PREPARATION OF COLOR REMOVING CHITOSAN COMPOSITES AND ASSESSMENTS ON ADSORPTION KINETICS

M.Sc. THESIS

Zeynep Ceren BUMİNOĞLU

Department of Polymer Science of Technology

Polymer Science of Technology Programme

Thesis Advisor: Prof. Dr. Nilgün KIZILCAN

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ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

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Zeynep Ceren BUMİNOĞLU
(515111025)

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

**RENK GİDERİCİ ÇİTOSAN KOMPOZİTLERİNİN
HAZIRLANMASI VE
ADSORPSİYON KİNETİĞİ ÇALIŞMALARI**

YÜKSEK LİSANS TEZİ

Zeynep Ceren BUMİNOĞLU
(515111025)

Polimer Bilimi ve Teknolojisi Anabilim Dalı

Polimer Bilimi ve Teknolojisi Programı

Tez Danışmanı: Prof. Dr. Nilgün KIZILCAN

MAYIS 2014

Zeynep Ceren Buminoğlu, a **M.Sc.** student of ITU **Institute of Science and Technology** student ID **515111025**, successfully defended the **thesis** entitled "**PREPARATION OF COLOR REMOVING CHITOSAN COMPOSITES AND ASSESSMENTS ON ADSORPTION KINETICS**", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor :   **Prof. Dr. Nilgün KIZILCAN**   ....
İstanbul Technical University

Jury Members :   **Prof. Dr. Name SURNAME**   ....
Yıldız Technical University

Prof. Dr. Name SURNAME   ....

Prof. Dr. Name SURNAME   ....

Prof. Dr. Name SURNAME   ....

Prof. Dr. Name SURNAME   ....

Date of Submission : 05 May 2014
Date of Defense :   28 May 2014

To my fiance and his unwavering smile,

FOREWORD

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May 2014

Zeynep Ceren BUMİNOĞLU
(Chemical Engineer)

x

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ABBREVIATIONS

CEC	**:** Cation Exchange Capacity
FTIR	**:** Fourier Transform Infrared Spectroscopy
SEM	**:** Scanning Electron Microscope
PVC	**:** Poly(vinyl chloride)
UF	**:** Urea-Formaldehyde
UV	**:** Ultra Violet

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SUMMARY

Many industries like textile, paper, plastic generate considerable amount of waste water since they use excessive amounts of water in their operations and they also use chemicals and colorants to color their products. These waste waters form a significant reason of worldwide water pollution, and if they are released before being treated, they bring an important harm to these waters. There are many studies in literature using modified or pure chitosan that aims for adsorption of dye molecules, detoxification of water and wastewater, and color removal. The objection of this study is the adsorption of textile dyes from water by chitosan derivatives. Chitosan-montmorillonite composites, and composites of Chi-MMT with urea and urea-formaldehyde were formed for this study. Chitosan was modified by mixing chitosan solutions and montmorillonite solutions with magnetic stirrer, washing with distilled water and subsequently drying. Urea-formaldehyde mixture was mixed with Chi-MMT mixture at 80 °C in order to form composites, and afterwards, this mixture was poured onto watch glasses and dried. Dye solutions (Reactive Blue 221, Reactive Red 195 and Reactive Black 5) were prepared in distilled water and sufficient amount of the ground composite flakes and composite films were added to each dye solution for several experiments in order to determine the effect of different conditions on adsorption. Adsorption experiments in different conditions such as different temperature values, different pH values, different amounts of adsorbate, different crosslinking contents were performed, these were compared for best outcome. UV analysis was performed for the assessment of color change in solutions after adsorption and with the help of these analyses adsorption capacities of the composites were determined. Studies on adsorption kinetics were performed by calculating adsorption rate and maximum adsorption capacity of the composites used in every experiment. Furthermore, chitosan derivatives underwent FT-IR analyses for characterization and SEM analyses were performed in order to determine the particle size and structure of the composites.

RENK GİDERİCİ ÇİTOSAN KOMPOZİTLERİNİN HAZIRLANMASI VE ADSORPSİYON KİNETİĞİ ÇALIŞMALARI

ÖZET

Tekstil, kağıt, plastik gibi birçok endüstri oldukça fazla oranda su kullanmaktadır ve ayrıca ürünlerini renklendirmek için kimyasal ve boya kullanmaktadırlar. Sonuç olarak, oldukça fazla oranda atık su üretirler. Bu atık sular dünya çapında su kirlenmesinin önemli bir sebebini oluşturur ve işlem görmeden bertaraf edilirlerse verildikleri sulara çok büyük zarar verirler. Renk, atık suda fark edilen ilk kontaminanttır ve çok küçük miktarda boyanın varlığı bile oldukça görünür ve istenmez bir durumdur. En küçük hacimdeki sıvı atıklar bile yüzey sularının normal olmayan şekilde renklenmesine sebep olabilir, bu durum da suyun netliğini etkiler. Renkli atık suların çevreye salınımı genellikle istenmeyen bir durumdur, fakat bu sadece renklerinden dolayı değildir. Bunun sebebi birçok boya ve bozunma ürününün toksik veya mutajenik etkilere sebep olmasıdır. Bu atık sular bu sebeple insanlar için ve suda yaşayan organizmalar için de tehlike oluşturmaktadır. Boya içeren atık suların işlenmesi çok zordur; zira boyalar inatçı organik moleküller olup ışık, ısı ve oksitleyici ajanlar karşısında stabildir. Toksik atık suları su kirlenmesinin ana sebeplerinden biridir ve işlenmeden bertaraf edilirse atıldıkları sulara önemli zararlar verebilirler. Su kaynaklarının korunabilmesi için atık su konusundaki mevzuatlar giderek daha sıkı hale getirilmektedir. Giderek azalan bu su kaynaklarını koruyabilmek için mevcut durumun daha kötüye gitmemesi amaçlı olarak atık sular üzerine düzenleyici mevzuatlar atık su işlenmesinde daha fazla işlem gerektirmektedir.

Tekstil atık sularındaki artık boyaların çok küçük miktarlarda bile çok fazla renk verebilmekte olması ve atık suyun içindeki güçlü tekstil boyaları yüzünden arıtma işlemi gördükten sonra bile rengini kaybetmemesi, bu konudaki yönetmelikler açısından zorluk oluşturmaktadır. Boyalar kalıcı ve ısrarcı moleküller oldukları için, boya içeren atık suların işlenmesi zor atıklar olduğu bilinir bir durumdur. Bir diğer zorluk da düşük konsantrasyonda boya içeren atık suları arıtmaktır. Bu durumda, yaygın boya giderme yöntemleri ekonomik açıdan tercih edilmeyen veya teknik açıdan zor yöntemlerdir. Eser miktarda safsızlık gidermek için kullanılan yöntemler çok masraflı olduğu için, atık suda boya gidermek için kullanılan birçok yöntem tekstil endüstrisinde büyük çapta kullanılmamaktadır. Pratikte, tek bir yöntem yeterli arıtma sağlayamamakta ve en ekonomik yoldan istenen su kalitesine ulaşmak için farklı proseslerin kombinasyonu kullanılmaktadır. Bu sebeple, endüstriyel kullanımda kabul edilebilir ve etkili olan yeni renk giderme yöntemlerinin geliştirilmesi gerekmektedir.

Düşük masraflı adsorbanlar kullanılarak yapılan adsorpsiyon çalışmaları bu konuda etkili ve ekonomik bir alternatif önermektedir, bu konuda birçok çalışma yapılmaktadır. Adsorpsiyon iyi bilinen bir ayırma işlemidir ve su dekontaminasyonu uygulamalarında etkili bir yöntemdir. Suyun yeniden kullanımında adsorpsiyon

masraf, tasarımın basitliği ve esnekliği, işlem kolaylığı, yüksek kapasiteye sahip olması ve toksik kontaminanlardan etkilenmeme açısından diğer tekniklerden daha iyi durumdadır. Adsorpsiyon ayrıca zararlı maddelerin oluşumuna da sebep olmamaktadır.

Adsorbanlar öncelikle sıvıdan bileşenleri giderebilecek derecede geniş iç hacme sahip olmalıdır. Bu şekilde gözenekli katı yapılar karbonlu veya inorganik olabilir, bazı durumlardaysa gerçek moleküler eleme özelliklerine sahip olabilir. Adsorbanlar dayanıklı olabilmek ve adsorbatları hızlı şekilde aktarabilmek için iyi mekanik ve kinetik özelliklere de sahip olmalıdır. Adsorbanları kullandıktan sonra yeniden kazanabilmek ekonomik ve idealdir, bu durumda yeniden kazanımı etkili ve mekanik ve adsorban özelliklere hasar vermeden gerçekleştirebilmek esastır. Ekonomik açıdan ham maddeler ve absorpsiyon yöntemleri, adsorpsiyonunu diğer alternatif ayırma proseslerine göre ideal olması için düşük masraflı olmalıdır.

Adsorbanlarla gerçekleştirilen çalışmalar henüz optimum duruma gelip, yani adsorban dozunu ve karşılaşılan sorunları en aza indirgemiş hale gelmemiştir. Fakat, bu konuda pratik ve yeniden kullanılabilir bir yöntem bulmak için aktif karbon gibi iyi bilinen adsorbanlar veya adsorban olarak kullanılabilir proses atıkları gibi birçok adsorban ile çalışmalar sürmektedir. Kullanılan adsorbanlar arasında özel bir ilgi doğal bir aminopolimer olan çitosana verilmektedir.

Çitosan sulu çözeltilerden boyanın ayrılması amacıyla çalışmalarda kullanılmaktadır. Bu doğal polimer, rengin giderilmesi için onu etkili bir biosorban haline getirecek içsel özelliklere sahiptir. Biosorban olarak kullanımı iki önemli avantaja sahiptir: ticari diğer adsorbanlara göre daha ekonomiktir (dünyada selülozdan sonra ikinci en bol bulunan polimer olan çitinin deasetilasyonu ile oluşur) ve önemli bağlama özelliğine sahiptir (bu aminopolimerin ana uygulama alanlarından biri kirletici maddeleri, özellikle ağır metalleri bağlama özelliğidir).

Çitosan çitinin deasetile bir türevi olup, temel olarak kabuklularda bulunan bir doğal polimerdir. Çitin ve çitosan arasındaki deasetilasyon düzeyini ayrıştırabilmek için genellikle %50 asetil içeriği bulunan polimerler çitosan olarak adlandırılır. Hem çitin hem çitosan kendilerine özgün yapıları nedeniyle yüksek derecede biyolojik ve mekanik özelliğe sahip olup, yenilenebilir ve biyofonksiyonel malzemelerdir. Çitosan gelişmiş çözünürlüğü ve ileri fonksiyonelliği sebebiyle bir çok uygulamada daha kullanışlıdır. Çitosan çitinden veya selülozdan kimyasal olarak daha çok yönlü olmakla beraber, biyobozunabilirliği, biyouyumluluğu, film oluşturma yetisi, polifonksiyonelliği, hidrofobisitesi ve adsorpsiyon özelliklerine sahiptir. Katyonik yapısı adsorpsiyon için umut vaat eden bir madde olmasını sağlar.

Çitosan kabuklular, böcekler ve mantarların dış iskeletinden elde edilmekte olup, gıda sektörünün bir atığı olduğu için ekonomik açıdan idealdir. Geçerli olarak bir çok ülkede üretilmekte olup, kozmetik, tekstil, gıda, tarım, kimya, dişçilik, ilaç, biyoteknoloji ve tıbbi uygulamalar olmak üzere birçok sektörde kullanılmaktadır. Çitosan bazlı maddelerin kullanışlı adsorbanlar olarak adsorpsiyon biliminde gelişmekte olan bir alandır. Çitosan aktif çamur, poliüretan, bentonit, kaolin, selüloz, magnetit, kum ve daha birçok malzeme ile birlikte boya gidermekte kullanılmıştır. Literatürde çitosanı ağır metaller, boyalar, fenoller, anyonlar ve çevreyi kirleten maddelerin adsorpsiyonunda kullanan birçok çalışma bulunmaktadır, ekonomik bir adsorban olması bu çalışmaları desteklemektedir.

Literatürde modifiye ve çitosan kullanılarak boya moleküllerinin adsorpsiyonu, su ve atık su detoksifikasyonu ve renk giderme üzerinde çalışmalar gerçekleştiren birçok

çalışma bulunmaktadır. Bu çalışmanın amacı çitosan türevleri kullanılarak tekstil boyalarının sudan adsorpsiyonudur. Bu çalışmada, çitosan-montmorillonit (Chi-MMT) kompozitleri ve üre-formaldehit ve üre ile Chi-MMT kompozitleri oluşturulmuştur. Çitosan, çitosan ve montmorillonitin sulu karışımları manyetik karıştırıcıda karıştırılarak modifiye edilmiş, distile su ile yıkanmış ve kurutulup öğütülmüştür. Üre-formaldehit karışımı Chi-MMT sulu karışımı ile 80 ˚C'de karıştırılarak kompozitler oluşturulmuş, ve sonrasında bu karışım saat camlarına dökülerek kurutulmuştur. Boya çözeltileri (Reaktif Mavi 221, Reaktif Kırmızı 195 ve Reaktif Siyah 5) distile suda hazırlanmış ve yeterli miktarda öğütülmüş kompozit tozu veya kompozit filmler her boya çözeltisine farklı koşulların adsorpsiyon üzerindeki etkisini belirlemek amaçlı olarak farklı deneyler için eklenmiştir. Farklı sıcaklık değerleri, farklı pH değerleri, farklı adsorban miktarları, farklı çapraz bağlı madde içerikleri içeren adsorbanlar gibi farklı koşullarda adsorpsiyon deneyleri gerçekleştirilmiş ve bunlar en iyi sonuç için karşılaştırılmıştır. Adsorpsiyondan sonra renk değişiminin değerlendirilmesi için UV analizi gerçekleştirilmiş ve UV analizlerinden alınan sonuçlar ile kompozitlerin adsorpsiyon kapasiteleri hesaplanmıştır. Adsorpsiyon kinetiği üzerine çalışmalar gerçekleştirilerek adsorpsiyon hızı ve her deneyde kullanılan kompozitlerin maksimum adsorpsiyon kapasitesi belirlenmiştir. Sentezlenen çitosan türevleri üzerinde FT-IR analizi gerçekleştirilerek karakterizasyonu gerçekleştirilmiştir. Ayrıca, partikül boyutu ve yapısını inceleyebilmek için kompozitler SEM ile karakterize edilmiştir.

1. INTRODUCTION

Biocomposites are a new class of hybrid materials composed of fillers incorporated into a bio-based matrix. Such an association between eco-friendly biopolymers and other materials, with the aim to obtain synergic effects, is one of the most innovating routes to enhance the properties of these bio-matrices. Depending on the geometry and the nature of the filler, new and improved propertiescan be obtained [1].

It is now recognized that adsorption using low-cost adsorbents is an effective and economic method for water decontamination. Low-cost adsorbents with high adsorption capacities are still under development to reduce the adsorbent dose and minimize disposal problems. Special attention has been given to polysaccharides such as chitosan, a natural aminopolymer. It is clear from the literature that the biosorption of dyes using chitosan is one of the more frequently reported emerging methods for the removal of pollutants. This natural polymer possesses several intrinsic characteristics that make it an effective biosorbent for the removal of color [2].

Chitosan is the partially N-deacetylated derivative of chitin, a natural polymer present mainly in shells of crustaceans. There are no standard discretion for the degree of N–deacetylation between chitin and chitosan; however, commonly polymers with more than 25% of acetyl content are named as chitosan. Chitosan is chemically more versatile than chitin or cellulose due to its biodegradability, biocompatibility, film-forming ability, bioadhesivity, polyfunctionality, hydrophobicity and adsorption properties. Its cationic nature allows it to be a promising material for adsorption purposes.

Chitosan is produced from the exoskeleton of crustaceans, insects and certain fungi, and it is economically feasible since it is a food industry waste from shellfish. Currently it is produced commercially in Japan, India, Australia, Poland, Norway and USA, along with many more smaller production plants among many other countries. Chitosan is used in many industries such as cosmetics, textile food, agriculture,

chemistry, dentistry, pharmaceutics, biotechnological and medical applications. The development of chitosan-based materials as useful adsorbents is an ever-expanding field in the area of adsorption science. Chitosan has been used in removal of dyes in combination with activated clay, polyurethane, bentonite, kaolin, cellulose, magnetite, sand, and many more materials of different varieties. There are many studies in literature using chitosan successfully in the adsorption of heavy metals, dyes, phenols, anions and pollutants since it is a low-cost adsorbent like activated carbon, kaolin, fired clay and montmorillonite [3].

Color removal from wastewaters is an important environmental aspect in textile industry. Color is easily recognized in wastewater as a contaminant and very small amount of dyes can give very visible, undesirable coloring in water.

Dyed wastewater is one of the most difficult industrial wastewaters to treat. Treatment difficulties are based on stability of recalcitrant dyes and their ability to bestow good coloring in very low concentrations. That being said, we can expect effective methods for dye removal to be overly complicated and that explains why they are assumed as unfavorable. Adsorption process provides an attractive alternative treatment especially if the adsorbent is selective and effective in various types of colorants, such as anionic, cationic and non-ionic dyes. At present, there is no single adsorbent capable of satisfying all of the necessary requirements. Composites of clay and natural polymers can give environmentally-friendly and economically-feasible adsorbents.

In this study, we aim to provide an analytical look into the differences of adsorbent effects of pure chitosan and its composites with montmorillonite clay and urea and formaldehyde, and after the assessment of these results, provide an opinion about what would be the most useful method in industry.

2. THEORETICAL PART

2.1 Chitin and Chitosan

Chitin and chitosan polymers are defined as natural aminopolysaccharides having unique structures, multidimensional properties, and highly sophisticated functions [4]. Both chitin and chitosan copolymers consist of N-acetylglucosamine and glucosamine. A copolymer is defined as chitin when it contains less than 7% nitrogen and it is defined as chitosan upon nitrogen content more than 7%. Both copolymers are found in nature, however, chitosan is generally defined as the deacetylated version of chitin. Chitin and its derivative chitosan both have similarities to cellulose [5]. They serve as an alternative to cellulose in terrestrial plants, and they serve as an alternative to collagen in animals [6].
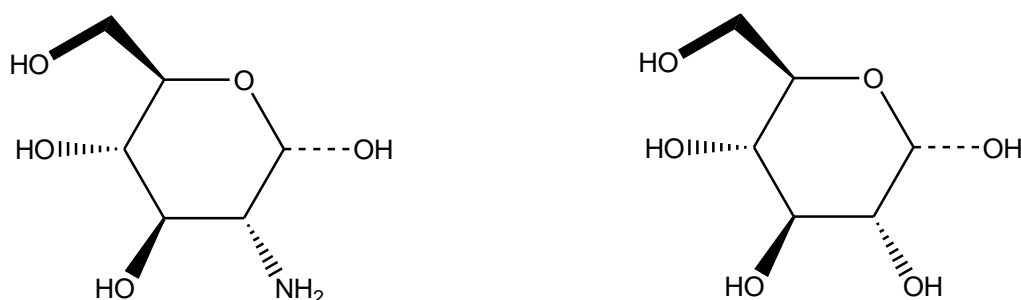
Figure 2.1 : Structure of glucosamine and glucose [4].

They are assumed to be an interesting option, among everything else, especially for the solution of problems of environmental toxicity. They possess high biological and mechanical properties due to their unique structures, as they are biorenewable, biodegradable, and biofunctional [7]. They have excellent adhesion characteristics, biocompatibility, and have versatile biological activities like antimicrobial activity and low immunogenicity, and low toxicity. These polymers are amino polysaccharides having the rare amide/amino functionality and hydroxyl groups that can undergo chemical modifications to give a variety of materials in a number of applications in healthcare, biotechnology, water treatment, cosmetics, food, agrochemicals, pulp and paper, textile finishes, photography, product separation and recovery, membranes and other miscellaneous applications [5].

3

2.2 Chitin

2.2.1 History of chitin

Use of chitin is known in ancient times in India, China and Korea. It was used mainly to alleviate spasms and convulsions. Ancient practices of folk medicine shows that some of the healing properties of chitosan were recognized by Indian and Korean ancestors, however they could isolate the ingredient or produce it repeatedly. They used it in powdered shell form or they boiled the shells to degrade the protein content. In modern times, first discovery of chitin was in a botanical garden in Nancy, France, by Henri Braconnot who noticed there was a material in the cell wall of mushrooms that did not dissolve in sulfuric acid. It was named as fungine at that time by himself, two years later in 1823 it was named as chitin, meaning tunic-envelop in Greek, by Odier. That was 30 years before the isolation of cellulose. In the year 1859, a French scientist C. Roget isolated chitosan from chitin, noting that insoluble chitin became soluble in acids when boiled in concentrated potassium hydroxide solution. In 1894, Hoppe-Seyler studied modified chitin and named it chitosan [4].

