

**Preparation and Characterization of Chitosan-  
Pullulan Hydrogel and Its Application for  
Adsorption of Erichrome Black T from Aqueous  
Solutions**

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## ABSTRACT

In this study, a superabsorbent hydrogel was synthesized by crosslinking chitosan and pullulan by glutaraldehyde. The Chitosan/Pullulan Hydrogel (CPH) as an adsorbent was then successfully used for adsorption of Erichrome Black T (EBT) dye from aqueous medium. The adsorbent capacity was investigated at different operational conditions such as initial concentration of dye, adsorbent dosage, pH, temperature, presence of salt and contact time.

The equilibrium data was observed to follow the Langmuir model and was observed that EBT sorption process favored the pseudo-second order kinetics. FT-IR characterization was used to demonstrate presence of the various functional groups; -NH<sub>2</sub>, -CONH<sub>2</sub>, -CO and -OH on the adsorbent.

From the data obtained from the experimental measurements, conclusion were drawn based on the eco-friendly and economical nature of the adsorbent material and thus may be a reliable material for treatment of contaminants from aqueous solutions.

**Key words:** Superabsorbent, Chitosan-Pullulan Hydrogel, EBT, Eco-friendly

## ÖZ

Bu çalışmada, kitosan ve pullulanın glutaraldehit ile çaprazbağlı superabsorbent hidrojel sentezlenmiştir. Kitosan/Pullulan hidrojel (CPH), Erichrome Black T (EBT) boyasının sulu ortamından adsorpsiyonu için başarılı bir adsorbenttir. Adsorbent kapasitesi, farklı boya başlangıç konsantrasyonu, adsorbent miktarı pH, sıcaklık, tuz varlığı ve etkileşim süreleri gibi farklı operasyon şartlarında incelenmiştir.

Adsorpsiyon denge verileri Langmuir adsorpsiyon modelini izlediği ve EBT adsorplama prosesinin yalancı ikinci mertebe kinetiğe uyduğu saptanmıştır FT-IR karakterizasyonu adsorbent üzerinde -NH<sub>2</sub>, -CONH<sub>2</sub>, -CO ve -OH gibi birçok fonksiyonel grubun varlığını göstermektedir.

Deneysel ölçümlerden elde edilen veriler adsorban materyalin çevre dostu ve ekonomik niteliğe sahip olduğunu ve böylece sulu çözeltilerden kirleticilerin temizlenmesi için güvenilir bir malzeme olabileceği sonucunu doğurmuştur.

**Anahtar Kelimeler:** Süperabsorbent, kitosan-Pullulan, Erichrome Black T, Çevre Dostu

*This thesis is dedicated to the greatest memories of  
my mother*

*It is also dedicated to my Father for his endless  
support and encouragement*

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# TABLE OF CONTENTS

ABSTRACT .....	iii
ÖZ.....	iv
DEDICATION.....	v
ACKNOWLEDGMENT.....	vi
LIST OF FIGURES .....	x
LIST OF TABLES .....	xi
LIST OF SYMBOLS/ABBREVIATIONS.....	xii
1 INTRODUCTION .....	1
1.1 Environmental Issue .....	1
1.2 Water Pollution .....	1
1.3 Methods of Dye Removal.....	2
1.4 Biopolymer .....	2
1.4.1 Chitosan.....	2
1.4.2 Pullulan.....	3
1.5 Objective of the research .....	4
2 LITERATURE REVIEW .....	5
2.1 Colorant .....	5
2.2 Dye.....	5
2.3 Treatment Technologies of Dyes Removal .....	6
2.3.1 Chemical Methods.....	7
2.3.2 Biological method.....	9
2.3.3 Physical Treatment .....	10
2.4 Adsorption Equilibria .....	12

2.5 Types of Adsorption Isotherms .....	12
2.5.1 Langmuir Isotherm .....	13
2.5.2 . Freundlich Isotherm .....	13
2.6 Adsorption Kinetics .....	14
2.6.1 Pseudo-First Order Equation.....	14
2.6.2 Pseudo-Second Order Equation .....	14
2.6.3 Intraparticle diffusion model.....	15
3 EXPERIMENTAL .....	16
3.1 Materials .....	16
3.2 Preparation of Solutions .....	17
3.2.1 Chitosan Solution Preparation .....	17
3.2.2 Pullulan Solution preparation .....	17
3.2.3 Preparation of Erichrome Black T Solution.....	17
3.3 Synthesis of Adsorbent (Chitosan/Pullulan hydrogel CPH) .....	17
3.4 Dye Adsorption .....	17
3.4.1 Effect of Initial Concentration of EBT Dye.....	19
3.4.2 Effect of Adsorbent Dosage.....	19
3.4.3 Effect of Initial pH.....	19
3.4.4 Effect of Temperature .....	19
3.4.5 Effect of Inorganic Salt .....	20
3.4.6 Effect of Ionic strength.....	20
3.4.7 Effect of Contact Time .....	20
4 RESULTS AND DISCUSSION.....	21
4.1 Adsorbent Characteristics.....	21
4.1.1 Fourier transform infrared spectroscopy (FT-IR) Analysis for Adsorbent	21



4.1.2 CPH properties.....	22
4.2 Dye Adsorption Batch Study.....	23
4.2.1 Effect of Initial Concentration of EBT Dye.....	24
4.2.2 Effect of Adsorbent Dosage.....	24
4.2.3 Effect of pH.....	25
4.2.4 Effect of Temperature on EBT Dye Adsorption.....	26
4.2.5 Effect of co-existing Salt.....	28
4.2.6 Effect of Ionic Strength.....	29
4.2.7 Effect of Contact Time.....	30
5 CONCLUSION .....	33
REFERENCES .....	34

## LIST OF FIGURES

Figure 1-1: Structure of Chitosan.....	3
Figure 1-2: Structure of Pullulan.....	4
Figure 2-1: Structure of Activated Carbon .....	11
Figure 3-1: Structure of Erichrome Black T.....	18
Figure 3-2: Calibration Curve for Erichrome Black T.....	18
Figure 3-3: dye solutions after and before the adsorption .....	18
Figure 4-1: FT-IR Analysis (a) Chitosan (b) Pullulan (c) Chitosan/Pullulan hydrogel (d) CPH with Dye. ....	22
Figure 4-2: Cross-linked Chitosan/ Pullulan Hydrogel.....	22
Figure 4-3: CPH (a) dried hydrogel, (b) swollen hydrogel.....	23
Figure 4-4: Effect of EBT Dye Concentration .....	24
Figure 4-5: Effect of Adsorbent Dosage .....	25
Figure 4-6: Effect of Medium pH.....	26
Figure 4-7: Effect of Temperature.....	27
Figure 4-8: Langmuir Isotherm .....	27
Figure 4-9: Freundlich Isotherm.....	28
Figure 4-10: Effect of Inorganic Salt .....	29
Figure 4-11: Effect of Ion Concentration.....	30
Figure 4-12: Effect of Contact Time .....	31
Figure 4-13: Pseudo first- order and pseudo second-order models.....	32

## **LIST OF TABLES**

Table 2-1: Classification of Dye by Methods of Application .....	6
Table 3-1: The Chemicals and their manufacturers .....	16
Table 4-1: Adsorption Parameters obtained from Langmuir and Freundlich Models	28
Table 4-2: Kinetic Parameters for EBT removal using CPH. ....	32

## LIST OF SYMBOLS/ABBREVIATIONS

CPH	Chitosan-Starch Hydrogel
EBT	Erichrome Black T
FT-IR	Fourier Transform Infrared spectrophotometer
$q_e$	Equilibrium concentration of adsorbed species in solid adsorbent ( mg g <sup>-1</sup> )
$C_e$	Equilibrium concentration of adsorbed species in solution (mg L <sup>-1</sup> )
$K_L$	Langmuir isotherm constant (L mg <sup>-1</sup> ).
$C_o$	Initial concentration (mg L <sup>-1</sup> )
$K_f$	Freundlich isotherm constant (mg.g <sup>-1</sup> )(L.mg <sup>-1</sup> ) <sup>1/n</sup>
$n$	Adsorption intensity;
$K_1$	Equilibrium rate constant of pseudo-first adsorption, (min <sup>-1</sup> ).
$K_2$	Equilibrium rate constant of pseudo-second order adsorption, (g mg <sup>-1</sup> min <sup>-1</sup> ).
$K_i$	The intra-particle diffusion rate constant (mg g <sup>-1</sup> min <sup>-1/2</sup> )
$t$	Time of diffusion (min)
$R$	Universal gas constant (8.314 Jmol <sup>-1</sup> K <sup>-1</sup> )
$T$	Absolute temperature (K)
$R_L$	Equilibrium parameter Langmuir isotherm

# Chapter 1

## INTRODUCTION

### 1.1 Environmental Issue

Colors are the beauty of earth, and they kill it with sweet venom. The technique of using color to promote our self-appearance, has been known since ancient days. Historical articles have been documented a pointing to the extraction of natural dyes from fruits, vegetables, some specific insects and fish since 3500 B.C (Kant, 2012)

Recently, dye pollution has triggered wide environmental concerns due to their ability to change water bodies' physicochemical properties even at trace amounts. Recent industrial growth have contributed to the large amount of poorly treated or unfixed dye molecules discharged into the water and the life-threatening effect is widely known (Badea, 2012).

