

Synthesis and Characterization of Superabsorbent Chitosan-Starch Hydrogel and its Application for Removal of Direct Red 80 Dye

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ABSTRACT

In this study, an eco-friendly superabsorbent hydrogel was prepared by crosslinking chitosan and starch using glutaraldehyde as the crosslinking agent. The chitosan-starch hydrogel (CSH) as an adsorbent was then successfully used for the sorption of Direct Red 80 (DR80) dye from aqueous medium. The adsorbent was evaluated using batch adsorption process by performing a series of batch investigations to identify the maximum sorption kinetics, thermodynamics and isotherms of DR80 onto the adsorbent by assessing different operational conditions such as pH, sorbent dose, initial DR80 concentration, salts and temperature. The sorption process was studied using the pseudo-first order, the pseudo-second order kinetic equations alongside the Freundlich and Langmuir isotherm equations at different temperatures. The equilibrium data was observed to follow the Freundlich model and was observed that DR80 sorption process favored the pseudo-second order kinetics correlation coefficient (R^2) value obtained. The negative and positive values of ΔG° and ΔH° demonstrated that the sorption process of DR80 onto the adsorbent was spontaneous and endothermic, respectively. FT-IR characterization was used to demonstrate presence of the various functional groups; $-\text{NH}_2$, $-\text{CONH}_2$, $-\text{CO}$ and $-\text{OH}$ on the adsorbent.

From the data obtained from the experimental measurements, conclusion were drawn based on the eco-friendly, low cost 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-Starch Hydrogel, Direct Red 80, Eco-friendly

ÖZ

Bu çalışmada, glutaraldehit çaprazbağlayıcı kullanılarak çevre dostu süper absorbent hidrojel olan çaprazbağlı kitosan ve nişasta hazırlanmıştır. Kitosan-nişasta hidrojel (CSH), sulu ortamda Direct Red 80 (DR80) boyası için başarılı bir adsorbandır. Adsorbanın, maksimum adsorpsiyon kapasitesi, kinetik, termodinamik ve adsorpsiyon izoterimleri, batch adsorpsiyon prosesleri kullanılarak pH, sorbent miktarı, DR80 başlangıç konsantrasyonu, tuz ve sıcaklık değişimlerinden faydalanılarak belirlenmiştir.

Bu adsorpsiyon prosesinde birinci ve ikinci dereceden kinetik eşitliklerinin yanında farklı sıcaklıkta Freundlich ve Langmuir izoterm eşitlikleri çalışılmıştır. Denge verileri Freundlich modelini takip etmekte ve DR80 tutma süreci yalancı 2. dereceden kinetik korelasyon katsayısı değeri (R^2) ile uyumludur. ΔG° ve ΔH° değerlerinin sırasıyla negatif ve pozitif oluşu, adsorban üzerinde DR80'in tutulma işleminin kendiliğinden ve endotermik olduğunu göstermektedir. FT-IR karakterizasyonu adsorbent üzerinde $-NH_2$, $-CONH_2$, $-CO$ ve $-OH$ gibi birçok fonksiyonel grubun varlığını göstermektedir.

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

Anahtar Kelimeler: Süperabsorbent, kitosan-Nişasta, Direct Red 80, Çevre Dostu

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NOMENCLATURE

| | |
|------------------|---|
| SAH | Superabsorbent Hydrogel |
| CSH | Chitosan-Starch Hydrogel |
| DR80 | Direct Red 80 |
| FT-IR | Fourier Transform Infrared spectrophotometer |
| UV-VIS | Ultraviolet Visible spectrophotometer |
| q_e | Equilibrium concentration of adsorbed species in solid adsorbent (mg g^{-1}) |
| C_e | Equilibrium concentration of adsorbed species in solution (mg L^{-1}) |
| Q_0 | Maximum adsorption capacity for forming monolayer (mg g^{-1}) |
| K_L | Langmuir isotherm constant (L mg^{-1}). |
| C_0 | Initial concentration (mg L^{-1}) |
| K_f | Freundlich isotherm constant (mg g^{-1})(L mg^{-1}) |
| n | Adsorption intensity; |
| k_1 | Equilibrium rate constant of pseudo-first adsorption, (min^{-1}). |
| k_2 | Equilibrium rate constant of pseudo-second order adsorption, ($\text{g mg}^{-1}\text{min}^{-1}$). |
| K_i | The intra-particle diffusion rate constant ($\text{mg g}^{-1}\text{min}^{-1/2}$) |
| t | Time of diffusion (min) |
| ΔH° | Enthalpy change (J mol^{-1}) |
| ΔS° | Entropy change (J mol^{-1}) |
| ΔG° | Gibbs free energy (J mol^{-1}) |
| R | Universal gas constant ($8.314\text{Jmol}^{-1}\text{K}^{-1}$) |
| T | Absolute temperature (K) |
| K_d | The distribution constant |
| R_L | Equilibrium parameter Langmuir isotherm |

Chapter 1

INTRODUCTION

Following historical studies, mankind has depended extensively on the use of biodegradable materials such as wool, leather, silk, starch and cellulose. As of nowadays, these biopolymers can be design to meet specific needs of our rapid growing population. The advent of modern technology has fundamentally transformed the way researchers and scientists view the materials they produce.

Recently, natural materials such as polysaccharides which are the major backbone of naturally derived superabsorbent hydrogel (SAH) have gained attention of researchers due to their peculiar properties such as being biocompatible, biodegradable, renewable, and non-toxic. Due to these properties exhibited by superabsorbent hydrogels, much interest has been paid to the synthesis of these materials with features such as high absorbency, gel strength, and absorption rate [Pourjavadi et al., 2009]. Through their different methods of processing, natural superabsorbent hydrogels have found extensive applications as biomaterials on account of their flexibility to be modified for specific use such in wound dressings, drug delivery systems, dental applications, implants and ophthalmic applications. They have also been used for applications in agriculture due to their potential influence on soil permeability, density, texture and infiltration rates of water through the soils [Kolybaba et al., 2003; Sadeghi & Soleimani, 2011].

1.1 Problem definition

1.1.1 Environmental Issues

Superiority in regards to environmental understanding has been an important driver for the increased use of bio-based superabsorbent hydrogels and this is believed to hold for the future. The use of bio-based derived superabsorbent hydrogels emerged as an important tool of this paradigm of economic growth due to the usage and massive discharge of dyes into water and our surroundings [Patel et al., Biopolymers, 1993].

With our environment being consumed by non-biodegradable, petroleum-based polymeric material, the increasing use for such materials has left the rivers, lakes, sea beaches and landfills overflowing with these indestructible materials thereby causing economic effects on our society. Due to this, interest by researchers and scientists has been drawn towards development of cheap, eco-friendly materials from readily available, renewable, inexpensive natural sources, such as Starch, cellulose (from plant resources) and chitin, chitosan (from animal resources). One of the main environmental problems is the industrial production of dyes, inks and paints.

1.1.2 Waste-water Pollution

Development of synthetic dyes as of the beginning of the twentieth century, things began to change. Accompanied by the fast growth rate of industrialisation, population increase and urbanisation led to the massive production of approximately ten thousands different dyes manufactured worldwide with a per annum market consumption of more than 700,000 tons per year of these cheaper, brighter, more color fast and easy to apply dyes, thereby causing the heavy water pollution [Bechtolda et al., 2003].

The discharge of dyes from dyeing manufacturing industries into wastewater contains highly coloured chemicals which lack an aesthetical appearance and in addition prevents the penetration of sunlight thereby affecting the intensity of light absorbed by hydrophytes and phytoplankton, causes a decrease in photosynthesis and dissolved oxygen concentration of the aquatic environment [Rangabhashiyam et al.,2013]. And moreover, most dyes are considered to be toxic or carcinogenic therefore being considered as pollutants to a given aquatic ecosystem due to the difficulty in treatment [Sharma et al., 2011]. For this reason scientists and researchers have developed fast and more eco-friendly means of adsorption treatment of the dyes from waste water [Malik, 2004].

1.2 Methods of Dye Removal

From analyses, most used dyes in textile and other manufacturing companies are reactive, basic and acidic dyes with the quantity of dyes discharged into water bodies being approximated 15-65%, 1-8% and 10-30% for reactive, basic and acidic dyes respectively. Therefore it is important and necessary to treat these dyes as their presence in high volumes and resistance to degradation within household and industries wastewater systems are unfriendly to our surroundings and health [Olapido, 2011].

Efficient treatment of dye from industrial and house colored wastewater is a challenge to engineers and scientists, as some of the methods are expensive and others are not efficient[Mondal, 2008]. Classification of the various removal technologies are shown in the table 1 [Gregorio & Pierre-Marie, 2008; Gregorio, 2006].

Table 1: Principles and different treatment technologies for dyes removal

| Existing principles | Processes |
|------------------------------------|---|
| Conventional treatment methods | <ul style="list-style-type: none"> ➤ Coagulation ➤ Precipitation ➤ Electro-coagulation ➤ Bio-degradation ➤ Adsorption |
| Established treatment technologies | <ul style="list-style-type: none"> ➤ Oxidation process ➤ Electrochemical process ➤ Membrane separation technology ➤ Ion-exchange method |
| Emerging treatment technologies | <ul style="list-style-type: none"> ➤ ➤ Advanced oxidation processes ➤ Biomass method ➤ Irradiation |

Notwithstanding these dye removal processes can be further classified into three different treatments ; i.) Physical treatment : by adsorption, membrane filtration, ion exchange ii.) Chemical treatment: by membrane separation, electro-coagulation, adsorption and chemical oxidation and iii.) Biological degradation: by decolorisation with white-rot fungi, microbial degradation and adsorption by biomass [Miroslava et al., 2008, Ozdemir et al., 2013].

1.3 Research Study Aim and Objectives

1.3.1 Aim

The main aim of this research work is to synthesize eco-friendly efficient chitosan-starch superabsorbent hydrogel and use for treatment of Direct Red 80 (DR80) from aqueous solution using the single batch adsorption technique.

1.3.2 Objectives

The research has an aim to be achieved and due to this some objectives were put in place as outlined below;

- To synthesize chitosan-starch SAH
- To examine the removal of DR80 from aqueous solution using chitosan-starch hydrogel as adsorbent.
- To establish and examine sorption isotherm equations for the dye (adsorbate) sorption based on the use of the chitosan-starch hydrogel (adsorbent).
- To investigate and study the kinetic and thermodynamic parameters of the adsorption process.
- To optimize performance of the removal of the dye by the chitosan-starch SAH.

The prepared hydrogel exhibited considerable swelling properties and capability to remove trace amount of dyes from polluted waste water. For this research, the swelling features of the hydrogel and treatment of DR80 dye by the synthesized SAH is investigated at different conditions and factors

Chapter 2

LITERATURE REVIEW

2.1 Superabsorbent Hydrogels

2.1.1 Historical Outline of Superabsorbent Hydrogels (SAH)

The first water sorbent hydrogels were prepared in early 1938; divinylbenzene and acrylic acid (AA) [Oladipo, 2011; Zohuriaan-Mehr & Kabiri, 2008]. With the earliest discovery and synthesis of hydrogels based on poly (hydroxyethyl methacrylate) (PHEMA) discovered by Otto Wichterle in the 1950s and having closely-linked monomers with swelling power up to 45% [Sannino et al., 2009]. This to the production of eye contact lenses which showed a breakthrough and change in the field of ophthalmology. The first commercially used SAH was prepared in the United States Department of Agriculture via alkaline hydrolysis starch-graft poly (acrylonitrile) in the 1960s [Oladipo, 2011; Zohuriaan-Mehr & Kabiri, 2008].

2.1.2 Criteria of Superabsorbent Hydrogels

Superabsorbent hydrogels (SAHs) are moderately crosslinked three dimensional hydrophilic network polymeric materials with properties to absorb and retain considerable amount of water or other aqueous fluids in aqueous environment with swelling of up to a hundred and more times its original size even under certain conditions such as heat or pressure with the ability to maintain its physical structure without dissolving [Oladipo, 2011; Sannino et al., 2009; Wanga et al., 2010; Saber-Samandari et al., 2012; Sadeghi & Hosseinzadeh, 2010].

Due to the similarities in the polymeric crosslinked network structure of gels alongside hydrogels, scientists and researchers use them indistinguishably. Gels are substantial dilute cross-linked systems with classification as being weak or strong depending on their flow properties at steady-state while hydrogels are 3-D network structures either synthesized from a group of synthetic and/or natural polymers which can absorb and retain considerable amount of water [Syed et al.]. In addition SAHs are different from normal hydrogels because of their ultrahigh absorbing ability to absorb deionized water as high as 1,000 to 100,000% whereas the adsorption capacity of normal hydrogels is between 100 to 1,000% [Zohuriaan-Mehr & Kabiri, 2008]. The diagram below demonstrates swelling of SAHs,



Figure 1: Schematic illustration of SAHs swelling with Comparison of the dry and swollen state particle

Based on the unique properties of SAHs: i) absorption capacity, ii) absorption rate and ii) gel strength making them superior to conventional absorbents, they have found a wide range of applications in fields such as agriculture, sanitary materials, wastewater treatment, DDS, foods and sealing materials etc [Olapido, 2011; Wanga & Wang, 2010; Zohuriaan-Mehr & Kabiri, 2008]. Notwithstanding they are some reaction variables such as i) crosslinker concentration, ii) polymerization temperature, iii) type of monomer and

iv) post-treatment which greatly affects the final properties of SAHs which if altered either increases or decreases the ability of the SAHs as shown in table 2.

With characteristics of the swelling medium such as pH, ionic strength, counter ions and valency, affects swelling properties of SAHs. As such SAHs are often sensitive to external stimuli such as heat, pH, electric field and chemical surroundings by so doing are called “intelligent or smart” polymeric materials [Saber-Samandari et al., 2012; Sadeghi & Hosseinzadeh, 2010].

Table 2: Effects of synthetic factors on absorption properties of SAHs

| Factors (↑) | Absorption capacity | Absorption rate | Swollen gel strength |
|---------------------------|---------------------|-----------------|----------------------|
| Crosslinker concentration | ↓ | ↓ | ↑ |
| Initiator concentration | ↑ | ↓ | ↓ |
| Monomer concentration | ↓ | ↑ | ↓ |
| Reaction temperature | ↑ | ↓ | ↓ |
| Particles porosity | x | ↑ | ↓ |
| Surface cross-linking | ↓ | ↑↓ | ↑ |
| Ionic Strength of Medium | ↓ | ↓ | ↑↓ |
| Temperature of Medium | x | ↑ | x |
| Photo-/Bio-degradation | ↑ | ↓ | ↓ |
| pH > 7 | ↑ | ↑ | ↑↓ |
| pH < 7 | ↓ | ↓ | ↑↓ |

↑ = increasing, ↓ = decreasing, ↑↓ = varied, x = non effective

2.1.3 Methods of Synthesizing Superabsorbent Hydrogels

Nowadays SAHs are mostly prepared from petroleum-based synthetic polymers with high cost of production and poor eco-friendly properties [Wanga & Wang, 2010]. But with a global awareness and decision supports, the replacement of synthetic materials

with good environmental friendly substitutes have been introduced due to the fast growing population and over consumption of these products leading to the depletion of the synthetic source [Oladipo, 2011; Zohuriaan-Mehr & Kabiri, 2008]. From studies, there are basically two ways for the preparation of bio-based SAHs; graft polymerization and crosslinking reaction [Zohuriaan-Mehr & Kabiri, 2008].

2.1.4 Categories of Superabsorbent Hydrogels

Depending on the functionality of SAHs, they can be classified into four different groups [Qui & Oark, 2001; Zohuriaan-Mehr & Kabiri, 2008];

- (i) available and non-available charges on the cross linked chains of the side groups
(Amphoteric, Ionic)
- (ii) on method of synthesis (copolymer, homo-polymer)
- (iii) physical structure (Amorphous, Semi-crystalline)
- (iv) Origin (Synthetic, Natural).

In addition an important class of SAH is the stimuli responsive gels.

2.2 Natural-based Polymers

Natural based polymers, as their name implies, are derived from natural sources. Natural based polymers are biocompatible and are typically composed of a polymeric network that can contain up to 99% or higher water content. Bio-based polymers are characterized of having batch-to-batch variations and low mechanical properties, cheap and easy to produce into hydrogels, making them good for various fields of applications [Hsu-Feng et al., 2010]. Due to properties such as biodegradability, biocompatibility, renewability and non-toxicity [Sadeghi & Soleimani, 2011] exhibited by these polysaccharides, extensive applications on account of their flexibility have been discovered for their usage in fields such as biomedicine, agriculture and industries. The presence of the bio-based parts assures biodegradability of the absorbing materials and

makes them to be eco-friendly. Natural based polymers in terms of source of origin are classified in three categories [[Hsu-Feng et al., 2010];

- 1.) Polysaccharides which are complex carbohydrates that are made up of repeating monomer units of monosaccharides and which occur widely in nature and are of either plant, animal, or microbial origins. Some examples of these polysaccharides include; starch, cellulose, agarose, chitosan and alginates. We do have other more complex carbohydrate polymers produced by bacteria and fungi, such as xanthan, pullulan and hyaluronic acid.
- 2.) The second class includes polypeptides which are mostly protein in nature and a good example is gelatin.
- 3.) The third class involves bacterial polyesters which are bio-macromolecules produced in nature by bacterial fermentation reactions of sugar or lipids .A good example is poly (3-hydroxy butyrate) PHB.

