact time, agitation speed of the shaker etc. The adsorption of color by Date seeds activated carbon for different agitation speeds of shaker ranging from 150 to 250 rpm with varying initial concentration from 800 to 1200 Pt-Co were studied. The amount adsorbed was found to increase from 120 to 130 Pt-Co (per gram of adsorbent per litre) for Date seeds activated carbon with increase in agitation speed of shaker from 150 to 250 rpm of an oscillator for a sample of 1200 Pt-Co initial color concentration.

The color removal percentage increased with the increase of agitation speed of shaker is shown in Figure 4.10. This is may be with low agitation speed of shaker, the greater contact time is required to attain the equilibrium and or reduction of particle size. With the increase of initial color concentration, removal percentage decreased in this study. For the sample of 1200 Pt-Co initial color concentration, color removal percentage increased from 65 to 71.25 percent with increasing of agitation speed of shaker from 150 rpm to 250 rpm, whereas for 1000 Pt-Co color concentration sample, removal percentage increased from 68 to 74 percent with increasing of agitation speed of shaker from 150 rpm to 250 rpm and for 800 Pt-Co concentration sample 70 to 76 percent color removed with increasing agitation speed of shaker from 150 rpm to 250 rpm.

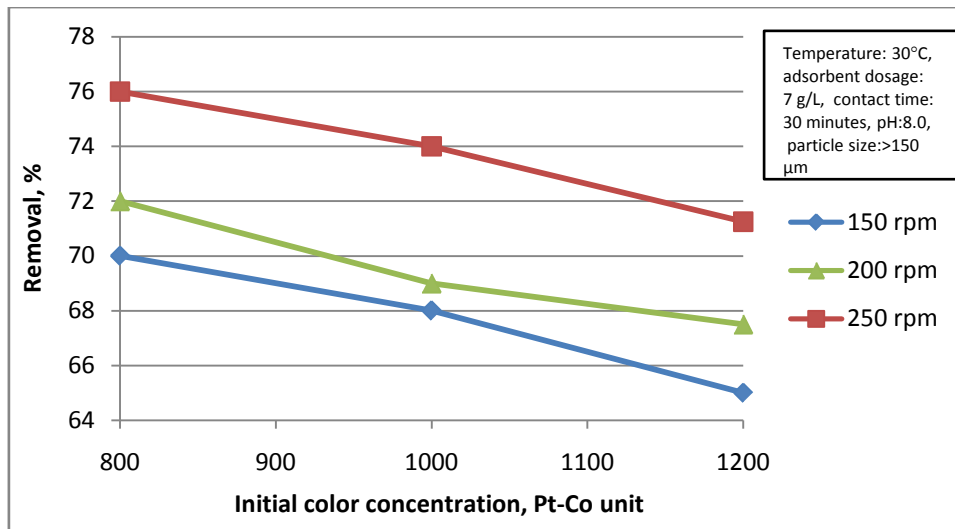


Figure 4.10: Effects of agitation speed with initial concentration on color removal

Effect of agitation speed with initial concentration on COD removal studies is shown in Figure 4.11. Similarly, like as color removal, COD removal percentage increased with increasing agitation speeds of shaker and decreasing initial concentrations. Maximum 84, 85 and 88 percent COD was removed for agitation speed 150, 200 and 250 rpm respectively for the sample with 185 mg/L initial COD concentration. COD adsorption rate per unit mass of adsorbent increased with the increase of initial concentration of the samples.

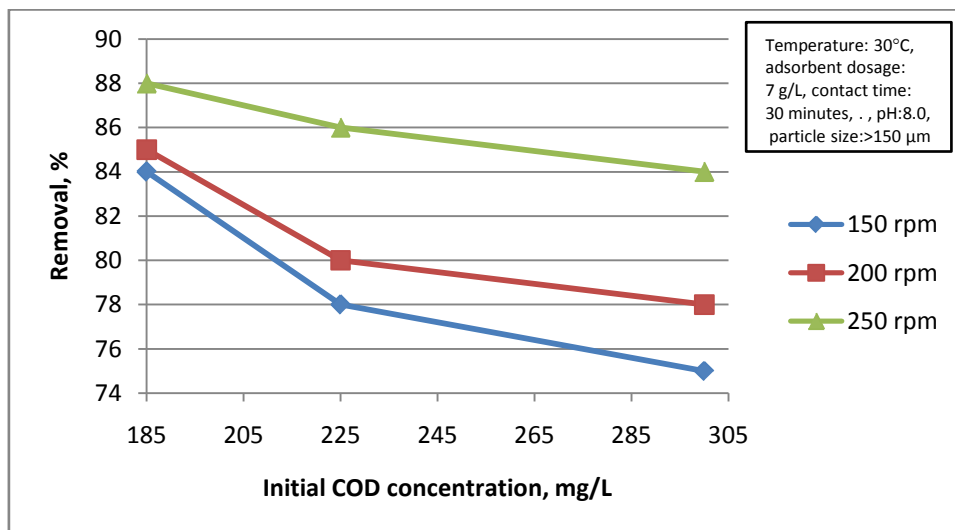


Figure 4.11: Effects of agitation speed with initial concentration on COD removal

4.3.2.5 Effect of particle size on color and COD removal

Effect of particle sizes on removal of color and COD for textile wastewater was investigated. Batch adsorption experiments were carried out for the removal of color and COD from aqueous solution of initial color and COD concentration 1200 Pt-Co and 300 mg/L respectively using Date seeds activated carbon for three different particle sizes >150 μm , (150-300) μm and (300-425) μm . Results are shown in Figure 4.12.