### 1.2 Water Pollution

Pollution can be defined as all the environmental changes caused by human action that cause damage to the ecosystem and the society. Turbidity, toxicity, and disagreeable conditions are all consequences of the pollution.

Textile trade is responsible for massive amounts of waste material. The polluted water is unfit for consumption and existence of species found in rivers which inflict damage to photosynthesis processes (Mariana, 2012).

Industrial plants and unregulated urban centers may continuously cause in dangerous water pollution due to their poorly treated or inefficient treatment methods of waste

before being released into the water bodies. (Zhang, 2012) Organic pollutants, such as polybrominated diphenyl ethers and polycyclic aromatic hydrocarbons (PAHs) contained in untreated industrial and domestic waste have been discharged into the aquatic environments worldwide and their health hazard is enormous (Zhang, 2012)

### **1.3 Methods of Dye Removal**

Classical wastewater technologies have been shown to be significantly unsuccessful for treatment of colored wastewater since these dyes are chemically stable. A wide range of methods have been developed for the removal of synthetic dyes from wastewaters to decrease their impact on the environment (Orosb, 2004). These include physical and chemical methods such as photochemical oxidation, ultrafiltration, ozone treatment, nanofiltration, reverse osmosis, cation exchange membranes, chemical coagulation, electrochemical degradation, biosorption, adsorption and ozonation, all of which have been used for dye removal from wastewater (Kama, 2011).

### **1.4 Biopolymer**

Polysaccharides exist in nature either as homopolysaccharides or heteropolysaccharides which are found in algae (e.g. alginate), plants (e.g. pectin, guar gum), microbes (e.g. dextran, xanthan gum), and animals (chitosan, chondroitin) (Sinha R. K., 2001). They have low toxicity, and they are safe, highly stable, hydrophilic and biodegradable.

#### **1.4.1 Chitosan**

Chitosan is a linear natural biopolymer obtained by deacetylation of chitin which is the second most abundant polysaccharide after cellulose. Chitin is the main protective of crustaceans such as shrimps, crabs, lobsters, and cell walls of some fungi such as mucor and aspergillus. Chitin can be defined as a linear homopolymer

that consists of N-acetyl-glucosamine, whereas chitosan consists of copolymers of both N-acetyl-glucosamine and glucosamine (Sinha, 2004). Chitosan has one free primary amino group and two hydroxyl groups per each repeat unit as shown in Figure 1-1 (Sinha, 2004).

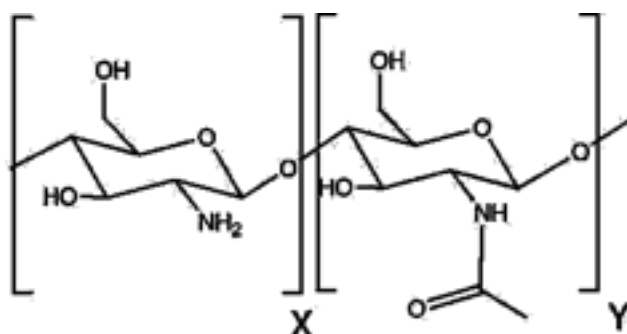


Figure 1-1: Structure of Chitosan

Due to the easy availability of free amino groups in chitosan, it carries a positive charge and thus in turn reacts with many negatively charged surfaces/polymers and also undergoes chelation with metal ions because of electron pair on N atom (Sinha, 2004).

Chitosan is a weak base and is insoluble in water and in organic solvents. However, it is soluble in dilute aqueous acidic solution ( $\text{pH} < 6.5$ ), which can convert the glucosamine units into the soluble form  $\text{R-NH}_3^+$  (Sinha, 2004).

#### 1.4.2 Pullulan

Pullulan is a polysaccharide biopolymer. Dry Pullulan is white to off-white powder which forms a viscous non-hygroscopic solution when dissolved in water at 5–10%. Pullulan starts to decompose at 250 °C and chars at 280°C. It is highly soluble in water and dilute alkali; insoluble in alcohol and other organic solvents except dimethylsulfoxide and formamide. As Pulllan is highly water soluble, it can be used as a carrier for drug and it helps in controlled release of drug in plasma. It has a

molecular weight within the range of 5000–9,000,000 g/mol with straight unbranched chain and is a very flexible molecule having the property of “random–coil” (depending on sedimentation coefficient and intrinsic viscosity measurement) (Vipul, 2013).

Pullulan is low-toxic, non-mutagenic, non-carcinogenic, odorless, tasteless, and edible. Pullulan has a considerable mechanical strength and other functional properties like adhesiveness, film formability, enzymatically mediated degradability (Vipul, 2013).

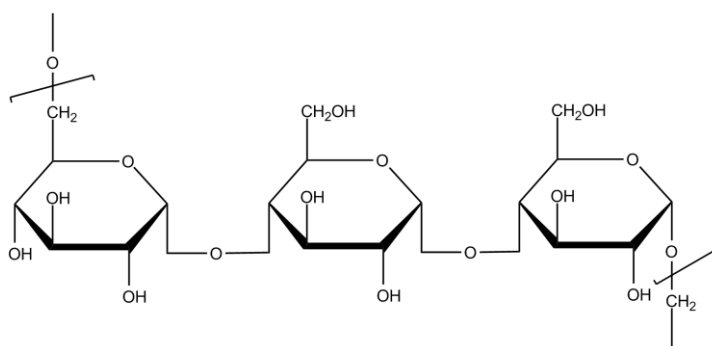


Figure 1-2: Structure of Pullulan

## 1.5 Objective of the research

- ▶ To prepare Full-polysaccharide environmentally friendly hydrogel.
- ▶ To examine the adsorptive properties of the adsorbent.
- ▶ To study the effect of different parameters such as temperature, pH, time, initial structure of dye, amount of adsorbent and effect of salts on the adsorption process.
- ▶ To study thermodynamics and kinetics of these adsorption processes.



## Chapter 2

### LITERATURE REVIEW

#### 2.1 Colorant

Colorant is an essential side of human life. We like to wear different types of colored clothes, eat colorful foods, even the medicines we take are decorated with colors. Nowadays, there are more than ten thousand different types of dyes available commercially and  $7 \times 10^5$  tons of dye manufactured yearly (Ratna, 2012).

Colorants are known for their ability to adsorb or emit electromagnetic radiation in the visible range (400-700 nm). Natural colorants were being used by human beings in the pre-historic times as mirrored by the cave drawings in Africa, Europe, Egypt and China. China and Egypt are particularly exceptional as the oldest glorious artificial pigments are found there, particularly Egyptian Blue ( $\text{CaCuSi}_4\text{O}_{10}$ ), and Han purple ( $\text{BaCuSi}_2\text{O}_4$ ), Han Blue (also  $\text{BaCuSi}_4\text{O}_{10}$ ) (Zollinger, 1987).

#### 2.2 Dye

Dyes are color substances of natural or synthetic source, which are resistant to fading upon exposure to chemicals, heat, light and water (Mark, 2013). There are over 100,000 commercially available dyes, and over  $7 \times 10^5$  tons of dye-stuff are produced yearly (Robinson, 2001). Additionally, dyes have high content of organic matters. They are not biodegradable, and they have complex aromatic structure (Mark, 2013). Recent studies show that about 12% of artificial dyes are lost while being produced or processed and 20% of the resultant dyes enter the environment through effluents

from industrial wastewater treatment plants. (Abdel-Mottaleb, 2008). Table 2-1 shows different types of dyes and their applications.

Table 2-1: Classification of Dye by Methods of Application

<b>Dying Method</b>	<b>Preference Substrate/ Typical Application</b>	<b>Principal Chemical Class</b>	<b>Solubility In Water</b>
<b>Reactive Dyes</b>	Cotton	Azo, Methallised Azo, Phthalocyanine, Anthraquinone	Soluble
<b>Disperse Dyes</b>	Polyester, Electronic Photography	Non-Ionic	Insoluble
<b>Direct Dyes</b>	Cotton, Regenerated Cellulose	Anionic, Poly-Azo	Soluble
<b>Vat Dyes</b>	Cellulose Fiber	Anthraquinone,	Insoluble, Soluble Leuco Salts
<b>Sulphur Dyes</b>	Cotton	Sulphur Dyes	Soluble
<b>Cationic or Basic Dyes</b>	Paper, Polyacrilonitril, Polyesters	Triarylmethan	Soluble
<b>Acid Dyes</b>	Nylon, Wool, Silk, Leather, Paper, Ink-Jets		Soluble
<b>Solvent Dyes</b>	Plastics, Gasoline, Oils, Waxes	Azo, Anthraquinone,	Insoluble

### 2.3 Treatment Technologies of Dyes Removal

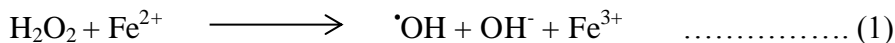
Several techniques have been described for the treatment of dye contaminated wastewater, and these are divided into three main classes: chemical, physical and biological (Gregorio, 2005).

### 2.3.1 Chemical Methods

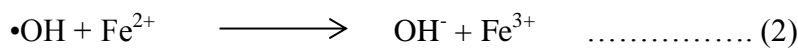
#### 2.3.1.1 Oxidative Processes

Chemical oxidation signifies the conversion or alteration of toxic waste by chemical oxidizing reagents other than oxygen or bacteria to similar but less toxic or hazardous compounds to organic components which are short-chained and biodegradable (Daniela, 2012). Research has shown that stronger oxidizing methods, such as ozone, chlorine, UV/ozone, UV/peroxide, Fenton's reagent (ferrous sulfate and peroxide), or other oxidizing techniques or a combination are necessary for oxidative chemical treatment. This is because some of the dyes are more resistant to weak oxidation condition (Robinson, 2001).