2.2.1 Chitosan-based Polymer

2.2.2.1 Structure and Origin

For present years, scientists and researchers have diverted their interest to a polysaccharide named chitosan an amino derivative of chitin. Chitosan was first discovered in 1859 by Professor C. Rouget [Bhatnagar & Sillanpää, 2009]. Chitosan is a natural amino polysaccharide derived from chitin via a deacetylation process to generate a linear structure of repeating units glucosamine (2-amino-2-deoxy- β -D-glucopyranose) and *N*-acetyl-glucosamine (2-acetamido-2-deoxy- β -D-glucopyranose) joined in a β -(1,4) manner and with a molecular formula of $C_6H_{11}O_4N$ [Bhatnagar & Sillanpää, 2009; Harish & Tharanathan, 2007]. The source of chitosan is mainly from exoskeleton of marine crustaceans such as crab (Dungeness crab), shrimp (Pacific shrimp), lobster, or crawfish shells [Fernandez-Kim, 2004]. Chitosan due to its non-toxicity,

biodegradability and biocompatibility over the last several years have gained so much attention and thus have been studied by various scientists as a fascinating adsorbent for the adsorption of dissolved dyes from aqueous medium. This biopolymer has fascinating characteristics that enables it to be an effective adsorbent for the treatment of color. Its application as an adsorbent is supported by two particular advantages: i) its cheapness and ii) its outstanding chelating ability. And in addition, this biopolymer possesses some other physico-chemical features such as being chemically stable, highly reactive and highly selective toward contaminants and as such chitosan has been modified by different methods either physically or chemically so as to improve the adsorption properties for different waste water dye contaminants [Bhatnagar & Sillanpää, 2007; Gregorio & Pierre-Marie, 2008].

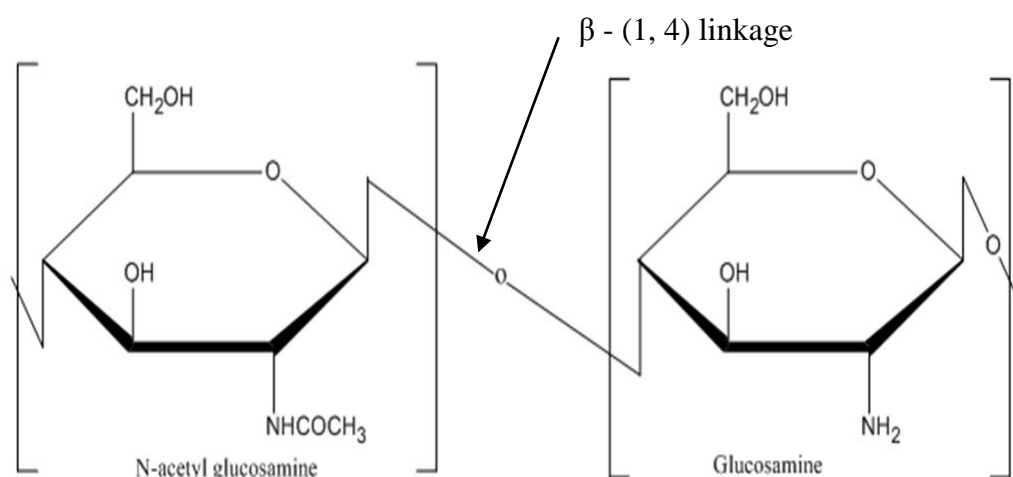


Figure 2: Chitosan structure showing the type of linkage between the glucose units

2.2.1.2 Functional Groups and Solubility of Chitosan

In regards to the versatile nature of chitosan and a wide range of applications, this has made chitosan more advantageous compared to other biopolymers like cellulose. The versatility of this biopolymer is due to the identification of three different functional groups present on the chitosan structure which include; an amino group at C-2 position, hydroxyl groups at C-3 and C-6 position [Harish & Tharanathan, 2007; Pradip et al.,

2004; Lu-E & Zhen-Xing, 2009]. With respect to solubility, chitosan is soluble in aqueous medium of some acids [Lu-E & Zhen-Xing, 2009].

2.2.1.3 Properties of Chitosan

With the outstanding properties exhibited by chitosan such as being biodegradable, biocompatible, film-forming, bio-adhesive, poly-functional, hydrophilic and adsorption properties, has led chitosan-based SAHs to be promising materials for waste water treatment purposes such as dye removal from aqueous medium. Table 3 illustrates the various physico-chemical and biological properties [Harish & Tharanathan, 2009; Gregorio & Pierre-Marie, 2008; Anwunobi & Emeje, 2011; Yogeshkumar et al., 2013; Fernandez-Kim, 2004].

Table 3: Intrinsic characteristics of chitosan

| | properties |
|--------------------------------|--|
| Physical and chemical features | <ul style="list-style-type: none"> ➤ Linear amino polysaccharide ➤ high crystallinity; hydrophilicity ➤ high viscosity ➤ Weak base; due to the deprotonated amino group ➤ Soluble in dilute aqueous acidic solutions and insoluble in water and other organic solvents ➤ Several reactive groups for chemical activation ➤ Ionic characteristics ➤ High charge density (one positive charge per glucosamine residue) |
| Biological features | <ul style="list-style-type: none"> ➤ Biocompatible ➤ Non-toxic ➤ Bio-degradable ➤ Bioactive ➤ Bio-adhesive |

2.2.1.4 Method of Preparation of Chitosan

Chitosan as earlier said is produced from crustacean shell such as crab, shrimp etc. The shells are composed of approximately 30-40% protein, 30-50% CaCO_3 , and 20-30% chitin dried [Fernandez-Kim, 2004].

Chitosan is mostly and commonly synthesized by deacetylation of chitin using 40-50% NaOH as reagent and water as a solvent at 100°C and for 30 minutes. With this reaction to completion a 98% yield product is obtained with the degree of deacetylation (DD) that can be determined by the use of an NMR spectroscopy [Yogeshkumar et al., 2013].

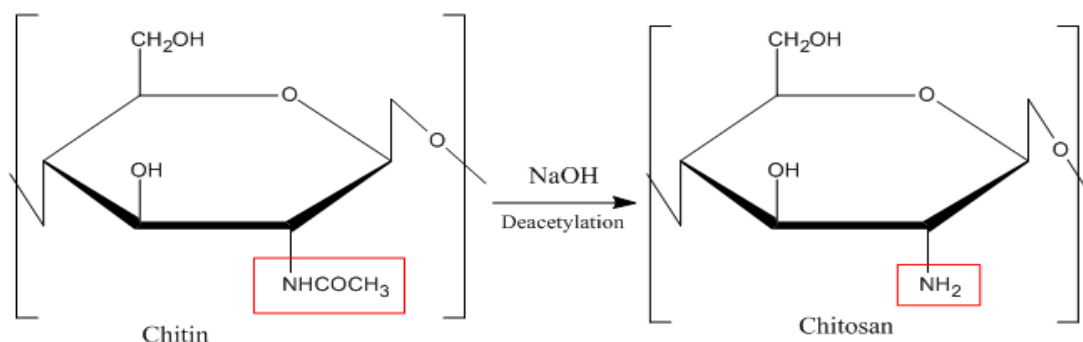


Figure 3: Synthesis of chitosan by deacetylation of chitin

2.2.1.5 Various Applications of Chitosan Based Polymer.

Chitosan as the only pseudo-natural polymer and due to its non-toxic, biodegradable and biocompatible and in addition its cheap and abundant availability in nature it has found many applications in the fields of biomedicine, industrial, agriculture and environmental.

Table 4: Applications of Chitosan based polymers

| Field of application | Applications |
|-------------------------|---|
| Industrial applications | <ul style="list-style-type: none"> ➤ Water purification ➤ Production of biodegradable packaging material ➤ Catalytic processes ➤ Cosmetics and sanitary materials ➤ Textile and paper production ➤ Food preservation and dietary food |
| Biomedical applications | <ul style="list-style-type: none"> ➤ Tissue engineering |

| | |
|----------------------------|---|
| | <ul style="list-style-type: none"> ➤ Ophthalmology ➤ Drug delivery systems ➤ Burn treatment ➤ Artificial skin ➤ Wound dressing/wound healing |
| Environmental applications | <ul style="list-style-type: none"> ➤ Water treatment (dye removal) |
| Agricultural applications | <ul style="list-style-type: none"> ➤ Water reservoirs ➤ Soil treatment |

2.2.2 Starch-based Polymer

2.2.2.1 Structure and Origin

Starch an abundant bio-based polymer have gained great interest since the 1970s [Lu et al., 2009], with a worldwide production of starch as estimated from 2008 was 66 million tons while production per year have been increasing still present due to increase in population with USA being the highest producer of starch followed by Europe and next by Asia [Sugih, 2008]. Starch is a common polysaccharide consisting of D-glucose units forming a homopolymer and is generally referred to as homoglucon or glucopyranose [Luc Averous, Agro polymers]. It has a general molecular formula of $C_6H_{12}O_6$ and occurs majorly in plants where they act as storage materials for energy.

The main source of starch is corn (maize) with other sources being wheat, potato, tapioca and rice. Starch granules consist of varying shapes (spheres and platelets) with size ranging from $0.5\mu-175\mu$ [Luc Averous, Agro polymers, Luc and Eric, biodegrade. Poly.]. Starch is chemically composed of two homopolymers: i) amylose (consist of about 10-20%) which is a linear polysaccharide composed of D -glucose units joined by α -(1,4) linkages and depending on the source and process of production amylose molecular weight ranges from $10^5 - 10^6$ g.mol⁻¹. ii) Amylopectin (consist of about 80-90%) which is highly branched and found occurring every 24-79 glucose units but which has the

same backbone and monomeric units like amylose. It mostly consist of 95% α -(1, 4) linkages with 5% α -(1, 6) linkages [Lu et al., 2009; Smith 2008; Luc and Eric, biodegrade. Poly.].

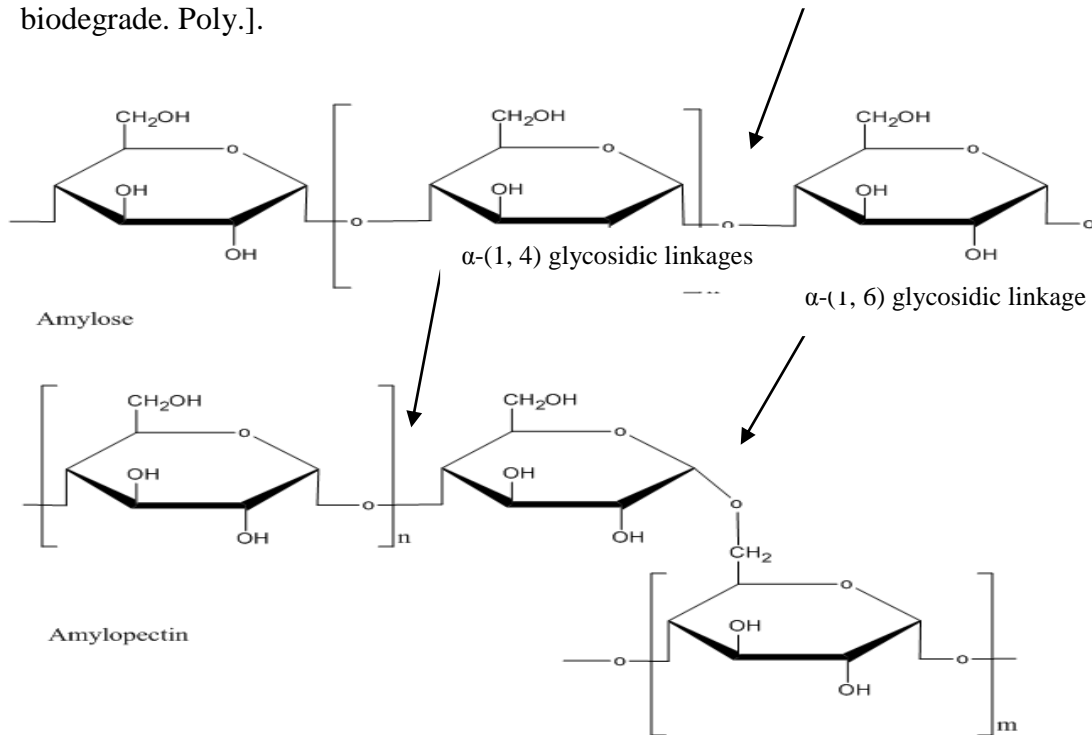


Figure 4: Starch structure showing the different linkages in a) amylose and b) amylopectin

Notwithstanding studies show that starch and cellulose belong to the same group of carbohydrates and are therefore very similar in structure. They are all polymeric forms of glucose units. Although these polymers are very similar, they differ in their physical and chemical characteristics and these differences are because of their glycosidic linkages. Cellulose is said to consist of beta (1, 4) glycosidic linkages and are arranged in a flip flop manner thereby contributing to their rigidity which is attributed to the orientation of the glycosidic linkage. While on the other hand starch constitute of alpha (1, 4) glycosidic linkage at linear points and alpha (1, 6) glycosidic linkages at branched points.

2.2.2.2 Processing of Starch

For full starch solubilization and extraction of starch from its source we do have different methods of starch processing and are outlined as follows [Sugih, 2008; Wanek et al., 2001]: i) By use of DMSO ii) By use of HCL iii) by use of enzymes iv) By use of the milling process.

2.2.2.3 Functional Groups and Solubility of Starch

In regards of the polymeric form and wide range use of starch, is due to the functional groups present on the starch which includes; hydroxyl groups at C-2, C-3 and C-6 positions. In addition to this due to the presence of numerous hydroxyl groups on starch, starch has been found to be partially soluble in water but when heated becomes completely soluble and may also be soluble in other organic solvents.

2.2.2.4 Physico - chemical Properties of Starch

With the versatile use of starch in different sectors of life, its applications are being enhanced by the various functional properties exhibited by this biopolymer such as [Sugih, 2008; Luc and Eric, biodegrade. Poly.];

- Its insolubility in cold water but gelatinizes on heating.
- Its high degree of crystallinity exhibited mostly by the amylopectin region.
- Moderate swelling ratio by forming a viscous solution.
- Exhibit retro-gradation which is characterized by low enthalpy, low gelatinization temperatures and weaker crystallinity.
- Shows past forming abilities which is also proven by increase in viscosity of starch solution accompanied by increase in heating.
- Exhibits a degree of hydrophilicity due to the presence of lots of OH groups on starch chains. This enables starch molecule to be able to be reduced or oxidized thereby forming hydrogen bonds, esters and ethers.

2.2.2.5 Applications of Starch Based Polymers

Starch and modified starches have a wide range of applications in fields like food industries, agricultural, medicine and pharmaceuticals, environmental and textile industries.

Table 5: Illustrating the various applications of starch in different fields of application

| Field of applications | applications |
|-------------------------------|--|
| Food and beverages industries | <ul style="list-style-type: none">➤ Use in the production of➤ Gravy and cream➤ Puddings➤ Bakery products➤ Confectionery➤ Syrups and disserts➤ Beverages |
| Agriculture | <ul style="list-style-type: none">➤ Use for producing biocides, molluscides and herbicides➤ Soil treatment |
| Medicine and pharmaceuticals | <ul style="list-style-type: none">➤ Use for drug production➤ Use for in tissue engineering➤ Use in drug delivery systems |
| Environmental applications | <ul style="list-style-type: none">➤ Use for water treatment(dye removal) |
| Textile industries | <ul style="list-style-type: none">➤ Use in making cosmetics➤ Use in producing spray for dresses➤ Use for weaving in textile industries➤ Use in the production of paper and glue➤ Production of colors and dyes |
| Construction industries | <ul style="list-style-type: none">➤ Use in the production of ceramics |

2.3 Colorants

In the past 145 years various kinds of colored substances have been produce with several million colored substances on an industrial scale. Colorants are natural or synthetic additives which enhance color, hiding power, and specialized physical qualities to a finished commodity or product thereby adding the bulk, durability, and corrosion resistance to an intended material.

They possess the ability to absorb and emit visible light within a wavelength range of 400-700nm [Zollinger, 2003]. While on the other hand color is a substance with important attribute which makes the visual appearance and quality of a given product or material appealing by increasing the freshness, safety and making the product or material have good aesthetic and sensual value [Binti, 2010].

2.3.1 Classification of Colorant in Terms of Origin and Application

With respect to chemical structure, colorants can either be inorganic or organic and are further subdivided into natural or synthetic source origin. i) Natural colorants which are of organic origin and are derived from edible sources using correct food preparation procedures. Examples include carotene, betalains, flavonoids and anthocyanins etc. ii) Synthetic colorants which are either organic or inorganic of origin are resemblance of vegetable, animal and mineral-based colorants which are synthesized in the laboratory. Some good examples include direct red 80, malachite green, brilliant blue. In terms of applications colorants are classified as dyes or pigments.