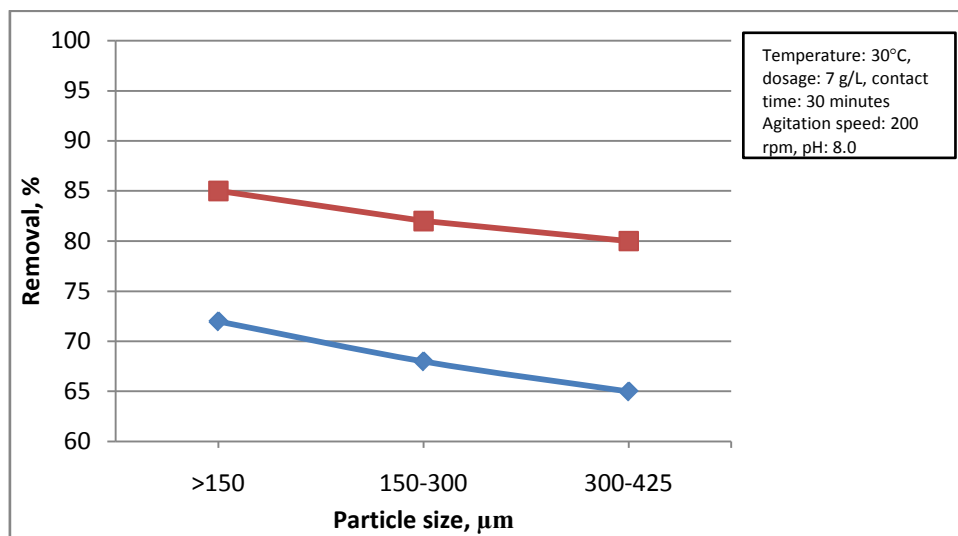


Figure 4.12: Effects of particle sizes on color and COD removal

It is shown that removal efficiency of both color and COD were decreased with increasing particle size of Date seeds activated carbon. About 72 percent of color removed with particle size >150 μm , whereas 68 percent color removed with particle size 150-300 μm and 65 percent removed with particle size 300-425 μm .

For COD removal, maximum 85 percent of COD removed with particle size >150 μm , whereas 82 percent removal efficiency was found with particle size 150-300 μm and 80 percent with particle size 300-425 μm . The removal efficiency decreased with the increase of particle size. This may be attributed as for the same amount of adsorbent, smaller the particle size, greater the total surface area that offered large number of active sites for removal of adsorbate by adsorbent.

4.3.2.6 Effect of pH on color and COD removal

Effect of pH on removal of color and COD using Date seeds activated carbon was investigated over a range of pH from 5 to 11. Batch adsorption experiment was studied with the sample of initial color and COD concentration 1200 Pt-Co and 300 mg/L respectively. The removal percentage of both color and COD increased with increasing pH from 5 to 11. Maximum color and COD removed using Date seeds activated carbon at pH 11 and minimum removed at pH 5. Both the results are shown in Figure 4.13.

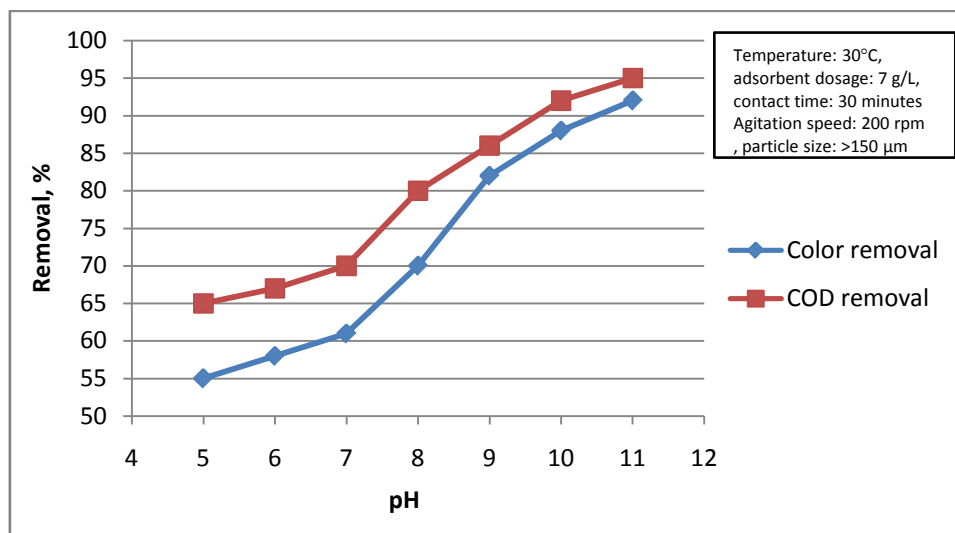


Figure 4.13: Effects of pH on color and COD removal

At pH 5, color and COD removal were 55 percent and 65 percent respectively and at higher pH 11, 92 percent color and 95 percent COD were removed. The increasing trend of removal of both color and COD with increasing pH is dependent on the nature of the adsorbent. Date seeds activated carbon was activated using $ZnCl_2$ activating agent and pH of Date seeds activated carbon was measured as 4.47 that denotes the property of Date seeds activated carbon is acidic in nature and reacts better with aqueous solution of basic in nature. This result concluded that the activated carbon having different surface functional groups such as acidic and basic, which have direct influence of pH.

4.3.3 Adsorption isotherm analysis

4.3.3.1 Freundlich isotherm for COD removal

The experimental data was fitted into both Freundlich and Langmuir isotherm to know the amount adsorbed. Freundlich and Langmuir COD removal isotherm for different temperatures (30°C, 35°C and 45°C) are shown in Figure 4.14 and Figure 4.15 respectively. Values of adsorption capacity, K_f and intensity of adsorption, n for Freundlich isotherm were determined from the slope and intercepts of the plot $\log q_e$ against $\log C_e$ (Figure 4.14) for 30°C, 35°C and 45°C temperature were given in Table 4.2.