In the Fenton oxidation method, ferrous ions react with hydrogen peroxide, releasing hydroxyl radicals with strong oxidizing abilities to degrade organic hazardous waste:



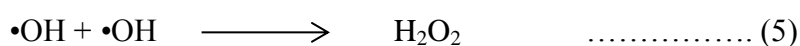
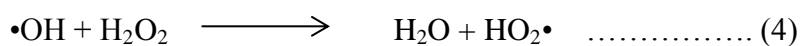
Hydroxyl radicals could react with  $\text{Fe}^{2+}$  ions to create  $\text{Fe}^{3+}$  ions or react with organics:



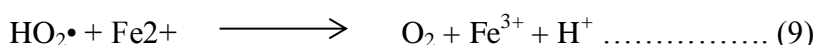
Hydroxyl radical generation is increased at low pH values (2.5-4.5). The oxidization products are typically low molecular mass oxygenated compounds that are simply

biodegradable or, in some instances, the organic compounds are reduced to CO<sub>2</sub> and water (Malik S. , 2003).

Hydroxyl radicals will react with hydrogen peroxide to provide different radicals, and should also combine together to provide hydrogen peroxide; the reactions being shown below:



Ferrous ions and radicals are made throughout the reactions. The reactions are as shown in Eqs. (6) – (9)



The reaction rate in equation (6) is much slower than that in equation (1). It is derived that ferrous ions are used quickly, still reproduce slowly (Malik, 2003).

Accordingly, when a large amount of ferrous ions are present rate of oxidation of organic compounds is faster because more amount of hydroxyl radicals are

generated. Though the Fenton's reaction may slow down because of the slow production of ferrous ion (Pignatello, 1992).

Fenton's reagent and Ultraviolet catalyzed peroxide techniques have also been estimated. The limited permeation of UV ray into dye solutions for UV/peroxide methods, the cost of the Fenton's reagent method, and the process complication in general have limited the progress of this kind of methods (Ogbeifum, 2001).

### **2.3.2 Biological method**

Biological technique is one of the methods for treating of the textile industry wastewater. In this method, dyes are degraded into less complicated materials and are finally mineralized to water and carbon dioxide through a variety of aerobic and also anaerobic bacterium. It can be accomplished in the presence of oxygen (aerobic degradation) and without oxygen (anaerobic degradation). Fungus of rotted wood, *Eubacterium sp*, *Rhizopus oryzae*, and *Proteus vulgaris* are some of the microorganisms used in which treatment (Hasan, 2008).

#### **2.3.2.1 Decolourisation by White-Rot Fungi**

A number of white-rot fungi have been reported to degrade textile dyes. The anthraquinone dyes are structurally similar to the phenolic units in lignin. To develop an easier assay for lignolytic activity, *Phanerochaete chrysosporium* for the ability to degrade three polycyclic aromatic carbonyl dyes are tested. The fungus decolorized the dyes, but only during secondary metabolism, when lignolytic activity appears in this fungus. Chemical inhibitors of lignin degradation also inhibited dye degradation. Likewise, a mutant lacking lignolytic activity was unable to decolorize the polymeric dyes.(Yatome, 1990).

White-rot fungi have the ability to degrade dye by exploiting enzymes, such as Mn dependent peroxidases (MnP), lignin peroxidases (LiP), or by other enzymes, like glucose-1-oxidase and glucose-2-oxidase, further a phenoloxidase accelerator and laccase (Reddy, 1995),(Yatome, 1990).

### **2.3.3 Physical Treatment**

Physical methods include adsorption on peat, wood, activated carbon, fly ash, silica, coal or processes such as ion exchange, membrane filtration, reverse osmosis and coagulation (Ratna, 2012).

#### **2.3.3.1 Adsorption**

Among classical methods, adsorption methods have received the priority as a result of their performance in removal of pollutants. Adsorption produces a top quality and economically friendly products. Adsorption is influenced by several physiochemical factors, such as adsorbent surface area, dye-adsorbent interaction, pH, temperature, particle size, and contact time (Robinson, 2001). Activated carbon is one of the adsorbents used for dye adsorption because of its high adsorption capacity due to its expanded surface area, micro-porous structure (Figure 2-1) and a high degree of reactive functional groups on its surface. It is very successful for adsorbing mordant, cationic, and acid dye and weaker for disperse, direct, extent, vat, reactive dyes and pigment (Malik, 2003).

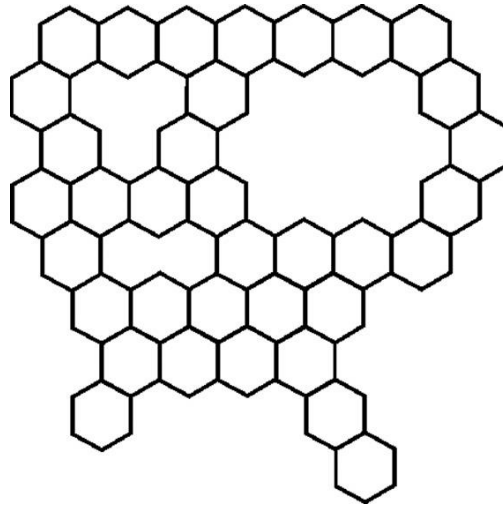


Figure 2-1: Structure of Activated Carbon

### **2.3.3.2 Membrane Filtration**

Membrane filtration is the method used to separate solids from the liquid via inflowing the mixture through media in which only liquid pass through. The membranes act as a wall which only allow one component of a mixture to permeate the membrane freely while hinder the permeation of other components. Cellulose acetate, polyvinylidenedifluoride and polysulfone are some of the industrial membrane materials. This technique consist four membrane processes which are nanofiltration (NF), reverse osmosis (RO), ultrafiltration (UF) and microfiltration (MF) (Wagner, 2001)

### **2.3.3.3 Ion exchange**

Ion exchange has not been vastly utilized for the treatment of effluents, because of their limited application for a wide-range of dyes (Robinson, 2001).

Preference of this method comprises no loss of adsorbent during regeneration, rehabilitation of solvent after using and removal of dissolvable dyes. This is an economically advantageous way to remove the dye. It includes the addition of ferric chloride and ferrous sulfate, which allows excellent removal of direct dyes from

wastewater. Unfortunately, the results with acid dyes are poor, with the high cost of ferric chloride and ferrous sulfate, which means that it is not an extensively used method. The main disadvantage is the preparation of resins cost. Organic solvent are not cheap, and the ion exchange process is not much effective for separation of various dyes (Robinson, 2001). The optimum coagulant concentration is depends on the static charge of the dye in the solution and the difficulty in removing the sludge formed as part of the curd problem. The production of large quantities of sludge occurs, and this leads to higher costs of disposal (Robinson, 2001).

## **2.4 Adsorption Equilibria**

Adsorption equilibria were analyzed on the basis of general equilibrium constant expression for the development of basic adsorption equations (Freundlich, Langmuir, and BET) in connection with the establishment of the general approach towards the physical interpretations of the parameters of adsorption. Theoretically; it is proved that Freundlich plot analysis can not be used to find useful parameters, such as the monolayer adsorption of an adsorbent. The present theory also proves that the adsorption process with the disclosed value of the monolayer adsorption capacity can be examined to find different equilibrium constants on the basis of the equation Franaeus, which is commonly used in the process of complication. And also it is discussed applications of the Langmuir equation to find the number of the ligand complex, as well as the size of the equilibrium constant required to analyze BET equation in the liquid phase adsorption process multilayer (Khan, 2012).

## **2.5 Types of Adsorption Isotherms**

Adsorption properties and equilibrium data, commonly known as adsorption isotherms describe how pollutants interact with adsorbent materials and are significant studies applied to optimize the use of adsorbents (Kama, 2011).



Adsorption equilibrium is established when the amount of dye being adsorbed onto the adsorbent is equal to the amount being desorbed (Kama, 2011).

### 2.5.1 Langmuir Isotherm

Langmuir adsorption isotherm is based on the assumption that the molecules of the adsorbate form a monolayer on the surface of the adsorbent. Adjacent adsorbed molecules do not interact, i. e., the adsorption of adsorbate at a particular site is independent whether the neighboring sites are adsorbed or not. Langmuir isotherm is widely used and can be represented as:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$$

Where  $q_e$  is the amount of dye per unit mass of adsorbent at equilibrium ( $\text{mg g}^{-1}$ ),  $q_m$  is the maximum amount of dye adsorbed per unit mass of adsorbent for the formation of complete monolayer on the surface of adsorbent ( $\text{mg g}^{-1}$ ),  $K_L$  is Langmuir constant related to energy of adsorption ( $\text{L mg}^{-1}$ ). Langmuir constant can be estimated from the linear plot of  $C_e/q_e$  versus  $C_e$  (Doguc, 2008).