2.4 Dyes

Dyes are said to be complex unsaturated aromatic compounds consisting of various coloring particles which are different from one another by their chemical composition and are characterized by their intense color, solubility, substantiveness and fastness in coloring [Klaus Hunger, Indus. Dyes, Suyamboo & Perumal, 2012].

2.4.1 Classification Systems of Dyes

There are different ways of dye classification with every class of dyes having its own chemistry, structure and manner of bonding. Some of the common ways of dye classification are; i) based on source of materials which are either natural or synthetic ii) based on their different chromophoric groups which can either be azo, indigoid, cationic

or sulfuric etc , iii) Based on the dye nuclear structure which either be anionic, cationic or non-ionic and iv) Based on industrial classifications which can either be protein textile, cellulose textile or synthetic textile. Table 6 shows different classes of dyes [Zollinger, 2003; Klaus Hunger, Indus. Dyes; Clark, 2011].

Table 6: Showing the various charges and nuclear structure of different dyes

| Dye class | charge | Nuclear structure |
|------------------|-----------------|--------------------------|
| Natural dyes | Mostly Negative | Anionic |
| Acid dyes | Negative | Anionic |
| Basic dyes | Positive | Cationic |
| Disperse dyes | Neutral | Non- ionic |
| Reactive dyes | Negative | Anionic |
| VAT dyes | Positive | Cationic |
| Sulfur dyes | Positive | Cationic |

2.4.2 Disadvantages of Dyes

Based on the recent survey carried out, the high usage of dyes in different fields of life and the fact of most dyes being produced these days are mainly of synthetic origin rather than natural calls for concern. In this regard most dyes produced from synthetic origin like any other chemicals make them similar in their reactions as other chemicals. Therefore due to this, it enables these dyes to have some effects when used [Klaus Hunger, Indus. Dyes; Clark, 2011; Yasmin, 2004];

- Dyes are considered to exhibits a level of toxicity supported by most dyes produced from some carcinogens such benzidine.
- Dye affect biological flow of energy in aquatic environment by preventing the penetration of light through water bodies thereby disrupting photosynthesis process and in addition to this dyes affect microbial and other living organism in water due to their mutagenic and carcinogenic ability.

2.4.3 Different Treatment Technologies for Dye Removal

Treatment of wastewater is a combination process which consists of physical, chemical or biological processes in their reactions. With the presence of more than a hundred thousand commercially available dyes existing alongside a per annum production of more than 7×10^5 tons has led to increased water pollution. Wastewater containing dyes are characterized by persisting organic molecules, resistance to aerobic digestion and stability to light rendering waste water difficult to treat. Thus several techniques have been developed for dye treatment and are classified into three groups; physical, chemical and biological processes [Mondal, 2008; Yasmin, 2004; Wang et al., Houzhong Univ.].

2.4.3.1 Physical Treatment Methods

Different physical methods have been widely used and they include;

2.4.3.1.1 Membrane Filtration Technology

The treatment and reusability of industrial effluents by membrane processes has gained more interest in the last few years due to with high separation efficiency, low energy consumption, easy operation and zero pollution. A membrane is said to be known as a permeable phase that hinders the movement of particular substances. This separation technique has the capability to concentrate and separate dye from effluent. This method is said to generate about 99% of color removal with 85% of salts an original water being reusable [Ahmad et al., 2002]. As of present days this method is mostly used for treatment of dyeing wastewater particularly based on the pressure of the membrane; reverse osmosis, ultrafiltration, nanofiltration and microfiltration [Yasmin, 2004; Ahmad et al., 2002]. Notwithstanding this technology has its limitation due to inability to be used in large scale and more prominently requires special equipments and very expensive to perform [Gregorio, 2006].

2.4.3.1.2 Adsorption

Adsorption is said to be the most widely used process for dye removal. The term adsorption is defined as a process wherein a material is concentrated at a solid interface from its liquid or gaseous surroundings [Guptaa & Suhas, 2009]. Adsorption has been found to be the most used method in physicochemical wastewater treatment thus is said to be preferred to other techniques for water reusability due to its inexpensive nature, flexible, simple design, easy operation, insensitivity to toxic contaminants and does not generate formation of harmful substances [Mondal, 2008; Wang et al., Houzhong Univ; Ahmad et al., 2002].

2.4.3.1.3 Ion Exchange Technique

This technique has been successfully use for color removal. This method is said to be a chemical reversible process where the ion from solution is interchanged with a similar charged ion bound to an immobilized solid particle. This method is use in treatment of drinking water in areas where hardness of water is abundant [Guptaa & Suhas, 2009].

2.4.3.2 Chemical Treatment Methods

Many chemical techniques have been developed for wastewater treatment and this include;

2.4.3.2.1 Adsorption

This process is one of the most widely used techniques for dye treatment by adsorption from wastewater due to its effectiveness for adsorbing cationic and anionic dyes. The advantages of this technique are due its wide surface area, micro-pore structure, high adsorption features and high degree of surface reactivity. But one disadvantage for this method is the inability to use this directly in textile dyeing wastewater treatment due to its high cost of regeneration [Yasmin, 2004; Wang et al., Houzhong Univ].

2.4.3.2.2 Electro-kinetic Coagulation

Coagulation method is mostly used in conventional treatment processes. Coagulation is a process that involves the destabilization of electrostatic actions that exists between reactive molecules of hydrolyzed dyes and water due to the addition of a chemical reagent called coagulant. The main advantage of this method is the efficient removal of insoluble dyes [Mondal, 2008; Guptaa & Suhas, 2009; Khouni et al., 2011].

2.4.3.2.3 Chemical Oxidation Processes

Chemical oxidation is a method wherein wastewater treatment is carried out by use of oxidizing agents such as hydrogen peroxide. These methods are often use in decolorisation processes of effluents since they require low amounts and less reaction times. These methods are generally used to partially or completely eliminate dyes. As of present the commonly used processes for wastewater treatment are; Fenton oxidation, ozone oxidation, photo-catalytic oxidation and electrochemical oxidation.

2.4.3.3 Biological Treatment Methods

These treatment techniques are often economical when compared to other physical and chemical techniques. Biological treatments is mostly based on the use of microorganism and thus has some favorable advantages such as being cheap, effective, ability to produce small amounts of sludge and are environmentally friendly. Nevertheless this treatment method has some drawbacks such as need for a large area, sensitive to diurnal changes as well as toxic nature of some chemicals, simple in design and incapability of getting efficient color removal with current conventional biodegradation methods. In regards to different demands of oxygen, biological treatment methods can be categorized into three different processes that is aerobic, anaerobic and both aerobic – anaerobic treatment [Haresh, 2012; Naresh, 2013].

2.4.3.3.1 Aerobic Treatment Process

This treatment process mostly involves use of activated sludge for treatment of textile dyeing wastewater by microorganisms utilizing dissolved oxygen to convert waste into biomass and CO₂. Under aerobic treatment the use of bacteria and fungi are the group of microorganisms that are mostly investigated because of their remediation of textile and dye wastewater [Wang et al., Houzhong Univ.; Naresh, 2013].

2.4.3.3.1.1 Fungal Decolorisation

The treatment of effluents by use of fungi has been of great researched interest. Various studies for dye treatment by fungi has been carried out and their mechanisms can be examined into three categories; bio-sorption, biodegradation and bio-accumulation; i) Bio-sorption which involves binding of solutes to the biomass by processes which do not involve metabolic energy. ii) Biodegradation which consist of breakdown of dye into different by-products via the action of some enzymes. iii) Bio-accumulation which involves the accumulation of contaminants by active generating cells. This process of treatment have some advantages such as increase in cell to surface ration thereby making this treatment process efficient in physical and enzymatic interaction with the surrounding [Yasmini, 2004; Naresh, 2013; Kaushik & Malik, 2009].

2.4.3.3.1.2 Bacteria Biodegradation

Experiments to isolate bacterial cultures with the ability to degrade dyes began in the 1970s with *Bacillus subtilis*, then *Aeromonas hydrophila*, followed by *Bacillus cereus*. This type of treatment process is said to be faster as compare to fungi treatment. The metabolizing process for dye is mainly by oxidative degradation which is the use of different enzymes from the microorganisms (bacteria). Notwithstanding these microbial systems do have some drawbacks like lack of fermentation reactions, and thus are therefore incapacitated to cope with huge volumes of textile effluents. Current studies

have shown that some bacterial strains can mineralize various dyes under aerobic conditions [Yasmini, 2004; Naresh, 2013].

2.4.3.3.2 Anaerobic Treatment Process

Anaerobic treatments first started in the early 1970s and later further investigated by several other researchers. The potential of anaerobic microorganisms to decolorize dyes by use of sludge is said to be effective and an economic treatment process for removal of textile effluents. This bioremediation process allows for water-soluble dyes to be degraded by an oxidation-reduction reaction with hydrogen. The degradation and decolorisation of these dyes mainly occurs by breaking dyes into amines using strong reduction agents such as sodium hydrosulphite, sodium formaldehyde and sodium borohydride. With anaerobic process, dyes are degraded and converted into aromatic compounds, which may be toxic, mutagenic or carcinogenic to other living organisms and thus a second step of biodegradation is necessary. The stage two mostly consists of conversion of the produced aromatic compounds by aerobic treatment [Naresh, 2013; Myrna et al., 2012].

2.4.3.3.3 Aerobic-anaerobic Treatment Process

Generally bacterial degradation of dyes is performed in two different stages. The stage one involves reductive cleavage of the dyes resulting in generation of colorless aromatic compounds. Stage two comprises of aerobic breakdown process of the aromatic compounds. Thus with some considerations put in place, effluents treatment process involving both anaerobic alongside aerobic treatment and combined is the most acceptable concept for treatment of dyes from wastewater [Nordin et al., 2013; Myrna et al., 2012]

2.5 Adsorption Theory

Adsorption is a process whereby a substance present in a given phase, is displaced from that phase by accumulation at interface between that phase and another phase. In general adsorption occurs at; i) gas to solid interface and ii) liquid to solid interface. The difference between adsorption and absorption; absorption is a process whereby a substance present in one phase is displaced from that phase by dissolution in another phase (liquid phase) as compared to adsorption is the accumulation at interface between one phase and another phase [Mohamed, 2013; Nhatasha, 2006].

2.5.1 Terminologies

Adsorbent

An adsorbent is a substance which is use in the solid phase of adsorption which is porous and characterized with a good surface area that can absorb solutes onto its surface by intermolecular forces.

Adsorbate

This is the solute material present at the liquid/gas phase of the adsorption and is said to be the adsorbed fluid.

2.5.2 Mechanism of Adsorption

Adsorption process proceeds in four stages; i) Bulk diffusion which involves diffusion of the adsorbate to the external surface of the adsorbent particle. ii) Film diffusion involving the movement of the adsorbate through the boundary layer at the adsorption interface. iii) Pore diffusion which involves the migration of the adsorbate from small area of the external surface to the pores within each adsorbent particle. iv) Chemical reaction which comprises of the adhesion of pollutant molecule to the surface in the pore. The retained solute in the sorption processes is called the sorbate, while the solid

on which the solute is bound is called the sorbent. Adsorption process can be classified into two classes; chemisorption and physisorption [Nhatasha, 2006].

2.5.3 Physical Adsorption or Physisorption

This is the adsorption type where the adsorbate adheres to the surface mainly via weak Van Der Waal's intermolecular interactions. This type of adsorption is generally efficient due to the rapid decrease in the quantity of dyes in solution. This process is characterized by varying temperature, type of interaction (Intermolecular weak Van Der Waal's forces), low enthalpy (0-40 KJ/mol) and low activation energy (5-40KJ/mol).

2.5.4 Chemical Adsorption or Chemisorption

Chemical adsorption is an adsorption process whereby a molecule interacts with the surface by adhesion thereby leading to the formation of a chemical covalent bond. This adsorption process is characterized by varying temperatures, kind of interaction that is covalent bonding, high enthalpy (80-400 KJ/mol) and high activation energy (40-800KJ/mol).

2.5.5 Factors Affecting Adsorption

For any process to proceed there must be some factors which will either slow or fasten the rate of that process. As regards to adsorption, the factors affecting this process include:

- Surface area of adsorbent : Larger sizes of an sorbent will lead to increase in adsorption amount of the solute in solution
- Size of adsorbent: Decrease in particle size of adsorbent leads to the increase in the external surface of adsorbent thereby exposing and creating more active sites for the adsorbate to interact.
- Contact time: The longer the time of adsorption process the better complete and efficient the adsorption will be.

- Solubility of adsorbate: Adsorbates partially soluble in water will be easily adsorbed from solution than those with increased solubility. And in addition non-polar substances will be easily adsorbed compared to polar substances due to the great affinity of polar substances for water.
- Affinity of the adsorbate for the adsorbent: Adsorbent will only interact more with solutes of which they have high affinities.
- Number of C-atoms: The larger the number of carbon atoms the lower the polarity and hence a greater potential for being adsorbed.
- Size of the pores: The larger the molecules the difficult it becomes to penetrate the pore thus decreasing sorption.
- Degree of ionization of the adsorbate molecule: Highly ionized molecules are adsorbed to a smaller extent than neutral molecules.
- pH: The extent of ionization of a species is affected by the pH and is best explained by the pH point zero charge of the sorbent used.
- Temperature: Explanation for any given sorption in respect to temperature is based on the information obtained from the enthalpy and entropy changes during adsorption process. But it is better worth noting that the use of any adsorbent for adsorption is based on research work being carried out [Gregorio & Pierre-Marie, 2008; Mohamed, 2013; Nhatasha, 2006].

2.6 Adsorption Equilibrium

On interaction of the adsorbent with wastewater containing absorbable substances, adsorption will occur and will continue until equilibrium is reached between the substance in solution and the substance adsorbed. Therefore at equilibrium a relationship is present between the concentrations of the substance in solution and the “concentrations” of the same species in the sorbed state. And in addition at equilibrium

the amount of dye adsorbed on the adsorbent equals the amount of dye desorbed from the adsorbent.

2.7 Adsorption Isotherms

The adsorption isotherm is an equation relating the amount of solute sorbed onto the solid adsorbent and the equilibrium concentration of the solute in solution at a given temperature;

$$q_e = f(C_e) \quad (1)$$

Where:

q_e = equilibrium concentration of adsorbed dye in solid adsorbent (mg g^{-1})

C_e = equilibrium concentration of adsorbed dye in solution (mg L^{-1})

2.8 Types of Adsorption Isotherms Equations

In general, an adsorption isotherm is a curve describing the phenomenon governing the retention or release or mobility of a substance from the aqueous solid phase at a constant temperature and pH. Adsorption equilibrium which is the ratio between the adsorbed substance to that retained in the solution can only be established when an adsorbate has interacted with the adsorbent for some given period of time, with the adsorbate concentration in bulk solution being in equilibrium with the interface concentration. During the last few years, various equilibrium isotherm models have been formulated such as : Langmuir, Freundlich, Brunauer–Emmett–Teller, Redlich–Peterson, Dubinin–Radushkevich, Temkin, Toth, Koble–Corrigan, Sips, Khan, Hill, Flory–Huggins and Radke–Prausnitz isotherm). These models were deduced based on three fundamental advances which include; i) Kinetic consideration where adsorption and desorption rates are the same. ii) Based on thermodynamics and iii) Based on potential theory which usually transmits the main idea in the plotting of characteristic curve [& Pierre-Marie, 2008; Yuh-Shan et al., 2005; Foo & Hameed, 2010; Desta, 2013; Dada et al., 2012].

2.9 Adsorption Isotherms Based on Wastewater Treatment

There are various models which can be used to determine equilibrium distribution but in the direction of wastewater treatment the function $q_e = f(C_e)$ most commonly take the form of Langmuir or Freundlich isotherm [Yuh-Shan et al., 2005; Desta, 2013].

2.9.1 Langmuir Isotherm

This sorption isotherm was primarily formulated to describe gas to solid phase adsorption onto activated carbon but was later used to quantify and contrast the performance of various bio-sorbents by describing the liquid-solid phase adsorption. This isotherm equation assumes the following for a given sorption process [Yuh-Shan et al., 2005; Foo & Hameed, 2010];

- Monolayer adsorption
- Adsorption is at specific sites
- Adsorbent has a finite capacity for adsorbate
- All sites are identical and energy equivalent
- The adsorbent is structurally homogenous

Langmuir adsorption theory relates rapid decrease of the intermolecular attraction forces to the increase in distance. This model is a two parameter isotherm as depicted by the mathematical expression below;

$$q_e = \frac{Q_o K_L C_e}{1 + K_L C_e} \quad (2)$$

By transforming the above equation into a linearized form gives;

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_o} + \frac{C_e}{Q_o} \quad (3)$$

Where;

C_e = the equilibrium concentration of adsorbate dye in solution (mg L^{-1})

q_e = equilibrium concentration of sorbed dye in solid adsorbent (mg g^{-1}).

Q_0 = maximum adsorption capacity for forming monolayer (mg g^{-1})

K_L = Langmuir constant (L mg^{-1}).

From the Langmuir linear equation a graph of C_e/q_e Vs C_e is deduce with Q_0 and K_L computed from the slope and intercept of the linearized plot.