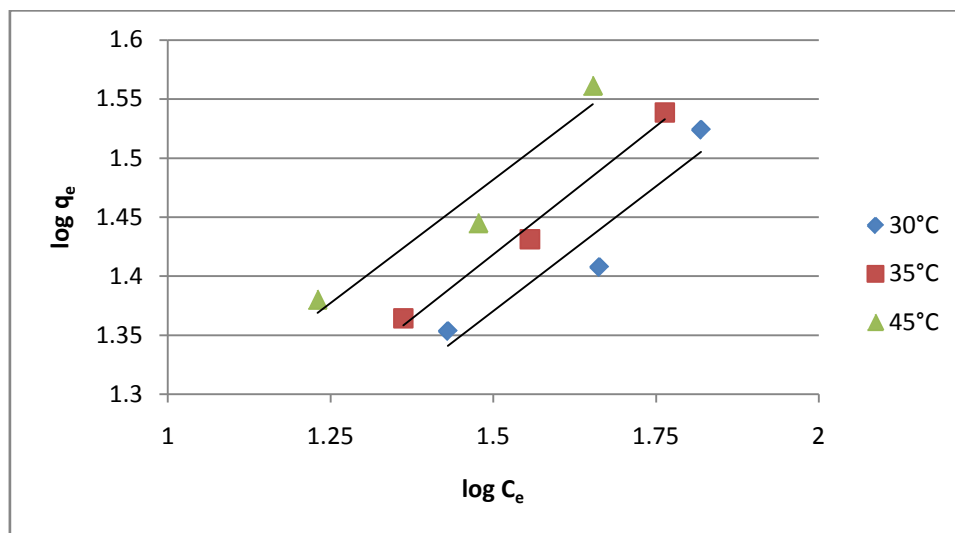


Figure 4.14: Freundlich isotherm for COD removal

The plots of $\log q_e$ against $\log C_e$ showed good linearity ($R^2 = 0.900$ to 0.986) indicating the removal of COD obeys the Freundlich adsorption isotherm. Values of n obtained from these plots were from 2.304 to 2.398 that lie between 2 to 3 indicates an effective adsorption (Potgeiter, et al., 2005). Adsorption capacity, K_f were increased from 5.44 to 7.16 with increasing temperature from 30°C, to 45°C represents an easy uptake of adsorbate from the solution with increasing temperature (Mahvi, et al., 2004). As shown in Table 4.2, relatively high regression coefficients (R^2) suggested that Freundlich models was more suitable for describing the removal behavior of COD by Date seeds activated carbon because of formation of multilayer of adsorbate species onto adsorbent.

4.3.3.2 Langmuir isotherm for COD removal

To fit the data of COD removal at temperatures 30°C, 35°C and 45°C in Langmuir isotherm model, C_e/q_e was plotted against C_e as shown in Figure 4.15. A linear plot of C_e/q_e against C_e suggested the applicability of the Langmuir isotherm models ($R^2 = 0.900$ to 0.979). Monolayer (maximum) adsorption capacity q_m and Langmuir constant related to energy of adsorption b were determined from slope and intercept of the plot given in Table 4.2. Monolayer (maximum) adsorption capacity, q_m obtained from Langmuir plots were 55.55 mg/g for 45°C and 52.63 mg/g for both 30°C and 35°C temperature.

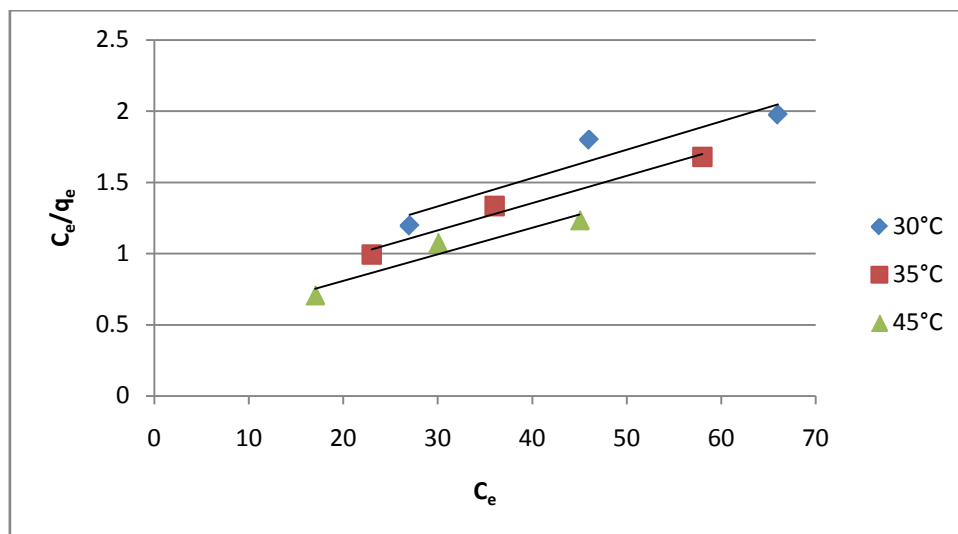


Figure 4.15: Langmuir isotherm for COD removal

The essential features of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor R_l which was obtained from the Eq. (5). In the present study, R_l values are obtained from 0.11 to 0.173 for Date seeds activated carbon that lie between 0 and 1 indicates favorable adsorption.