### 2.5.2 Freundlich Isotherm

Freundlich adsorption isotherm is applicable for heterogeneous systems and involves the formation of multilayers. Freundlich isotherm can be represented as:

$$q_e = K C_e^{1/n}$$

In which,  $K$  and  $n$  are the Freundlich constants.  $K$  is a measure of the amount of adsorption and  $n$  is a measure of the heterogeneity of the adsorption energy across

the surface. The value of  $K$  and  $n$  can be obtained from the slope and intercept of a linear plot of  $\log q_e$  versus  $\log C_e$  (Khan, 2012).

## **2.6 Adsorption Kinetics**

An ideal adsorbent for wastewater pollution control must not only have a large adsorption capacity but also a fast adsorption rate. Therefore, the adsorption rate is another important factor for the selection of the material and adsorption kinetics must be taken into account since they explain how fast the chemical reaction occurs and also provides information on the factors affecting the reaction rate (Gregorio, 2008). Three kinetic models have been widely used in the literature for adsorption processes: pseudo-first-order kinetic model (Lagergren model), pseudo-second-order kinetic model and Intraparticle diffusion model (Webber and Morris model) (Gregorio, 2008).

### **2.6.1 Pseudo-First Order Equation**

The pseudo-first-order kinetic model also known as the Lagergren kinetic equation is widely employed to understand the kinetic behavior of the system, which is given by the equation:

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

Where  $q_e$  and  $q_t$  are amounts of dye adsorbed at equilibrium and at time  $t$  ( $\text{mg}\cdot\text{g}^{-1}$ ),  $k_1$  is the pseudo first order rate constant ( $\text{min}^{-1}$ ) (HO, 2004).

### **2.6.2 Pseudo-Second Order Equation**

The pseudo-second-order kinetic model is given by the equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

Where,  $q_t$  and  $q_e$  are the amount of dye adsorbed at equilibrium and at time  $t$ . The constant  $K_2$  is the equilibrium rate constant of pseudo-second-order model ( $\text{gmol}^{-1} \text{min}^{-1}$ ). The pseudo second-order model is based on the assumption that the rate limiting step may be chemisorption which involves valence forces by sharing or electron exchange between the adsorbent and the adsorbate (Wang, 2008).

### **2.6.3 Intraparticle diffusion model**

The intraparticle diffusion model indicates that the ratelimiting step is the transport of the solute from the bulk of solution into adsorbent pores through an intraparticle process This equation is given as:

$$q_t = K_{id} t^{0.5} + C_i$$

Where  $K_{id}$  is the intraparticle diffusion rate constant ( $\text{mg/g min}^{1/2}$ ) and  $C_i$  is the thickness of the boundary layer.

## Chapter 3

### EXPERIMENTAL

#### 3.1 Materials

The materials used and their manufacturers are listed in Table 3-1.

Table 3-1: The Chemicals and their manufacturers

No	Chemical	Company
1	Chitosan	Fluka- Germany
2	Pullulan	Freda-China
3	Glutaraldehyde	Aldrich-Germany
4	Eriochrome black t	Merck-Germany
5	Acetic acid	Riedel-deHaen-Germany
6	Hydrochloric acid	Riedel-deHaen-Germany
7	Sodium hydroxide	Aldrich-Germany
8	Sodium Chloride	Analar-UK
9	Sodium Sulfate	Analar-UK
10	Sodium Hydrogen Phosphate	Analar-UK
11	Sodium Iodide	Analar-UK

## **3.2 Preparation of Solutions**

### **3.2.1 Chitosan Solution Preparation**

Firstly 0.5 g of chitosan was weighed by an analytical balance and dissolved in 40 mL of 1% (v/v) acetic acid, under constant magnetic stirring about 450rpm for 5 hours to get homogenous solution of chitosan of concentration 1.25% (W/V).

### **3.2.2 Pullulan Solution preparation**

0.5 g of Pullulan was weighed by an analytical balance then dissolved into 10 mL of distilled water by using a magnetic stirrer by stirring about 450 rpm for 3 hours, to set a solution of 5% (W/V).

### **3.2.3 Preparation of Erichrome Black T Solution**

A stock solution of EBT was prepared by dissolving 100 mg of EBT in 500 ml of distilled water to make a 200 mg/L solution while working solutions were prepared by dilution, using the equation  $N_1V_1=N_2V_2$ .

## **3.3 Synthesis of Adsorbent (Chitosan/Pullulan hydrogel CPH)**

Full polysaccharide hydrogel was prepared by mixing 40 mL of 1.25% (w/v) of chitosan and 5% (w/v) of pullulan and were stirred overnight to get homogenous solution of chitosan and pullulan, then 0.8 ml of 25% of glutaraldehyde was added gently and at about 20 minutes solid gel was obtained.

## **3.4 Dye Adsorption**

The prepared gel has the ability to adsorb the Erichrome black T (Figure 3.3) from aqueous solutions; several different effects on adsorption were studied. UV-visible adsorption analysis at  $\lambda_{\max}=530$  nm for 200, 100, 75, 50, 25 and 12.5 mg/L of EBT dye have been measured to draw calibration curve as shown in Figure 3.4 by using intercept and slope of this curve we can calculate unknown concentration of dye. Figure 3.5 shows the EBT dye solutions before and after the adsorption.

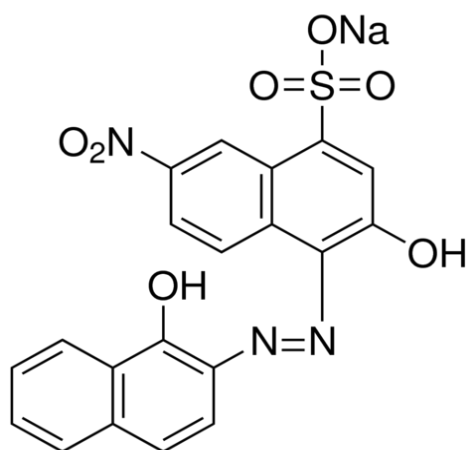


Figure 3-1: Structure of Erichrome Black T

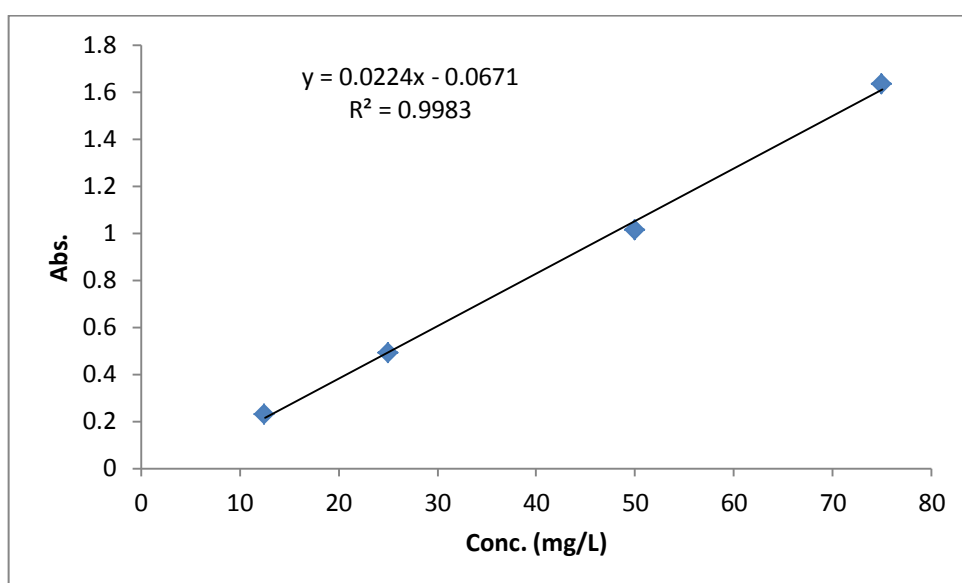


Figure 3-2: Calibration Curve for Erichrome Black T



Figure 3-3: dye solutions after and before the adsorption

### **3.4.1 Effect of Initial Concentration of EBT Dye**

In order to be able to find out the effect of different initial concentrations of dye on adsorption behaviour, 200 mg of gel is submerged into 50 ml of 3 separate dye solutions; 20, 40 and 60 mg/L respectively. All of the samples are put on a shaker, then 5 ml is taken from each of them after 1, 3, 6, 9 and 12 hours and finally UV-Visible adsorption of each one was measured.

### **3.4.2 Effect of Adsorbent Dosage**

To find out the effect of gel dosage in adsorbing the dye, a sample of gel weighting 100, 150, 200 and 300 mg is put in 50ml of 40 mg/L of dye solution and placed on a shaker. Then take 5ml each 1, 3, 6, 9 and 12 hours and took UV-Visible adsorption of each one.

### **3.4.3 Effect of Initial pH**

For the purpose of investigating the effect of pH on the adsorption, buffer solutions of pH of 2 (50 ml 0.2 M KCl and 13.0 ml of 0.2 M HCl were mixed) , 5 (mixing of 100 ml 0.1 M potassium hydrogen phthalate with 45.2 mL of 0.1 M NaOH) and 10 (mix of 100 mL of 0.05 M NaHCO<sub>3</sub> with 21.4 ml of 0.1 M NaOH) were prepared and then 25 ml of each solution was mixed with 25ml of the 80 mg/L of EBT dye solution in presence of 200 mg of CPH, placed in a shaker and after three hours UV-Visible absorption of dye remaining in solution was measured.

### **3.4.4 Effect of Temperature**

A 40mg/L of dye solution containing 200mg gel in conical flasks was placed in a pre-set water bath of 25, 50, 75 and 100 °C for 3 hours. Then UV-Visible analysis of was performed for each sample.