Important features of the Langmuir isotherm can be shown in terms of an equilibrium parameter R_L , with no dimensions referred to as separation factor.

$$R_L = \frac{1}{1+K_L C_0} \quad (4)$$

Where;

C_0 = initial concentration (mg L^{-1})

K_L = Langmuir constant (L mg^{-1})

R_L shows the sorption nature to be either unfavorable for $R_L > 1$), linear for $R_L = 1$, favorable for $0 < R_L < 1$ and irreversible for $R_L = 0$ [Foo & Hameed, 2010; Gimbert et al., 2008].

2.9.2 Freundlich Isotherm Equation

This isotherm is said to be the earliest formulation explaining the non-ideal and reversible sorption which is not tight down to the formation of monolayer. This equation is typically a two parameter isotherm as shown in its formulated equation below. This model assumes the following;

- Multilayer adsorption
- Adsorption occurs on heterogeneous surfaces
- Adsorption energy decreases exponentially on completion of the adsorption process.

According to history this model was formulated purposely for the adsorption of charcoal [Foo & Hameed, 2010]. Of recent times, Freundlich isotherm is mostly used in heterogeneous medium. The mathematical formulation of this model is given below;

$$q_e = K_f C_e^{1/n} \quad (5)$$

Where;

K_f = Freundlich constant (mg g^{-1}) (L mg^{-1})

n = adsorption intensity;

C_e = equilibrium concentration of adsorbate dye in solution (mg L^{-1})

q_e = equilibrium concentration of adsorbed dye in solid adsorbent (mg g^{-1})

By linearization the equation above becomes;

$$\log q_e = \log K_f + \left(\frac{1}{n}\right) \log C_e \quad (6)$$

By deducing a plot of $\log q_e$ Vs $\log C_e$, the values of K_f and $1/n$ are determined from the intercept and slope. Nevertheless some peculiarities have been observed in this model that is range of slope between 0 and 1 is a determination of adsorption intensity or surface heterogeneity and the heterogeneous nature is said to increase as the value approaches zero and a value below unity indicates a chemisorption process and value of $1/n$ above one indicates physical adsorption [Yuh-Shan et al., 2005; Foo & Hameed, 2010; Desta , 2013; Dada et al., 2012; Gimbert et al ., 2008]

2.10 Kinetic Models of Adsorption

These models are used to correlate the sorbate uptake rate with concentration of the sorbate. The models use to describe the adsorption mechanism include;

2.10.1 Pseudo-first Order Equation

This kinetic equation was first formulated in 1898 by Lagergren and was use to explain the kinetic process of liquid-solid phase adsorption of oxalic acid and malonic acid onto charcoal. As of present years, this equation has been widely applied to explain the adsorption of contaminants from effluents in different fields. The integrated linear mathematical equation is expressed below;

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (7)$$

Where;

q_e = equilibrium concentration of adsorbed dye in solid adsorbent, (mg g⁻¹)

q_t = equilibrium concentration of adsorbed dye at time t, (mg g⁻¹)

k_1 = equilibrium rate constant of pseudo-first equation, (min⁻¹).

Plotting a graph of $\log(q_e - q_t)$ Vs t gives a straight line of which values of q_e and K_1 are determined from the intercept and slope respectively.

2.10.2 Pseudo-second Order Equation

This equation was first explained by Ho in 1995 in the adsorption of divalent metal ions onto peat. The integrated linear equation is depicted as follows;

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (8)$$

Where;

q_e = equilibrium concentration of adsorbed dye in solid adsorbent (mg g⁻¹)

k_2 = equilibrium rate constant of pseudo-second order equation, (g mg⁻¹ min⁻¹).

A graph of t/q_e Vs t can be deduce with values of $1/K_2 q_e^2$ and $1/q_e$ obtained as intercepts and slope [Feng-Chin et al., 2008; Ho & Mckay, 1998; Qiu et al., 2009]. In addition the initial adsorption rate of the adsorption process can be determined by $h_0 = K_2 q_e^2$.

2.10.3 Intra-particle Diffusion Equation

This equation was suggested by Weber and Morris in 1962 which described the fractional advance to equilibrium variance. The formulated equation is shown below;

$$q_t = K_i t^{1/2} \quad (9)$$

Where;

K_i = the intra-particle diffusion rate constant (mg g⁻¹ min^{-1/2})

t = diffusion time ($\text{min}^{-1/2}$)

q_t = equilibrium concentration of adsorbed dye at time t , (mg g^{-1})

A plot of q_t Vs $t^{1/2}$ can be deduce to determine value of K_i . Studies showed that such plots can demonstrate multi-linearity demonstrating that two or more stages occurred. Stage 1 which is the instantaneous adsorption stage, stage 2 gradual adsorption stage, for which the rate of intra-particle diffusion is controlled and stage 3 the equilibrium stage which is the beginning of a decrease for intra-particle diffusion due to very low solute concentrations in solution [Feng-Chin et al., 2001; Ho & Mckay, 1998].

Chapter 3

EXPERIMENTAL

3.1 Apparatus/Materials

A medium molecular weight (Mwt) chitosan (Sigma Aldrich) with molecular formula $C_{12}H_{24}N_2O_9$ and molar mass of 4.0×10^5 was used as starting material. Soluble starch (Merck) with molecular formula $C_6H_{10}O_5$, glutaraldehyde 25wt% (Sigma Aldrich) with molecular formula $OHC(CH_2)_3CHO$ and density of 1.06, glacial acetic acid of 100% purity, C.I. Direct Red 80 with molecular weight of 1373.08 and molecular formula as $C_{45}H_{46}N_{10}Na_6O_{21}S_6$ were used. Instruments such as mechanical stirrer (Heidolph MR Hei-standard), electronic balance, UV-spectrophotometer (T80+ UV/Vis spectrometer) PG instrument Ltd, Perkin Elmer spectrum 65 FT-IR spectrometer and a mechanical agitator were all used.

3.2 Methods

3.2.1 Preparation of Chitosan Solution

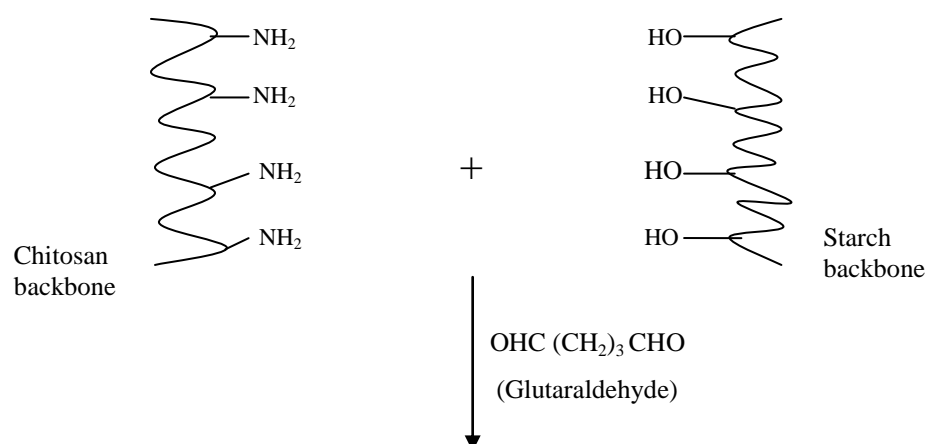
Firstly 2g of chitosan was weighed using an analytical balance and the weighed chitosan was then transferred into a 250mL beaker. Into the beaker containing the weighed chitosan 100mL of 2% v/v acetic acid was added and using mechanical stirrer under magnetic stirring of about 450rpm, the solution was then stirred thoroughly for about 3hrs at room temperature and pressure of 298K to have a homogenous solution and thereby obtaining a 2% w/v chitosan solution.

3.2.2 Preparation of Starch Solution

A weighed amount of 2g of soluble starch was transferred into a 250mL beaker and to it 100mL of distilled water was added. The starch was then dissolved by heating at a temperature between 353K to 363K for a time of 30mins under magnetic stirring to obtain a homogenous and decolorized 2% w/v starch solution.

3.3 Adsorbent Synthesis (Crosslinking Experiment)

The eco-friendly hydrogel was synthesized via chemical crosslinking method. 10mL 2% w/v chitosan solution was collected and mixed with 10mL of 2% w/v starch solution in a 50mL beaker. The solutions were mixed using a magnetic stirrer for about 15mins at 450rpm to obtain a homogenous solution and to the solution was then added 0.4mL of 25% wt glutaraldehyde using a pipette. The solution was then allowed for thorough stirring at 450rpm for crosslinking to occur by observation at different time intervals. The viscosity of the gel gradually increasing due to the crosslinking taking place and at about time of 30mins a solid gel was obtained. The CSH was then used for further investigations. The crosslinking reaction is depicted as shown below;



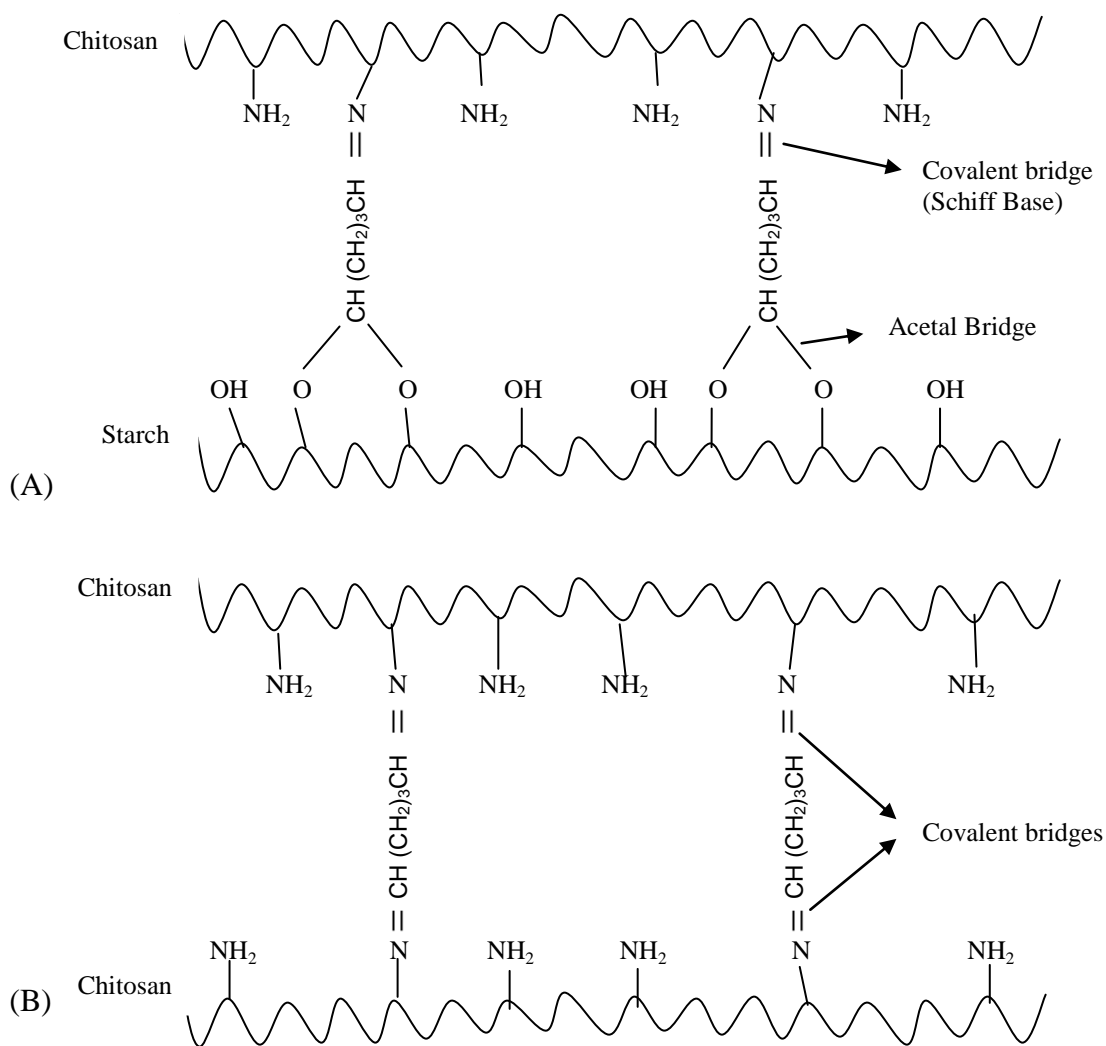


Figure 5: Schematic representation of crosslinking reaction (A) chitosan starch GLA, (B) chitosan-chitosan GLA

3.4 Adsorbate Preparation

Direct Red 80 (DR80) purchased and used without further treatment was prepared by dissolving 0.1g of the dye in 500mL of distilled water to give 200mg/L dye concentration. The working concentrations were gotten by diluting the stock solution accurately to known initial concentrations of 20, 40, 60, and 80, 100mg/L. The physicochemical characteristics of DR80 are illustrated in the table below

Table 7: Physicochemical characteristics of DR80

| Commercial name | IUPAC name | Molecular formula | percent composition | Mwt (g/mol) | λ_{\max} (nm) |
|-----------------|---|-----------------------------------|---|-------------|-----------------------|
| Direct Red 80 | 7,7-(Carbonyldiimino)bis[4-hydroxy-3-[[2-sulfo-4-[(4-sulphophenyl)azo]phenyl]azo]-2-naphthalene sulfonic acid]hexasodium salt | $C_{45}H_{26}N_{10}Na_6O_{21}S_6$ | C= 39.36%, H= 1.91%, N= 10.20%, Na= 10.05%, O= 24.47%, S =14.01% | 1373.08 | 530 |

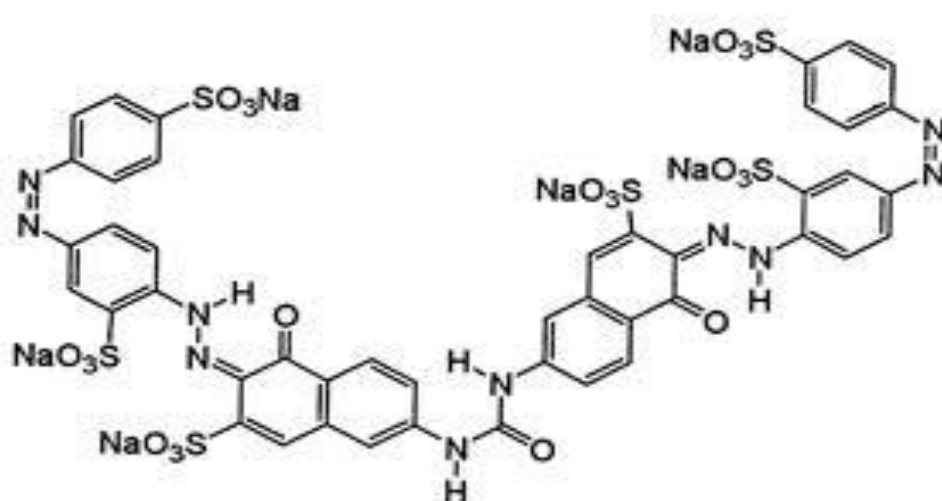


Figure 6: Molecular structure of DR 80 dye

3.5 CSH Characterization

The characterization of the CSH was carried out by using standard protocol of FT-IR spectrophotometer of which powdered samples were prepared into pellets with KBr. The adsorbent was also characterized using UV-Vis spectrophotometer.

3.6 Concentration Determination and Calibration

For determination of concentration of the samples from the experiment carried out, a calibration curve of the DR80 was first prepared. The concentrations were prepared and absorbance was determined using a UV-spectrophotometer (T80+ UV/Vis spectrometer) at λ_{\max} of 530nm. Calibration checks were performed in duplicate and the maximum absorbance of DR80 was plotted Vs concentration.

3.7 Studies on Swelling Behavior of CSH

The swelling of CSH was examined by immersing 1g of wet synthesized CSH into 100mL of distilled water and another 1g into a 100mL of dye solution of concentration 80mg/L at 298K. At given time intervals the swollen hydrogels were withdrawn from the beaker and the excess water and dye solution were eliminated using filter tissue. The samples were weighed and immersed into the beakers as many times as possible still an equilibrium swelling was attained (the point at which there is no further absorption), which occurred in less than 2days. After the swelling process the swollen hydrogels were then decantated and later air dried until a constant weight this occurred in 24hrs. The CSH mass increase permitted the calculation of the swelling percentage as shown below:

$$\text{Swelling ratio (\%)} = \frac{W_s - W_d}{W_d} \times 100 \quad (10)$$

Where W_s and W_d are the weights of the swollen gel after given times and dry gel samples respectively.