2.2.2 Place of chitin in nature

Chitin is a natural polysaccharide shown as poly (β-(1→4)-N-acetyl-D-glucosamine).Chitin is abundant in nature and synthesized by an enormous number of living organisms. While chitin can be found abundantly in nature, up to this day chitin is mainly produced from crab and shrimp shells commercially. It occurs in nature as in ordered crystalline state, being structural components in the exoskeleton of arthropods or in the cell walls of fungi and yeast, and it is present in a certain number of other viable organisms in the lower plant and animal populations, supplying mainly reinforcement and strength for the organisms containing it [8].

Shellfish chitin is an exoskeletal component in a complex network containing proteins and minerals ($CaCO_3$) while the main components in the complex network of fungal chitin are other polysaccharides such as α and β-glucan, mannan and cellulose. Shellfish chitin is more crystalline and chemically more stable while fungal chitin is softer and less crystalline. Shellfish chitin is more acetylated compared to fungal chitin that has a lower degree of acetylation. Therefore, these differences have impact on the extraction processes utilized to produce chitin [9].

4
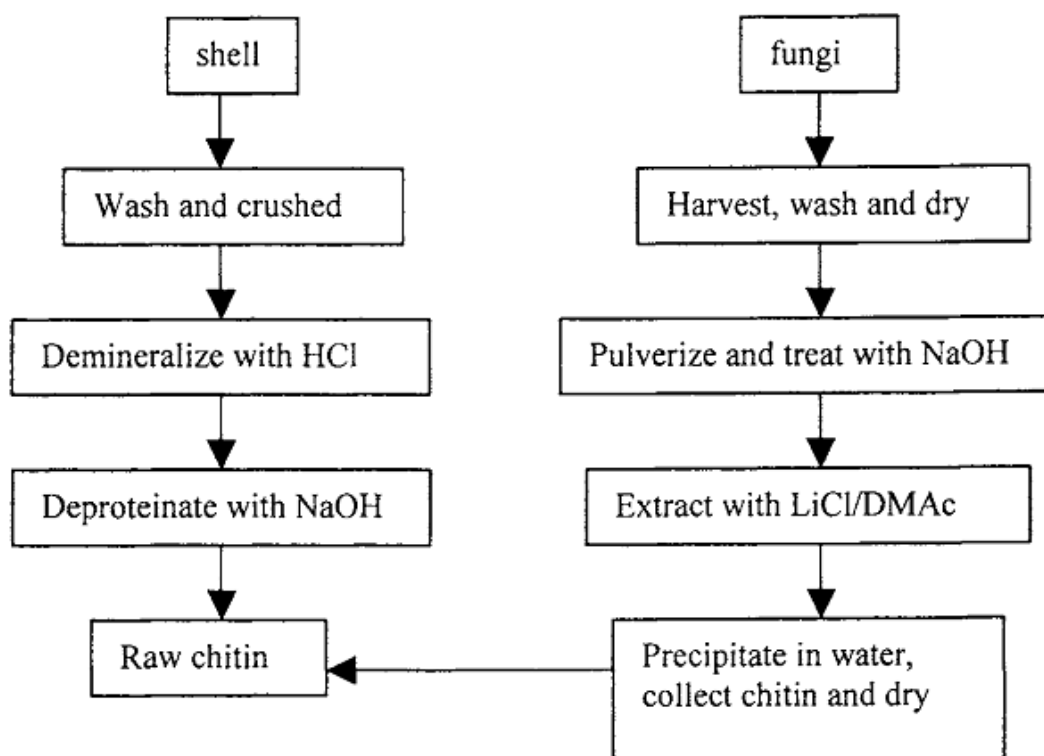
Figure 2.2 : Different steps involved in chitin production [9].

It has been estimated that the crustacean chitin present in the sea amounts to 1560 million tons. Chitin acts as a structural component and provides strength and protection to the organisms in the shell and cuticle. Chitin acts as a constituent to form a complex network of proteins and calcium carbonate deposits forming the rigid shell in crustaceans. The interaction between chitin and protein is constituted by covalent bonding, and basically is a polysaccharide-protein complex. Chitin is found in algae, protozoa and in the cell wall of several fungi in the plant kingdom. Chitin is present in fungi in contents varying from 0.45% in yeasts, and up to 10-40% in filamentous fungi species with high proteolytic activity [9]. Chitosan is not native to animal sources and is normally obtained by deacetylating chitin. In addition, some number of fungal strains produce chitosan instead of chitin [10].

2.2.3 Commercial aspects of chitin

Taking into account the annual production amount of chitin, it can be said that it is the most abundant biopolymer after cellulose. A great structural similarity exists between chitin and cellulose. The difference between them is in that the hydroxyl group of carbon C2 in cellulose is substituted by an acetamide group in chitin [11].

Figure 2.3 : Exoskeleton of crustacea, the source of commercial chitin[12].

Commercial chitin is extracted from crustacean wastes of the fishing industry, the main chitin sources being the shells of shrimp, crab, lobster, prawn and krill. These crustacean wastes consist of chitin (20–30 per cent), protein (30–40 per cent), inorganic salts (mainly calcium carbonate and phosphate) (30–50 per cent) and lipids (0–14 per cent). These percentages vary considerably with the species and the season [9]. There are some deacetylation and chain scission steps in its processing. The process used, the source of the raw chitinous material, and its treatment before processing determines the properties of the chitin obtained [6]. In industrial processing, chitin is extracted from crustaceans by acid treatment and alkaline extraction in order to dissolve calcium carbonate and solubilize proteins, respectively. In general, a color removal step is often added to remove leftover pigments and attain a colorless product. After being subjected to these processes, chitin is graded in terms of purity and color, since residual protein and pigment can cause problems especially for biomedical products [8]. There are certain basic necessities in the production of a biomaterial, these are in brief high purity and batch consistency. Only when these conditions are supplied, the product can be called a biomedical grade material. These are particularly important in the production of chitin as its biological origin corresponds to a wider variation in its raw materials, they can be summarized as properties differing in the shells like sex, age and habitat of the animal such as calcium and protein content. Also chitin can be obtained from several marine and plant sources. Different sources differ in extraction and isolation methods and these all lead to a different product depend on all of these considerations [9].

2.2.4 Processing of chitin

The isolation of chitin starts with selection of shells. Quality of the final product is determined by this selection, that is important especially for crabs and lobsters. Ideally, shells that have the same size and species are chosen. Shells are then cleaned and dried, afterwards thorough crushing is performed as the next step. The crushed shell pieces are treated with dilute hydrochloric acid in order to remove calcium carbonate. Proteins and organic impurities are removed by an alkali treatment [9]. Protein extraction is usually performed with a mild alkaline solution, at 60-70 C for a few hours, and then the extracted proteins are removed. These proteins can be put to use, if wanted, such in animal feeds [5]. In deproteinization, covalent chemical bonds have to be destroyed between the chitin-protein complex. Removing the protein content is important especially for some applications since some people are allergic to shellfish, more precisely towards its protein components. Pigments, primarily carotenoids are removed by extraction with ethanol or acetone after the demineralization process. Demineralization is performed by the decomposition of calcium carbonate into the water-soluble calcium salts. Most commonly used reagent is dilute hydrochloric acid (HCI) that produces water-soluble calcium chloride ($CaCI_2$). Demineralization is straightforward process, however, for deproteinization this cannot be said [9].
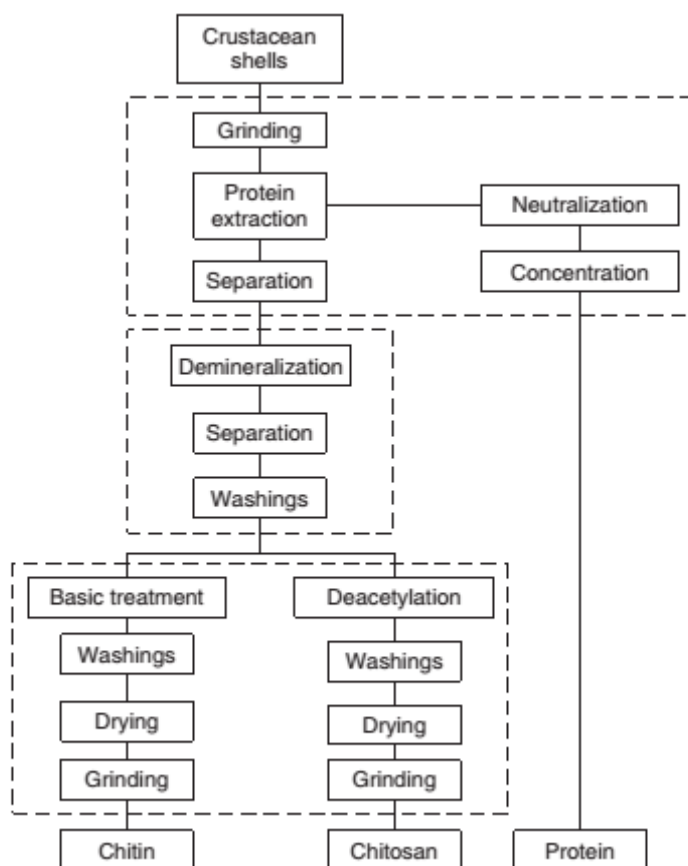
Figure 2.4 : Steps involved in chitin/chitosan preparation [11].

2.3 Chitosan

By partial deacetylation of chitin under alkaline conditions, chitosan, the most important chitin derivative used in a variety of applications, is obtained.

When the degree of deacetylation of chitin reaches above 50% (depending on the origin of the polymer), it becomes soluble in aqueous acidic media and is called chitosan. The solubilization occurs by protonation of the –NH2 function on the C-2 position of the D-glucosamine repeat unit, whereby the polysaccharide is converted to a polyelectrolyte in acidic media [8].

CH₂OH ... (chemical structure diagram)
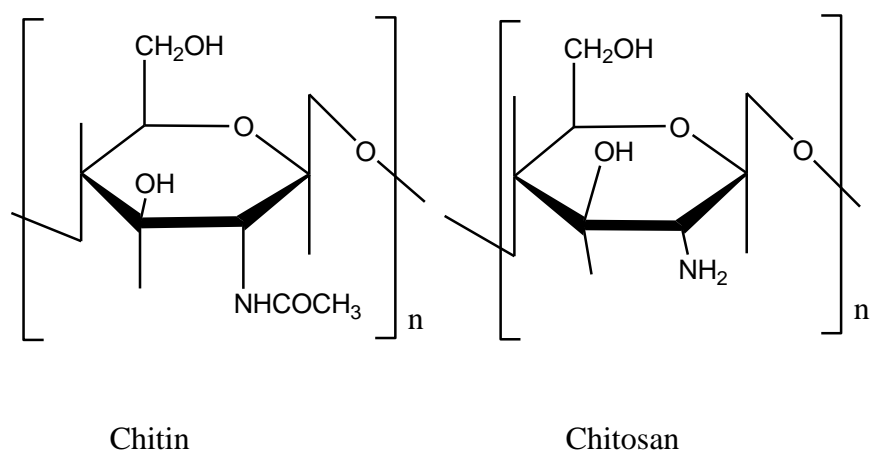
Chitin   Chitosan

Figure 2.5 : Chemical structure of chitin and chitosan [11].

2.3.1 Structure of chitosan

Despite its easy availability, chitin still remains an under utilized resource primarily because of its intractable molecular structure. However, chitosan as a derivative of chitin is better placed for a variety of applications due to its improved solubility and enhanced functionality [5].

Chitosan is a linear polysaccharide obtained by extensive deacetylation of chitin. It is obtained commercially from shrimp and crabshell chitin [13]. It is mainly composed of two kinds of β(1 →4) linked structural units which are 2-amino-2-deoxy- D - glucose and N-acetyl-2-amino-2-deoxy- D –glucose.

Chitosan, due to the presence of amino groups at the C2 position, and primary and secondary hydroxyl groups at the C3 and C6 positions, has many applications in various fields. Chitosan, being its simplest and least expensive derivative, is obtained from chitin. Along the chitosan polymer chain, the presence of positively charged amino groups enables it to bind with negatively charged surfaces via ionic or hydrogen bonding unlike most polysaccharides [7].

2.3.2 Degree of N–deacetylation

Chitosan is the partially N-deacetylated derivative of chitin, it is a natural polymer present mainly in shells of crustaceans. There is no standard discretion for the degree of N–deacetylation between chitin and chitosan since it is virtually impossible to completely deacetylate chitin. Commonly, polymers with more than 25% of acetyl content are named as chitosan.

The process of deacetylation involves the removal of acetyl groups from the molecular chain of chitin, leaving behind a compound (chitosan) with high degree of chemically reactive amino groups [5]. Chitin deacetylation is based on the hydrolysis of the acetamide groups at high temperature and strongly alkaline conditions. These conditions are supplied by using concentrated (40–50 per cent) NaOH or KOH solutions at temperatures above 100°C, the reaction is performed heterogeneously preferably in an inert atmosphere or in the presence of reducing agents to avoid depolymerization, such as $NaBH_4$ or thiophenol [11]. Chitin flakes are treated in suspension at 80-120 °C with constant stirring for 4-6 hours and this process is repeated for obtaining a high amino-content product [5]. Other factors that have an effect on conducting the reaction are the starting material, the previous treatment and the desired degree of acetylation. That being said, if the deacetylation process is performed with the help of only one alkaline treatment, maximum deacetylation degree attained will be 75–85 per cent. Nevertheless, several treatments have been developed in order to prepare fully deacetylated chitosan [11]. Deacetylation of chitin can also be done enzymatically. Here powdered chitin is treated with N-deacetylase or with microbes that secrete N-deacetylase. The enymatic method gives chitosan with low degree of deacetylation and polymerization [5].

Chitin is a semi-crystalline polymer, resembling cellulose in that manner. Conditions of deacetylation process affects the product of the process, such that when it is performed in heterogeneous conditions, mainly the amorphous regions are converted, while the process is performed under homogeneous conditions, the resulting polymer bring about a more uniform modification. Homogenous reaction is carried out using alkali chitin, which is obtained by conducting successive freezing–thawing cycles of an alkaline aqueous chitin suspension until it dissolves. Moreover, homogeneous deacetylation can be performed under more moderate alkali concentrations (about 13 wt%), and at 25–40°C. The products of the heterogenous process are polydispersed in terms of the acetylation degree of their chains, while products of the homogeneous conditions do not exhibit chain compositional dispersion.

2.3.3 Structural advantages of chitosan

Chitosan is chemically more versatile than chitin or cellulose due to its biodegradability, biocompatibility, film-forming ability, bioadhesivity, polyfunctionality, hydrophobicity and adsorption properties.

Its cationic nature allows it to be a promising material for adsorption purposes. The unique structural advantage of chitosan is the presence of the primary amine in the C-2 position of the glucosamine. Few biological polymers have such a high content of primary amines, and these primary amines bring important functional properties to chitosan that can be exploited for chemical modification. Apart from the amino group, chitosan possesses a primary and secondary hydroxyl group good chemical modification so that its properties can be altered to incorporate improved physical, mechanical, solution and biological properties. Therefore it can be said that the presence of acetamodo and amine groups in chitin and chitosan influences their properties and make them different from cellulose. With regard to its improved functionality, modification of chitosan is more preferred than chitin. The properties of chitosan depend on the degree of N-acetylation and distribution of N-acetyl groups. Chitosan is a high molecular weight polysaccharide similar in structure to cellulose, differing in hydroxyl group in 2- position is replaced by the amino group [5].

Chitosan is positively charged due to the acidic environment and therefore it can interact with electrostatic forces. For its antimicrobial effect, its interaction with the anionic groups at the cell surface due to its cationic nature, is caused by the formation of an impermeable layer around the cell, which prevent the transport of essential solutes. The second mechanism involves the inhibition of the RNA and protein synthesis by permeation into the cell nucleus. Also, it is suggested its wound-healing properties are caused by its ability to stimulate fibroblast production by affecting the fibroblast growth factor. As a result of its cationic character, chitosan is able to react with polyanions giving rise to polyelectrolyte complexes [5].

2.3.4 Adsorption studies with chitosan

Besides being natural and plentiful, chitosan possesses interesting characteristics that also make it an effective biosorbent for the removal of color with outstanding adsorption capacities. Compared with conventional commercial adsorbents such as

commercial activated carbons (CAC) for removing dyes from solution, adsorption using chitosan-based materials as biosorbents offers several advantages [14].The effectiveness of chitin and chitosan to adsorb dye molecules has been reported by numerous workers from as early as 1958 [15].

Polymer/montmorillonite composites have improved properties such as excellent mechanical properties, thermal stability, gas barrier, and flame retardation in comparison to conventional composites [16]. Wang and colleagues found in their studies that molar ratio of chitosan to montmorillonite could influence the chemical environment of the composites and hence the adsorption properties. Increment in the molar ratio of chitosan to montmorillonite increases the adsorption capacity of Congo Red until the molar ratio exceeds 1:1 after which the adsorption remains almost constant. It may be caused by the montmorillonite being saturated by the amount of intercalated chitosan [17]. X-ray diffraction (XRD) analysis showed that chitosan intercalated into montmorillonite interlayer led to the destruction of montmorillonite crystalline structure. Wang and Wang [18] suggested two mechanisms of adsorption — electrostatic interaction and chemisorption.

Won et al. [19] used polyurethane to form chitosan composites in adsorbing Acid Violet 48.The preparation of chitosan/polyurethane composites is different fromother methods, as chitosan does not undergo dissolution using acetic acid. According to the study of Lyoo et al. [20], at 0.25 wt% of glutaraldehyde concentration, chitosan was found to be most efficient in immobilizing into the polyurethane matrix foam. The scanning electron microscope (SEM) image revealed the composites to have open structures which had been proven in previous literatures [21]. The open structures of the composites enhance the accessibility of acid dyes into the chitosan adsorbent which had been immobilized in the composite foams [20].

Chang and Juang [22] studied the chitosan/activated clay composites. Based on specific gravity values, they concluded that the addition of activated clay could enhance the ability of chitosan to agglomerate and improve the hardness of the beads based on the Stokes Laws. In the adsorption studies of methylene blue and reactive dye (RR22), the chitosan composites had a comparable adsorption in comparison to chitosan beads.

Wan Ngah, Ariff, and Hanafiah [23], prepared crosslinked chitosan/bentonite composites to adsorb tartrazine, a dye which contains azo group that is harmful to living things, found that the experimental data correlated well with the pseudo-second order model and an adsorption capacity of 435.0 mg/g of Malachite Green was achieved.

Similarly, Hameed et al. [24] prepared crosslinked chitosan/oil palmcomposite beads to remove Reactive Blue 19.

Zhu et al. [25] prepared a new chitosan bead which was blended with maghemite (γ-Fe2O3) and kaolin. From the SEM and tunneling electron microscope (TEM) images, it was found that there were many pores and pleats on the surface of the composites which provided active sites for dye entrapment. The composites exhibited good adsorption ability as it could adsorb up to 70% methyl orange at pH 6.

Alumina is suitable to use as an adsorbent due to the amphoteric character of hydrous aluminum hydroxides. A number of works have been carried out on the application of chitosan/ceramic alumina composites as an adsorbent to remove anionic and cationic heavy metals such as As(III) [26], As(V) [26], Cr(VI) [27], Cu(II) [28] and Ni(II) [28].

Chitosan/perlite composites have been applied as an adsorbent to remove heavy metals such as cadmium [29], chromium [30], copper [31; 32] and nickel [31].

Sand can be modified to adsorb heavy metals and dyes in wastewater.Wan, Kan, Lin, Buenda, and Wu [33] have reported on the application of chitosan immobilized on sand in the adsorption of Cu(II).

Chitosan/sand composites have shown better adsorption capacity than any of its component used alone. This is due to the three dimensional structure of the adsorbent used. Amine groups in chitosan provide active sites for the formation of complexes with metallic ions, which are stabilized by coordination [2].

In addition, PVA has been used to immobilize chitosan to form chitosan/PVA composites [34,35]. This type of composite has been used to remove Cu(II) [35] and Cd(II) [34] from wastewater. Desorption studies were carried out with more than 60% recovery, suggesting that the adsorbent was recyclable [34,35].

Another biosorbent was developed by coating chitosan onto PVC beads [36]. The composite beads were used to adsorb copper and nickel ions from aqueous solution.

In contrast, Yang and Chen [37] found that chitosan/bentonite composites were a good adsorbent for removing mercury ions from wastewater.