### **3.4.5 Effect of Inorganic Salt**

0.2 M of each of NaCl, NaI, Na<sub>2</sub>HPO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub> were prepared and 25ml of each were mixed with 80mg/L of dye containing 200mg of the gel under mechanical shaker for 3 hours. 5ml of solution was withdrawn after the pre-set time and analyzed.

### **3.4.6 Effect of Ionic strength**

0.2, 0.4, 1 and 2 M of sodium chloride solutions were prepared then 25ml of each solution mixed with 25ml of 80mg/L of dye, after 3 hours UV-Visible analyses of solutions were taken.

### **3.4.7 Effect of Contact Time**

The effect of contact time was followed by withdrawing at interval 5ml of solutions from 40mg/L of dye containing 50mg of gel at the following hours 1, 3, 6, 9 and 12 under constant agitation.



## Chapter 4

### RESULTS AND DISCUSSION

#### 4.1 Adsorbent Characteristics

##### 4.1.1 Fourier transform infrared spectroscopy (FT-IR) Analysis for Adsorbent

FT-IR spectra in the 4000–400  $\text{cm}^{-1}$  wave number range for (a) Chitosan, (b) Pullulan, (c) Chitosan/Pullulan hydrogel and (d) CPH with Dye were compared as shown in Figure 4.1. In case of pure chitosan, it has strong peaks observed at  $3442.57\text{cm}^{-1}$  due to OH group and the bands at  $2922.73\text{ cm}^{-1}$  and  $1080$  are due to C-H stretching and C-O-C stretching respectively. Chitosan shows a band at  $1641\text{ cm}^{-1}$  which refers to the amide group.

For Pullulan FTIR spectroscopy peaks of O-H stretch ( $3406.06\text{cm}^{-1}$ ), CH stretch ( $2928.17\text{ cm}^{-1}$ ), C-O-C stretch ( $1642.39\text{ cm}^{-1}$ ), C-O-H bend ( $1638\text{ cm}^{-1}$ ), and C-O-C stretch ( $1155\text{ cm}^{-1}$ ) are present.  $1080$  and  $1019\text{ cm}^{-1}$  are due to coupled valent vibrations of the C-O and C-C bonds and distortional vibrations of the CCH, COH, and HCO bonds. The shift in  $1641\text{cm}^{-1}$  of Chitosan and  $1642\text{cm}^{-1}$  of Pullulan to  $1638\text{cm}^{-1}$  due to stretching vibration of C=N of schiff-base. Two new signatures appear at  $1566\text{ cm}^{-1}$  (C=C), and  $1638\text{ cm}^{-1}$  (C=N), providing support that crosslinking between the amine group of Chitosan and the aldehyde group of Glutaraldehyde has occurred. In comparison of CPH and CPH-Dye the peaks  $1413\text{cm}^{-1}$  and  $1153\text{cm}^{-1}$  were decreased, and the absorption at  $1075\text{cm}^{-1}$  was increased, these changes refer to adsorption of EBT dye onto CPH.

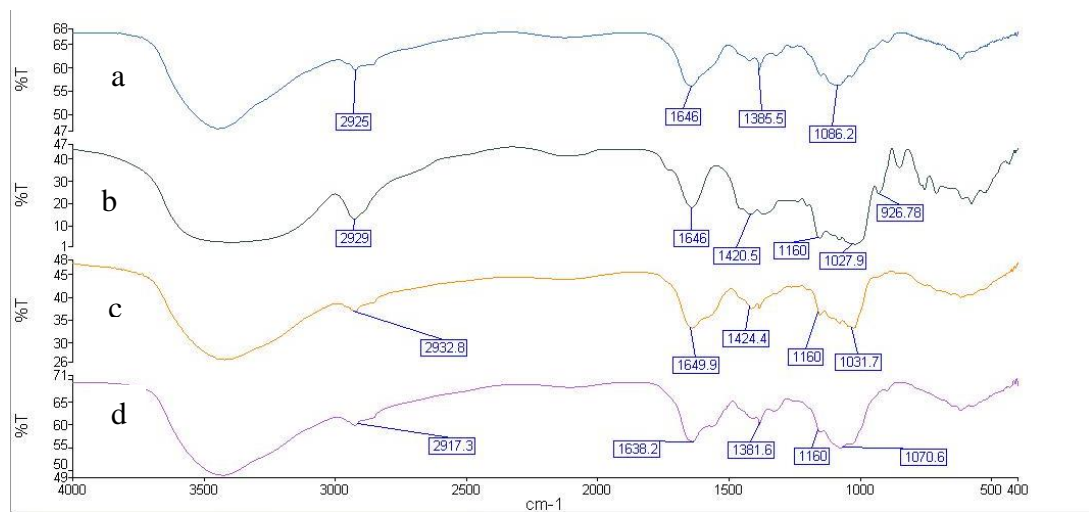


Figure 4-1: FT-IR Analysis (a) Chitosan (b) Pullulan (c) Chitosan/Pullulan hydrogel (d) CPH with Dye.

#### 4.1.2 CPH properties

Chitosan/pullulan hydrogel (CPH) made from cross-linking of chitosan and Pullulan backbone by glutaraldehyde. There is possibility of cross-linking by physical cross-linkers such as H-bonding it is because of presence of  $-OH$  groups on Pullulan and  $OH$  and  $NH_2$  groups on Chitosan, as shown in backbone Figure 4.2. Figure 4.3 shows the dry and swollen gel.

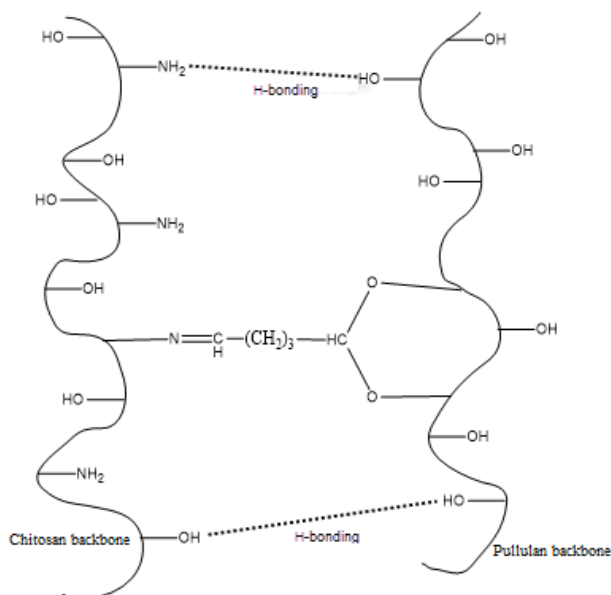
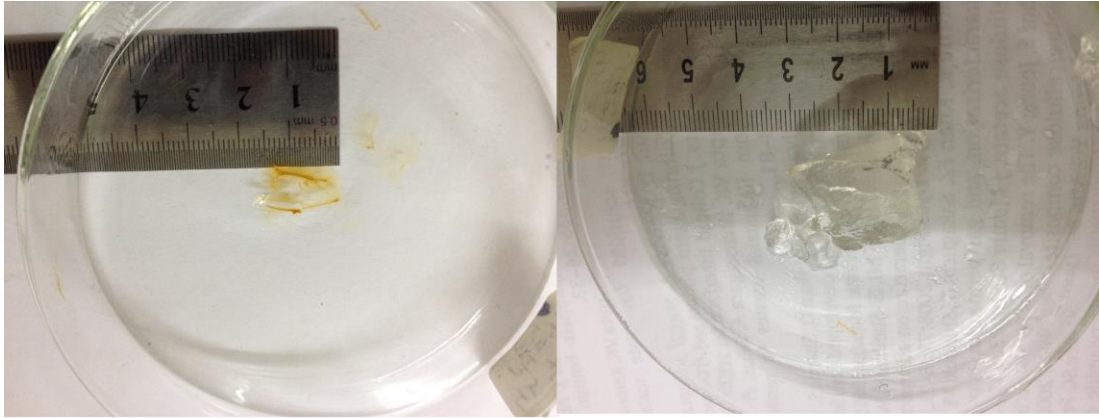


Figure 4-2: Cross-linked Chitosan/ Pullulan Hydrogel



**(a)**

**(b)**

Figure 4-3: CPH (a) dried hydrogel, (b) swollen hydrogel

## 4.2 Dye Adsorption Batch Study

The capacity of dye adsorption from solution was investigated based on changes in its concentration in the solution. The quantity of the adsorbed dye was calculated from the following equation:

$$q_e = (C_i - C_e) \frac{V}{W}$$

Where:

$q_e$ : the quantity of dye absorbed, in mg/g.

$C_i$ : initial concentration of dye, in mg/L

$C_e$ : concentration of dye after sorption, in mg/L

$W$ : sorbent mass, in mg

$V$ : solution volume

While, adsorption percentage was calculated from the following equation:

$$R\% = \left( \frac{C_i - C_e}{C_i} \right) 100$$

Where: R%= Percentage removal

$C_i$ : initial concentration of dye, in mg/L

$C_e$ : concentration of dye after sorption, in mg/L

#### 4.2.1 Effect of Initial Concentration of EBT Dye

At an adsorbent dosage of 200 mg, the effect of initial EBT concentration on % removal is shown in Fig. 4.2. It was observed that an increase in % removal of EBT is caused by an increase in dye concentration. At higher dye concentration, greater number of EBT molecules would quickly saturate the binding sites found on the surface area of CPH which lead to increasing the amount of dye removed. This would cause a decrease in the % removal due to the limited adsorption sites at an initial concentration of 40mg/L, similar trend has been reported elsewhere.