3.8 Batch Adsorption Analysis

The adsorption investigations were performed by single batch method and the effect of different parameters like sorbent dosage (25mg, 50mg, 75mg), pH (1-10), initial DR80 concentration (20, 60, 100mg/L), temperature (313, 333, 353K) were studied. The adsorption measurements were performed at constant agitation speed of 150rpm by using 200mL conical flasks containing various amounts of CSH with 25mL of DR80 solution known concentrations at 298K. The pH of the solution was fixed to the desired value by addition of small amount of 1M HCL or 1M NaOH. The flasks were shaken for various time intervals to allow for adequate contact time for equilibrium to be established between the CSH and the DR80 solution. The absorbance of the samples was observed and established at known time intervals to determine the residual DR80 concentration

using UV-Vis spectrophotometer at λ_{\max} of 530nm. The quantity of DR80 absorbed at equilibrium was then solved using the following equation;

$$q_e = (C_i - C_e) \frac{V}{W} \quad (11)$$

Where q_e is the DR80 concentration in adsorbent at equilibrium, C_i initial concentration of DR80, C_e equilibrium concentrations of DR80 in liquid phase, V volume of DR80 solution and W weight of the CSH. The percentage of DR80 removal was calculated as follows;

$$\text{Removal \%} = \left(\frac{C_i - C_e}{C_i} \right) 100 \quad (12)$$

Where C_i is the initial concentration of DR80 and C_e is the concentration of DR80 at equilibrium at time t . However the obtained adsorption data and contact time of the DR80 adsorption onto CSH were used in testing the use of the kinetic model equations and the two-parameter equilibrium isotherms such as Langmuir and Freundlich isotherms.

$$q_e = \frac{Q_o K_L C_e}{1 + K_L C_e} \dots\dots\dots (\text{Langmuir equation}) \quad (13)$$

$$q_e = K_f C_e^{1/n} \dots\dots\dots (\text{Freundlich equation}) \quad (14)$$

The Freundlich isotherm is suitable for heterogeneous adsorbent surface with a non-uniformity distribution of heat of sorption across the given surface while the Langmuir isotherm makes assumptions that the adsorption occurs at specific homogeneous active sites within the adsorbent.

The effect of varying conditions such as dosage, concentration, pH, time and temperature on CSH swelling feature was also investigated. During investigation studies, the other

varying conditions were kept constant while studying one factor. Kinetic adsorption of DR80 solution for the CSH was also investigated using various kinetic equations as shown below;

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \dots \text{(Pseudo-first order rate equation)} \quad (15)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \dots \text{(Pseudo-second order rate equation)} \quad (16)$$

$$q_t = K_i t^{0.5} + C \dots \text{(Intra-particle diffusion equation)} \quad (17)$$

Where: q_e = equilibrium concentration of DR80 adsorbed in solid adsorbent (mg g^{-1})

q_t = equilibrium concentration of DR80 adsorbed at time t (mg g^{-1})

k_1 = equilibrium rate constant of pseudo-first equation (min^{-1})

t = time take for DR80 to be adsorbed (mins)

k_2 = equilibrium rate constant of pseudo-second order sorption, ($\text{g mg}^{-1} \text{min}^{-1}$)

k_i = intra-particle diffusion rate constant, ($\text{mg g}^{-1} \text{min}^{-1/2}$)

C = boundary layer effect.

3.9 Error Analysis

The evaluation of the best fit for which isotherms to the obtained experimental equilibrium values in this present work was done by statistical error functions to determine the most convenient kinetic and isotherm equation to represent the experimental data using the linearized correlation coefficient R^2 . The closer the value of R^2 to unity the more confident and favorable the experimental data is considered.

Chapter 4

RESULTS AND DISCUSSION

4.1 Characterization of Samples

4.1.1 FT-IR Spectroscopy

Prepared cross linked Chitosan-starch blend was analyzed by FT-IR in the wavelength between 4000cm^{-1} and 400cm^{-1} and was carried out in solid state using KBr pellets. The CSH samples were pulverized in an agate mortar and homogenized with KBr followed by pressing the mixture in a hydraulic press to cast pellets thin thickness then Perkin-Elmer spectrophotometer was used for the FT-IR studies.

For the IR spectrum of pure chitosan, the bands appearing between the range of 3750 cm^{-1} to 3000 cm^{-1} are due to OH groups stretching vibrations, the band at 2884 cm^{-1} indicate stretching vibrations of NH and CH bonds in $-\text{CH}_2$ and $-\text{CH}_3$ groups. The band at 2124 cm^{-1} is related to CH stretching vibrations. The bands between the range of $1680-1480\text{ cm}^{-1}$ describe vibrations of C-O bonds of the amide group RNHCO (secondary amide at 1657 cm^{-1}). Bending vibrational stretch of $-\text{CH}_2$ and $-\text{CH}_3$ groups were attributed to the bands formed at 1421 cm^{-1} , 1385cm^{-1} and 1327 cm^{-1} . The absorption bands in the range 1160 cm^{-1} to 1000 cm^{-1} are related to stretching vibrations of C-O groups. The small peaks at 895 cm^{-1} and 620 cm^{-1} relates to wagging of the polysaccharide morphology of chitosan.

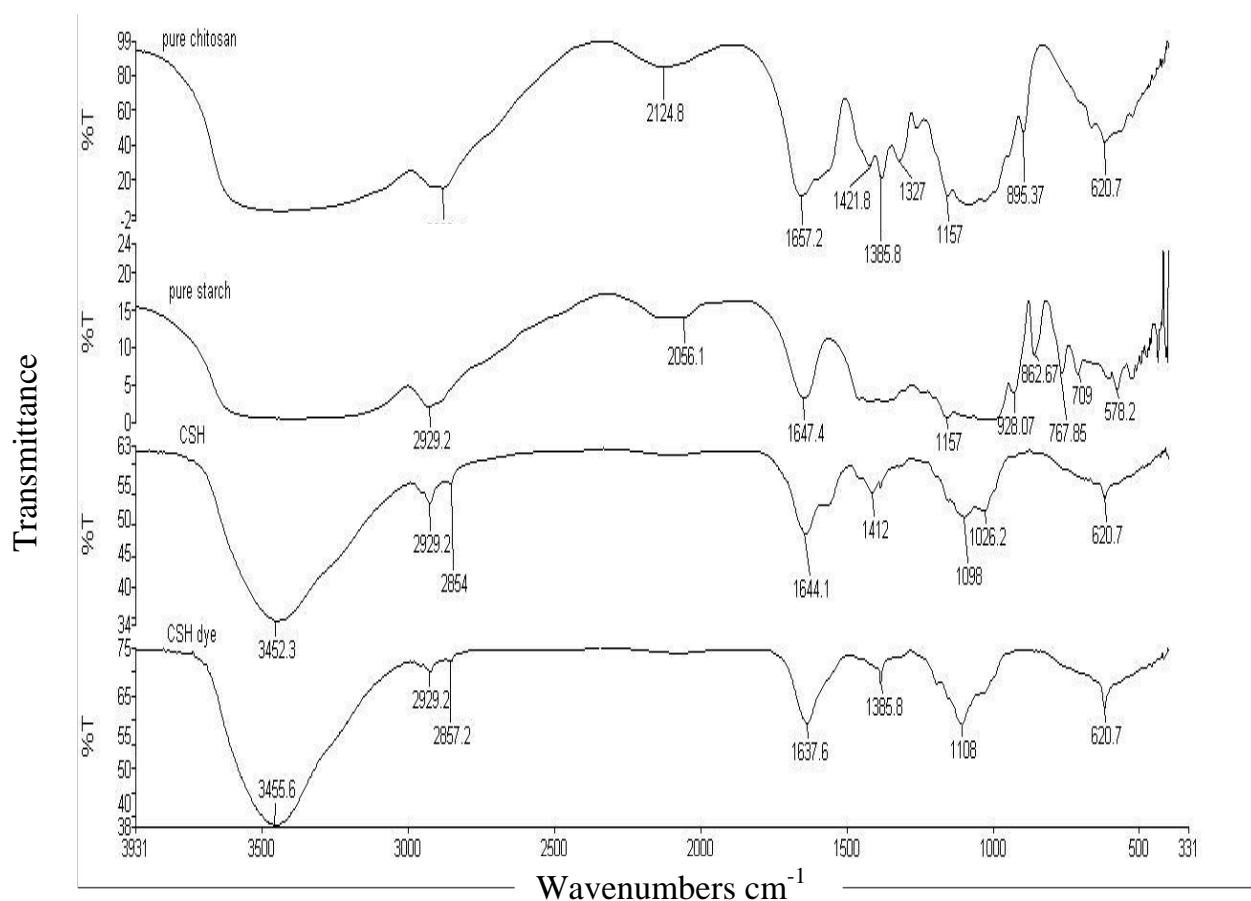


Figure 7: FT-IR spectrum of pure chitosan, pure starch, CSH and CSH dye

As for the IR spectrum of pure starch, the wide band range from 3670 cm^{-1} to 3348 cm^{-1} is ascribed to the O-H stretching of amylose due to the forming of inter and intra-molecular H-bonds. Band at 2929 cm^{-1} relates to asymmetric stretching of CH bond and the band at 2056 cm^{-1} which is attributed to symmetrical stretching of $-\text{CH}_2$ group while the band at 1647 cm^{-1} is ascribed to OH bending vibration showing water adsorbed in the amorphous part of starch. Band at 1157 cm^{-1} relates to the C-O vibrations within the anhydroglucose ring. The bands at 928 cm^{-1} , 862 cm^{-1} , 767 cm^{-1} , 709 cm^{-1} and 578 cm^{-1} C-H bending of starch in the benzene ring.

As regards to the IR spectrum of the crosslinked CSH with GLA, the peak band at 3452 cm^{-1} is ascribed to O-H stretching in the crosslinked CSH. Bands at 2929 cm^{-1} and 2854 cm^{-1} are ascribed to the C-H vibrations of $-\text{CH}_2$ and $-\text{CH}_3$ groups. Shift of peaks from

the parent polymers 1657 cm^{-1} (pure chitosan) to 1644 cm^{-1} is due to C=N stretching vibrations of schiff's base. Band 1412 cm^{-1} relates the -CH bending of -CH₂ in glutaraldehyde. Band at 1098 cm^{-1} and 1026 cm^{-1} represents C-O-C and C-H bending in the CSH structure. In Comparison of the IR spectrum of CSH and that of CSH-dye, there is a decrease in intensity of the bands 2929 cm^{-1} and 2854 cm^{-1} in CSH to CSH dye and a decrease in bands at 1644 cm^{-1} in CSH to 1637 cm^{-1} in CSH dye and a decrease from 1412 cm^{-1} in CSH to 1385 cm^{-1} in CSH dye. All these decreases are due to the adsorption of DR80 onto adsorbent and thus an interaction between the N-H, C-H, C=C and C-O groups of the adsorbent and DR80. But there is an increase from the band of 1098 cm^{-1} in CSH to 1108 cm^{-1} in CSH dye.

4.1.2 pH point Zero Charge (pH_{pzc}) Analysis

To better understand adsorption mechanism, is important to determine the pH point of zero charge of adsorbent. The pH at point zero charge (pH_{pzc}) of CSH was investigated by pH drift equilibrium technique. A pH solution (50mL) of 0.01 M NaCl was used and was altered between 1 and 10 by addition of small amounts of either 1M HCl or NaOH solution. To the prepared pH solution 50mg of the adsorbent was added. After 24hrs, when the pH stability was attained, the final pH was taken. Plots of the final pH and initial pH were used to calculate the point at which the initial and final pH intersects. This point of intersection is the point taken to be the pH_{pzc} of the adsorbent. The pH_{pzc} of CSH was found to be 3.5. At any pH below this point the surface of the adsorbent becomes positively charged, which enhances the sorption of negatively charged dye anions (DR80) via the electrostatic force of attraction.

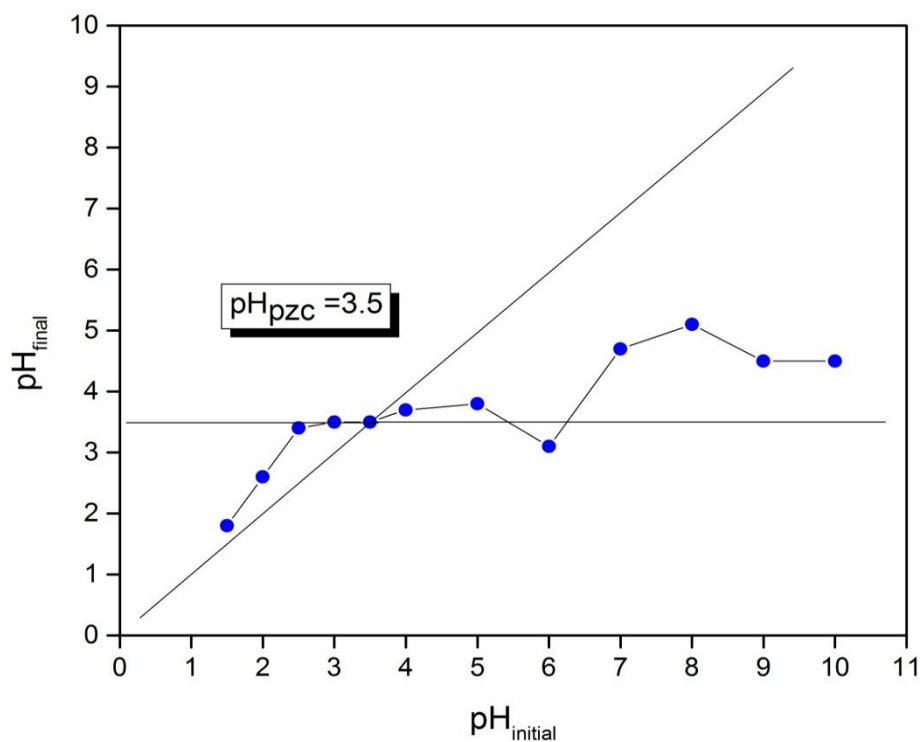


Figure 8: Determinations of pH_{pzc} of CSH by the pH drift method

4.1.3 Swelling Behavior of CSH

Some factors do affect the swelling behavior of SAHs and these factors may include; immersion time, composition of polymers, swelling medium of sorbent specific size area, crosslinking percentage and other chemical conditions.

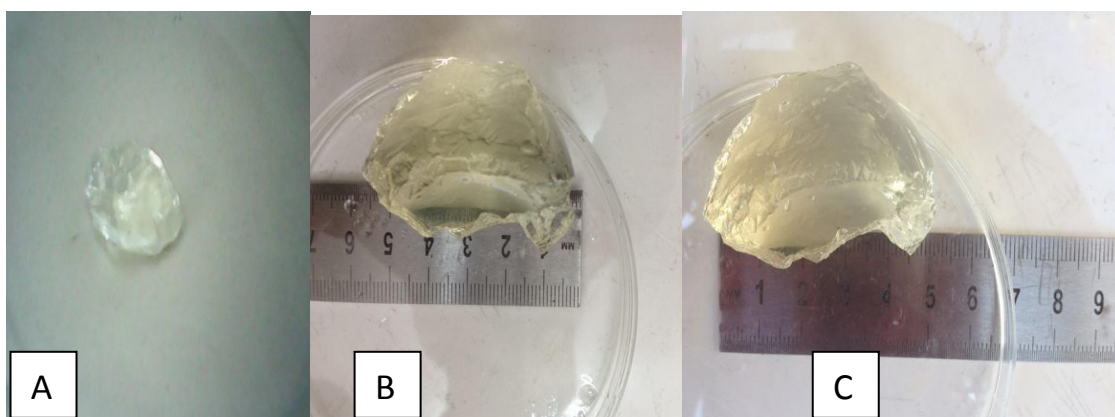


Figure 9: Photos of CSH (A) wet hydrogel before immersion in water, (B) and (C) swollen hydrogel

4.1.4 Swelling Kinetics of CSH in Water and Dye

Swelling behavior of CSH was investigated both in water and DR80 solutions with immersion of 1g of wet CSH in two different beakers. This immersion process was performed for 1560 minutes and the data collected at different time intervals are given in table 8 below.

Swelling of CSH in both water and DR80 increased at a fast rate up to 480 minutes. After this time it was observed that the uptake of CSH in both water and DR80 increased but with more contact time needed and at this point the CSH reached a state of equilibrium. The highest swelling percentages of CSH for both water and DR80 was 80000 % (800.0g/g) and 28250% (282.5g/g) respectively. This large amount of swelling is because of the hydrophilic nature of the CSH chains and its good water holding ability. This feature can be attributed to weakening of H-bonds due to dissolving of the starch in the blend polymer when immersed in solution.