Table 4.2: Isotherm parameters and correlation coefficients for COD removal

Temperature °C	Freundlich isotherm parameters			Langmuir isotherm parameters		
	K_f	n	R^2	q_m (mg/g)	b (mg ⁻¹)	R^2
30	5.44	2.369	0.900	52.63	0.0258	0.900
35	5.83	2.304	0.986	52.63	0.032	0.979
45	7.16	2.398	0.934	55.55	0.041	0.930

4.3.3.3 Freundlich isotherm for color removal

Both Freundlich and Langmuir color adsorption isotherm for different temperatures (30°C, 35 °C and 45 °C) are shown in Figure 4.16 and Figure 4.17 respectively. Freundlich isotherm parameters such as adsorption capacity, K_f and intensity of adsorption, n for color adsorption were obtained from the slope and intercept of the plot $\log q_e$ against $\log C_e$ (Figure 4.18) for 30°C, 35°C and 45°C temperature were given in Table 4.3.

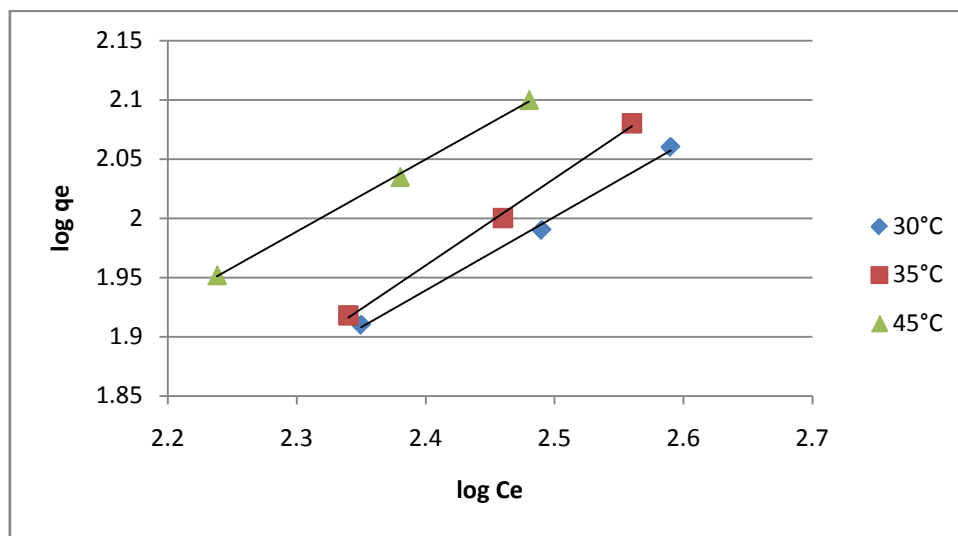


Figure 4.16: Freundlich isotherm for color adsorption

Though the correlation coefficient of the plots of $\log q_e$ against $\log C_e$ showed good linearity ($R^2 = 0.996$ to 0.999) indicating the adsorption of color obeys the Freundlich adsorption isotherm. Values of n obtained from slope of these plots were from 1.36 to 1.64 that is more than 1 that indicates adsorption of color at different temperature is a favourable process (Potgeiter, et al., 2005). Values of adsorption capacity, K_f is increasing with the increase of temperature, but not linearly. So the Freundlich isotherm explains the data obtained for color adsorption using Date seeds activated carbon at different temperatures. As shown in Table 4.3, relatively high regression coefficients (R^2) suggested that Freundlich models was more suitable for describing the removal behavior of color by Date seeds activated carbon because of formation of multilayer of adsorbate species onto adsorbent.

4.3.3.4 Langmuir isotherm for color removal

Langmuir isotherm model was used to fit the data of color removal at different temperatures 30°C, 35°C and 45°C by plotting C_e/q_e against C_e as shown in Figure 4.17. A linear plot of C_e/q_e against C_e suggested the applicability of the Langmuir isotherm models ($R^2 = 0.962$ to 0.986). Monolayer (maximum) adsorption capacity q_m and Langmuir constant related to energy of adsorption b were determined from slope and intercept of the plot given in Table 4.2. Monolayer (maximum) adsorption capacity, q_m obtained from Langmuir plots were from 333 to 500 Pt-Co (per gram of adsorbent per litre) for temperature from 30°C to 45°C as shown in Table 4.3.

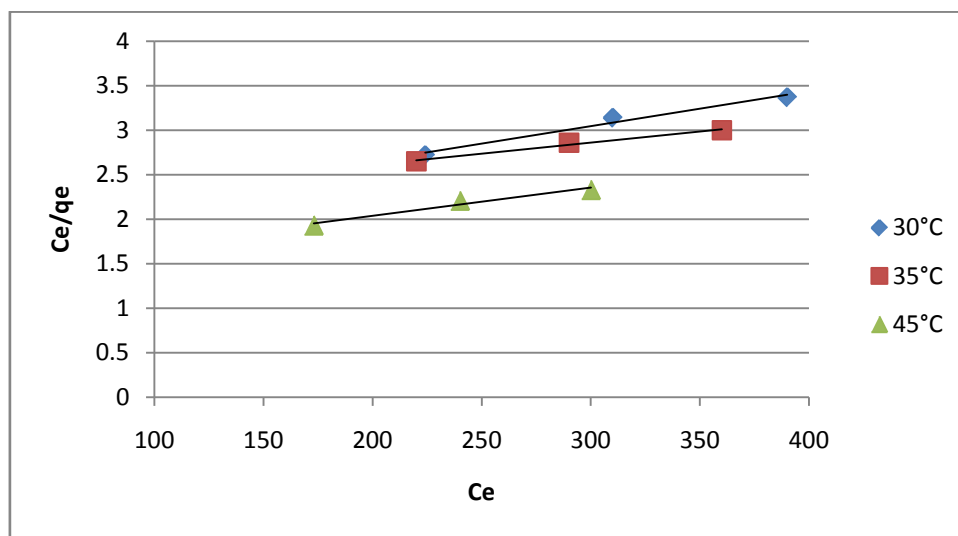


Figure 4.17: Langmuir isotherm for color adsorption

In the present study, for Date seeds activated carbon color adsorption, the values of dimensionless separation factor R_l obtained using Eq. (5) were from 0.284 to 0.581 that lie between 0 and 1 indicates favorable adsorption.