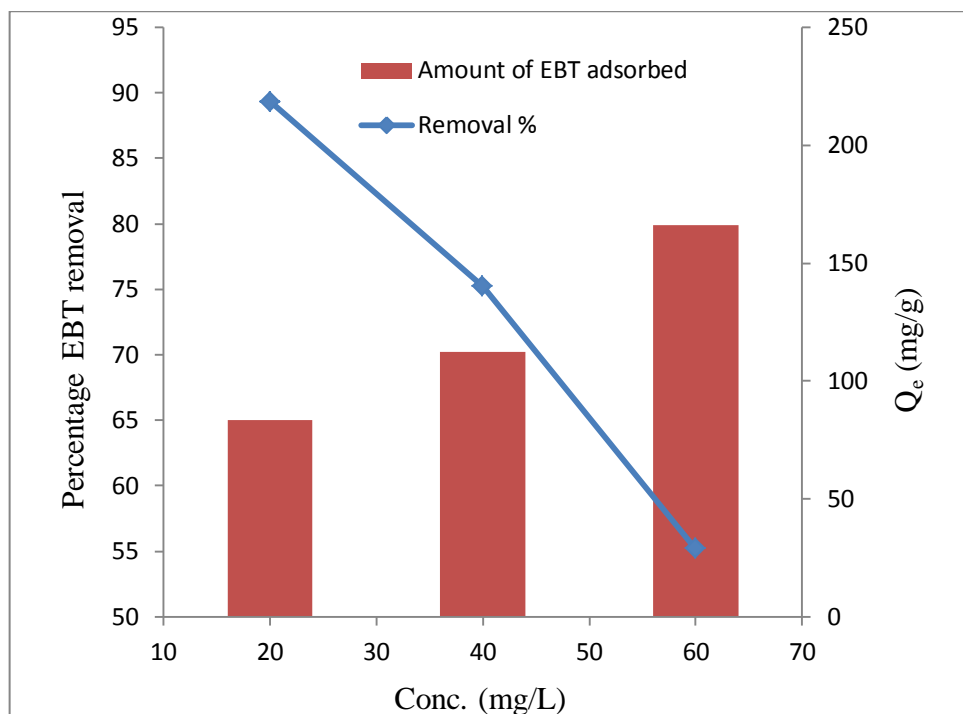


Figure 4-4: Effect of EBT Dye Concentration (Amount of Gel = 0.2 g)

#### 4.2.2 Effect of Adsorbent Dosage

The adsorption of EBT on CPH was studied by varying the adsorbent dosage (100, 150, 200, 300 mg) at initial dye concentration of 40 mg/L, at 25°C and in shaker.

Percentage removal of EBT increased with increasing of adsorbent dosage. As shown in Figure 4-2, after 720 minutes the percentage of adsorption of EBT dye increase from 43.31% of 100mg of CPH to 65.75% of 300mg of CPH. This can be attributed to increased availability of active sites on the CPH surfaces, leading to further increase in dye adsorption.

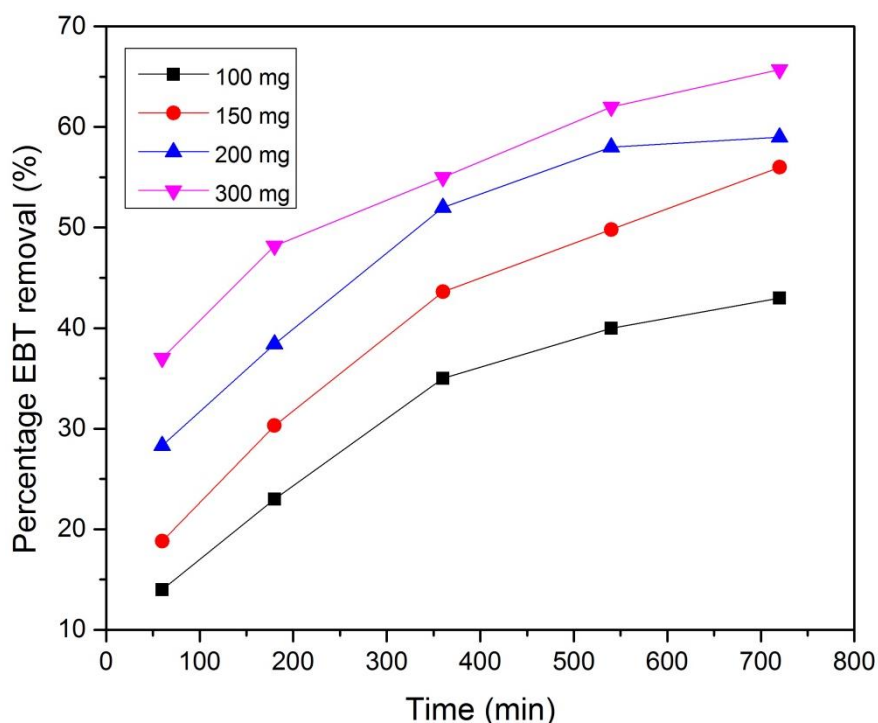


Figure 4-5: Effect of Adsorbent Dosage (EBT Concentration = 40 mg/L)

#### 4.2.3 Effect of pH

In this study, the effect of pH was carried out by adding 25ml of buffer solutions of pH (2-10) to 25ml of 80mg/L of dye in the presence of 200mg of adsorbent, at room temperature. In Figure 4-4, it can be observed that the removal of EBT decreased as the solution pH was increased from 2 to 5 due to competition between the EBT sulphonate groups ( $\text{SO}_3^-$ ) and the negative surfaces of the adsorbent. At an acidic pH, the functional groups of CPH become protonated, and, the surface charge of CPH

becomes more positively charged, which enhances EBT adsorption through electrostatic attraction.

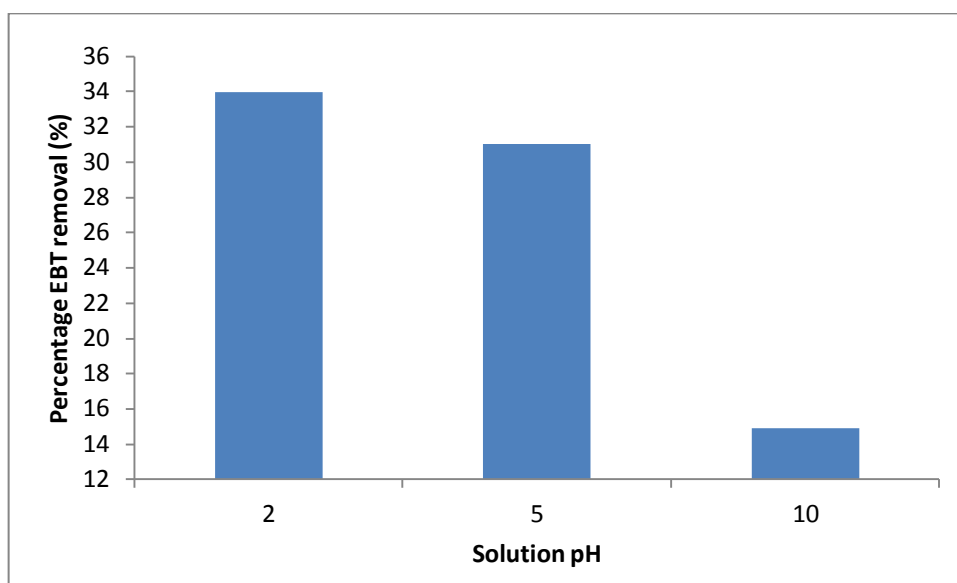


Figure 4-6: Effect of Medium pH (EBT Concentration = 40 mg/L, Adsorbent Dosage = 200 mg)

#### 4.2.4 Effect of Temperature on EBT Dye Adsorption

The obtained experimental results are elucidated by Langmuir (Figure 4-8) and Freundlich (Figure 4-9) models, and the resultant parameters are summarized in Table 4-1. As indicated in the Table 4-1, the fit is well suitable with Langmuir model based on the correlation coefficient ( $R^2$ ). Freundlich isotherm does not satisfactorily fit the experimental data in spite of the high values of  $n$  ( $1/n < \text{unity}$ ) in the model equation, which indicate that EBT is favorably adsorbed onto CPH. The increasing values of  $K_L$  in the Langmuir equation as the temperature increases reflect increasing affinity of EBT-CPH relationship. The satisfactory fit of Langmuir isotherm maybe due to homogenous distribution of active adsorption sites on the CPH surface since Langmuir model assumes monolayer adsorption.