All of these studies suggest that chitosan is a suitable material for adsorption and a versatile raw material for water treatment purposes.

2.4 Clays

Clays are fine-grained natural materials present in soil or rocks [38]. They are also described as an aggregate of minerals and colloidal substances [39]. Generally they are hydrous aluminosilicate minerals that dominantly make up the colloid fraction ($<2\mu$) of soil, rocks and water [40].

Multiple layers ofhydroxylated and coordinated tetrahedral and octahedralsheets generally constitutesclay minerals [38]. Their uniquechemical and physical properties are originated by the layered structure[41].

Clay minerals have good ion exchange capacity. They are an important constituent of soil and take up various contaminants from water, from both sources flowing over soil or penetrating underground. They have this effect by ion exchange and adsorption mechanisms. Chemical composition, nature of the surface atoms, the type and extent of defect sites, layer charge and the type of exchangeable cations are the factors effective on the surface activity of clays [42]. Parameters like pH, ionic strength, pressure and temperature of the surrounding environment affect the environmental effect of clays [43]. Also characteristics of clays like large surface area, cation exchange capacity (CEC), chemical and mechanical stability, layered structure determine the usefulness of the clays on this issue [44].It is observed that when the uptake of pollutants by the clays does not exceed the CEC, the mechanism of adsorption is dominated by ion exchange, but if the uptake is more than the CEC, the ions may be held through hydrophobic bonding. [45].

The edges and the faces of the clays are generally effective in taking up different types of species (cations, anions and polar organic contaminants) from water. The strength of such interactions is determined by the particular structural and related features of the clay. Accumulation of adsorbed pollutants on clay surface is likely to

face certain steric constraints as they enter into the interlayer space. Clay-adsorbate interactions may proceed via van der Waals type weak bonding, hydrophobic effects and even H-bonding, all of which are likely to play important roles in holding the pollutants to the clay surface. Crystal imperfections in the clay minerals may also affect adsorption and reaction processes on the clay surface [46].

Clay-based composites and biocomposites have become materials of increasing interest due to their nanosized structural and functional properties. Organic–inorganic nanohybrid materials possessing the properties of both types of compounds are commonly developed by combining the nanometric scale of the expansive surface areas and reactive surfaces of clays with the functional behavior of organic polymers as an attractive way.

2.4.1 Montmorillonite

Sodium montmorillonite (MMT) is a naturally occurring 2:1 phyllosilicate, capable of forming stable suspensions in water [47]. Origin of the name of montmorillonite (MMT) is the French town Montmorillon, in this town it was discovered by Damour and Salvetat in 1847. MMT is derived from the process of weathering of eruptive rock material (generally tuffs and volcanic ash) [48]. MMT contains trace amounts of crystobalite, zeolites, biotite, quartz, feldspar, zirconia in its pure form [49]. MMT is composed of a crystalline structure of a pyrophyllite model. Structure of pyrophyllite model is composed of two silica tetrahedral sheets sandwiching an edge-shared octahedral sheet of either aluminum or magnesium hydroxide, known as t-o-t sheets [48]. Stacking of the layers leads to a regular van der Waals gap between the layers called the interlayer or gallery. Isomorphic substitution within the layers generates charge deficiency (i.e. Fe^{2+} or Mg^{2+} replacing Al^{3+} in montmorillonite and Li^+ replacing Mg^{2+} in hectorite). The deficit charges are compensated by cations (usually Na^+ or K^+) sorbed between the three-layer clay mineral sandwiches. These are held relatively loosely and give rise to the significant cation-exchange properties [50].
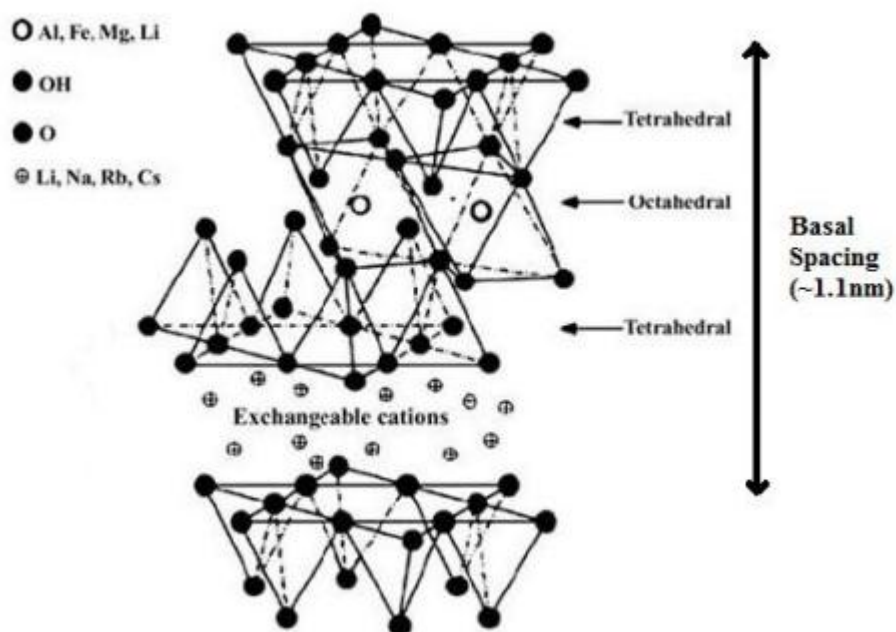
Figure 2.6 : Structure of montmorillonite clay.

Montmorillonite is one of the layered clay minerals, and it is well known that it is composed of 1 nm-thick silicate layers. Organic ammonium ions and neutral organic molecules are intercalated in the interlayer space between the silicate layers [51].

Some of the most commonly used smectite-type layered silicates for composite preparation are hectorite and montmorillonite. Smectites have high cation exchange capacities, surface area, surface reactivity, adsorptive properties, and therefore they are a valuable mineral class for industrial applications [52].Smectite clays, such as the common mineral montmorillonite, are characterized by substitution of lower-valency metal cations (Mg^{2+} for Al^{3+} or Al^{3+} for Si^{4+}) within the sheets to create a net negative charge that is compensated by interlayer cations that are typically solvated by water molecules [41].

MMT is capable of absorbing certain cations and maintain them in exchangeable state thus facilitating the exchange of intercalated cations by other cations in a water solution. The most common exchangeable cations are Na^+ and Ca^{2+} cations. Sodium MMT (Na^+-MMT) and calcium MMT (Ca^{2+}-MMT) are the two main classes of montmorillonites [48].

The most commonly used layered silicate is montmorillonite. MMT owes this attention to its ability to show extensive interlayer expansion or swelling which, in turn, is related to its peculiar structure. The efficiency of the MMT in improving the

properties of the polymeric materials is primarily determined by the degree of its dispersion in the polymer matrix [50].

2.5 Urea-Formaldehyde

Urea-formaldehyde (UF) resins are based on the manifold reaction of two monomers, urea and formaldehyde. By using different conditions of reaction and preparation more or less innumerable variety of condensed structures is possible. UF resins are the most important type of the so-called aminoplastic resins [53].

Urea–formaldehyde (UF) resins are polymeric condensation products of the chemical reaction of formaldehyde with urea, mainly being adhesives extensively used for the production of wood-based composite panels [54]. UF resins are thermosetting duromers and consist of linear or branched oligomeric and polymeric molecules, which also always contain some amount of monomer. Non-reacted urea is often beneficial to achieve special effects, e.g. better stability during storage. However, the presence of free formaldehyde is ambivalent. On the one hand, it is necessary to induce the hardening reaction. On the other, it causes formaldehyde emission during the press cycle as well as subsequent, displeasing, formaldehyde emission from the pressed boards, a fact that has led to a total change in the formulation of UF resins. After hardening, UF resins form an insoluble, threedimensional network and cannot be melted or thermoformed again. In their stage of application UF resins are still soluble or dispersed in water or in the form of spray dried-powders, which, in most cases however, are redissolved in water for application. The main differences between UF resins with high and with low contents of formaldehyde are their reactivity as a consequence of the different free formaldehyde content and their degree of crosslinking in the cured network. The degree of crosslinking is directly correlated to the molar ratio of the two components. Taking into consideration that an ideal linear UF chain has a molar ratio of 1.0, assuming that there are no ether bridges, no unreacted branch-site methylol groups and no other free formaldehyde, then the small molar excess of formaldehyde above molar equality is what yields the final crosslinking. In practice this calculation is not really exact, because there are always ether bridges and some unreacted methylol groups in the resin, even after hardening [53].

It can be said that UF resins are major raw materials of wood panel industry and they are seen as one of the most important types of adhesive in the wood-based panel industry [54]. Urea is rather inexpensive compared with melamine and phenol. Formaldehyde also is relatively inexpensive, and thus, together, they give a resin of low cost but nevertheless high performance. All aminoplastic glue resins usually give clear and unvisible gluelines after hardening, contrary to phenolic or polyphenolic gluelines [53]. UF resins have advantagessuch as fast curing, good performance in the panel,water solubility, and lower pricecompared tophenol–formaldehyde (PF) resins and diphenylmethanediisocyanate. Concordingly, disadvantages are lower water resistance that is limiting the use of wood-based panels bonded with UF resin to interior applications and formaldehyde emission (FE) from the panels [55]. The reversibility of the aminomethylene link is also the cause of low resistance UF resins possess againstthe influence of water and moisture, especially at highertemperatures. This is also one of the reasons for their subsequent formaldehyde emission, when hardenedand in service [53]. FE release from wood-based panels is caused by free formaldehyde present in UF resin and hydrolytic degradation of UF resin under moisture conditions [55]. Additionally, the reversibility of the aminomethylene link and its susceptibility to hydrolysis also are also reasons for lower resistance against water and moisture and subsequently FE [53]. It has been the main challenge for UF chemists over the last 20 years to reduce the content of formaldehyde in UF resins, and this without any major changes in the performance of the resins. In theory this is not possible, because formaldehyde is one of the two main reactive partners in the reaction with urea during the condensation reaction and during curing. Decreasing the F/U molar ratio means lowering the degree of branching and crosslinking in the hardened network, which unavoidably leads to a lower cohesive bonding strength [53]. However, chemists managed to work around this issue, lowering F/U molar ratio of UF resin from approximately 1.6 to a lower range, and keeping the same board performance requirements asgiven in the relevant quality standards [56].

2.6 Wastewaters in Textile Industry

Textile industry uses a substantial amount of dyes for colorization and also consumes large volumes of water in the process. As a result of this process, a great amount of colored wastewater is created. Color is the first contaminant to be recognized in

wastewater. The presence of very small amounts of dyes in water (less than 1 ppm for some dyes) is highly visible and undesirable [57]. Even minor releases of effluents may cause abnormal coloration of surface waters, affecting the clarity of the water [58]. In particular, the release of coloured effluents into the environment is undesirable, not only because of their color, but also because many dyes from wastewater and their breakdown products are toxic and/or mutagenic to life [59]. These wastewaters are also dangerous for humans, as some of the dyes are reported to cause allergy, dermatitis, skin irritation bodies is essential [14]. Many of these dyes are also toxic and even carcinogenic and this poses a serious hazard to aquatic living organisms. However, wastewater containing dyes is very difficult to treat, since the dyes are recalcitrant organic molecules, resistant to aerobic digestion, and are stable to light, heat and oxidizing agents [57]. Their toxic effluents are a major source of aquatic pollution and will cause considerable damage to the receiving waters if discharged untreated. Thus, the removal of dyes from effluents before they are mixed up with unpolluted natural water wastewater is chemically very complex in nature [60]. There are several ways in which colorants cause problems in waters, some of which are; acute and/or chronic effects on exposed organisms, or affecting the growth of bacteria that biologically degrade impurities in the water [58].

Today, pollution of aquatic habitats is a universal phenomenon, due to the discharge of mostly untreated or partially treated municipal and industrial wastewaters into them [60].Legislation about toxic substances in industrial wastewaters is becoming increasingly strict; consequently, a large number of researchers are addressing the variety of issues in this area [58].

2.7 Dyes

2.7.1 Structure of dyes

Organic molecules that contain unsaturated double bonds are capable of absorbing light within a given wavelength range (usually in the ultraviolet). If these double bonds are conjugated and alternate within the molecule, they are able to mutually interact with one another as a cloud of n electrons. If sufficient conjugation exists, the molecule will partially absorb light in the lower energy visible wavelength range and will be considered a dye or a pigment. In general, dyes are colored molecules

soluble or dispersible in water or solvent media, which can penetrate the fiber on coloration. The unsaturated groups, which can be conjugated to make the molecule colored, are referred to as chromophores. Groups that enhance or alter the color within a conjugated system through alteration of the electron density are referred to as auxochromes [61]. A series of typical chromophores and auxochromes can be seen in Fig. 2.8.
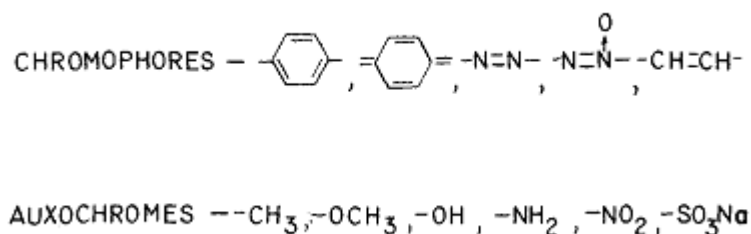
Figure 2.7 : Structure of typical chromophores and auxochromes.

Dyes are classified according to their application and chemical structure. Chromophores are azo (–N=N–), carbonyl (–C=O), methine (–CH=), nitro (–NO₂) and quinoid groups [59]. The chromophore and auxochrome are part of the chromogen, which is defined as suitable substituents that is attached to color a compound [62]. The most important auxochromes are amine (–NH₃), carboxyl (–COOH), sulfonate (–SO₃H) and hydroxyl (–OH). It is worth to mention that the sulfonate groups confer very high aqueous solubility to the dyes. The auxochromes can belong to the classes of reactive, acid, direct, basic, mordant, disperse, pigment, vat, anionic and ingrain, sulphur, solvent and disperse dye. While azo dyes constitute a mixture of red, yellow and blue dyes, anthraquinone dyes have a wide range of colors in almost the whole visible spectrum, but they are most commonly used for violet, blue and green colors [59].

2.7.2 Types of dyes

Disperse, azoic and sulfur dyes belong to the class of nonionic dyes; acid, reactive, and direct dyes belong to the class of anionic dyes; and basic dyes belong to the class of cationic dyes [63].

2.7.2.1 Anionic dyes

2.7.2.1.1 Direct dyes

Direct as are named as such due to the directness and simplicity of their application. Direct dyes are relatively large and linear molecules. Thanks to their sodium sulfonate substituents, ($-SO_3Na$) they are soluble in water. These groups dissociate in water to give colored sulfonate anions and the corresponding number of sodium cations. Direct dyes generally can be described by the general formula: dye-(SO_3^-)$_n$•nNa^+, where n is 1-5.Direct dyes have relatively poor resistance towards washing, moderate resistance towards fading in exposure to light, and they give good color, however they are not characterized due to their brightness. They are moderate in cost and easy to apply [64].

2.7.2.1.2 Acid dyes

Acid dyes are large molecules containing one or more sulfonic or carboxylic acid salt functional groups [61]. Synthetic acid dyes can be denoted with the same formula as direct dyes, which is dye-(SO_3-)n•nNa+. These molecules are smaller than direct dyes, and the number of sulfonate groups is lower. "n" value can be between 1-4, often 1 [64].

These dyes are applied onto fibers with an acid solution, and with the help of positive charges developed within the material to be dyed, acid solutions act as a driving force for dye diffusion and migration into the fiber. Because of that, only fibers which develop a positive charge in the presence of acid can be dyed by acid dyes, these are wool, nylon, and certain modified synthetics. Acid dyes are resistant to light and laundering, however, these properties can be improved [61].
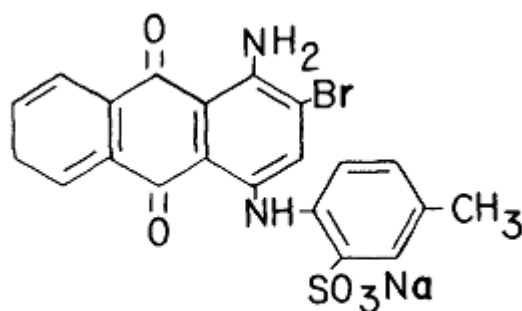
Figure 2.8 : General structure of an acid blue dye.

2.7.2.1.3 Reactive dyes

Reactive dyes are usually solubilized by the inclusion of sodium sulfonate groups, -SO_3Na, to act like direct dyes, and thus their anions obtain some substantivity, although not as much as direct dyes, in the presence of electrolytes. In order to explain their difference from direct dyes, one needs to explain that they have additional groups for facilitating reaction with cellulose fibers to produce new, colored cellulose derivatives. These colored covalent derivatives obtained have extremely high resistance to color removal by washing. These dyes can be represented by the general formula dye-X, where –X is a leaving group. The leaving group is displaced from the original dye molecule by reactive nucleophiles and becomes the X- anion.

Overall reaction can be summarized as the release of an anion, X^-, and the formation of a cellulose-dye bond. The primary activating groups are s-triazinyl ring and the masked vinyl sulfone side chain, $-S0_2-CH_2CH_2-OSO_3Na$. Here, the hydroxide ion firstly unmasks the reactive vinyl group. While reactive dyes have a wide range of bright colors, they are expensive, their applications are not so easy, and they can produce an excessive amount of colored effluent [64].
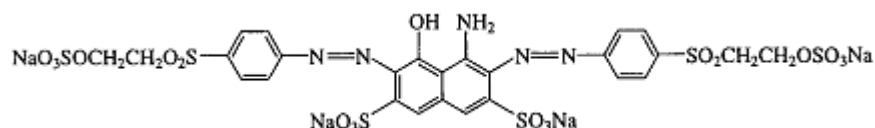

Figure 2.9 : An important AZO reactive dye, Reactive Black 5.

2.7.2.2 Cationic dyes

2.7.2.2.1 Basic dyes

Basic or cationic dyes consist of a single highly colored cation, with a simple inert counter-ion: Dye+X- where, X- may be a chloride ion [64]. Cations of the basic dyes migrate toward negative charges in the material to be dyed. These dyes can be applied to protein, nylon, acrylic, and specially modified synthetic fibers. These dyes are applied from mildly acidic or neutral solutions. Generally basic dyes have good intensity, several of which are fluorescent, however, resistance of the color of the dyes on protein and nylon fibers is poor. This resistance can be improved through mordanting [61].

When dyed onto hydrophobic fibers, their light-resistance is good. This can be explained as the presence of water always has a material effect in accelerating the fading of colors exposed to light [64]. Their biggest utility today is for dyeing hydrophobic manmade fibers with anions attached to the polymer molecules [61].
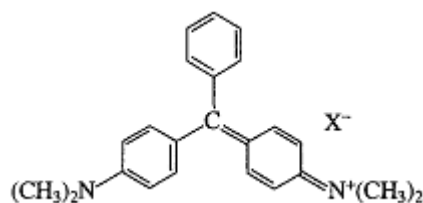
Figure 2.10 : Structure of Basic Green 4.

2.7.2.3 Nonionic dyes

2.7.2.3.1 Disperse dyes

Disperse dyes are hydrophobic, nonionic products and are sold as fine ground powders or dye pastes. Disperse dyes have found some utility on many hydrophobic fibers. They are often applied to nylon, on which they have generally poorer resistance properties than acid dyes. Disperse dyes are derived largely from simple monoazo and anthraquinonoid chromophores. [64].Coloring with disperse dyes are usually provided by small polar molecules that contains anthraquinone or azo groups and they don't have charged cationic or anionic groups in their structure. The disperse dyes are sparingly soluble in water and must be dispersed with the aid of a surfactant in the dye bath. Resistance to washing and light of these dyes is generally good [61].
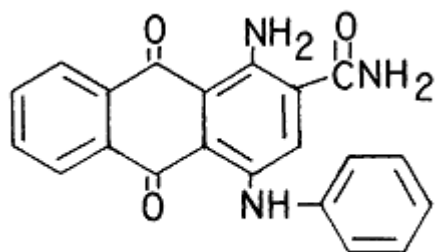
Figure 2.11 : General structure of a Disperse Blue 6.