Table 4.3: Isotherm parameters and correlation coefficients for color removal

Temperature °C	Freundlich isotherm parameters			Langmuir isotherm parameters		
	K_f	n	R^2	q_m	b (mg^{-1})	R^2
30	2.80	1.64	0.996	333	0.0016	0.978
35	1.57	1.36	0.997	500	0.0009	0.986
45	3.85	1.61	0.999	333	0.0021	0.962

4.3.4 Adsorption kinetic study

Adsorption kinetic study is used to investigate the mechanism and rate controlling steps of adsorption. The mechanism of adsorption involves the chemical reactions of the functional groups present on the surface of the adsorbent and adsorbate, temperature and pH (Baseri et al., 2012). In the literature, several models have been applied to know the order of adsorbent-adsorbate interactions and the rate of adsorption of color. In this present study, the following three kinetic models were applied for the experimental data. Kinetic study for color adsorption was only analyzed using these kinetic models but a analysis could not be carried out for COD because of limitation of time.

4.3.4.1 Pseudo first order kinetic model

In Pseudo first order kinetic model The plots of $\log(q_e - q_t)$ against t for color adsorption for three different initial color concentrations 800 Pt-Co, 1000 Pt-Co and 1200 Pt-Co respectively were shown in Figure 4.18. The plots gave a straight line with a slope of $-k_1/2.303$ and intercept of $\log q_e$ that allows to determine pseudo first order rate constant, k_1 and theoretical amount of color adsorbed per unit mass of adsorbent per litre, q_e (*theoretical*) respectively. Pseudo first order rate constant k_1 and theoretical adsorption q_e (*theoretical*) were obtained from the slope and intercept of plot $\log(q_e - q_t)$ against t .

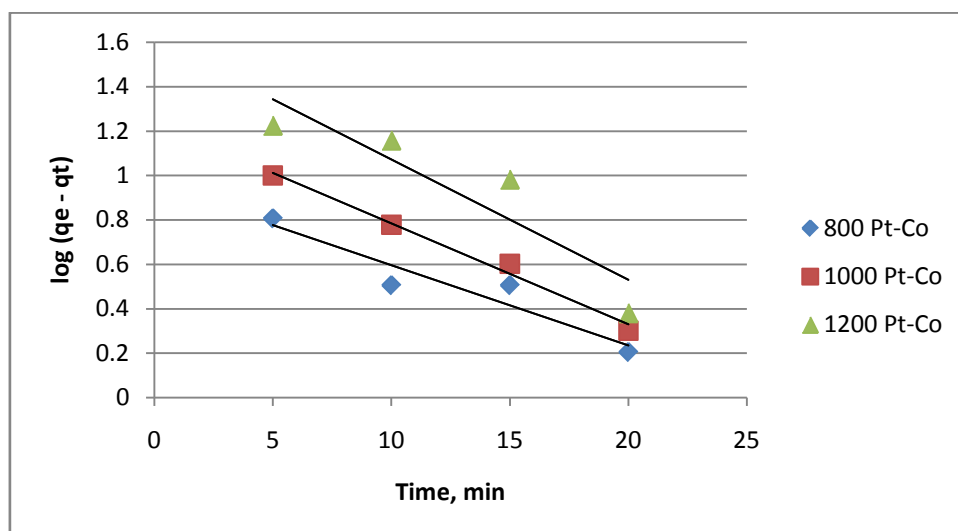


Figure 4.18: Pseudo first order plot for color adsorption

Table 4.4: Parameters of Pseudo-first order kinetic model

Initial color concentration	q_e (experimental)	k_1	q_e (theoretical)	R^2	$t_{1/2}$
800	120	0.083	9.036	0.900	0.83
1000	146	0.104	17.3	0.988	1.14
1200	168	0.124	41.11	0.827	1.70

Note: Unit of q_e in Pt-Co (per gram of adsorbent per litre).

Theoretical adsorption q_e (theoretical) were compared with the experimental adsorption q_e (experimental) values as shown in Table 4.4. Experimental adsorption, q_e (experimental) values differ widely from the corresponding theoretical values q_e (theoretical) and also correlation coefficient values (R^2) are not high for all concentrations which show that pseudo first order kinetic study of Langergen does not fit well with whole range of contact time and is generally applicable for initial stage of adsorption (Ho and Mckay, 1998).

4.3.4.2 Pseudo second order kinetic model

Since pseudo first order equation does not fit well, the Langergen pseudo – second order kinetic model was used to find out the rate of adsorption. The pseudo second order kinetic model plots t/q_t against t for color adsorption for three different initial concentrations 800 Pt-Co, 1000 Pt-Co and 1200 Pt-Co respectively are shown in Figure 4.19.