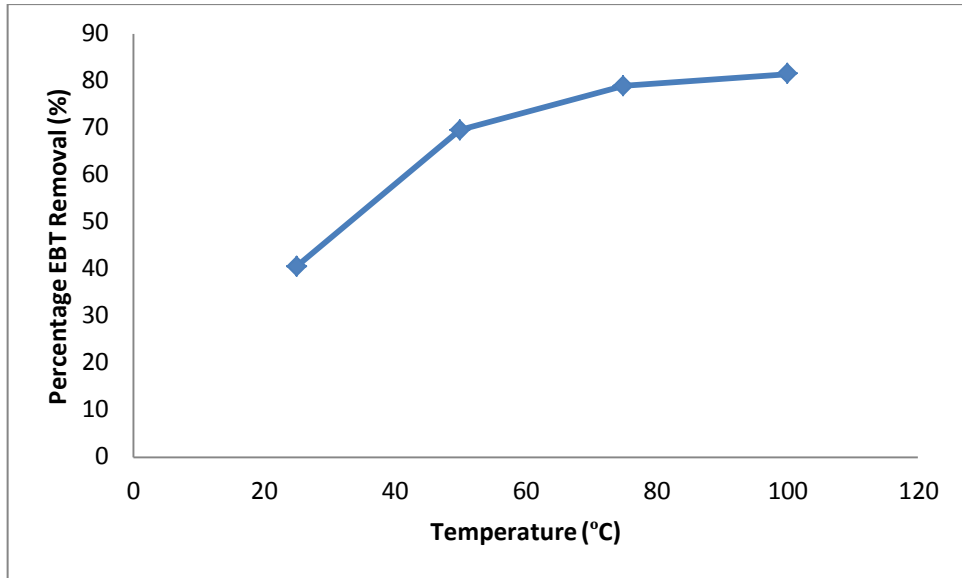


Figure 4-7: Effect of Temperature (EBT Concentration = 40 mg/L, Adsorbent Dosage = 200 mg)

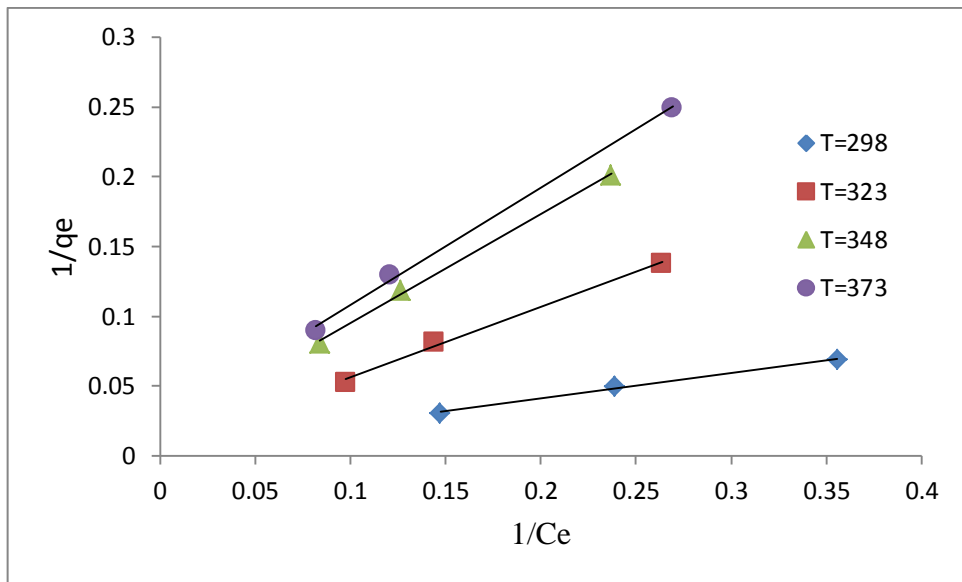


Figure 4-8: Langmuir Isotherm (EBT Concentration = 40 mg/L, Adsorbent Dosage = 200 mg)

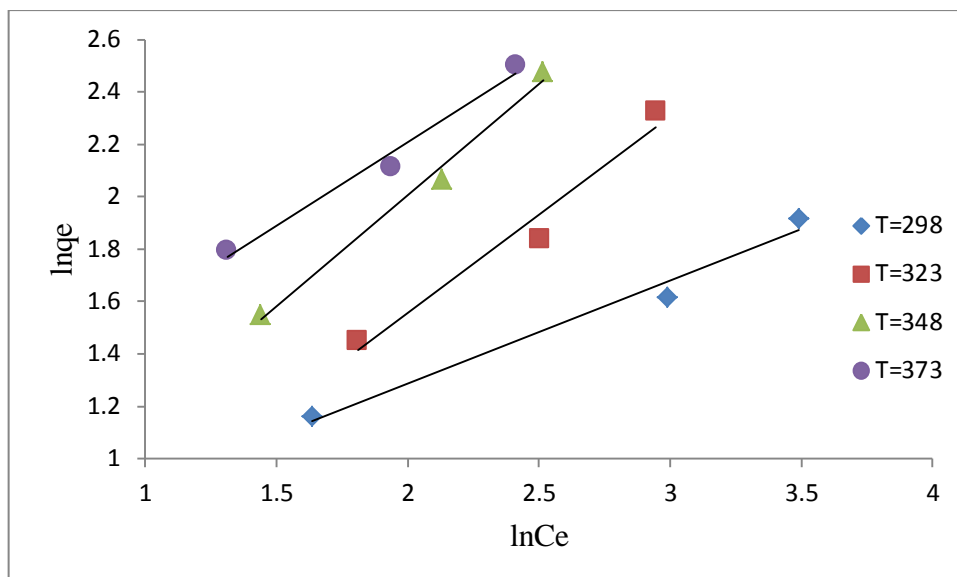


Figure 4-9: Freundlich Isotherm (EBT Concentration = 40 mg/L, Adsorbent Dosage = 200 mg)

Table 4-1: Adsorption Parameters obtained from Langmuir and Freundlich Models  
 Conditions: contact time: 6hr, Initial concentration: 40mg/L, EBT dose: 200mg, pH:2.0

Langmuir parameter	T (K)	$q_m$ (mg/g)	$K_L$ (L/mg)	$R_L$	$R^2$
EBT	298	222.222	0.0112	0.504	0.9982
	323	175.438	0.0218	0.688	0.9986
	348	58.4795	0.0245	0.533	0.9952
	373	41.841	0.0284	0.467	0.9931
Freundlich parameter	T (K)	1/n	n	$K_f$ (mg/g)(L/mg)	$R^2$
EBT	298	1.99561	0.5011	89.32	0.9817
	323	19.0472	0.0525	93.33	0.9903
	348	3.25203	0.3075	100.36	0.9626
	373	1.07089	0.9338	108.45	0.9803

#### 4.2.5 Effect of co-existing Salt

Industrial wastewater from textiles, paper mills, medicines and dyestuffs not only contain dyes, but also different types of dissolved materials, such as nitrates, salts, chloride, sulphates, surfactants etc. Consequently, the experimental tests were conducted on effects of  $Cl^-$ ,  $I^-$ ,  $SO_4^{2-}$  and  $HPO_4^{2-}$  on the adsorption of EBT on CPH. In this study 25ml of 0.2 M of Sodium salts of  $Cl^-$ ,  $I^-$ ,  $SO_4^{2-}$  and  $HPO_4^{2-}$  were added



into 25ml of 80 mg/L at 25°C and shaker. The effect was referred to competition between the salts anions ( $\text{Cl}^-$ ,  $\text{I}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{HPO}_4^{2-}$ ) and the EBT molecules for the unoccupied sites on the adsorbent. As shown in Figure 4-6, the highest reduction of adsorption percentage is in the presence of  $\text{HPO}_4^{2-}$  ion (23.7%), and lowest decreasing is in existence of Chloride anion (40.63%) which in the adsorption percentage of EBT dye in the absence of salts is 71.63.  $\text{HPO}_4^{2-}$  showed more competition due to its high negative charges compared to chloride ions competing with the sulfonic groups of EBT.

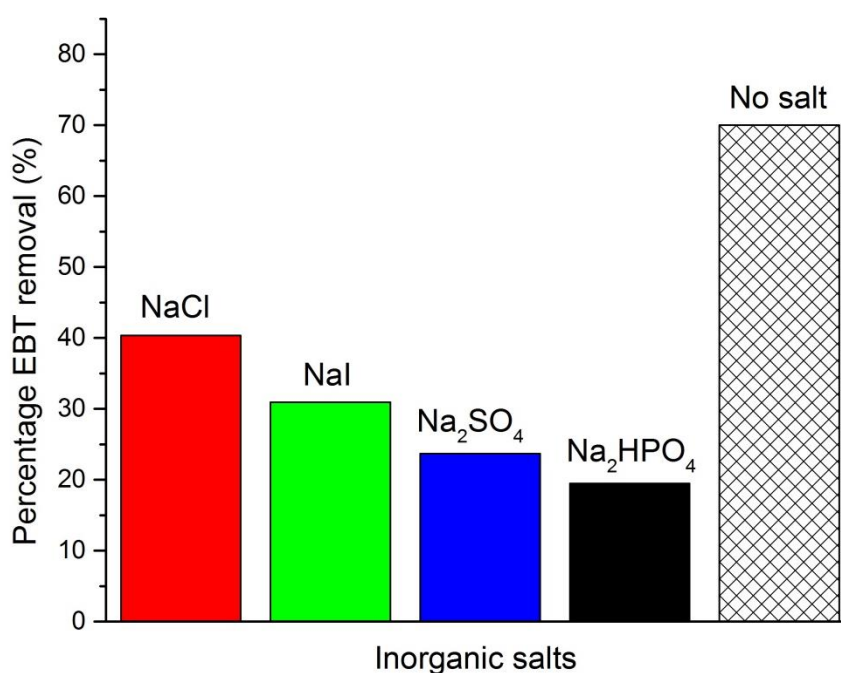


Figure 4-10: Effect of Inorganic Salt (EBT Concentration = 40 mg/L, Adsorbent Dosage = 200 mg)

#### 4.2.6 Effect of Ionic Strength

Effect of ionic strength on sorption of EBT onto CPH was studied at room temperature and different concentration of NaCl (0.2, 0.4, 1, 2 M), over all initial concentration of dye of 40 mg/L and 200 mg.