2.7.2.3.2 Vat dyes

Vat dyes are a good example of the cross-over between dyes and pigments. Large, planar and often containing multi-ring systems, vat dyes come exclusively from the carbonyl class of dyes (for example, indigo). The ring systems of the vat dyes help to strengthen the Van-der-Waals forces between dye and fibre. Vat dyes(colors) are sold in very finely divided pigmentary form either as pastes or powders. Vat colors are costly and complex chemicals, generally based on derivatives of anthraquinone. Vat dyeings generally have excellent wet, light and abrasion resistance. Vat dyeings are more limited in their color gamut than are direct dyeings. However, as a group, vat dyeings have outstanding resistance to bleaching [64].
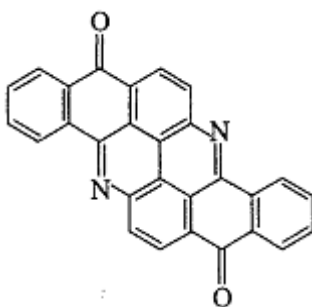
C.I. Vat Yellow 1

Figure 2.12 : General structure of Vat Yellow 1.

2.7.2.3.3 Sulfur dyes

Sulfur dyes are pigmentary, but reducible to water-soluble anionic forms which dye cellulosic fibers readily. Sulfur colors reduce more readily than vat colors and require only sodium sulfides to dissolve them. They are more difficult than vat colors to oxidize.

Sulfur colors are the most economical of colors, but have, as a group, the narrowest color gamut of all. Their dyeings lack true reds, have only dull yellows and are mostvaluable for heavy blacks, navy blues, browns and dark greens. Resistance to light of their dyeings is moderate to good in heavy shades and their resistance to washing is good. In many ways the fastness properties parallel those of indigo dyeings, and sulfur colors are often used for denim goods [64].

2.7.2.3.4 Azoic dyes

These are precursors of azo pigments. These, when dissolved in alkali, ionize to give anionic naphtholates, which have some substantivity for cellulose (just like other anionic dyes) in the presence of electrolytes. Starting with basic intermediates, which are in expensive, cost advantage these dyes supply is largely sacrificed to the complexity of a 2-step dyeing process. However, azoic combinations are still the only way the very deepest shades of orange, scarlet, red and bordeaux can be economically achieved on cotton and cotton/polyester blends [64].

2.8 Adsorption

The term adsorption refers to the accumulation of a substance at the interface between two phases such as solid and liquid or solid and gas. The substance that accumulates at the interface is called 'adsorbate' and the solid on which adsorption occurs is 'adsorbent'. At the surface of the solids, there are unbalanced forces of attraction which are responsible for adsorption. In cases where the adsorption is due to weak van der Waals forces, it is called physical adsorption. On the other hand, there may be a chemical bonding between adsorbent and adsorbate molecule and such type of adsorption is referred as chemisorption [65].

Adsorption is a well known equilibrium separation process and an effective method for water decontamination applications. Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants. Adsorption also does not result in the formation of harmful substances [66].

Adsorption enables the separation of selected compounds from dilute solutions. Compared to alternative technologies, adsorption is attractive for its relative simplicity of design, operation and scale up, high capacity and favorable rate,

insensitivity to toxic substances, ease of regeneration and low cost. Additionally, it avoids using toxic solvents and minimizes degradation [67].

Adsorption is a mass transfer process occurring at the liquid–liquid, gas–liquid, gas–solid, or liquid–solid interfaces by the accumulation of substances within [68]. Adsorption occurs at the boundary between two phases, change in concentration of a given substance at the interface as compared with the neighboring phases is referred to as adsorption [69]. The term 'adsorption' deals with the process in which molecules accumulate in the interfacial layer, but desorption denotes the converse process.

As a surface phenomenon, adsorption arises from interactions among individual atoms, ions or molecules of an adsorbate and those present in the adsorbent surface. The process involves the separation of a substance from one phase and its accumulation at the surface of another [70]. Upon contact of some fluid (gas or liquid) with a solid adsorbent, some of these fluid molecules (adsorbates) are concentrated at the surface with fluid–solid intermolecular attraction forces. Therefore, these fluid molecules become denser, and molecular diameters near the surface (adsorbed phase) extends. On the basis of differences in the fluid–solid forces of attraction between the components, desired components of the mixture are selectively adsorbed at the surface. Thereby separation provided by adsorption process is attained by creating an adsorbed phase with a composition different from the composition of bulk fluid phase. Energy is released during adsorption process, thus we can say it is an exothermic process [71].

The adsorbed state material is defined as adsorbate. Adsorption is defined as the penetration of these adsorbate molecules into the bulk solid phase. Terms, sorption, sorbent, sorbate and sorptive is used for indicating both adsorption and absorption, especially when both occur simultaneously or cannot be distinguished [69].

The action of the adsorbed molecules from the surface to the bulk fluid phase is called desorption, a reverse process of adsorption. Since adsorption process is exothermic, desorption process is endothermic and requires energy. Adsorbent is repeatedly used in this a practical separation process. Regenerative use of the adsorbent is the key to the practical use of this technology [71].

Another term is named adsorption isotherm, referred as the fundamental concept in adsorption science. It is the relation of equilibrium between the quantity of the adsorbed material and the concentration in the bulk fluid phase at constant temperature. Adsorption isotherms are stated as the primary source of information on the adsorption process [69].

The process has become one of the preferred methods for removal of toxic contaminants from water into a solid phase and has been prescribed variously as very effective, economical, versatile and simple method of separation.[70]. The technique is applicable at very low concentrations, and can be followed through both batch and continuous processes, having ease of operation, little sludge generation, possibility of regeneration and reuse, and low capital investment, etc[72].

The fundamental practical applications of adsorption and related areas are following:

- ✓ separation and purification of liquid and gas mixtures, bulk chemicals, isomers and air;
- ✓ drying gases and liquids before loading them into industrial systems;
- ✓ removal of impurities from liquid and gas media;
- ✓ recovery of chemicals from industrial and vent gases; and
- ✓ water purification [69]

2.8.1 Adsorption kinetics

In order to transport an adsorbate molecule from the bulk fluid phase to the adsorption site, a finite amount of time is required. Resulting rate process is denoted as adsorption kinetics. Sources of resistance to mass transfer resistance are the presence of fluid film outside the adsorbent particle and anisotropic skin at the particle surface, and internal macro- and microporous diffusional resistances. The presence of other adsorbates in the pores and temperature changes by releasing/absorbing energy by adsorption/desorption process affect the transport of the adsorbate. Reducing the size of adsorbent particle increases the rate of the adsorption process. In addition, gas phase adsorption is faster than liquid phase adsorption [71].

The amount of adsorbate that can be taken up by an adsorbent is a function of both temperature and concentration of adsorbate, and the process, at constant temperature, can be described by an adsorption isotherm according to the general Equation **(2.1).**

$$q_t = \frac{(C_0 - C_t)V}{m} \qquad \text{(2.1)}$$

Where qt (mg/g) is the amount of adsorbate per mass unit of adsorbent at $t = t$, C_0 and C_t (mg/L) are the initial and at time t concentration of adsorbate, respectively, Vis the volume of the solution (L), and m is the mass of adsorbent (g).

The pseudo-first order equation of Lagergren is generally expressed as follows in Equation (2.2):

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad \text{(2.2)}$$

Where q_e and q_t are the sorption capacities at equilibrium and at time t, respectively (mg/g), and k_1 is the rate constant of pseudo-first-order sorption (1/min). After integration and applying boundary conditions, $t = 0$ to $t = t$ and $qt = 0$ to $qt = qt$; the integrated form of equation (2.2) becomes

$$q_t = q_e(1 - e^{-k_1 t}) \qquad \text{(2.3)}$$

However, equation (2.3) is transformed into its linear form for use in the kinetic analysis of data.

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \qquad \text{(2.4)}$$

Second rate order equation Equation (2.5):

$$\frac{1}{q_e - q_t} = \frac{1}{q_t} + kt \qquad \text{(2.5)}$$

Pseudo second order equation is Equation (2.5):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad \text{(2.6)}$$

Where;

q_e= amount of dye absorbed in equilibrium (mg/g)

q_t= amount of dye absorbed at $t=t$ (mg/g)

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

k= rate constant of first order equation (g/ mg.min)

k_2= rate constant of pseudo second order equation (g/ mg.min)

2.8.2 Parameters affecting adsorption and desorption

In adsorption studies, the influence of the major operational variables on the whole process should be known in order to achieve high recovery rates and economical production [67].

Surface area, functionality, porosity, irregularities, strongly bound impurities, internal porous structure, particle size, nature and initial concentration of adsorbate, solution pH, temperature, interfering substances, nature and amount of adsorbent can be listed as factors affecting adsorption.

Adsorption is proportional to the specific surface area since it is a surface phenomenon, meaning total surface area that is available for adsorption can limit or enhance the adsorption. For this reason, more porous and finely divided solid adsorbents can give better adsorption per unit weight [73, 74]. Surface area is mostly composed of the pores of molecular dimensions [68].

The solubility of the solute can affect adsorption to a great degree. If the solute is very soluble, its adsorption into the pores of the adsorbant will be harder. Also, molecular size will affect the transport into the pores. [75, 76].

Capacity of adsorption is significantly affected by the physicochemical nature of the adsorbent. In general, an inverse relationship can be expected between the extent of adsorption of a solute and its solubility in the solvent where the adsorption takes place.

Changes in pH affects adsorption because the distribution of surface charge of the adsorbent can change, and therefore composition of raw materials and the technique of activation vary dependent on this change and affects adsorbate functional groups [77-78].

Adsorption process can also be affected by temperature. Adsorption reactions are generally exothermic reactions; therefore it can be said that the extent of adsorption increases with decreasing temperature [79,80,81].

Final parameter affecting adsorption is concentration of coexistent organic and inorganic compounds. Many compounds present in water and wastewater strongly influence adsorption. This effect can be enhancing adsorption, or interfering with one other, or independent different effects of different compounds can be present [68].

Adsorption is also influenced by the adsorbate characteristics. Adsorption from a multicomponent solution is a complex problem. Interactions between adsorbates may improve the adsorption capacity of some compounds in binary and ternary systems [67].

The effectiveness of the treatment depends not only on the properties of the adsorbent and adsorbate, but also on various environmental conditions and variables used for the adsorption process, e.g. pH, ionic strength, temperature, existence of competing organic or inorganic compounds in solution, initial adsorbate/adsorbent concentration, contact time and speed of rotation, particle size of adsorbent, etc. These parameters should also be taken into account while examining the potential of low-cost adsorbents [65]. Cost factor should not be ignored. Low production cost with higher removal efficiency of adsorbents would make the process economical and efficient.

2.8.3 Adsorbents

Adsorbents should firstly possess high internal volume that will facilitate the components being removed from the fluid. Such highly porous solid structure may be either carbonaceous or inorganic in nature, and synthetic or naturally occurring, and in certain circumstances may have true molecular sieving properties. Adsorbents should also have good mechanical and kinetic properties in order to be resistant and able to transfer adsorbates rapidly. Regenerating adsorbents after use is economical and ideal, and performing regeneration efficiently and without damage to mechanical and adsorptive properties is crucial. In terms of economical aspects, raw materials and methods of adsorbents should be inexpensive for adsorption to be ideal in comparison with other alternative separation processes [82].

Internal surface area is generally consists of pores of various size. interconnected micropore, mesopore and macropore networks form total surface area in many of the adsorbent materials as carbons, silica gels etc. These pore sizes are in following volumes respectively: diameters of macropores are more than 50 nm, diameters of mesopores (known also as transitional pores) are between 2 - 50nm, and diameters of micropores are smaller than 2 nm. Even the largest pores in an adsorbent are in submicron levels and they can only consist of a small part of the total pore volume. While passing through this complex structure, adsorbate molecules first pass through the fluid film on the external surface of adsorbent particle, then passes through the macroporous structure and into the micropores.
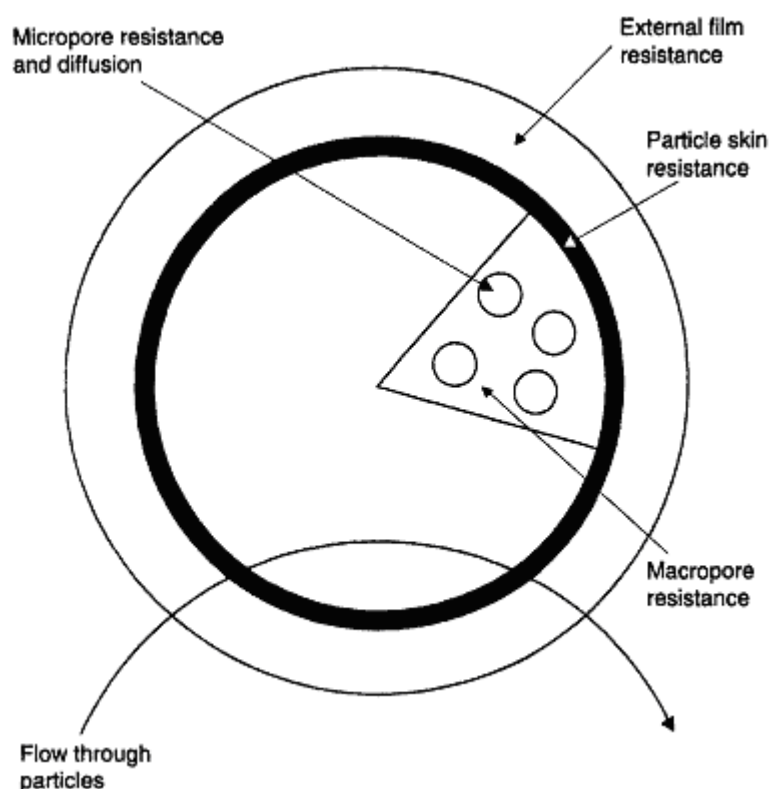

Figure 2.13 : An adsorbent molecule and resistances in the uptake of adsorbate [82].

2.8.4 Types of adsorbents

A number of materials have been extensively investigated as adsorbents in water pollution control [65]. These include activated carbons, minerals, biosorbents, zeolites, aluminas, silica gels, polymeric adsorbents, and ion-exchange resins. The presence of a variety of micro- and mesoporous adsorbents has been the origin of the development of adsorption technology. Large specific surface area (500 to 1500

m2/g), varying pore structure, and polar and nonpolar surface properties can facilitate the selective adsorption[71].

Main types of adsorbents used in industry have been specified in Table 2.1.

Table 2.1 : Types of industrial adsorbents [82].

Carbon Adsorbents	Mineral Adsorbents	Other Adsorbents
Carbon Adsorbents	Mineral Adsorbents	Other Adsorbents
Active carbons	Silica gels	Synthetic polymers
Activated carbon fibers	Activated alumina	Composite adsorbents
Molecular carbon sieves	Oxides of metals	Mixed sorbents
Monocarbon microbeads	Hydroxides of metals	Monocarbon microbeads
Fullerenes	Zeolites	Fullerenes
Heterofullerenes	Clay minerals	Heterofullerenes
Carbonaceous nanomaterials	Pillared clays	Carbonaceous nanomaterials
	Porous clay-hetero structures	
	Inorganic nanomaterials	

2.8.4.1 Activated carbons, resins, minerals

Mineral adsorbents include siliceous materials and natural clays, which also show ion exchange ability. Chemical modification can increase the affinity of minerals towards the adsorption of several compounds [67]. These are strong adsorbents with high surface area. For example, for activated carbons, only about 0.0003% of the total surface is the external surface of the carbon particle assuming spherical particles [83]. Since clay minerals have low cost, high surface area, high porosity, and abundance in most continents, clays are good candidates as adsorbents. There are many kinds of clays:smectites (montmorillonite, saponite), mica (illite), kaolinite, serpentine, pylophyllite (talc), vermiculite, sepiolite, bentonite, kaolinite, diatomite, and Fuller'searth (attapulgite and montmorillonite varieties) [84]. Ion exchange resins and minerals are also used extensively in adsorption.

2.8.4.2 Low cost adsorbents

These can be listed as fly ash, lignin and lignocellulosic materials, and polysaccharide-based adsorbents. This group includes chitin, chitosan, cyclodextrin, starch, crosslinked starch, starch derivatives, hybrid materials such as cyclodextrin bound to silica, non-woven fabrics immobilized on polypropylene, chitosan immobilized on sand, alginate–chitosan gels or chitosan–cyclodextrin derivatives Polysaccharide materials show versatility, chemical stability, high reactivity, ability to interact with a variety of molecules. Some functional groups provide excellent chelating and complexing properties, allowing an easy regeneration[67].

2.8.4.3 Biosorbents

The term biosorption designs a number of metabolism-independent processes involving the uptake of solutes from aqueous solutions by material of microbial origin. Biosorbent materials such as wastes from fermentation and activated sludges are abundant and cost-efficient. Living biomass can also act as a biosorbent in degradation processes, but nutrient supply and toxicity should be considered. Dead cells can be regenerated and reused, although limitations derived from adsorbate separation and mass loss may occur. Sewage sludge might be used as a cheap biosorbent for phenolics alone or in combination with other adsorbents. Adsorption of model phenolics onto macroalgae, fungi, sponge, and olive mill phenolics onto bacterial cells was reported [67].

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3. EXPERIMENTAL

3.1 Chemicals

Chitosan is supplied from Sigma-Aldrich. Product form is coarse ground flakes and powder and color is off-white to beige. Deacetylation ratio is 75%. Montmorillonite is supplied from Süd-Chemie. Average particle size of montmorillonite used in this thesis is smaller than 10 µm. Its cation exchange capacity is 80 meq/100g. Urea is supplied from Carlo Erba. It is an A.C.S. grade reagent with 99.8% assay. 37% formaldehyde solution was obtained from Merck. Acetic acid was supplied from Glacier Chemicals. Sodium hydroxide pellets used were supplied from Sigma Aldrich. Reactive Blue 221, Reactive Red 195 and Reactive Black 5 was obtained from Solar Fine Chemicals.

3.2 Equipments

Adsorbance values of dye solutions at certain wavelengths were measured by UV-visible spectrophotometer the trademark Hitachi U-0080D able to measure wavelengths between 200 nm to 1100 nm.

Trademark of FTIR used for characterization of composites is Perkin Elmer Spectrum 65.

Trademark of drying oven used for drying composite films and composite flakes is Binder, it can be heated up to 300˚C.

Trademark of magnetic stirrer used is Heidolph MR and it can be heated and stirred up to 350˚C and 1250 rpm.

For SEM analyses, trademark of the device used is Philips ESEM–FEG XL-30.

3.3 Synthesis

3.3.1 Synthesis of Chitosan-Montmorillonite Composites

For the synthesis of chitosan-montmorillonite composites, firstly 0.5 g of montmorillonite (MMT) is mixed in 100 ml of distilled water in a magnetic stirrer at 800 rpm for at least half an hour. Concurrently, 0.5 g of chitosan is mixed in 100 ml of 2% (v/v) distilled water and acetic acid solution. Chitosan solution is close to gel form upon mixing with dilute acid solution and attention must be paid the chitosan to completely dissolve. Then chitosan solution is thoroughly mixed with montmorillonite solution in a magnetic stirrer at 800 rpm for at least half an hour. Mixture is poured to a container to be dried in drying oven at 60 ˚C until it is dried completely. After drying, chitosan-montmorillonite composites are ground into fine flakes (Chi-MMT). Reactive Blue 221, Reactive Red 195 and Reactive Black 5 dye solutions are formed in 50 mg/L in concentration.

Upon changing the ratio of chitosan to montmorillonite in composites, 0.25 mg of montmorillonite is mixed in 100 ml of water at 800 rpm for at least half an hour and 0.5 g of chitosan is mixed in 100 ml of 2% acetic acid solution. The same operations are performed as explained above for these composites.

Lastly, 0.5 mg of montmorillonite is mixed in 100 ml of water at 800 rpm for at least half an hour and 0.25 g of chitosan is mixed in 100 ml of 2% acetic acid solution. The same operations are performed as explained above for these composites.

Table 3.1: Ratios of chitosan-montmorillonite in composites.

Composite Name	Chitosan Amount	Montmorillonite Amount	Chi-MMT ratio
Chi/MMT-a	0.25 g	0.5 g	1:2
Chi-MMT	0.5 g	0.5 g	1:1
Chi/MMT-b	0.5 g	0.25 g	2:1

3.3.2 Synthesis of Chitosan-Montmorillonite Composites Crosslinked with Urea-Formaldehyde

For the synthesis of chitosan-montmorillonite composites crosslinked with urea-formaldehyde, 0.5 mg of montmorillonite is mixed in 100 ml of water at 800 rpm for at least half an hour and 0.5 g of chitosan is mixed in 100 ml of 2% acetic acid

solution. Then chitosan solution is thoroughly mixed with montmorillonite solution in a magnetic stirrer at 800 rpm for at least half an hour. 0.6 g of urea is dissolved in 3 ml of 37% formaldehyde solution. Urea-formaldehyde mixture is added dropwise to chitosan-montmorillonite mixture under stirring in a magnetic stirrer at 75°C. After 3 hours of mixing at this temperature, mixtures (Chi-MMT-UF) were cast on watch glasses and left to dry at room temperature.