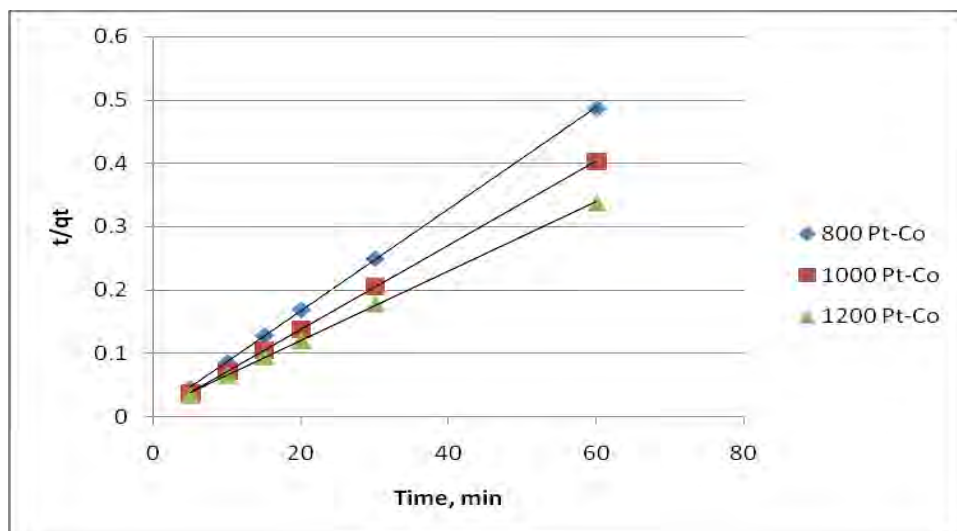


Figure 4.19: Pseudo second order plot for color adsorption

Rate constant of second order adsorption, k_2 and theoretical adsorption, q_e (*theoretical*) values are calculated from the intercepts and slopes of plot t/q_t against t . From highly linear plots it is clear that there may be a possibility of chemisorptions playing a significant role in the rate determining step.

The pseudo second order parameters q_e (*theoretical*), h and k_2 obtained from the plot are presented in Table 4.5. Where h , initial adsorption rate was obtained from Eq. (9). The correlation coefficient, R^2 for second order adsorption model has very high values for the adsorbents ($R^2 = 0.999$) and theoretical adsorption, q_e (*theoretical*) values are consistent with experimental adsorption, q_e (*experimental*) that showed Pseudo second order kinetic model of Langergen fitted well with whole range of contact time and adsorption process appears to be controlled by chemisorptions.

Table 4.5: Parameters of Pseudo-second order kinetic model

Initial color concentration	q_e (<i>experimental</i>)	k_2	q_e (<i>theoretical</i>)	h	R^2
800	120	0.01	125	129.6	0.999
1000	146	0.006	166.67	191.8	0.999
1200	168	0.0035	200	169.3	0.999

Note: Unit of q_e in Pt-Co (per gram of adsorbent per litre).

4.3.4.3 Intra particle diffusion model

The overall adsorption process may be indeed controlled either by one or more 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. Compared to the external or internal diffusion step, the adsorption step is usually vary fast for the adsorption of organic compounds on porous adsorbents (Sarker et al., 2003). In a rapidly stirred batch adsorption process, the diffusive mass transfer is related to an apparent diffusion coefficient, which will fit the experimental adsorption rate data. Generally, a process is diffusion-controlled if its rate depends on the rate at which components diffuse towards one another (Fierro et al., 2008). To realize the exact diffusion mechanism, the adsorption kinetic data were further analyzed by an intra-particle diffusion model (Weber and Morris, 1963).

The intra particle diffusion rate constant (k_i) and I , a constant that gives idea about the boundary layer thickness are obtained from the Eq. (10). k_i and I are obtained from the slope and intercept of the plot q_t against $t^{1/2}$ shown in Figure 4.20. The intercepts I and k_i values of plots q_t against $t^{1/2}$ increases with increase of initial color concentration is given in Table 4.6. The larger the value of I , the greater the boundary layer effect is. Figure 4.20 presents the data points that are related to two or more straight lines, indicating a desorption was not only controlled by only intra-particle diffusion; both external film and intra-particle diffusion mechanism were the rate controlling steps. The first linear portion was due to film diffusion of color through solution onto the external surface of Date seeds activated carbon. The later portion refers to slow intra-particle pore diffusion. This indicates that both external film and intra-particle pore diffusion mechanism were involved in the adsorption of color onto Date seeds activated carbon.