Table 8: Swelling data of CSH in water and DR80

| Swelling Medium | Mass of wet CSH used (g) | Dry weight of CSH (g) | Swollen weight of CSH (g) | Time (mins) | Swelling percentage (%) |
|-----------------|--------------------------|-----------------------|---------------------------|-------------|-------------------------|
| Dye (80mg/L) | 1.00 | 0.02 | 2.61 | 30 | 12950 |
| | | | 3.29 | 60 | 16350 |
| | | | 3.94 | 120 | 19600 |
| | | | 4.48 | 240 | 22300 |
| | | | 4.64 | 360 | 23100 |
| | | | 4.84 | 480 | 24100 |
| | | | 5.05 | 900 | 25150 |
| | | | 5.43 | 1320 | 27050 |
| | | | 5.67 | 1560 | 28250 |
| Water | 1.00 | 0.02 | 2.84 | 30 | 14100 |
| | | | 5.00 | 60 | 24900 |
| | | | 8.19 | 120 | 40850 |
| | | | 10.94 | 240 | 54600 |
| | | | 12.29 | 360 | 61350 |
| | | | 13.32 | 480 | 66500 |
| | | | 14.68 | 900 | 73300 |
| | | | 15.68 | 1320 | 78300 |
| | | | 16.03 | 1560 | 80050 |

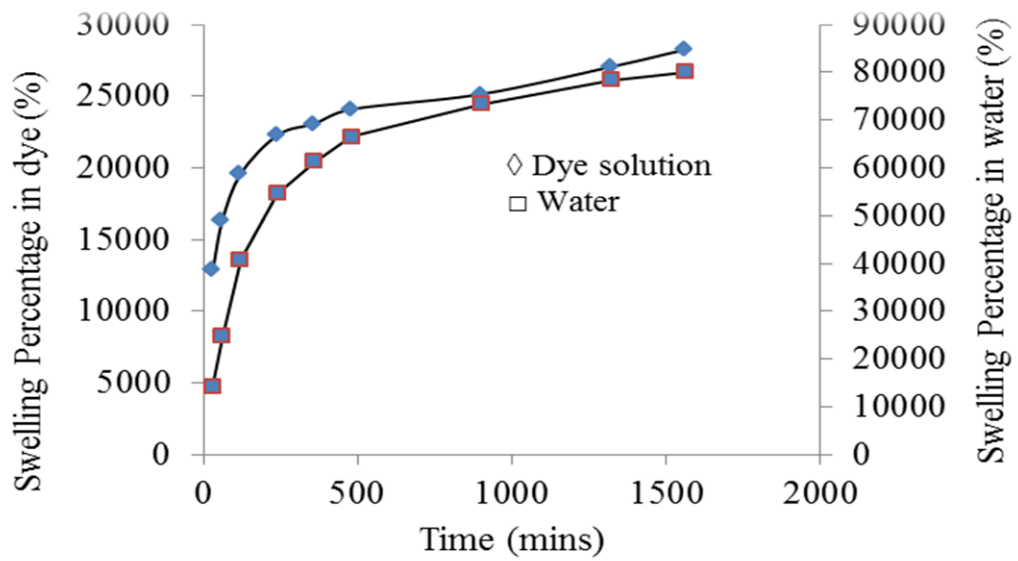


Figure 10: Swelling of CSH in water and DR80 with time

4.1.5 Adsorption Calibration

For the DR80 dye five different concentrations were prepared by correct serial dilution from the stock solution (200mg/L) and absorbance were measured for each dye concentration using the Perkin–Elmer UV-VIS Spectrophotometer. A plot of absorbance (abs) against concentration (mg/L) for the results obtained and the calibration graph is depicted as follows;

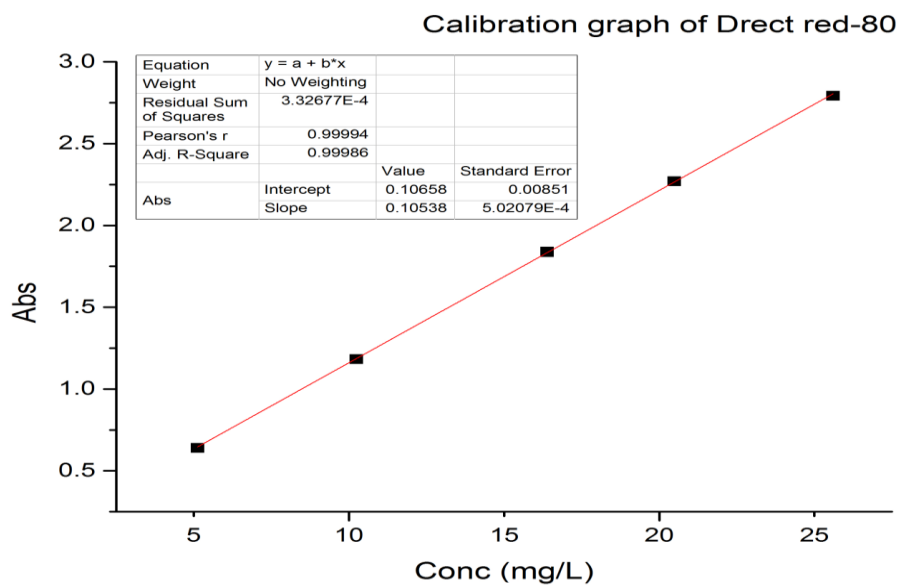


Figure 11: Calibration curve of DR 80

4.1.6 Dye Adsorption Batch Investigation

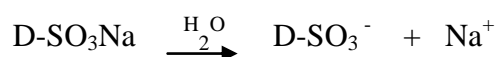
The dye investigation was carried out in an agitator at 150rpm for 15h as explained in section 3.6. The adsorption capacity by the adsorbent after spectrophotometer reading was gotten using the equation below alongside the DR80 solution concentration was determined at wavelength corresponding to the highest absorbance of each DR80 solution.

$$q_e = (C_i - C_e) \frac{V}{W} \quad (19)$$

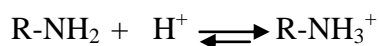
Where q_e is the equilibrium concentration of sorbed DR80 in solid adsorbent, C_i initial DR80 concentration and C_e the equilibrium concentrations of DR80 (mg/L). V which is the volume of DR80 solution (L), and W , the weight of the CSH (g).

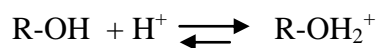
4.1.7 Adsorption Mechanism

As regards the adsorption of acid dyes (DR80) onto the surface of CSH, various mechanisms are taken into considerations such as ionic interaction between anionic sulphonate group(s) of the dissolved DR 80 dye with the protonated amino groups (NH_3^+) of chitosan and protonated hydroxyl groups (OH_2^+) alongside hydrophobic interaction of alkyl groups in CSH. Mechanism of sorption process of CSH and DR 80 dye involves dissolving of DR 80 in aqueous solution and sulphonate groups of DR 80 dye ($\text{D-SO}_3\text{Na}$) are dissociated and changed to anionic dye ions as shown in the chemical equation below;

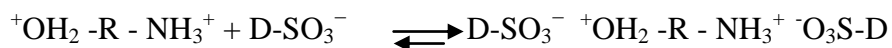


In addition in the presence of excess H^+ , the amino groups of chitosan (R-NH_2) and the hydroxyl groups (R-OH) are protonated.





The adsorption process then proceeds due to electrostatic interaction between the ions in CSH and that in the dye (the counter ions reaction).



In this case the DR 80 is a multivalent dye thus a favorable adsorption capacity is observed for DR 80 which suggests that adsorption takes place close to the outer surface of the CSH and due to the large DR80 ions there is no complete penetration of the dye into the CSH.

4.1.8 Dye Adsorption Studies of CSH

The present study examines the dye uptake capacity with time, variation of concentration, dosage, temperature and pH with time for the CSH.

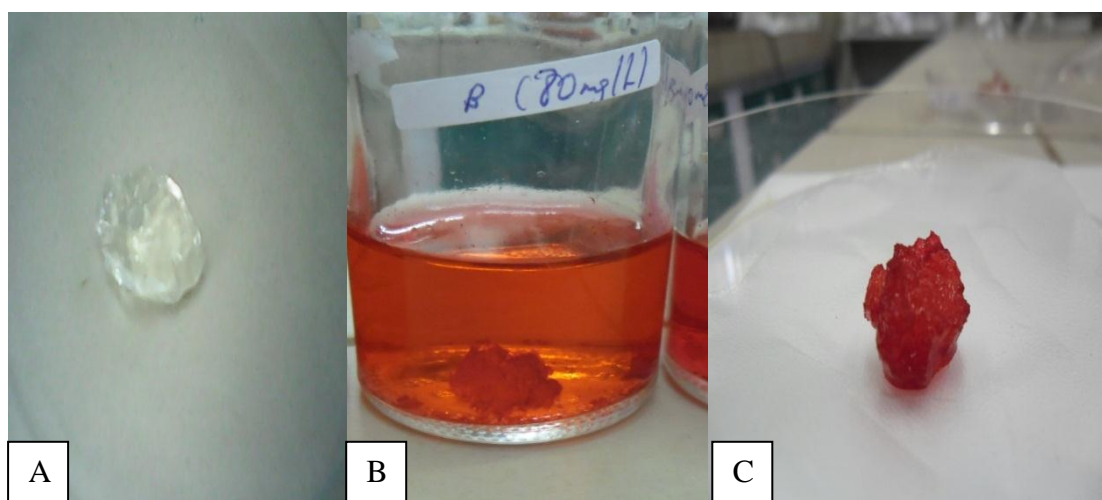


Figure 12: Photos of A) wet hydrogel before dye adsorption B) hydrogel in DR 80 dye solution C) loaded hydrogel with DR 80 dye

4.1.9 Effects of Operational Parameters on DR80 Removal

4.1.9.1 Effect of Initial Concentration on DR80 Adsorption

Higher initial DR80 concentration provides significant driving force to overcome the mass transfer resistances of the DR80 between the aqueous and solid phases, therefore increasing sorption. And in addition, increasing initial DR80 concentration leads to an increase in the collisions between DR80 anions and adsorbent, thereby enhancing the sorption process. Effect of the initial DR80 concentration on the DR80 sorption amount by sorbent was studied for 15h with initial DR80 concentration of 25mL at 20, 60, and 100mg/L, at a constant pH value of 3.0, adsorbent dosage 50mg/L, temperature of 298K and an agitation speed of 150rpm, the results are depicted as shown on the figure below. It is clear in the figure that the percentage of DR 80 dye removal dropped with the increase in initial DR80 concentration. However, the quantity of DR80 sorbed increased with increase in DR80 concentration. The data stipulates that the sorption was highly dependent on the initial DR80 concentration for increasing concentrations.

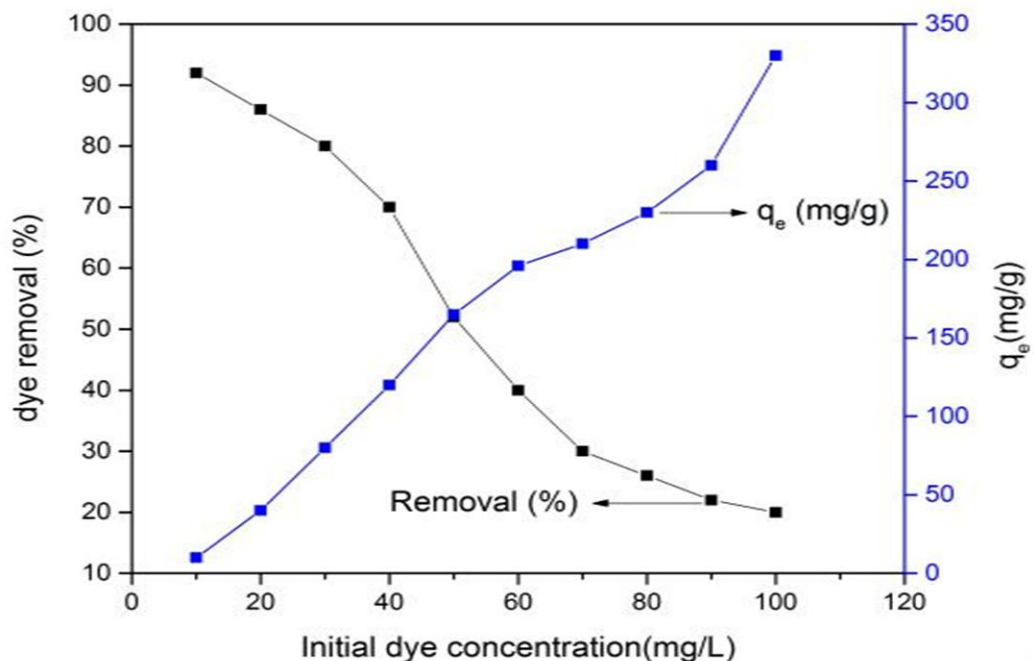


Figure 13: Effect of initial DR80 concentration for the adsorption onto CSH

4.1.9.2 Effect of pH on DR80 Adsorption

The is an important factor because of the dye-binding capacity of each adsorbent. Generally adsorption depends on initial pH and pH point zero charge of the adsorbent (pH_{pzc}). The CSH adsorbent used in this study is a multifunctional adsorbent that containing functional amine and hydroxyl groups and these functional groups are said to be greatly affected by the pH of the DR80 solution. Thus at high acidity, the functional amino and hydroxyl groups of CSH are protonated and due to counter ion reaction the negative ions of the DR 80 are adsorbed by the ion exchange process [Oladipo et al., 2013]. The pH_{pzc} of CSH was investigated by the drift equilibrium method and at this pH_{pzc} , the CSH adsorbent is said to have zero potential charge on its surface therefore below the pH_{pzc} the CSH surface becomes positively charged thereby leading to electrostatic interaction with the negatively charged DR 80 dye.

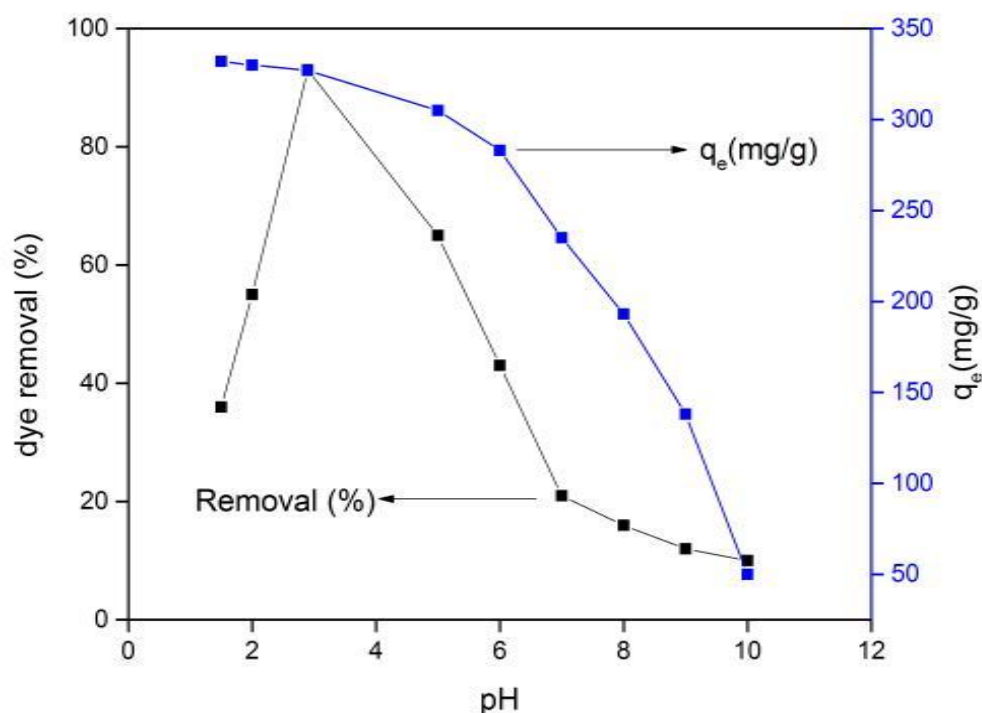


Figure 14: Effect of pH on adsorption capacity of DR 80 onto CSH

The pH_{pzc} of CSH occur at pH 3.5. The figure above shows the equilibrium DR80 sorbed at different initial pH ranging between 1.0 to 10.0 for CSH. For each pH, 25mL of the DR 80 concentration (60mg/L), adsorbent dosage (50mg), temperature (298K) and agitation speed (150rpm) constant. Maximum decolorisation percentage was observed at pH 2.8. The higher sorption capacity of DR80 solution is due to availability of more protonated NH_3^+ and OH^+ thereby increasing binding sites. The sorption capacity of DR80 dropped from 340.86 to 45 mg/g with increase in pH from 2.8 to 10. This is attributed to the increase in the number of negatively charged sorption sites of CSH sorbent thereby leading to an electrostatic repulsion between CSH and DR 80 dye.

4.1.9.3 Effect of Adsorbent Dosage on DR80 Adsorption

Effect of CSH dose (25mg, 50mg, 75mg) on quantity removal of DR 80 dye at steady concentration 25mL of 40mg/L, pH value of 3.0, temperature 30°C and an agitation speed of 150rpm is represented in the figure below. It was noted that the percentage of color removal increased as sorbent dosage increased.