For the synthesis of chitosan-montmorillonite composites crosslinked with urea-formaldehyde with low formaldehyde content, 0.5 mg of montmorillonite is mixed in 100 ml of water at 800 rpm for at least half an hour and 0.5 g of chitosan is mixed in 100 ml of 2% acetic acid solution. Then chitosan solution is thoroughly mixed with montmorillonite solution in a magnetic stirrer at 800 rpm for at least half an hour. 0.6 g of urea is dissolved in 1.5 ml of 37% formaldehyde solution. Urea-formaldehyde mixture is added dropwise to chitosan-montmorillonite mixture under stirring in a magnetic stirrer at 75°C. After 3 hours of mixing at this temperature, mixtures (Chi-MMT-UF2) were cast on watch glasses and left to dry at room temperature. The ratio of formaldehyde content of these composites to priorly formed Chi-MMT-UF composites is 1:2.

For the synthesis of chitosan-montmorillonite composites crosslinked with urea-formaldehyde with no formaldehyde content, 0.5 mg of montmorillonite is mixed in 100 ml of water at 800 rpm for at least half an hour and 0.5 g of chitosan is mixed in 100 ml of 2% acetic acid solution. Then chitosan solution is thoroughly mixed with montmorillonite solution in a magnetic stirrer at 800 rpm for at least half an hour. 0.6 g of urea is dissolved in 3 ml of distilled water. Urea mixture is added dropwise to chitosan-montmorillonite mixture under stirring in a magnetic stirrer at 75°C. After 3 hours of mixing at this temperature, mixtures (Chi-MMT-U) were cast on watch glasses and left to dry at room temperature.

3.4 Adsorption Experiments

3.4.1 Chitosan-montmorillonite composites

In the experiments which Chi-MMT amount was changed, first experiment was performed with 5 mg of dye and 50 mg adsorbent in 100 ml of distilled water. Three

solutions were prepared in this way for three dyes (Reactive Blue 221, Reactive Red 195 and Reactive Black 5). In the other three experiments, dye amount was not changed (5 mg) and adsorbent amount was increased to 100 mg, 200 mg and 300 mg added to 100 ml dye solution.

In the experiments which pH value amount was changed, 3 sets of solutions were prepared in pH values of 4, 6 and 8 by adjusting with NaOH solution. Nine solutions were prepared in this way for three dyes (Reactive Blue 221, Reactive Red 195 and Reactive Black 5). These solutions contained 5 mg of dye and 100 mg of adsorbent in 100 ml dye solution.

In the experiments which temperature was changed, 2 sets of solutions were prepared in room temperature (25 °C) and refrigerated conditions (10 °C). Six solutions were prepared in this way for three dyes (Reactive Blue 221, Reactive Red 195 and Reactive Black 5).These solutions also contained 5 mg of dye and 100 mg of adsorbent in 100 ml dye solution.

In the experiments which chitosan ratio in composite was changed, 3 sets of solutions were prepared with composites possessing chitosan:montmorillonite ratio of 1:1, 1:2 and 2:1. Nine solutions were prepared in this way for three dyes (Reactive Blue 221, Reactive Red 195and Reactive Black 5). These solutions contained 5 mg of dye and 100 mg of adsorbent in 100 ml dye solution.

3.4.2 Chitosan-montmorillonite composites with urea and urea-formaldehyde

In these experiments, composites of chitosan-montmorillonite with urea and urea-formaldehyde was used. Three kinds of composites were formed, two of which with had 1:2 formaldehyde ratio among them (Chi-MMT-UF and Chi-MMT-UF2, respectively) and the third one had no formaldehyde content (Chi-MMT-U).

2 sets of solutions were prepared with composites possessing formaldehyde ratio of 2:1. Six solutions were prepared in this way for three dyes (Reactive Blue 221, Reactive Red 195and Reactive Black 5).These solutions contained 5 mg of dye and 100 mg of adsorbent in 100 ml dye solution.

Three solutions were prepared with composites possessing no formaldehyde content for three dyes (Reactive Blue 221, Reactive Red 195 and Reactive Black 5).These solutions contained 5 mg of dye and 100 mg of adsorbent in 100 ml dye solution.

4. RESULTS AND DISCUSSION

In this study, Chi-MMT composites and urea-formaldehyde and Chi-MMT composites were formed for the adsorption of dye molecules from aqueous solutions. Chi-MMT composites were formed in ratios 1:1, 2:1 and 1:2 in order to determine the effect of different amounts of the clay. Chi-MMT composites containing urea and urea-formaldehyde were formed for improving adsorption properties of the composites, urea to formaldehyde ratio was 1:2, 1:1 in these composites, except for one composite in which no formaldehyde was used. Characterization of Chi-MMT composites and urea-formaldehyde and Chi-MMT composites is performed with FTIR and SEM.

Changes of adsorption capacities (q_t) with time data were plotted on q_t-t graph values. After determination of adsorption capacities, the effect of adsorption data on rate equations was investigated and second order rate equations were fitted to data. The effect of adsorption amount, temperature and pH on adsorption capacity was investigated. Also, adsorption equilibrium constants were calculated.

4.1 Characterization of Samples

4.1.1 FTIR spectrophotometric analysis

The FTIR spectra of urea and Chi-MMT-UF, Chi-MMT-UF2 and Chi-MMT-U composites and Chi-MMT composites are presented in Figure 4.1, Figure 4.2, Figure 4.3 and Figure 4.4.
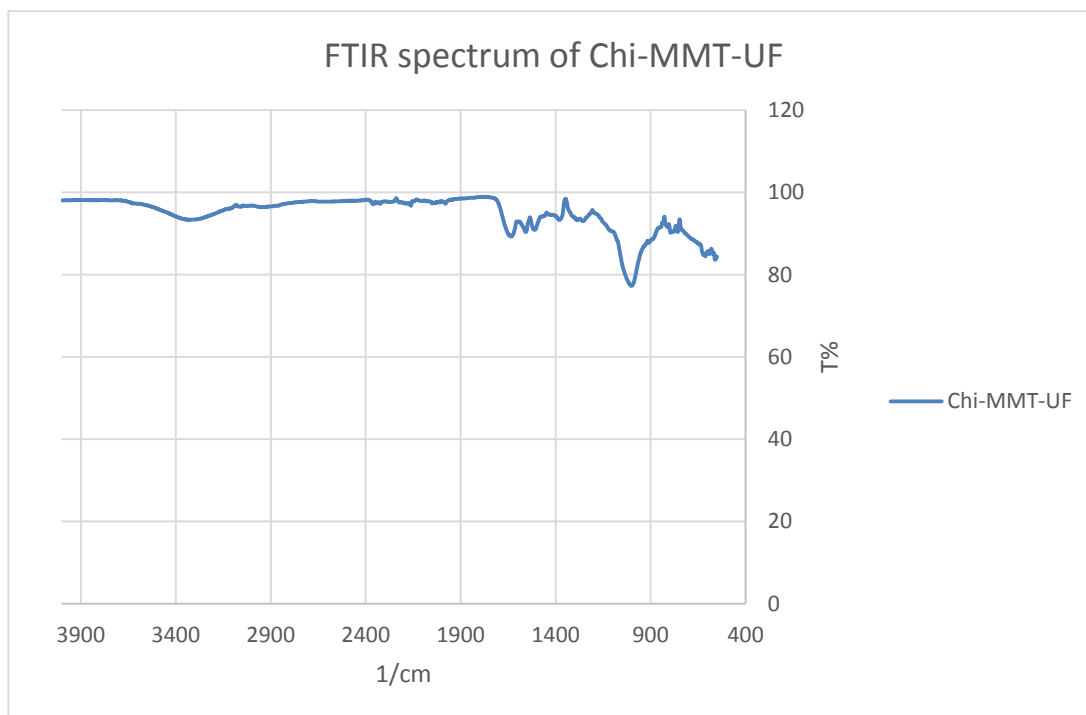
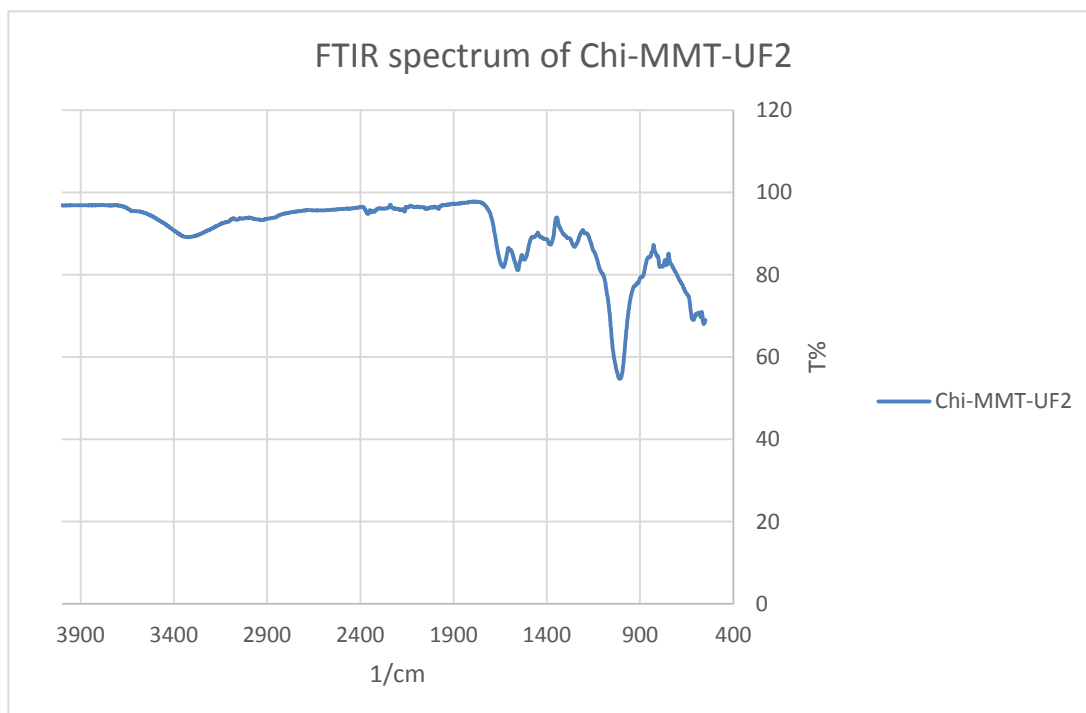**Figure 4.1 :** FTIR spectrum Chi-MMT-UF composites.
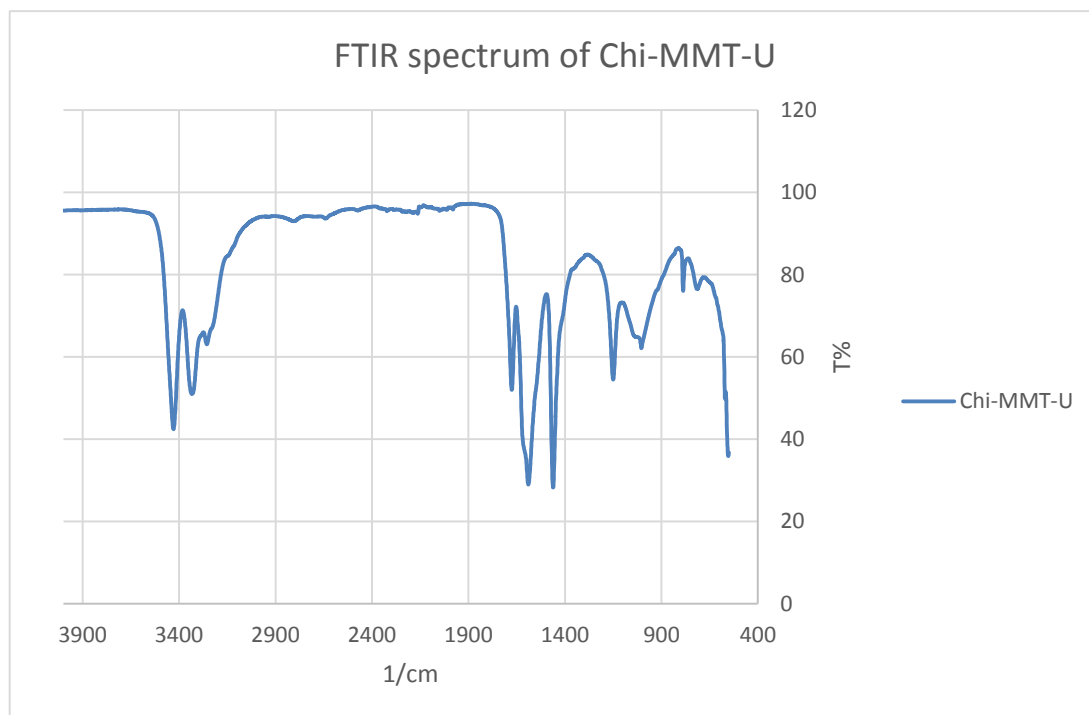

Figure 4.2 : FTIR spectrum Chi-MMT-UF2 composites.

Figure 4.3 : FTIR spectrum Chi-MMT-U composites.

It can be seen that near 1550-1560 cm^{-1} a specific peak for urea-formaldehyde resins is observed due to N-H stretching. Also, due to C-N stretching, a peak near 1240 cm^{-1} is observed. Approximately at 1640 cm^{-1}, due to –NH-C=O- stretching, another peak is observed. Near 3330 cm^{-1}, another peak can be observed due to N-H stretching. Proceeding to the other FTIR spectra, specific peaks for chitosan is examined in Figure 4.4 and 4.5.
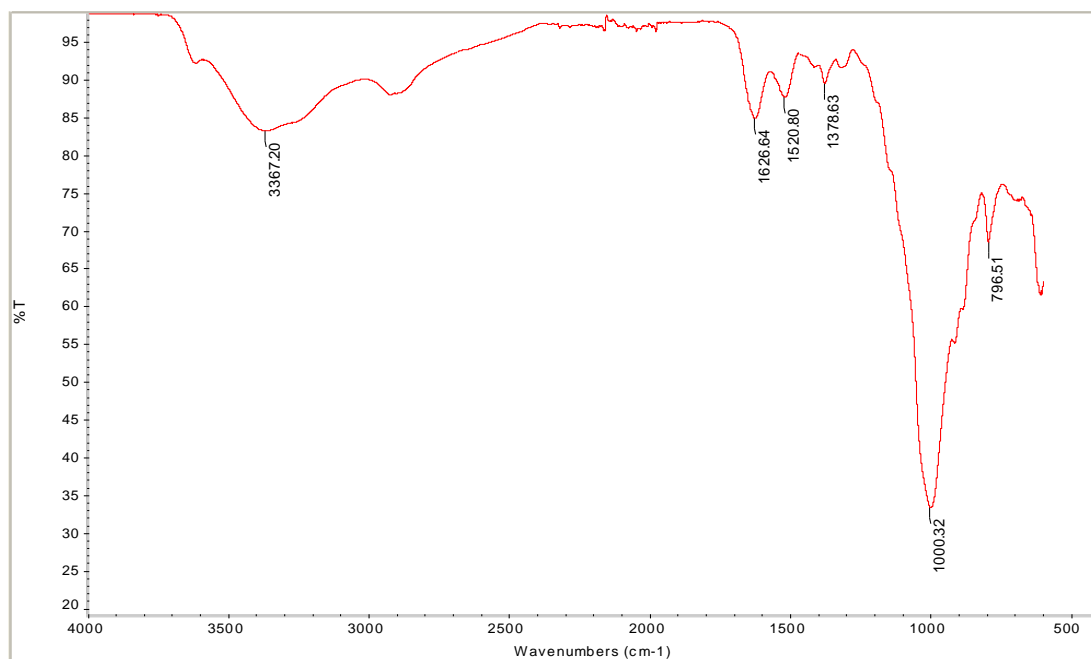
Figure 4.4 : FTIR spectrum Chi-MMT composites.

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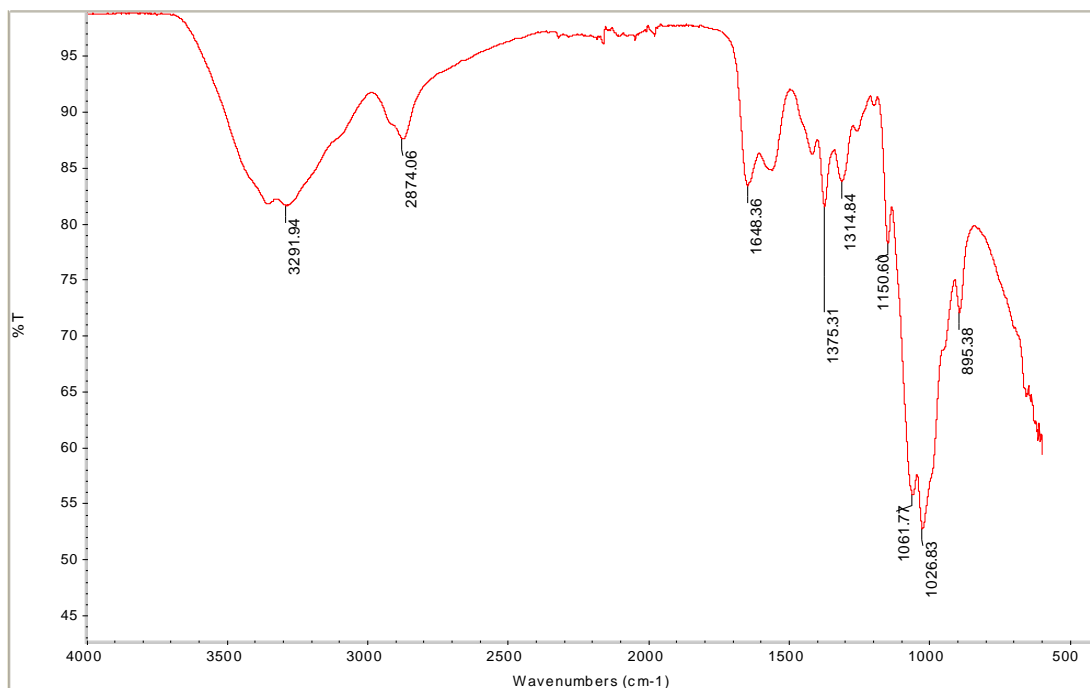
Figure 4.5 : FTIR spectrum chitosan flakes.

It can be seen from Figure 4.5 that a specific peak for N-acetylglucosamine is present near 1314 cm^{-1}. This band is smaller in Figure 4.4 due to interaction with montmorillonite. Also, the peak near 1648 cm^{-1} indicating presence of amide groups in Figure 4.5 is present in smaller size in near 1626cm^{-1} in Figure 4.4 for the same reason. Also, the large band due to–OH group and –NH stretching vibration near 3291 cm^{-1} in Figure 4.5 is smaller in Figure 4.4 near 3367 cm^{-1} because of its interaction with montmorillonite. The peak at 2874cm^{-1} refers to aliphatic C-H stretching, also smaller in Figure 4.4 due to interaction. At 796 cm^{-1}, a peak due to montmorillonite presence (Si-O) is observed, with another one at 1000 cm^{-1}.due to Si-O stretching.

4.1.2 SEM analysis

Images obtained with Scanning Electron Microscope is presented in Figure 4.6 for Chi-MMT molecules.
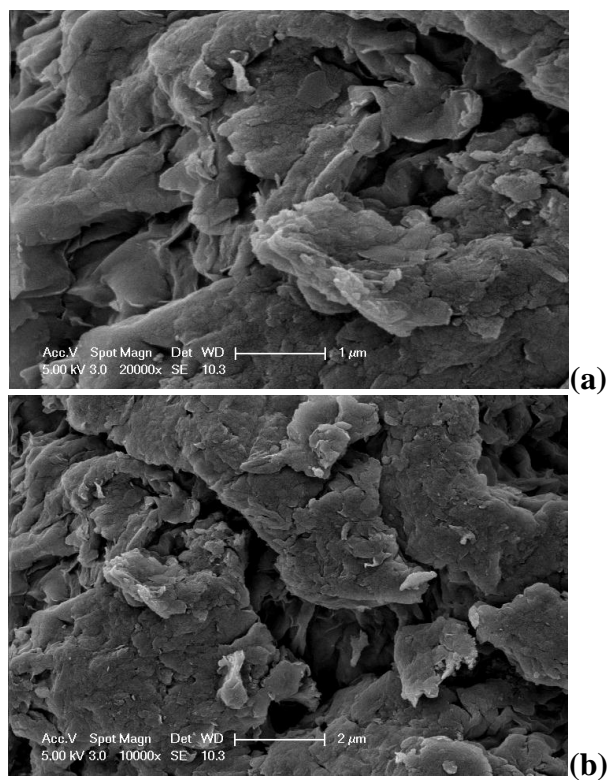
Figure 4.6 : SEM images of Chi-MMT flakes (a) 1 µm (b) 2 µm.