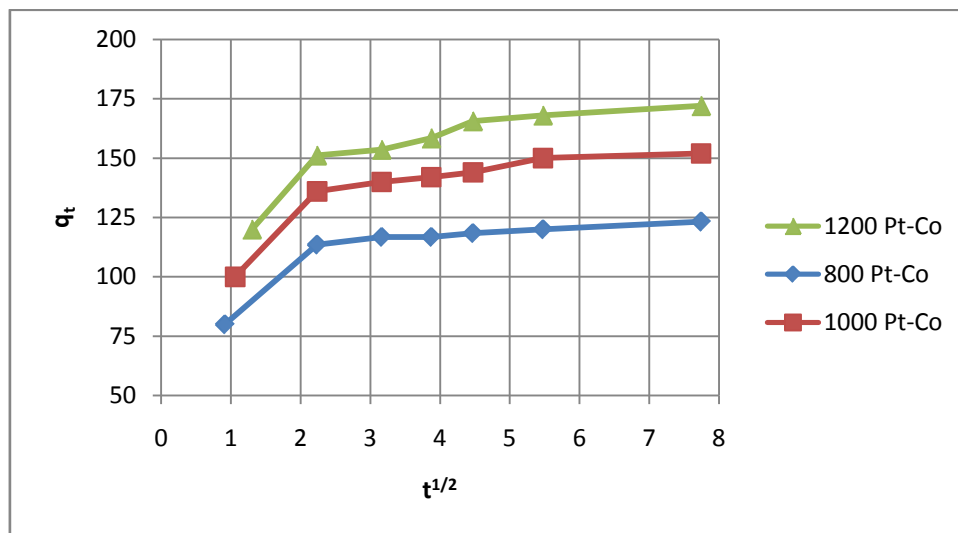


Figure 4.20: Intra particle diffusion plot for color adsorption

Assuming spherical geometry of the adsorbents, the overall rate constant of the process can be correlated to the pore diffusion or film diffusion in accordance with the pore diffusion coefficient and film diffusion coefficient obtained from the Eq. (11) and Eq. (12). For this study r_o radius of the adsorbent (cm) was 0.0075 cm, $t_{1/2}$, the time necessary to obtain half the initial concentration is obtained from the Eq. (13). Assuming δ the film thickness is of 0.001 cm (Helfferich, 1962) and $t_{1/2}$ values are

given in Table 4.6, using these values; the film diffusion coefficient (D_f) and pore diffusion coefficient (D_p) were calculated are given in Table 4.6.

Michelson et al., (1975) suggested if the diffusion coefficient lies between $10^{-6} - 10^{-8}$ cm^2/sec , the film diffusion will be rate limiting while if pore diffusion coefficient is in the range of $10^{-11} - 10^{-13}$ cm^2/sec , the pore diffusion will be the rate limiting. In order to find out the nature of process responsible for adsorption on chosen adsorbent, attempts were made to calculate the diffusion coefficient of the process. It was found that estimated film and pore diffusion were in the range of 0.563×10^{-7} to 1.38×10^{-7} cm^2/sec and 1.65×10^{-8} to 3.389×10^{-7} cm^2/sec for color as shown in Table. Thus, it may be concluded from the calculated diffusion coefficients from this study that as the diffusion values were more or less equal and were also in range within the two limits; either of the two (i.e., film diffusion or pore diffusion) or both might be rate controlling.

Table 4.6: Film diffusion and pore diffusion coefficients for color removal

Initial color Conc. (Pt-Co)	Intra particle diffusion model			$t_{1/2}$, sec	D_p cm^2/sec	D_f cm^2/sec
	k_i	I	R^2			
800	1.656	110.6	0.967	49.8	3.389×10^{-7}	1.38×10^{-7}
1000	3.008	130.4	0.924	68.4	2.467×10^{-8}	1.009×10^{-7}
1200	4.051	143.2	0.887	102	1.65×10^{-8}	0.563×10^{-7}

4.3.5 Thermodynamics of adsorption

Spontaneity of a process can be determined by thermodynamic parameters such as enthalpy change (ΔH°), free energy change (ΔG°) and entropy change (ΔS°) using Eq. (17) and Eq. (18). A spontaneous process will show a decrease in ΔG° and ΔH° values with increasing temperature. The temperatures used in the thermodynamic study were 303, 308 and 318 K. K_o is the ratio of concentration in solid phase (values are obtained by the subtraction of liquid phase concentration from initial concentration) and liquid phase concentration. Values of ΔH and ΔS for COD and color removal (presented in Table 4.7 and Table 4.8) are obtained from the slope and intercept of plot $\ln K_o$ against $1/T$ are shown in Figure 4.21 and Figure 4.22 respectively.

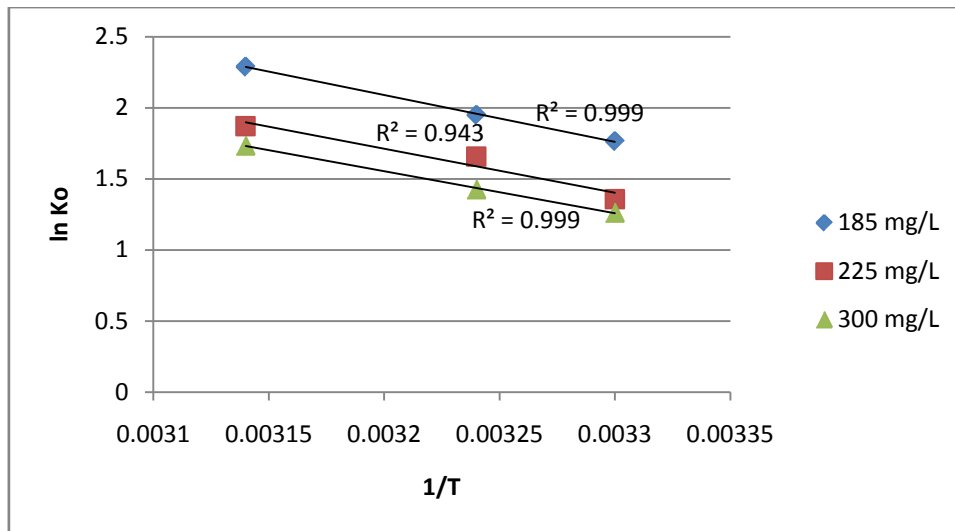


Figure 4.21: Von't Hoff plot for COD removal

The negative value of ΔG indicates the adsorption is favorable and spontaneous. ΔG increases with increase in temperature and decreases with increase in initial concentration of COD. The positive values of ΔH for both COD and color indicate that the removal of COD and color onto Date seeds activated carbon is endothermic in nature, which is supported by the increase in removal of COD by Date seeds activated carbon with the increase in temperature. This may be attributed to increased surface coverage at higher temperature, expansion and creation of reactive and active sites.