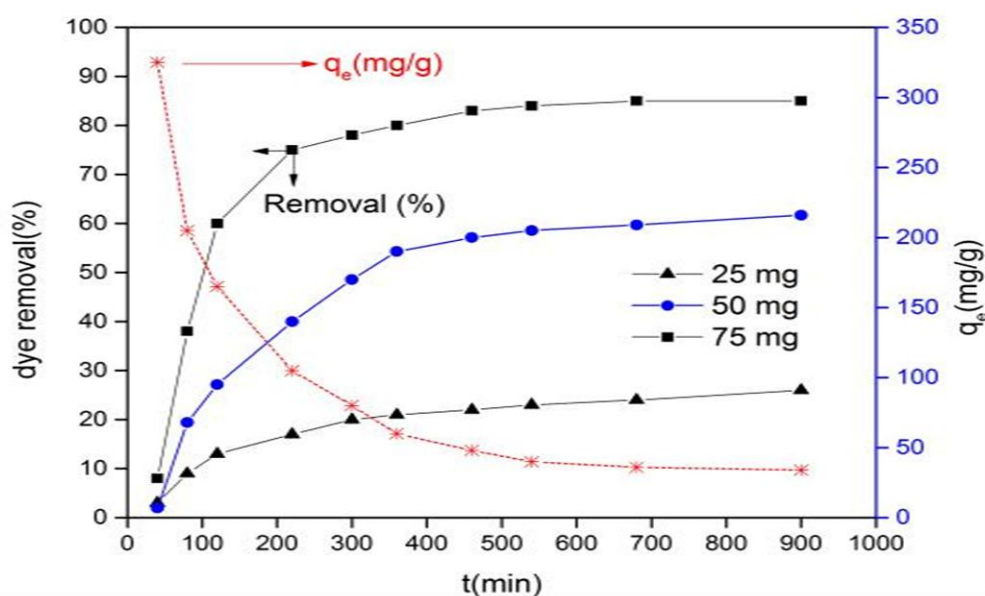


Figure 15: Effect of CSH dose on the adsorption capacity of DR80

It increased from 26.24% to 60.12% after 900 mins of reaction by increasing sorbent dose from 25mg to 50mg. As sorbent dose was further added to 75mg, the percentage of DR80 removal only increased by 24.88%. The graph shows that the quantity of DR80 sorbed decreased from 325.86 mg/g to 34.28 mg/g due to decreased of adsorption sites.

4.1.9.4 Effect of Co-existing Inorganic Salts on Dye Adsorption

Effluents from textile and dyestuff industries do not only comprises of dye but also contains different salts such as phosphates, sulphates and nitrates which are usually present at great levels, resulting in decrease of removal efficiency of the target contaminants. Thus experimental investigations were carried out on the effects of PO_4^{3-} , SO_4^{2-} and NO_3^- on the adsorption of DR 80 onto CSH. The effects of addition of various salts affects a given adsorption process in two different ways [Oladipo et al., 2013]; i) coulombic potential screening amongst the charged adsorbent and adsorbing ions or ii) preferential sorption on the active sites of the given sorbent. In this study, 0.01 M corresponding sodium salts of PO_4^{3-} , SO_4^{2-} and NO_3^- were added into 25mL of DR80 solutions of 60 mg/L at temperature of 298K and agitation speed of 150rpm. As depicted on the figure below, the presence of the inorganic salts drastically reduces the sorption rate of DR80 onto CSH. The inhibition effect can be attributed to the competitive adsorption of inorganic anions with DR80 anions onto the surface of CSH. The influence of phosphate ion was strongest due trivalent negative charges (high ionic strength thus increase in adsorption of the anions onto CSH) followed by the divalent (sulphate ions) and univalent (nitrate ions) anions with less effect. Normally increasing ionic strength will decrease adsorption capacity when the electrostatic interaction between the DR80 ions and CSH surface are attractive and on the other hand adsorption capacity will increase when the electrostatic interaction is repulsive [Yahya et al., 2007, Oladipo et al., 2013].

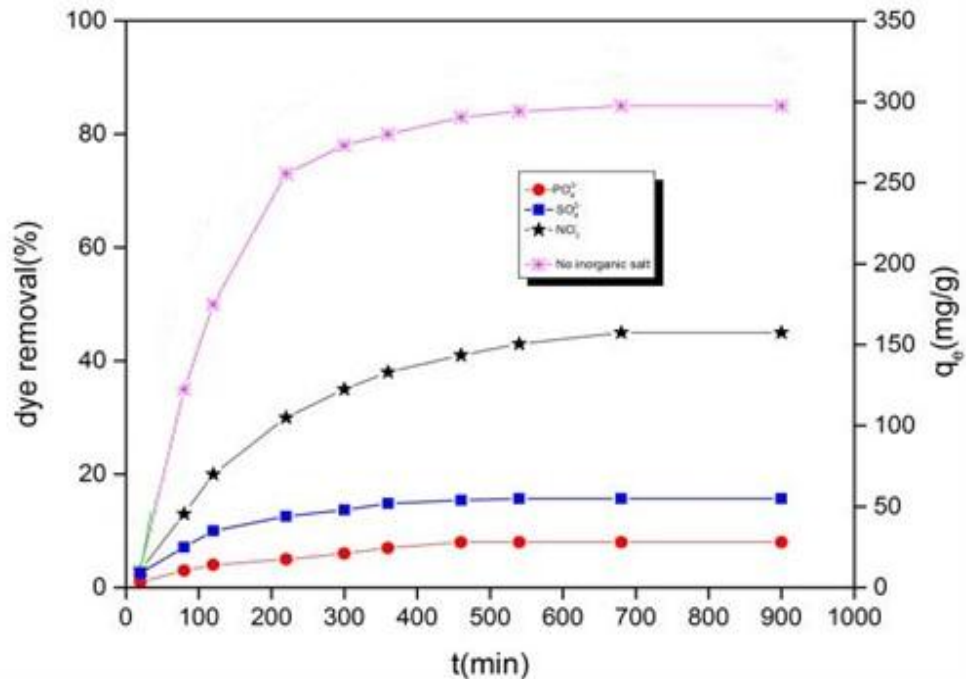


Figure 16: Effect of ionic strength of various anions on adsorption capacity of DR80 onto CSH

4.1.9.5 Effects of temperature on DR80 sorption and Thermodynamic parameters

Effect of temperature on sorption of DR 80 onto CSH was studied at 313 K, 333 K and 353 K at steady DR 80 concentration of 60mg/L, pH 3.0, adsorbent dosage 50mg and 15h of contact time. Data obtained demonstrated that the sorption capacities DR80 increased with increase in temperature, showing that the sorption process is endothermic. This increase in sorption relatively with temperature increased was attributed to the high number of activated sites generated on the CSH as temperature was increasing. As regards to the thermodynamic parameters, they are used in the determination of whether the adsorption process will spontaneously occur.

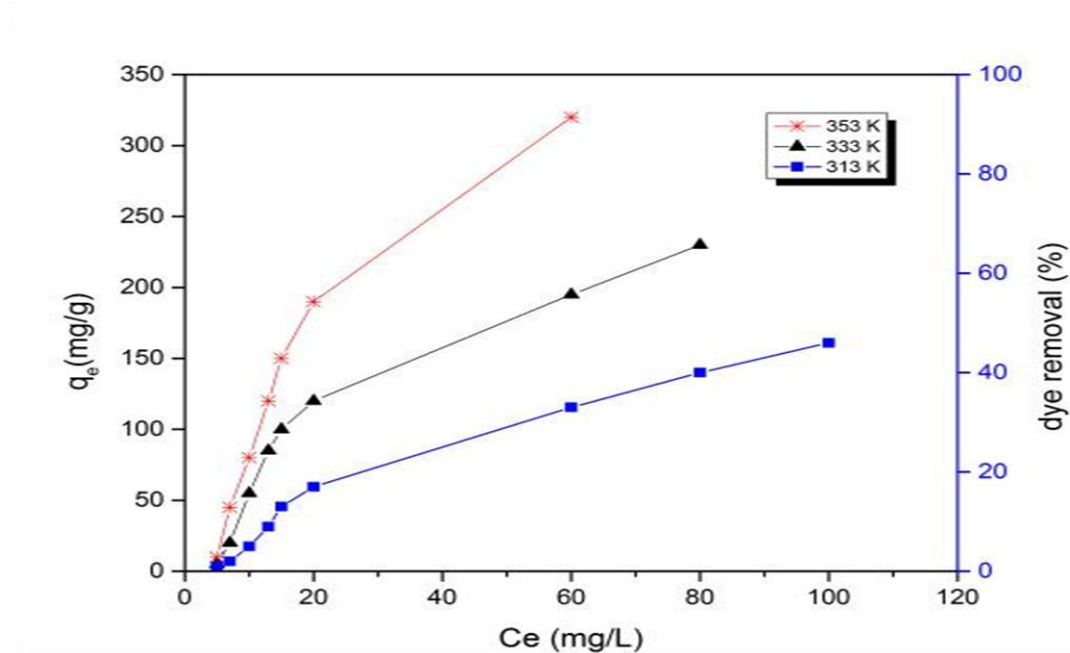


Figure 17: Effect of temperature on the adsorption capacity of DR 80 onto CSH

For equilibrium reactions, K_d , the distribution constant, can be applied to calculate the Gibbs free energy. In addition the thermodynamic behavior of the adsorption of DR 80 onto CSH using the thermodynamic parameters such as free energy ΔG° , enthalpy ΔH° and entropy ΔS° have been use following the equations below;

$$K_d = \frac{q_e}{C_e} \quad (20)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (21)$$

$$\Delta G^\circ = -RT \ln K_d \quad (22)$$

$$\ln K_d = -\frac{\Delta G^\circ}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (23)$$

Where R is the universal gas constant, $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, and T absolute temperature in K. ΔS° and ΔH° were deduced from the slope and intercept of Van't Hoff plot of $\ln K_d$ versus $1/T$, as shown from the plot below.

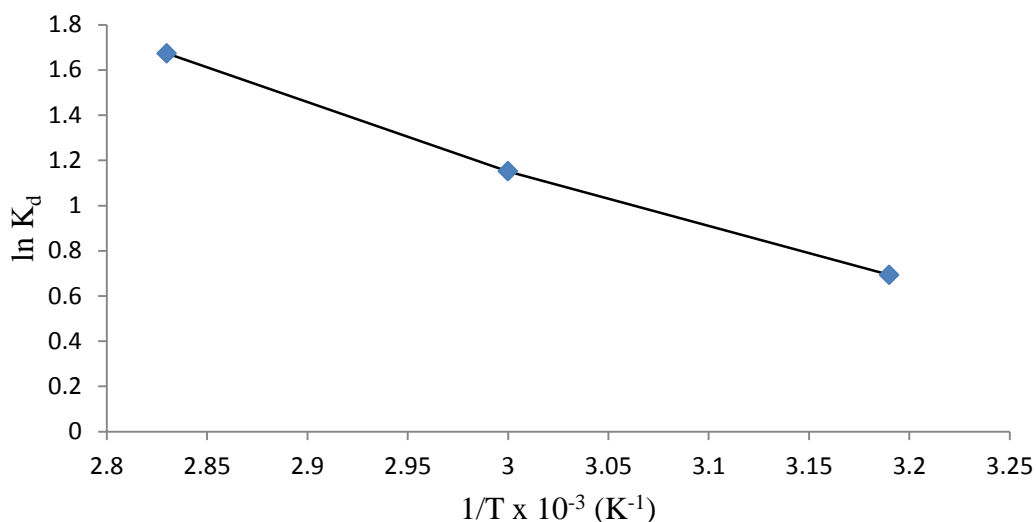


Figure 18: Plot of $\ln K$ versus $1/T$ for determination of thermodynamic parameters.

Values of ΔG° were calculated from the two parameter equation above and the data obtained for all the thermodynamic parameters are given in the table below.

Table 9: Thermodynamic parameter values for adsorption of DR 80 onto

| Acid dye | T (K) | K_s | r^2 | ΔG° (KJmol ⁻¹) | ΔH° (KJmol ⁻¹) | ΔS° (Jmol ⁻¹ K ⁻¹) |
|----------|-------|-------|-------|---|---|--|
| DR80 | 313 | 2884 | 0.982 | -7.15 | 83.68 | 290.19 |
| | 333 | 3602 | 0.979 | -13.01 | | 290.35 |
| | 353 | 4889 | 0.992 | -18.78 | | 290.26 |

The negative data of ΔG° at the various given temperatures on the table above shows that DR 80 adsorption onto CSH indicates a spontaneous process and the mixed adsorbent has good affinity at high temperatures. In addition the decrease in values of ΔG° with increase in the temperature is attributed to a decrease in the spontaneity extent at the various given temperatures Value of standard enthalpy, ΔH° is given as 83.68KJmol⁻¹. This positive ΔH° value indicates that sorption of DR 80 dye onto CSH is an endothermic reaction and thereby shows the affinity of CSH for DR 80. This reaction

is due the available active sites of the sorbent at higher temperatures due to increased surface activity and kinetic energy of the DR80 molecules. Since standard enthalpy changes for physical adsorption is less than 20 KJ/mol, while chemical sorption is in the range between 80-400kJ/mol, studies suggest that the adsorption is chemical sorption. The positive ΔS° values indicates the randomness at the solid–solute interface increases with DR80 sorption onto the adsorbent thereby suggesting suitable affinity of DR80 of adsorbent and indicates some structural alterations in the adsorbate and adsorbent.

4.1.10 Comparative Adsorption of Different Adsorbent for DR80

Comparing the maximum adsorption obtained in this study to other already studied works on this same DR80 dye, it is observed as shown on the table below that CSH demonstrates a better adsorption capacity for DR80 and is better suitable for adsorption of this dye as of different studies carried out on this dye.

Table 10: Comparative adsorption capacities of different adsorbents for DR80

| Adsorbent | Dye | Max.Adsorption capacity (mg/g) | Reference |
|-------------------------------|----------------|--------------------------------|-----------------------|
| CSH | Direct Red 80 | 340.86 | Present study |
| Orange peel | Direct Red 80 | 21.0 | Arami et al. (2005) |
| Soy meal hull | Direct Red 80 | 178.6 | Arami et al. (2006) |
| SA/n-TiO ₂ | Direct Red 80 | 163.9 | Niyaz et al. (2011) |
| Mixture almond shells | Direct Red 80 | 22.422 | Doulati et al. (2007) |
| | Acid Red 18 | 249.87 | |
| Poly(APTAC-co-DMAAm) hydrogel | Acid Yellow 36 | 199.96 | Patel et al. (2013) |
| | Acid Red 73 | 198.16 | |
| m-CS/PVA HBs | Congo Red | 470.1 | Zhu et al. (2012) |
| Chitosan Hydrogel Beads | Crystal violet | 76.9 | Anjali et al. (2013) |

4.1.11 Adsorption Isotherm Models

Freundlich model fit the experimental results well compared to Langmuir equation based on the correlation coefficient (r^2) as indicated in table 11. In all the investigated

temperature it indicated that the CSH surface is majorly made up of heterogeneous sorption sites and less homogenous sorption sites. As indicated in table 11, the values of $1/n$ for all the experimental temperatures were lower than 1 indicating high adsorption intensity. The increasing values of K_f as the temperature increases indicate endothermic adsorption processes while increasing $1/n$ values with temperature suggest reducing adsorption intensity.

Table 11: Isotherm parameters obtained from Freundlich and Langmuir equations.

| <i>Langmuir parameter</i> | T (K) | Q_0 ($mg\ g^{-1}$) | K_L ($L\ mg^{-1}$) | R_L | r^2 |
|-----------------------------|---------|------------------------|---|-------|-------|
| DR80 | 313 | 287.55 | 3.76 | 0.013 | 0.948 |
| | 333 | 303.65 | 3.08 | 0.016 | 0.896 |
| | 353 | 330.86 | 2.38 | 0.021 | 0.935 |
| <i>Freundlich parameter</i> | T (K) | $1/n$ | K_f ($mg\ g^{-1}$) ($L\ mg^{-1}$) | r^2 | |
| DR80 | 313 | 0.345 | 299.54 | 0.994 | |
| | 333 | 0.456 | 310.45 | 0.998 | |
| | 353 | 0.562 | 340.86 | 0.996 | |

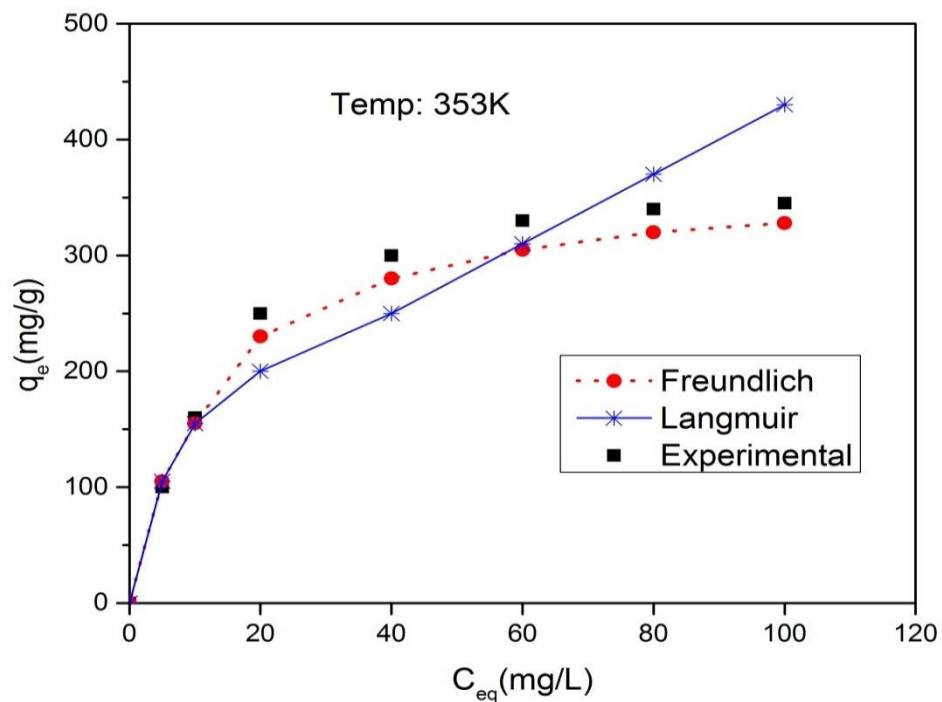


Figure 19: Adsorption isotherm of DR80 at 353K-Freundlich, Langmuir and experimental

4.1.12 Adsorption Kinetics Models

Adsorption rate parameters for DR80 onto CSH were calculated using the mentioned kinetics and the obtained data were utilized to explain the adsorption mechanism. As indicated in table 12, the $q_{e,cal}$ values of pseudo second-order agrees with the $q_{e,exp}$ values and its relatively high r^2 show that the model is suitable to describe DR80 adsorption while the low values of r^2 and the marked difference between the $q_{e,cal}$ and $q_{e,exp}$ show that the pseudo first-order is not suitable to describe DR80 adsorption onto CSH. The kinetic data were fitted to the intra-particle diffusion equation to elucidate the diffusion mechanism of DR80. The intercept (C) of the q_t vs. $t^{1/2}$ plot shows the boundary layer effect. The C values increases with increasing initial DR80 concentration as shown indicating higher contribution of surface adsorption in the rate determining step. Also the linear plot of q_t vs. $t^{1/2}$ (graph not shown) shows that intra-particle diffusion model was not the only rate determining step since the plots do not pass through the origin.