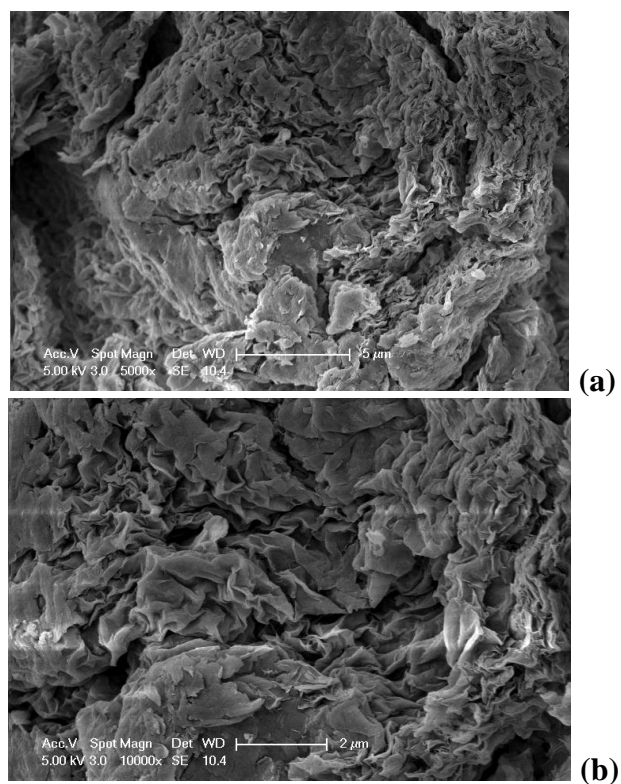It can be seen that Chi-MMT composites have a porous structure favorable for adsorption.

Figure 4.7 : SEM images of Chi-MMT (a) 5 µm (b) 2 µm.

It can also be seen from more distant images of Chi-MMT flakes that the surface area of composites is quite large as essential for adsorption.
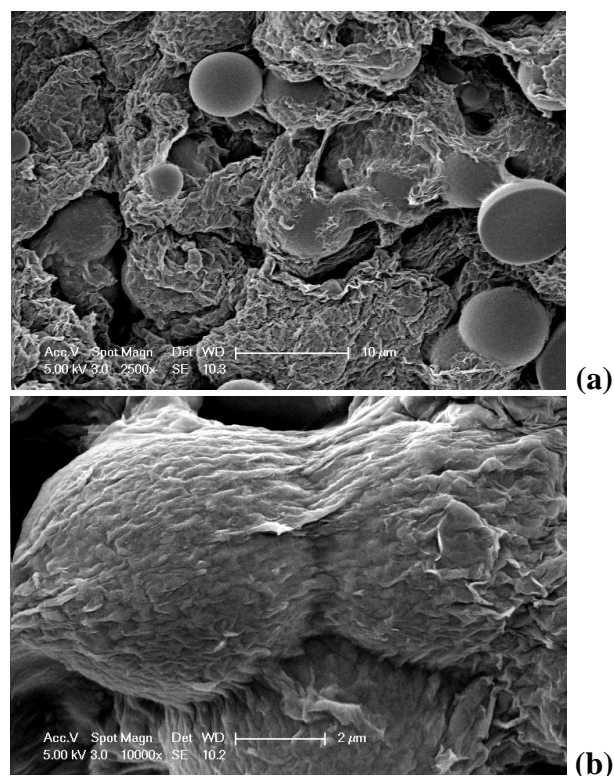

(a)

(b)

Figure 4.8 : SEM images of Chi-MMT-UF2 composites (a) 10 µm (b) 2 µm.

It can be seen from SEM images of Chi-MMT-UF2 molecules that urea-formaldehyde and Chi-MMT molecules have formed a porous structure suitable for adsorption.

4.2 Adsorption Plots

4.2.1 Experiments with changes in adsorbent amount

The experiments were performed with dye solutions 50 mg/L in concentration. Four experiments were performed with 500 mg/L, 1000 mg/L, 2000 mg/L and 3000 mg/L adsorbent in 100 ml dye solutions. The data were plotted in q_t/t graphs in Figure 4.9.
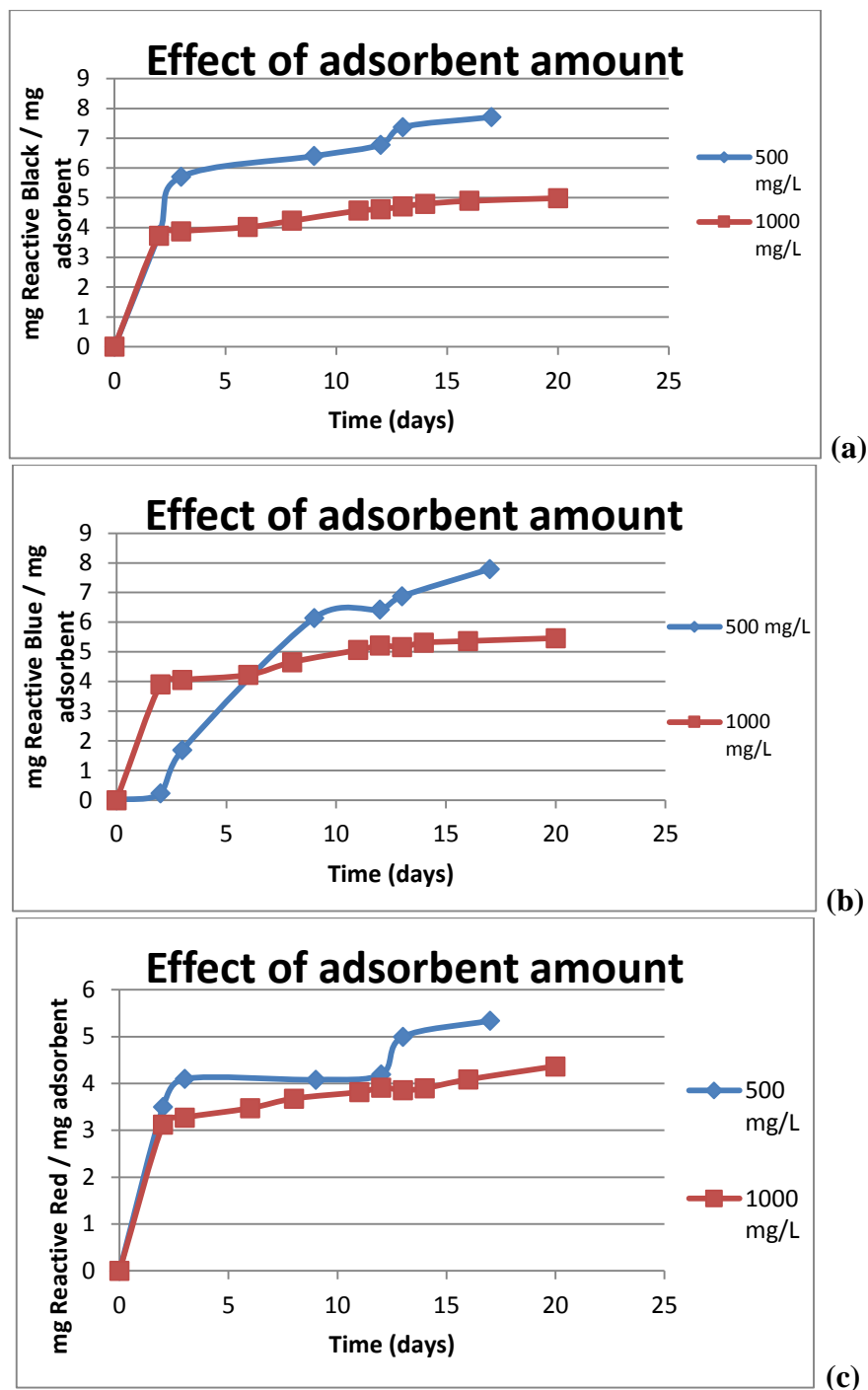
Figure 4.9 : Values of q_t versus time for three different dyes by Chi-MMT composites of different amounts (a) RB5 (b) RB221 (c) RR195 (Dye concentration=50 mg/L, Temperature=25˚C).

The experiments performed with 2000 mg/L and 3000 mg/L adsorbent in 100 ml dye solutions were plotted in qt/t graphs in Figure 4.10.
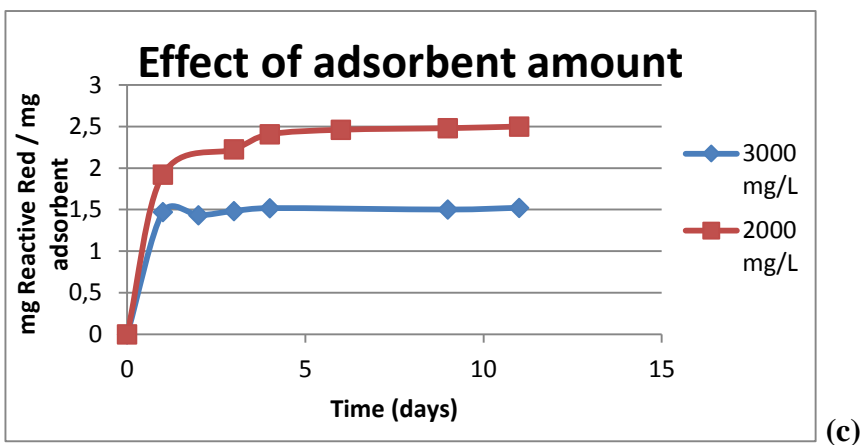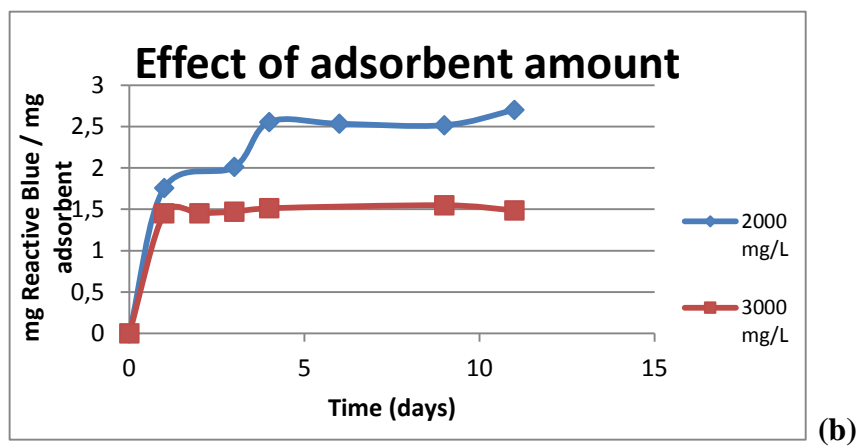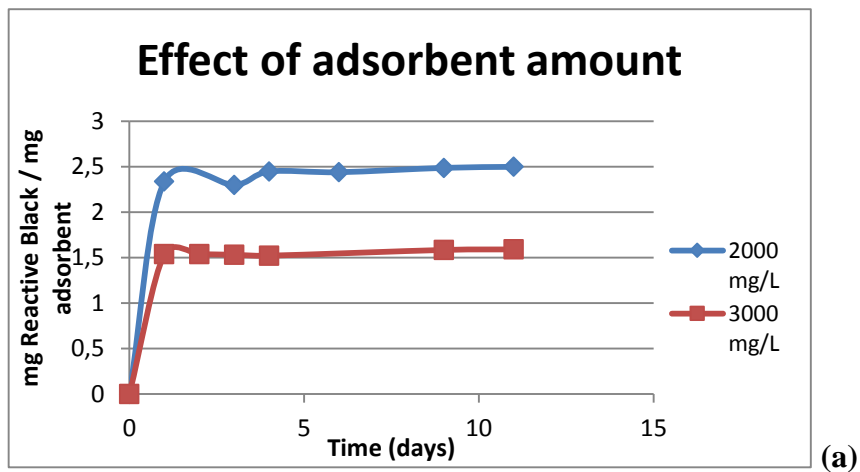
Figure 4.10 : Values of q_t versus time for three different dyes by Chi-MMT composites of different amounts (a) RB5 (b) RB221 (c) RR195 (Dye concentration=50 mg/L, Temperature=25˚C).

Experiments with 50 mg of adsorbent gave the best q_t values since these adsorbate amounts are lower than the best capacity of this adsorbent and experiments were

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performed in order to find optimum amount of adsorbent for the fastest adsorption and respective optimum conditions. Another experiment will be performed in order to find the best q_t value. By increasing adsorbent amount from 500 mg/L to 1000 mg/L, q_t values were changed from 7.70 mg dye/mg adsorbent to 4.98 mg dye/mg adsorbent for Reactive Black, 7.79 mg dye/mg adsorbent to 5.46 mg dye/mg adsorbent for Reactive Blue and 5.34 mg dye/mg adsorbent to 4.36 mg dye/mg adsorbent for Reactive Red since dye amount is stable and milligram of dye for each milligram of adsorbent decreases with increasing adsorbent amounts.

Experiments with 200 mg of adsorbent gave better q_t values than the ones with 300 mg of adsorbent. q_t value was changed from 2.48 mg dye/mg adsorbent to 1.32 mg dye/mg adsorbent for Reactive Black, 2.68 mg dye/mg adsorbent to 1.48 mg dye/mg adsorbent for Reactive Blue and 1.52 mg dye/mg adsorbent to 2.48 mg dye/mg adsorbent for Reactive Red since dye amount is stable and milligram of dye for each milligram of adsorbent decreases with increasing adsorbent amounts.

4.2.2 Experiments with adsorbents of different chitosan ratios

The experiments were performed with 100 ml dye solutions 50 mg/L in concentration. Three experiments were performed with 1000 mg/L adsorbent with different chitosan:montmorillonite ratios of 1:1 (Chi-MMT), 2:1 (Chi-MMT-b), 1:2 (Chi-MMT-a). The data were plotted in qt/t graphs in Figure 4.11.
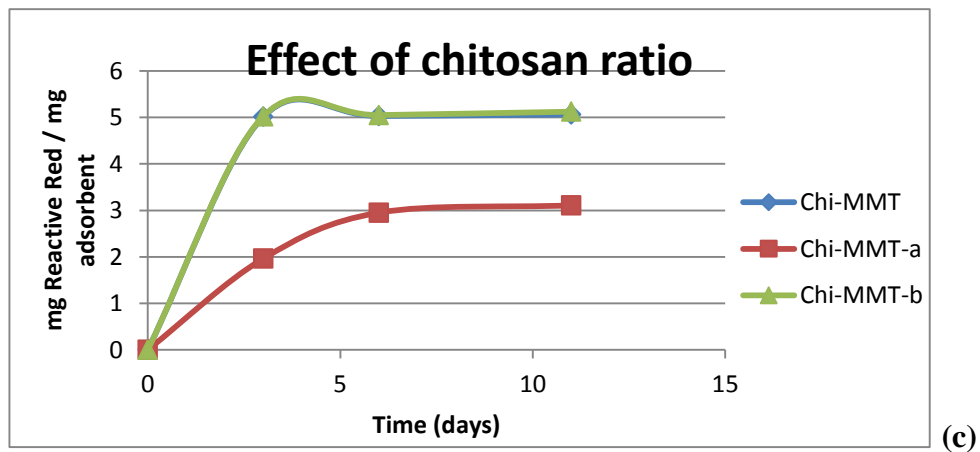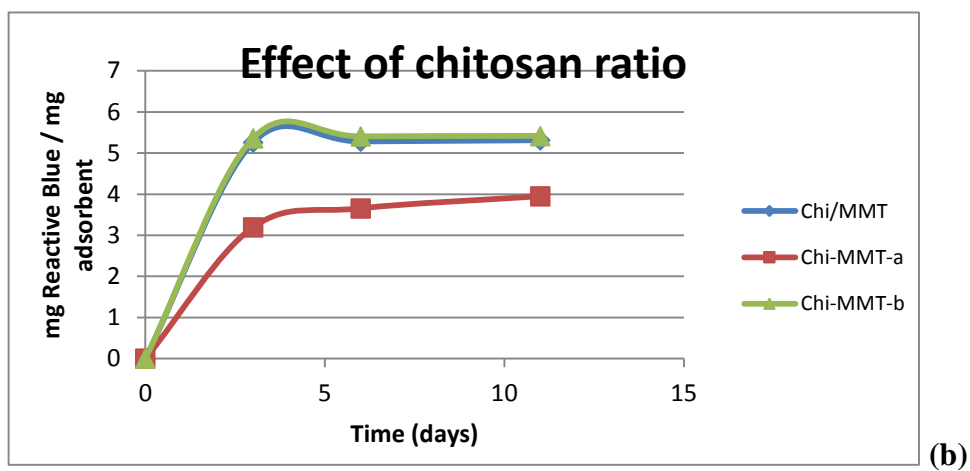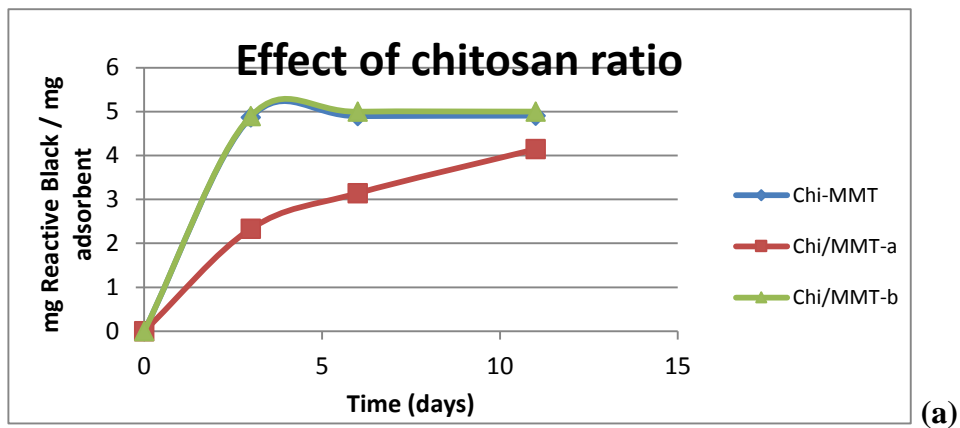
Figure 4.11 : Values of q_t versus time for three different dyes by Chi-MMT composites of different chitosan ratios (a) RB5 (b) RB221 (c) RR195 (Dye concentration=50 mg/L, Temperature=25˚C).

Experiments with Chi-MMT-b gave best q_t values than the ones with Chi-MMT-a and Chi-MMT. q_t value was changed with Chi-MMT-a, Chi-MMT and Chi-MMT-b from 4.14 mg dye/mg adsorbent to 4.90 mg dye/mg adsorbent and 4.99 mg dye/mg

adsorbent for Reactive Black, 3.95 mg dye/mg adsorbent to 5.31 mg dye/mg adsorbent and 5.41 mg dye/mg adsorbent for Reactive Blue and 3.10 mg dye/mg adsorbent to 5.06 mg dye/mg adsorbent and 5.12 mg dye/mg adsorbent for Reactive Red. This can be explained by the increasing chitosan amount in composites.