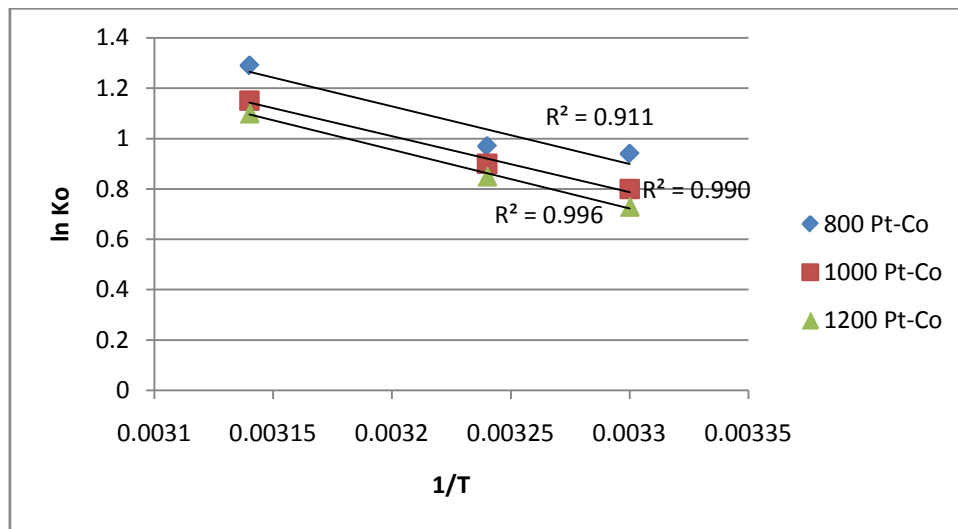


Figure 4.22: Von't Hoff plot for color removal

The low positive values of ΔH (2.956 to 3.286 KJ/mole) indicate physisorption and endothermic nature of adsorption (Arivoli, 2007 and Renmin et al., 2005). Further

more if ΔG decreases with increase in temperature it indicates an endothermic process. The positive values of ΔS indicate the increased disorder and randomness at the solid liquid interface of adsorbate with the adsorbent. The increase of adsorption capacity of the adsorbent at higher temperatures was due to enlargement of pore size and activation of adsorbent surface (Weber, 1967 and Vedivelan and Vasanthkumar, 2005).

Table 4.7: Thermodynamic parameters for COD removal

Initial COD conc. (mg/L)	K_o			ΔG (kJ/mole)			ΔH (kJ/mole)	ΔS (J/K/mole)
	303 K	308 K	318 K	303 K	308 K	318 K		
185	5.85	7.04	9.88	-4.450	-4.998	-6.056	0.39	1.51
225	3.89	5.25	6.5	-3.422	-4.246	-4.949	0.37	1.39
300	3.54	4.17	5.67	-3.185	-3.656	-4.588	0.35	1.32

Table 4.8: Thermodynamic parameters for color adsorption

Initial color conc. (Pt-Co)	K_o			ΔG (kJ/mole)			ΔH (kJ/mole)	ΔS (J/K/mole)
	303 K	308 K	318 K	303 K	308 K	318 K		
800	2.57	2.63	3.62	-2.37	-2.47	-3.40	0.27	1.01
1000	2.22	2.45	3.16	-2.00	-2.29	-3.04	0.26	0.97
1200	2.07	2.33	3.00	-1.83	-2.16	-2.90	0.28	1.01

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The quality of the textile raw effluent was evaluated through laboratory analysis and the sample used for this study was prepared from raw sample through filtration to avoid the effect of filtration in the final treated effluent. The residual concentration of Date seeds activated carbon treated effluent meets ECR-97 discharge standards. The main objective of this thesis was to evaluate the efficiency of Date seeds activated carbon for the treatment of textile effluent and to understand the treatment process.

Following conclusions can be drawn from this study:

1. The adsorption capacity of Date seeds activated carbon for the treatment of textile effluent was satisfactory. Maximum 92% color and 95% COD removed at equilibrium contact time and optimum dosage under basic aqueous solution.
2. The data obtained from adsorption isotherms are fitted well with both Langmuir and Freundlich isotherm model; but Freundlich isotherm model fitted better. The possible reason may be likely the formation of multilayer of solute over adsorbent.
3. Removal of both color and COD were found to increase with increasing contact time, adsorbent dosage, temperature, agitation speed, pH and decreasing particle sizes.
4. Kinetic studies showed that the adsorption of color followed pseudo second-order model with multi-step intra-particle diffusion model.
5. Thermodynamic study showed that the removal of color and COD using Date seeds activated carbon is spontaneously favourable, endothermic and increased disorder and randomness at the solid liquid interface of adsorbate with adsorbent.

5.2 Recommendations for further studies

Tertiary treatment of textile effluent is the ultimate treatment prior to discharge to the environment. So discharged effluent must fulfill the discharge criteria mentioned in ECR-97. Most of the textile industry owners are unwilling to invest in effluent treatment cost, so it could be investigated the potentiality of use of low-cost available waste materials for the treatment of textile effluent.

1. The present study was carried out for 30 minutes equilibrium contact time but in real field retention of flowing wastewater for 30 minutes will require holding facility. So contact time may be reduced for further study.
2. The study was carried out for different temperature from 30°C to 45°C; but the actual temperature was recorded that might have some error. So the error of temperature should be taken into consider in future study.
3. Color scanning for determining the optimum wavelength for best adsorption should be done prior to use of Spectrophotometer in future study.
4. Granular activated carbon can be prepared from Date seeds for using in fixed bed column treatment to know the volume of wastewater can be treated.
5. The applicability of Date seeds activated carbon for the treatment of drinking water, for the treatment of effluent from other industries (paper and leather) and for the removal of pesticide from aqueous solution can be investigated.

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