For the adsorption of EBT using the CPH, the interactions between the dyes and the hydrogel are mainly electrostatic attractions. The adsorption amount of EBT decreases with increasing ionic strength (Figure 4.7). As a result of increasing of competition of attracting to CPH active sites, the electrostatic attraction between the dyes and the CPH decreases with increasing ionic strength.

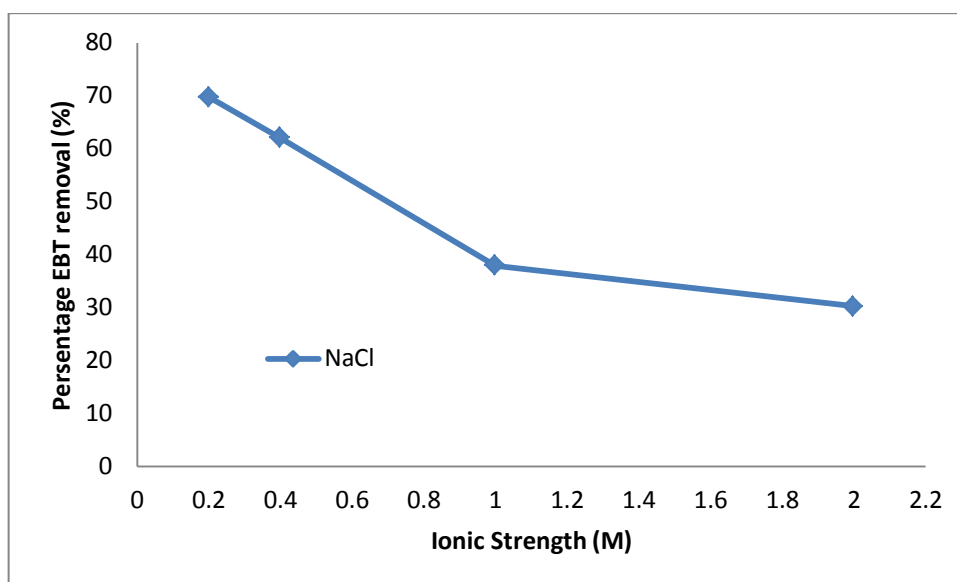


Figure 4-11: Effect of Ion Concentration (EBT Concentration = 40 mg/L, Adsorbent Dosage = 200 mg)

#### 4.2.7 Effect of Contact Time

One of the most important parameters is the contact time. According to Figure 4-8, the EBT was rapidly adsorbed in the first 120 min, and then the adsorption rate decreased gradually from 240 to 540 min and finally reached to equilibrium in about 720 min. The fast adsorption at the initial stage may be due to a large number of positive charged surface site (functional groups) that are available for adsorption of EBT on CPH. Dye molecules spread from the bulk solution of the outer surface of the hydrogel particles.

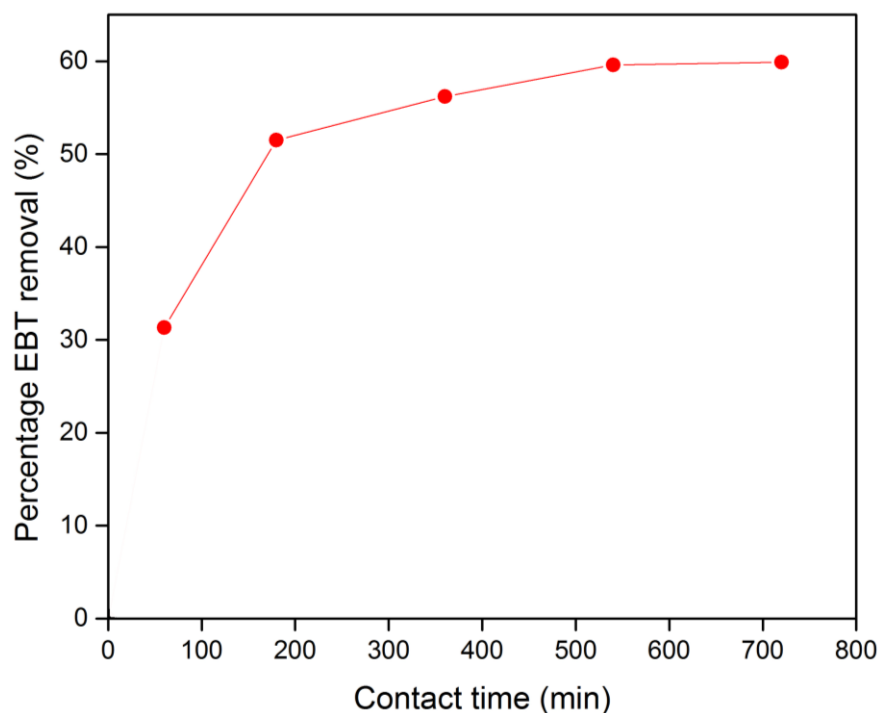


Figure 4-12: Effect of Contact Time (EBT Concentration = 40 mg/L, Adsorbent Dosage = 200 mg)

Kinetic models parameters for EBT onto CPH were evaluated by both pseudo first-order and pseudo second-order equations and the results obtained were applied to explain the EBT adsorption mechanism onto CPH. As shown in Table (4-2) the  $q_{e,cal}$  values of pseudo first-order do not fit well with the  $q_{e,exp}$  values which are around 5.5 mg/g and its relatively low  $R^2$  show that the model is not suitable to describe EBT adsorption mechanism while the high values of  $R^2$  and the comparable  $q_{e,cal}$  and  $q_{e,exp}$  values indicate that pseudo second-order is better suited for EBT adsorption and description of the mechanism. Figure 4-13 shows Pseudo first- order and pseudo second-order models of EBT dye adsorption on CPH adsorbent.

Table 4-2: Kinetic Parameters for EBT removal using CPH.  
 Conditions: contact time: 6hr, Temperature: 323K, EBT dose: 200mg, pH: 2.0 and  
 dye concentration: 40 mg/L

<i>Kinetic model</i>	<i>Pseudo first-order</i>	<i>Pseudo second-order</i>
$k \times 10^{-2}$	0.01 (min <sup>-1</sup> )	24.6 (g.mg <sup>-1</sup> .min <sup>-1</sup> )
$q_{e,cal}$ (mg/g)	57.512	6.68
$q_{e,exp}$ (mg/g)	5.69	5.23
$R^2$	0.8805	0.9988

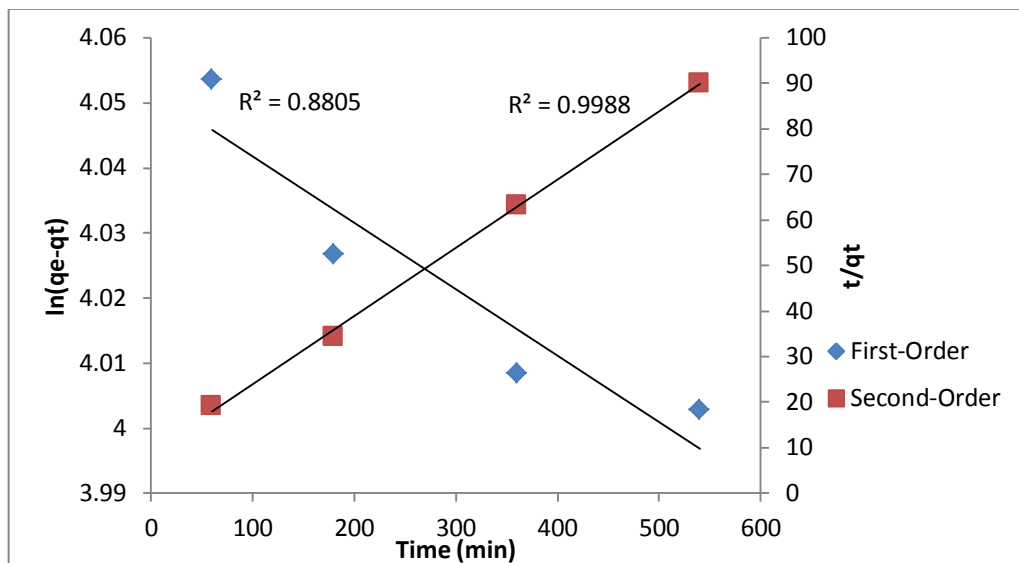


Figure 4-13: Pseudo first- order and pseudo second-order models

## Chapter 5

### CONCLUSION

In this study, the achievement of CPH as a sorbent to remove EBT from aqueous medium was examined. Characterization of CPH adsorbent has been studied using the FT-IR technique and furthermore adsorption batch study, kinetic studies and improvement were achieved experimentally, the following were gained;

- The CPH shows good efficiency for removing EBT dye from aqueous medium
- Kinetic data fits well as the pseudo second-order equation, which gave the best match with experimental data.
- The fit is well in line with Langmuir model based on the correlation coefficient ( $r^2$ ).
- The collected data showed that the best adsorption can be achieved at high adsorbent dosage, high temperature, without inorganic salt and in acidic medium.

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