4.2.3 Experiments with different temperature values

Two experiments were performed at 25˚C and 10˚C with 1000 mg/L adsorbent in 100 ml dye solutions 50 mg/L concentration. The data were plotted in qt/t graphs in Figure 4.12.
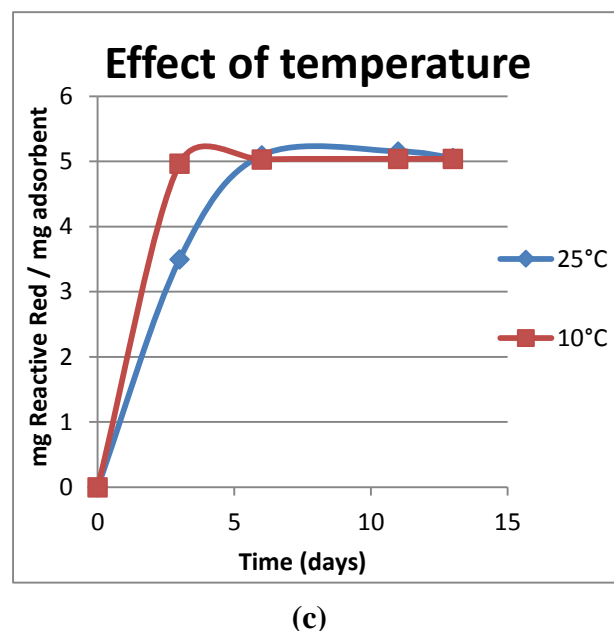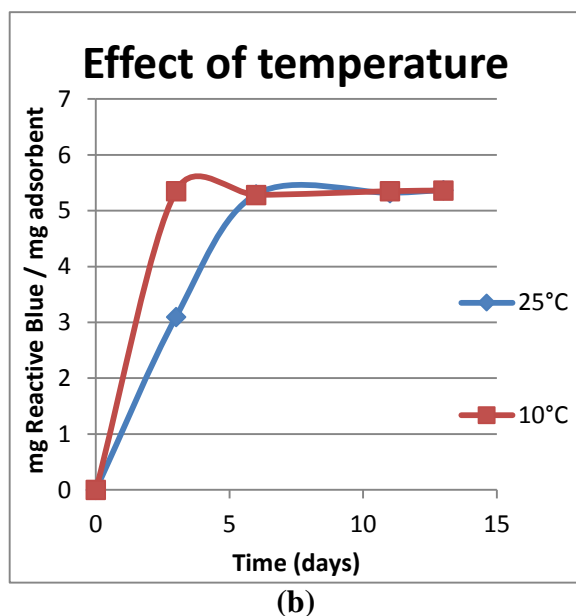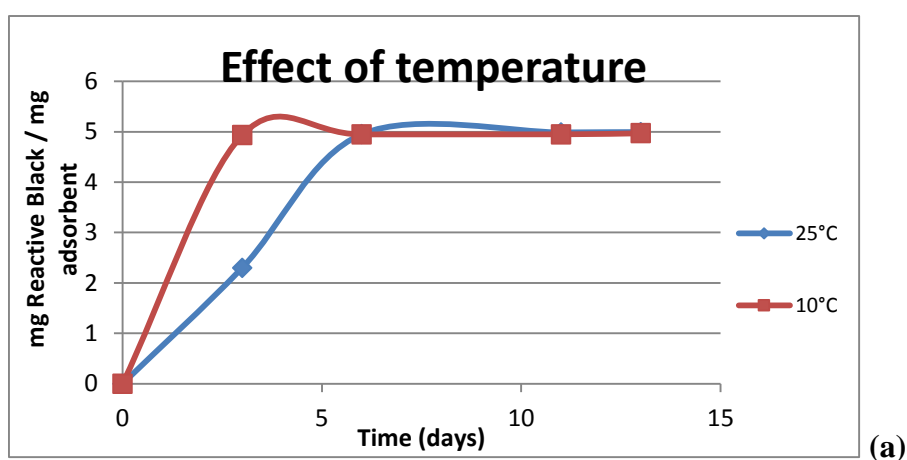

Figure 4.12 : Values of q_t versus time for three different dyes by Chi-MMT composites in different temperature values (a) RB5 (b) RB221 (c) RR195 (Dye concentration=50 mg/L, Adsorbent amount=1000 mg/L).

Experiments with 25°C and 10°C gave similar results since temperature only affects the rate of adsorption and does not affect q_t values significantly. For 10°C q_t value is 4.94 mg dye/mg adsorbent for Reactive Black, 5.28 mg dye/mg adsorbent for Reactive Blue and 5.03 mg dye/mg adsorbent for Reactive Red. q_t value obtained with 25°C is 4.99 mg dye/mg adsorbent for Reactive Black, 5.37 mg dye/mg adsorbent for Reactive Blue and 5.05 mg dye/mg adsorbent for Reactive Red. The fact that 10°C gave slightly lower q_t value can be explained by faster adsorption and shorter adsorption period.

4.2.4 Experiments with different pH values

Three experiments were performed at pH 4, pH 6 and pH 8 with 1000 mg/L adsorbent in 100 ml dye solutions 50 mg/L in concentration. The data were plotted in qt/t graphs in Figure 4.13.
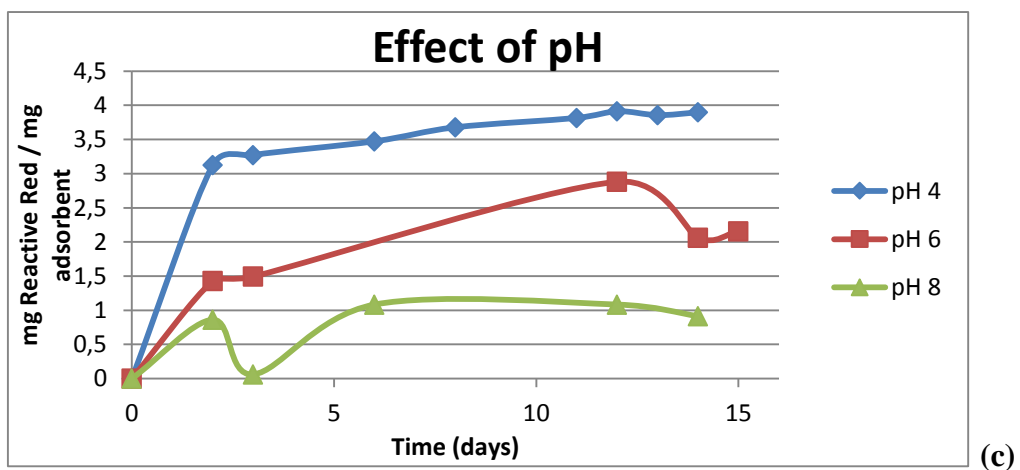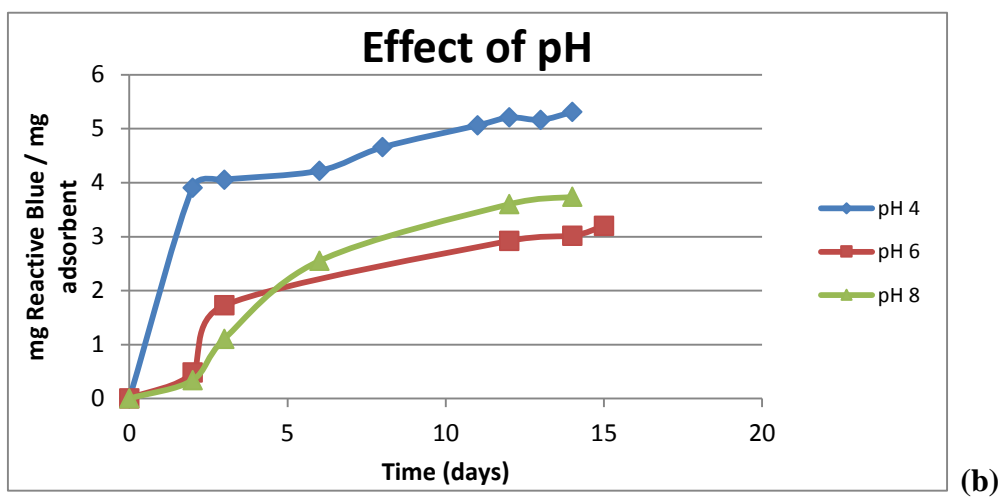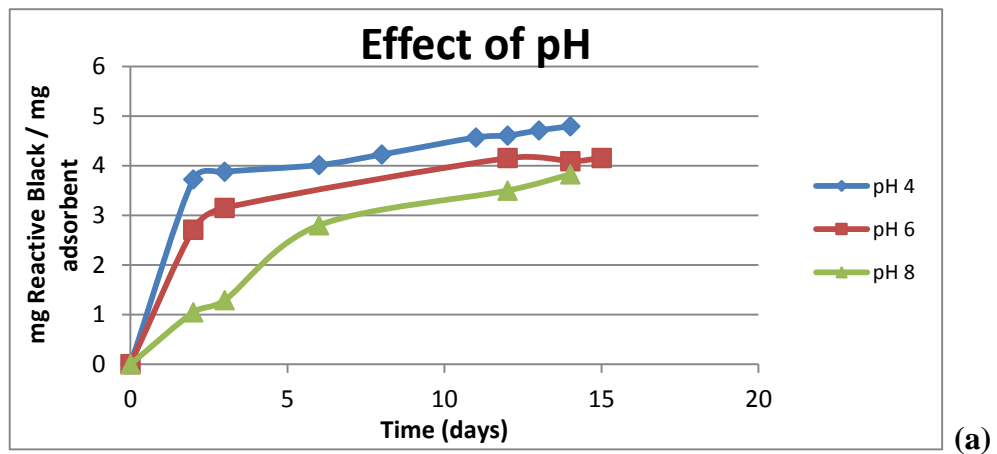
Figure 4.13 : Values of q_t versus time for three different dyes by Chi-MMT composites in different pH values (a) RB5 (b) RB221 (c) RR195 (Dye concentration=50 mg/L, Adsorbent amount=1000 mg/L).

Experiments with pH value 4 gave best q_t values than other ones with pH 6 and pH 8. q_t values were changed with pH values of 4, 6 and 8 from 4.98 mg dye/mg adsorbent to 4.57 mg dye/mg adsorbent and 3.82 mg dye/mg adsorbent for Reactive Black, 5.46 mg dye/mg adsorbent to 3.40 mg dye/mg adsorbent and 3.73 mg dye/mg adsorbent for Reactive Blue and 4.36mg dye/mg adsorbent to 2.51 mg dye/mg adsorbent and 1.08 mg dye/mg adsorbent for Reactive Red. Best results were obtained by pH value 4.

4.2.5 Experiments with Chi-MMT-UF, Chi-MMT-UF2 and Chi-MMT-U

Three experiments were performed with Chi-MMT-UF, Chi-MMT-UF2 and Chi-MMT-U with 1000 mg/L adsorbent in 100 ml dye solutions 50 mg/L concentration. The data were plotted in qt/t graphs in Figure 4.14.
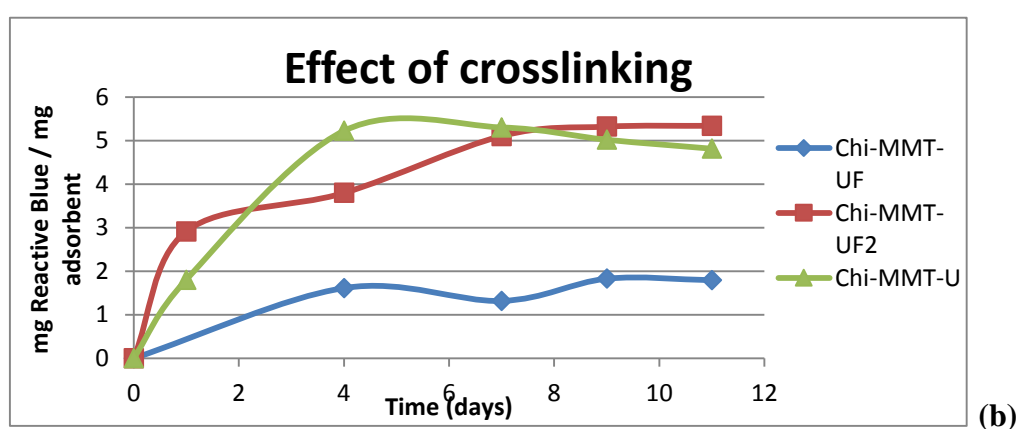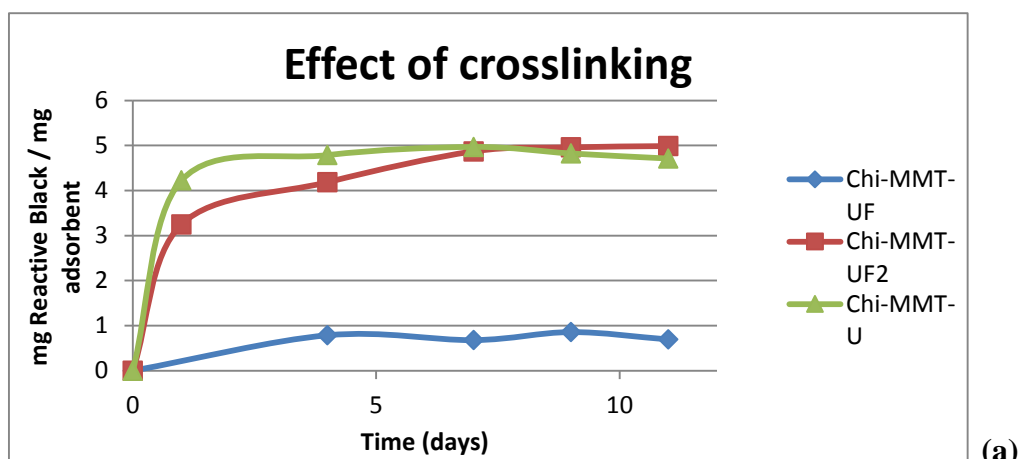
Figure 4.14 : Values of q_t versus time for three different dyes by Chi-MMT-UF composites with different formaldehyde ratios (a) RB5 (b) RB221 (c) RR195 (Dye concentration=50 mg/L, Adsorbent amount=1000 mg/L).

Experiments with Chi-MMT-UF2 gave best qt values than other ones with Chi-MMT-UF and Chi-MMT-U. qt values were changed with Chi-MMT-UF, Chi-MMT-UF2, and Chi-MMT-U from 0.82 mg dye/mg adsorbent to 4.98 mg dye/mg adsorbent and 4.87 mg dye/mg adsorbent for Reactive Black, 1.86 mg dye/mg adsorbent to

5.34 mg dye/mg adsorbent and 4.81 mg dye/mg adsorbent for Reactive Blue and 0.27 mg dye/mg adsorbent to 5.13 mg dye/mg adsorbent and 4.93 mg dye/mg adsorbent for Reactive Red.

4.2.6 Experiments with optimum conditions

Optimum conditions were determined from the previous experiments. An experiment was performed with Chi-MMT composites with 1000 mg/L adsorbent in 100 ml dye solutions in 50 mg/L dye concentration at 10 °C and pH 4. The data were plotted in qt/t graphs in Figure 4.15. Also, dye amount was increased and the same experiment was repeated at 10 °C and pH 4 with 1000 mg/L adsorbent in 100 ml dye solutions in 200 mg/L dye concentration. Highest q_t values were obtained with this experiment since amount of dye for each mg of adsorbent has been increased.
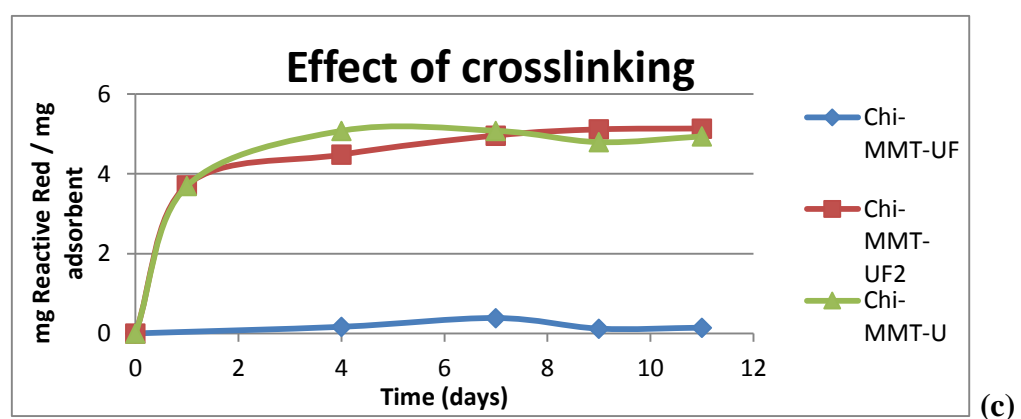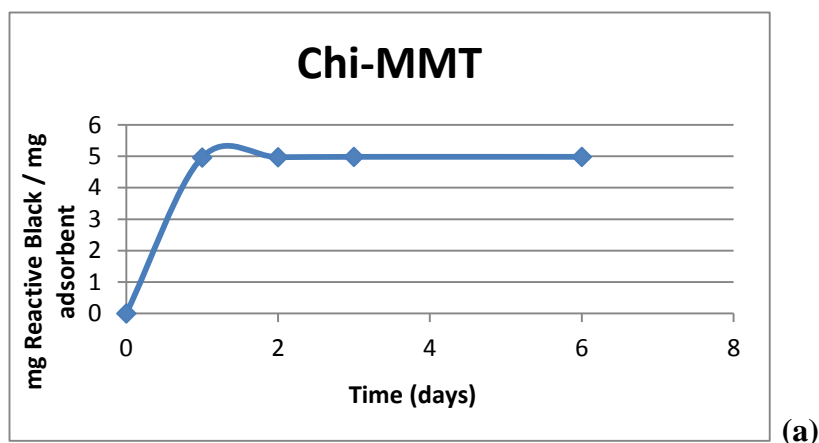

(a)
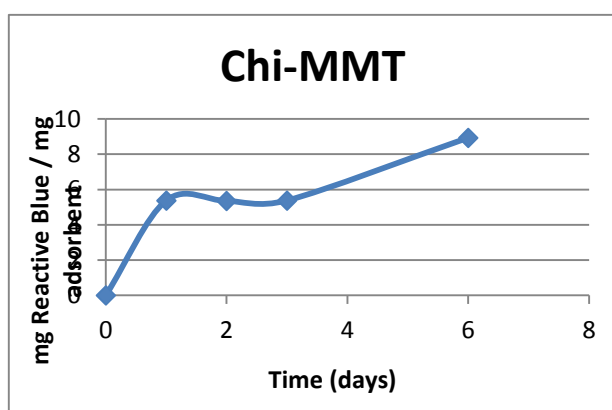
(b)
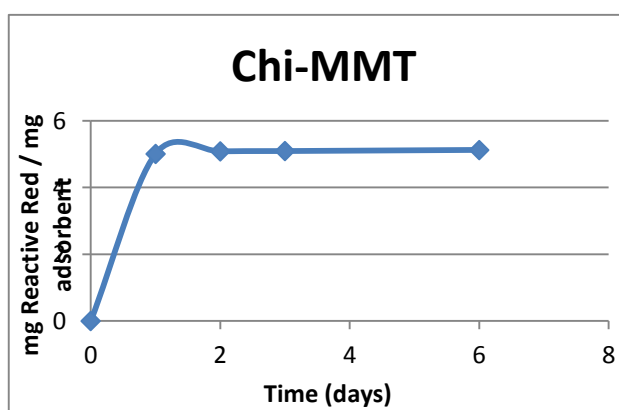
(c)

Figure 4.15 : Values of q_t versus time for three different dyes by Chi-MMT composites in optimum conditions (a) RB5 (b) RB221 (c) RR195 (Dye concentration=50 mg/L, Adsorbent amount=1000 mg/L).

Values of q_t were determined to be 4.98 mg dye/mg adsorbent for Reactive Black, 8,93 mg dye/mg adsorbent for Reactive Blue and 5.09 mg dye/mg adsorbent for Reactive Red.
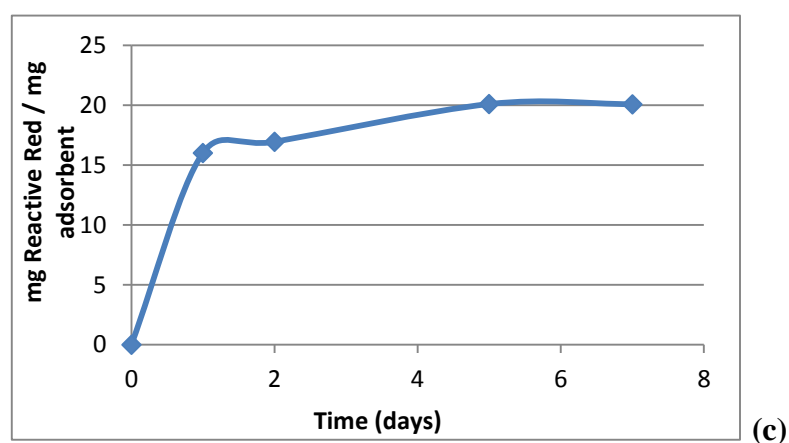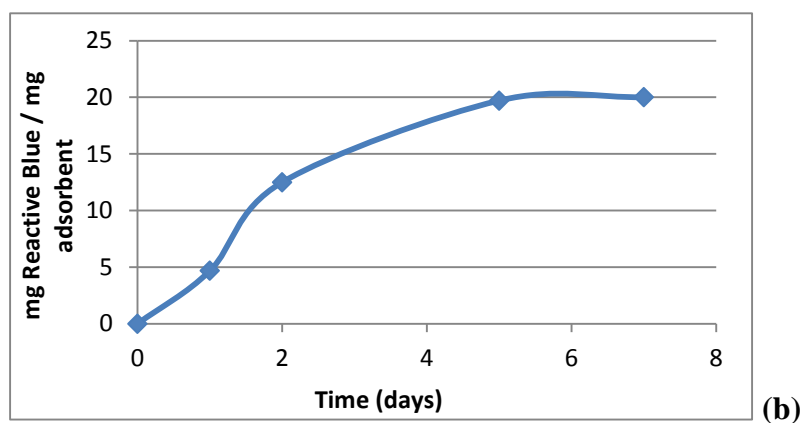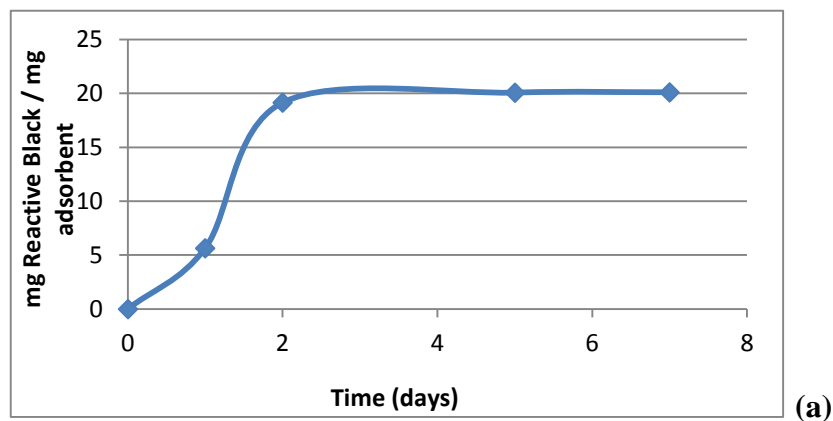
Figure 4.16 : Values of q_t versus time for three different dyes by Chi-MMT composites in optimum conditions (a) RB5 (b) RB221 (c) RR195 (Dye concentration=200 mg/L, Adsorbent amount=1000 mg/L).