Table 12: Adsorption kinetic parameters of DR80 dye onto CSH

| DR80 Concentration | 20mg/L | 40mg/L | 60mg/L | 80mg/L | 100mg/L |
|--|--------|--------|--------|--------|---------|
| Kinetic model | | | | | |
| <i>Pseudo first-order</i> | | | | | |
| k_1 (min^{-1}) | 0.66 | 0.31 | 0.6 | 0.74 | 1.2 |
| $q_{e,cal}$ (mg g^{-1}) | 110.34 | 145.56 | 198.67 | 232.45 | 216.56 |
| $q_{e,exp}$ (mg g^{-1}) | 174.99 | 198.12 | 266.89 | 290.38 | 312.77 |
| r^2 | 1.000 | 0.978 | 0.985 | 0.988 | 0.968 |
| <i>Pseudo second-order</i> | | | | | |
| k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) | 18.66 | 1.77 | 0.54 | 0.18 | 0.09 |
| $q_{e,cal}$ (mg g^{-1}) | 178.45 | 200.88 | 270.45 | 303.43 | 345.23 |
| $q_{e,exp}$ (mg g^{-1}) | 174.99 | 198.12 | 266.89 | 290.38 | 312.77 |
| r^2 | 1.000 | 1.000 | 0.998 | 0.997 | 0.999 |
| <i>Intra-particle diffusion</i> | | | | | |
| k_{int} ($\text{mg g}^{-1} \text{min}^{-1/2}$) | 4.87 | 10.64 | 14.98 | 17.54 | 11.75 |
| C (mg g^{-1}) | 187.67 | 205.56 | 245.89 | 198.78 | 239.67 |
| r^2 | 0.959 | 0.999 | 0.987 | 0.923 | 0.897 |

Chapter 5

CONCLUSION

In this study, the performance of CSH as a sorbent to remove DR80 from aqueous medium was investigated. Characterization of CSH adsorbent has been studied using the FT-IR technique and in addition adsorption equilibrium isotherms, kinetic studies and optimization were carried out experimentally and analyzed, the following were obtained;

- The CSH adsorbent demonstrated a high capacity of DR80 removal from aqueous medium in the batch sorption process.
- The Freundlich isotherm was proof to provide the best correlation for the adsorption of DR80 onto CSH because of the heterogeneous sorption capacity depicted by this isotherm.
- The batch studies illustrated that the kinetics of the sorption process was well explained by the pseudo-second order equation in the temperature ranges investigated.
- The data that depended on temperature demonstrated that the sorption process was spontaneous and endothermic due to the ΔG° and ΔH° values obtained.

In addition the sorption process was observed to be a chemical sorption due to the value of ΔH° obtained from the experiment. In conclusion, the adsorbent used in this study is an economic, non-toxic, efficient, eco-friendly material and an alternative to more expensive sorbents for the treatment of acidic dyes from aqueous media.

REFERENCES

Pourjavadi A., Soleyman R., Bardajee G.R., Ghavami S. (2009). Novel Superabsorbent Hydrogel Based on Natural Hybrid Backbone: Optimized Synthesis and its Swelling Behavior. *Bull. Korean Chem. Soc*, 30(11).

Kolybaba M., Tabil L.G., Panigrahi S., Crerar W.J., Powell T., Wang B. (2003). Biodegradable Polymers: Past, Present, and Future, *The society of Engineering in Agriculture, Food and Biological systems*, Paper number: RRV03-0007.

Patel M., Bastioli C., Marini L., Dipl. Würd-inger E., Environmental assessment of bio-based polymers and natural fibres.

Bechtolda T., Turcanua A., Ganglbergerb E., Geissler S. (2003). Natural dyes in modern textile dye houses: how to combine experiences of two centuries to meet the demands of the future, *Journal of Cleaner Production*, 11, 499–509.

Sadeghi M., Soleimani F.(2011). Synthesis of Novel Polysaccharide-Based Superabsorbent Hydrogels Via Graft Copolymerization of Vinylic Monomers onto Kappa-Carrageenan, *International Journal of Chemical Engineering and Applications*, 2(5).

Mondal S. (2008). Methods of Dye Removal from Dye House Effluent: An Overview, *Environmental Engineering Science*, 25(3), DOI: 10.1089/ees.2007.0049.

Sharm S. K., Sanghi R. (2012). *Advances in water treatment and pollution prevention*, www. Springer.com.

Rangabhashiyam S., Anu N., Selvaraju N. (2013). Sequestration of dye from textile industry wastewater using agricultural waste products as adsorbents, *Journal of Environmental Chemical Engineering*.

Olapido, A. A. (2011). Synthesis and Characterization of Modified Chitosan-based Novel Superabsorbent hydrogel Swelling and Dye Adsorption behavior. Eastern Mediterranean University, Gazimagusa, North Cyprus.

Miroslava V., Vitale K., Gallios G.P., Lucia I. (2008). Water treatment technologies for removal of high toxicity pollutants, *NATO science for peace and security C: Environmental security*.

Sharma P., Kaur H., Sharma M., Sahore V. (2011). A review on applicability of naturally available adsorbents for the removal of hazardous dyes from aqueous waste, *Environ Monit Assess*, 183,151–195, DOI 10.1007/s10661-011-1914-0.

Ozdemir U., Ozbay I., Ozbay B., Veli S. (2013). Application of economical models for dye removal from aqueous solutions: cash flow, cost–benefit, and alternative selection methods, *Clean Techn Environ Policy*, DOI 10.1007/s10098-013-0638-y.

Sannino A., Demitri C., Madaghiele M. (2009). Biodegradable Cellulose-based Hydrogels: Design and Applications, *Materials*, 2, 353-373, doi:10.3390/ma2020353.

Wanga W., Wang A. (2010). Synthesis and swelling properties of pH-sensitive semi-IPN superabsorbent hydrogels based on sodium alginate-g-poly (sodium acrylate) and polyvinylpyrrolidone, *Carbohydrate Polymers*, 80, 1028–1036.

Saber-Samandari S. Gazi M. Yilmaz E. (2012). UV-induced synthesis of chitosan-g-polyacrylamide semi-IPN superabsorbent hydrogels, *Polym. Bull*, 68, 1623–1639, DOI 10.1007/s00289-011-0643-4.

Sadeghi M., Hosseinzadeh H. (2010). Synthesis and super-swelling behavior of a novel low salt-sensitive protein-based superabsorbent hydrogel: collagen-g-poly(AMPS), *Turk. J. Chem* 34, 739 – 752.

Qui Y., Oark K. (2001). Environmental sensitive hydrogels for drug delivery, *Adv. Drug Delivery*, 53, 321.

Hsu-Feng K., Charles S.F., Prashant N.K. (2010). Novel synthesis strategies for natural polymer and composite biomaterials as potential scaffolds for tissue engineering. *Phil. Trans. R. Soc.* 368 (1917), 1981-1997

Syed K. H., Al-Assaf G. S., Phillips G. O. *Hydrogels: Methods of Preparation, Characterisation and Applications*. Glyndwr University, Wrexham, United Kingdom.

Sadeghi, M. and Soleimani, F. (2011). Synthesis of Novel Polysaccharide-Based Superabsorbent Hydro Gels Via Graft Copolymerization of Vinylic Monomers onto Kappa-Carrageenan. *Inter. J. Chem. Eng. and Applications*, 2(5).

Bhatnagar A., Sillanpää M. (2009). Applications of chitin- and chitosan-derivatives for the detoxification of water and wastewater: A short review, *Advances in Colloid and Interface Science*, 152, 26–38.

Ekebafé L. O., Ogbeifun D. E., Okieimen F.E. (2011). Polymer Applications in Agriculture, 23(2), 81 – 89.

Malik P. K. (2004). Dye removal from wastewater using activated carbon developed from sawdust: adsorption equilibrium and kinetics, *J. Hazardous Materials*, B113, 81-88.

Harish K. V., Tharanathan R. N. (2007). Chitin/chitosan: modifications and their unlimited application potential: An overview, *Trends in Food Sci. & Tech*, 18, 117-131.

Gregorio C., Pierre-Marie B. (2008). Application of chitosan, a natural aminopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: A review of recent literature, *Prog. Polym. Sci.* 33, 399–447.

Anwunobi A. P., Emeje M O. (2011). Recent Applications of Natural Polymers in Nano-drug Delivery. *J. Nanomedic Nanotechnol.* S4:002. doi:10.4172/2157-7439.S4-002

Yogeshkumar N.G., Gurav A. S., Yadav A.V. (2013). Chitosan and Its Applications: A Review of Literature, *Inter. J. Res. Pharm. and Biomed. Sci*,4(1)

Fernandez-Kim S. O. (2004). Physicochemical and functional properties of crawfish chitosan as affected by different processing protocols, Louisiana State University.

Zohuriaan-Mehr M. J., Kabiri K. (2008). Superabsorbent Polymer Materials: A Review, *Iranian Polymer Journal*, 17 (6), 451-477.

Lu D. R., Xiao C. M., Xu S. J. (2009). Starch-based completely biodegradable polymer materials, *eXPRESS Polymer Letters*, 3(6), 366–375

Pradip K. D., Joydeep D., Tripathi V. S. (2004). Chitin and Chitosan: Chemistry, properties and applications, *J. of Scientific and Indus. Res.* 63, 20-31.

Sugih A. K. (2008). Synthesis and properties of starch based materials, University of Groningen.

Luc Averous, Agro polymers and starch based materials.

www.biodeg.net/biomaterial.html.

Luc Avérous and Eric Pollet, Biodegradable Polymers.

www.springer.com/cda/content/.../cda.../9781447141013-c2.pdf

Wanek W., Heintel S., Richter A. (2001). Preparation of starch and other carbon fractions from higher plant leaves for stable carbon isotope analysis, *Rapid Commun Mass Spectrum*, 15, 1136-1140.

Binti Hassan N. A. (2010). Color stability of natural colorant in Turmeric, University of Malaysia.

Zollinger H. (2003). Color Chemistry “Synthesis, properties and applications of organic dyes and pigments”: Third edition revised version. ISBN-10: 3906390233 | ISBN-13: 978-3906390239

Klaus Hunger, (2004). Industrial dyes: Chemistry, properties and applications. ISBN: 9783527304264

Clark M. (2011). Handbook of textile and industrial dyeing: Principles, processes and types of dyes, Vol. 1. ISBN: 978-1845696955

Yasmin Binti C. A. (2004). Adsorption studies of dyes using clay-based and activated carbon adsorbents, University of Sains Malaysia.

Lu-E S., Zhen-Xing T. (2009). Absorption of Nuclease P1 on Chitosan nano-particles, *Braz. J. Chem .Eng*, 26(2).

Gregorio Crini, (2005). Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment, *Prog. Polym. Sci.* 30, 38–70.

Suyamboo B. K., Perumal R. S. (2012). Equilibrium, Thermodynamic and Kinetic Studies on Adsorption of a Basic Dye by Citrullus Lanatus Rind, *Iranica Journal of Energy & Environment*, 3 (1), 23-34, DOI: 10.5829/idosi.ijee.2012.03.01.0130.

Wang Z., Xue M., Huang K., Liu Z. Textile Dyeing Wastewater Treatment, Huazhong University of Science and Technology China.

Ahmad A. L., Harris W. A., Syafiie, Seng O. B. (2002). Removal of dye from wastewater of textile industry using membrane technology, *Journal of Technology*, 36(F), 31–44.

Guptaa V. K., Suhas. (2009). Application of low-cost adsorbents for dye removal: A review, *Journal of Environmental Management*, 90, 2313–2342.

Gregorio Crini. (2006). Non-conventional low-cost adsorbents for dye removal: A review, *Bioresource Technology*, 97, 1061–1085.

Khouni I., Marrot B., Moulinb P., Amar R. B. (2011). Decolorisation of the reconstituted textile effluent by different process treatments: Enzymatic catalysis, coagulation/flocculation and nano-filtration processes, *Desalination*, 268, 27-37.

Kariyajjanavar et al, (2011). Degradation of Textile Wastewater by Electrochemical Method, *Hydrol Current Res*, 2(1).

Nordin N., Amir S. F. M., Riyanto, Othman M. R.(2013). Textile Industries Wastewater Treatment by Electrochemical Oxidation Technique Using Metal Plate, *Int. J. Electrochem. Sci.*, 8, 11403 – 11415.

Naresh B., Jaydip J., Prabhat B., Rajkumar P. (2013). Recent Biological Technologies for Textile Effluent Treatment: A Review, *Int. Res. J. Biological Sci*, 2(6), 77-82.

Kaushik P., Malik A. (2009). Fungal dye decolourization: Recent advances and future potential, *Environment International*, 35, 127–141.

Myrna S., Aida S., Pérez H. I., Manjarrez N., Floresa M. (2012). Microbial decoloration of azo dyes: A review, *Process Biochemistry*, 47, 1723-1748.

Mohamed Nageeb Rashed. (2013). Adsorption Technique for the Removal of Organic Pollutants from Water and Wastewater, DOI:10.5772/54048 <http://dx.doi.org/10.5772/54048>.

Nhatasha binti S. S. J. (2006). Adsorption study – dye removal using clay, University College of Engineering and Technology Malaysia.

Oladipo A. A., Gazi M., Saber-Samandari S. (2013). Adsorption of anthraquinone dye onto eco-friendly semi-IPN biocomposite hydrogel: Equilibrium isotherms, kinetics studies and optimization, *Journal of the Taiwan Institute of Chemical Engineers*.

Yuh-Shan H., Wen-Ta C., Chung-Chi W. (2005). Regression analysis for the sorption isotherms of basic dyes on sugarcane dust, *Bioresource Technology*, 96, 1285–1291.

Foo K. Y., Hameed B.H. (2010). Insights into the modeling of adsorption isotherm systems, *Chem. Eng. J.* 156, 2–10.

Desta M. B. (2013). Batch Sorption Experiments: Langmuir and Freundlich Isotherm Studies for the Adsorption of Textile Metal Ions onto Teff Straw (*Eragrostis tef*) Agricultural Waste, *Journal of Thermodynamics*, [http://dx.doi.org/ 10.1155/ 2013/ 375830](http://dx.doi.org/10.1155/2013/375830).

Dada A.O., Olalekan A.P., Olatunya A.M., DaDa O. (2012). Langmuir, Freundlich, Temkin and Dubinin–Radushkevich Isotherms Studies of Equilibrium Sorption of Zn²⁺ Unto Phosphoric Acid Modified Rice Husk, *Journal of Applied Chemistry*, 3(1), 38-45.

Gimbert F., Morin-Crini N., Renault F., Pierre-Marie B., Grégorio C. (2008). Adsorption isotherm models for dye removal by cationized starch-based material in a single component system: Error analysis, *Journal of Hazardous Materials*, 157, 34–46.

Chan L. S., Cheung W. H., Allen S. J., McKay G. (2012). Error Analysis of Adsorption Isotherm Models for Acid Dyes onto Bamboo Derived Activated Carbon, *Chinese Journal of Chemical Engineering*, 20(3), 535—542.

Feng-Chin W., Ru-Ling T., Ruey-Shin J. (2001). Kinetic modeling of liquid-phase adsorption of reactive dyes and metal ions on chitosan, *Wat. Res.* 35(3), 613–618.

Ho Y. S., Mckay G. (1998). Kinetic models for the sorption of dye from aqueous solution by wood, *Trans IChemE*, Vol 76, Part B.

Qiu et al. (2009). Critical review in adsorption kinetic models, *J Zhejiang Univ Sci A*, 10(5),716-724.