Values of qt were determined to be 29.41 mg dye/mg adsorbent for Reactive Black, 40 mg dye/mg adsorbent for Reactive Blue and 21.73 mg dye/mg adsorbent for Reactive Red.

4.3 Adsorption Kinetics Studies

4.3.1 Application of pseudo first and second order rate equation for experiments with different adsorbent amounts

Results of adsorption experiment were tested for composite samples in different conditions. The results fitted pseudo-second order kinetic model and plots of t/q_t against time for every experiment was added. Results of pseudo-first order kinetic model were presented in Table 4.1 for comparing against experimental q_e values in order to prove the results have fit pseudo-second order kinetic model.

Equilibrium adsorption capacities (q_e) values were calculated from the slope of obtained trend lines and adsorption rate constant k_2 values were calculated from the intercepts according to Equation **(2.4)** for pseudo first order rate calculations and Equation **(2.5)** for pseudo second order rate calculations.
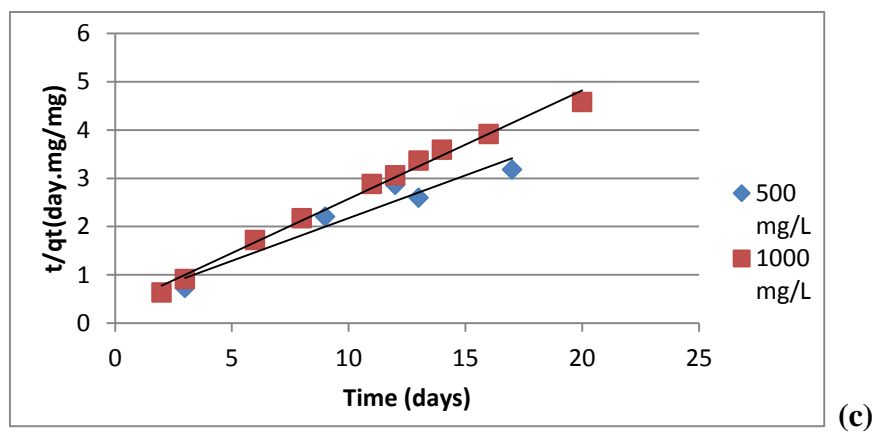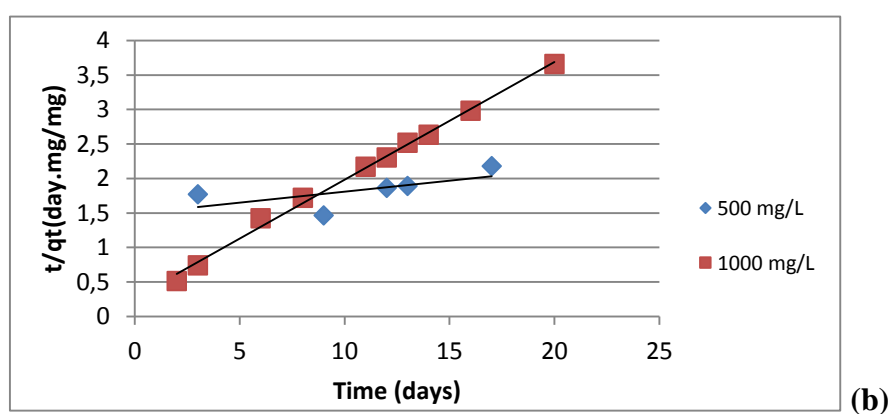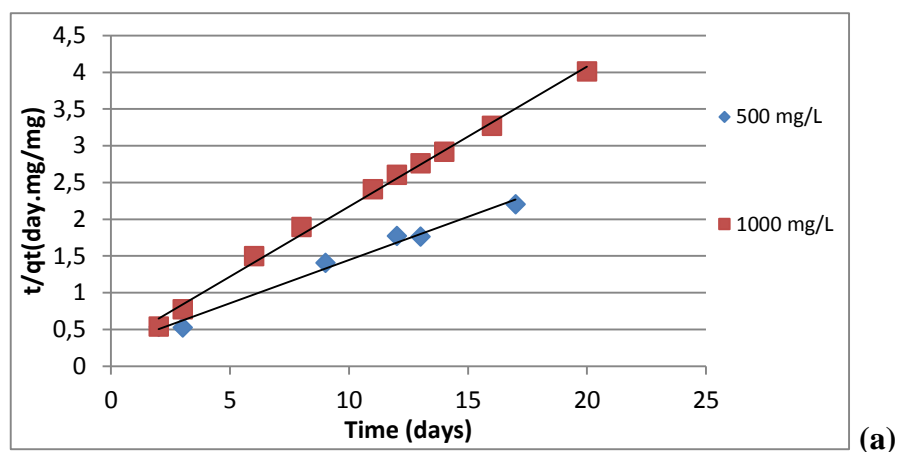
Figure 4.17 : Pseudo-second order rate equation for adsorption results of Chi-MMT composites (a) RB5 (b) RB221 (c) RR195 (Dye concentration=50 mg/L, pH=4, T=25˚C).

The experiments performed with 2000 mg/L and 3000 mg/L adsorbent in 100 ml dye solutions were plotted in qt/t graphs in Figure 4.18.
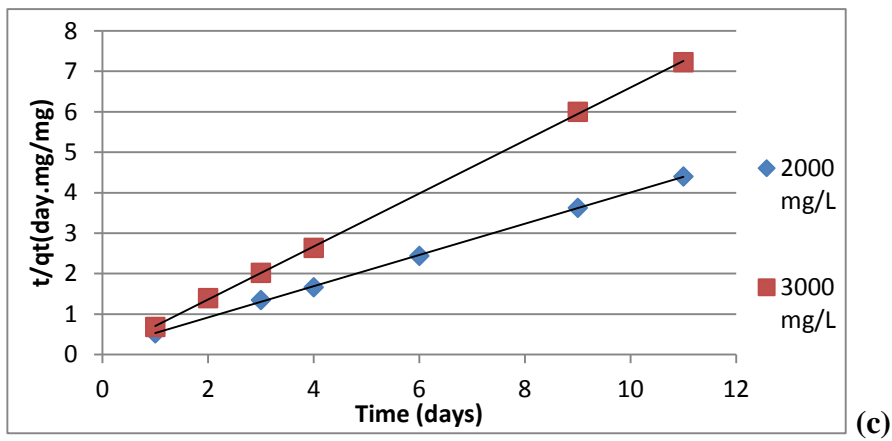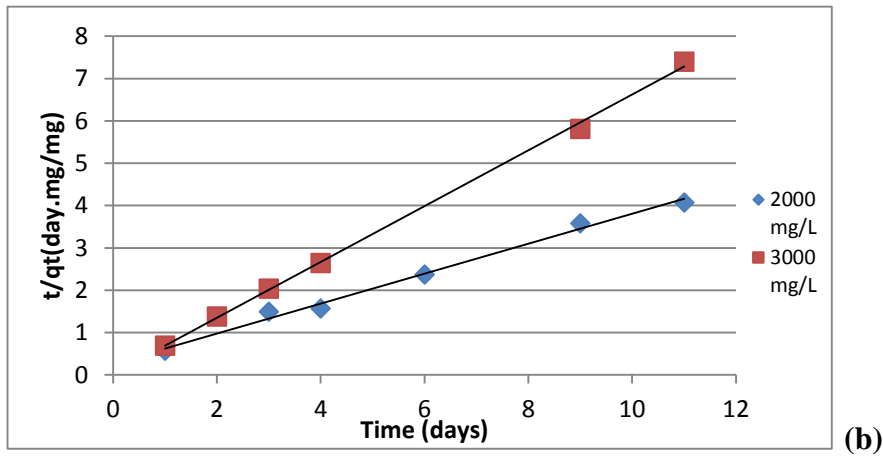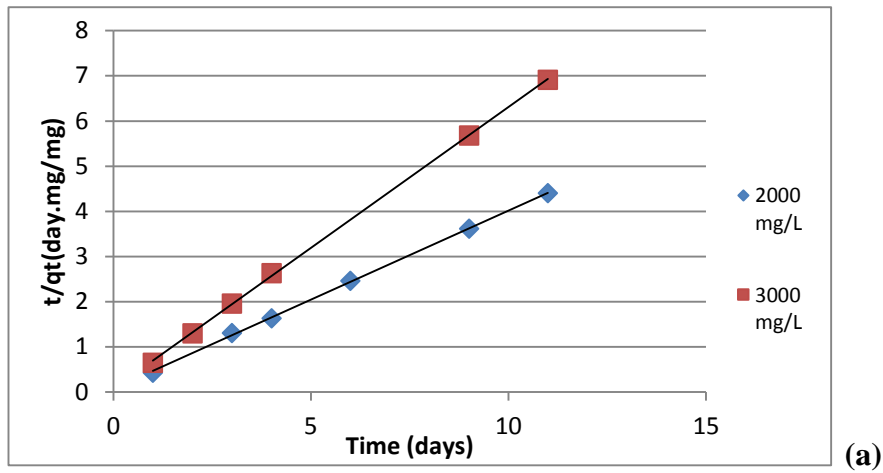
Figure 4.18 : Pseudo-second order rate equation for adsorption results of Chi-MMT composites (a) RB5 (b) RB221 (c) RR195 (Dye concentration=50 mg/L, pH=4, T=25°C).

For pseudo first and pseudo second kinetic models, values of k_1, k_2, q_e, and R^2 are listed in Table 4.1 and 4.2.

Table 4.1 : Kinetic parameters of Chi-MMT composites for pseudo-first order model (Dye concentration=50 mg/L, pH=4, T=25˚C).

Dye	Sample	k_1(day^{-1})	q_e(mg/mg)	R^2
Reactive Black 5	50 mg adsorbent	0.056	6.12	0.904
	100 mg adsorbent	0.14	2.21	0.964
	200 mg adsorbent	0.167	0.27	0.787
	300 mg adsorbent	0.092	0.05	0.949
Reactive Blue 221	50 mg adsorbent	0.276	17.81	0.846
	100 mg adsorbent	0.122	2.49	0.972
	200 mg adsorbent	0.209	0.84	0.554
	300 mg adsorbent	0.308	0.15	0.765
Reactive Red 195	50 mg adsorbent	0.178	3.57	0.651
	100 mg adsorbent	0.154	2.47	0.733
	200 mg adsorbent	0.439	0.77	0.943
	300 mg adsorbent	0.343	0.15	0.626

Kinetic parameters for pseudo second order model were given in Table 4.2.

Table 4.2 : Kinetic parameters of Chi-MMT composites for pseudo-second order model (Dye concentration=50 mg/L, pH=4, T=25˚C).

Dye	Sample	k_2(mg/mg.day)	q_e(mg/mg)	R^2
Reactive Black 5	50 mg adsorbent	0.050	8.54	0.987
	100 mg adsorbent	0.135	5.26	0.995
	200 mg adsorbent	2.514	2.51	0.997
	300 mg adsorbent	2.440	1.37	0.983
Reactive Blue 221	50 mg adsorbent	0.006	31.25	0.419
	100 mg adsorbent	0.106	5.88	0.995
	200 mg adsorbent	0.417	2.92	0.994
	300 mg adsorbent	13.571	1.51	0.998
Reactive Red 195	50 mg adsorbent	0.075	5.68	0.928
	100 mg adsorbent	0.151	4.46	0.991
	200 mg adsorbent	1.056	2.59	0.999
	300 mg adsorbent	8.938	1.52	0.999

It can be seen from the tables that pseudo second order kinetic model has fit better for experimental values. Highest k_2 values are achieved with 300 mg absorbent. This can be explained that as the amount of the adsorbent increases, the adsorption becomes faster. However, the highest q_e values are achieved with 50 mg adsorbent. This can be explained by the fact that dye amount is stable for all experiments and as the adsorbent amount increases, dye amount is distributed throughout the adsorbent molecules.

4.3.2 Application of pseudo first and second order rate equation for experiments with adsorbents of different chitosan ratios

Adsorption kinetic studies were applied for composites with different chitosan ratios with initial dye concentration of 50 mg/L, pH 4 and 1000 mg/L adsorbent. The results are presented in Figure 4.19. Kinetic parameters calculated applying pseudo-first and second order kinetic model are given in Tables 4.3 and 4.4.
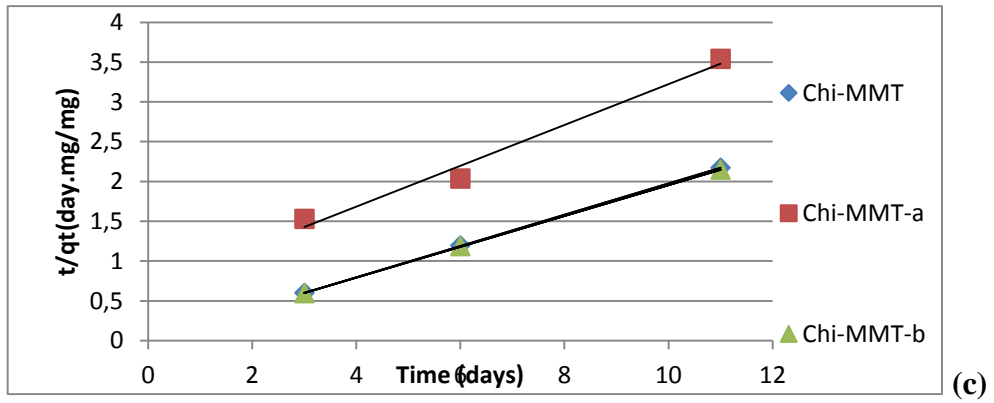
Figure 4.19 : Pseudo-second order rate equation for adsorption results of Chi-MMT composites with different chitosan ratios (a) RB5 (b) RB221 (c) RR195 (Dye concentration=50 mg/L, pH=4, T=25˚C).

For pseudo first order kinetic model, values of k_1, k_2, q_e, and R^2 are listed in Table 4.3.

Table 4.3 : Kinetic parameters of Chi-MMT composites for pseudo-first order model (Dye concentration=50 mg/L, pH=4, T=25˚C).

Dye	Sample	k_1(day^{-1})	q_e(mg/mg)	R^2
Reactive Black 5	0.25/0.5 Chi/MMT	0.324	6.17	0.967
	Chi-MMT	0.027	0.189	0.898
	0.5/0.25 Chi/MMT	0.046	0.316	0.641
Reactive Blue 221	0.25/0.5 Chi/MMT	0.172	1.62	0.994
	Chi-MMT	0.03	0.26	0.998
	0.5/0.25 Chi/MMT	0.031	0.25	0.794
Reactive Red 195	0.25/0.5 Chi/MMT	0.051	3.42	0.761
	Chi-MMT	0.058	0.16	0.993
	0.5/0.25 Chi/MMT	0.203	0.26	0.944

Kinetic parameters for pseudo second order model are given in Table 4.4.

Table 4.4 : Kinetic parameters of Chi-MMT composites for pseudo-second order model (Dye concentration=50 mg/L, pH=4, T=25˚C).

Dye	Sample	k_2(mg/mg.day)	q_e(mg/mg)	R^2
Reactive Black 5	0.25/0.5 Chi/MMT	0.034	5.95	0.991
	Chi-MMT	6.868	4.92	1
	0.5/0.25 Chi/MMT	2.8	5.05	1
Reactive Blue 221	0.25/0.5 Chi/MMT	0.211	4.34	1
	Chi-MMT	3.885	5.34	1
	0.5/0.25 Chi/MMT	4.784	5.46	1
Reactive Red 195	0.25/0.5 Chi/MMT	0.099	3.90	0.981
	Chi-MMT	3.841	5.10	1
	0.5/0.25 Chi/MMT	1.862	5.18	0.999

It can be seen from the tables that pseudo second order kinetic model have fit better for experimental values. Lower k_2 values are achieved with samples including less chitosan. This can be explained that low chitosan ratio in the adsorbent lowers adsorption rate.

4.3.3 Application of pseudo second order rate equation for experiments with different temperature values

Adsorption kinetic studies were applied for composites in different temperatures with initial dye concentration of 50 mg/L, pH 4 and 1000 mg/L adsorbent. The results are presented in Figure 4.20. Kinetic parameters calculated applying pseudo-first and second order kinetic model are given in Table 4.5 and 4.6.
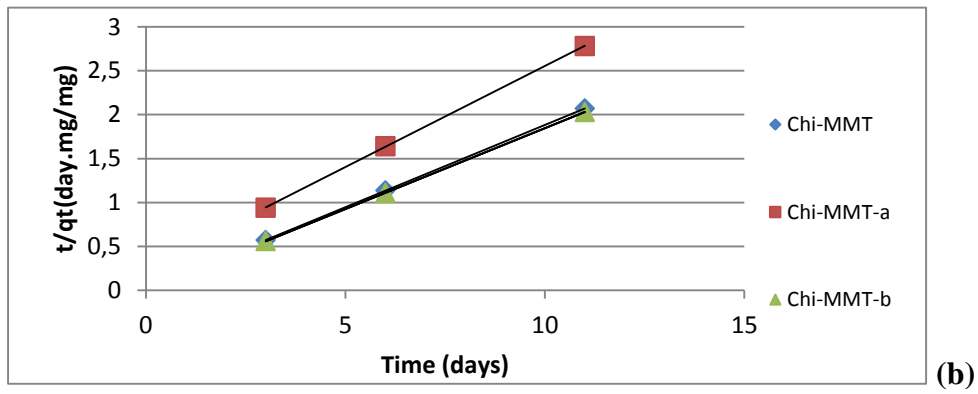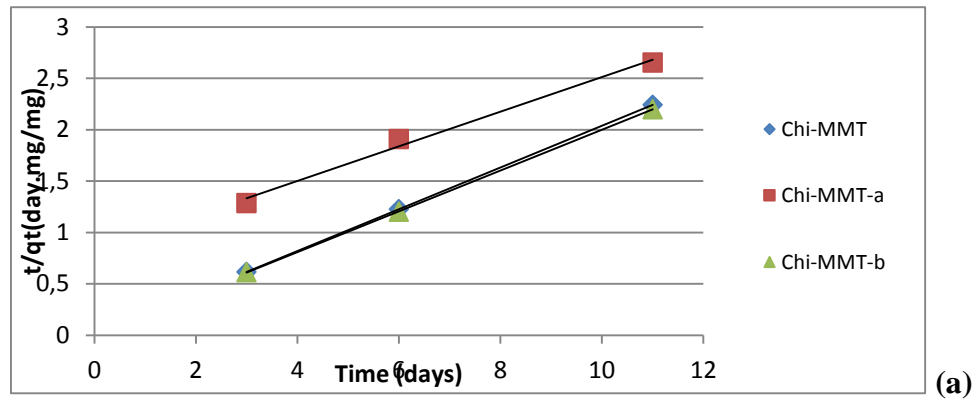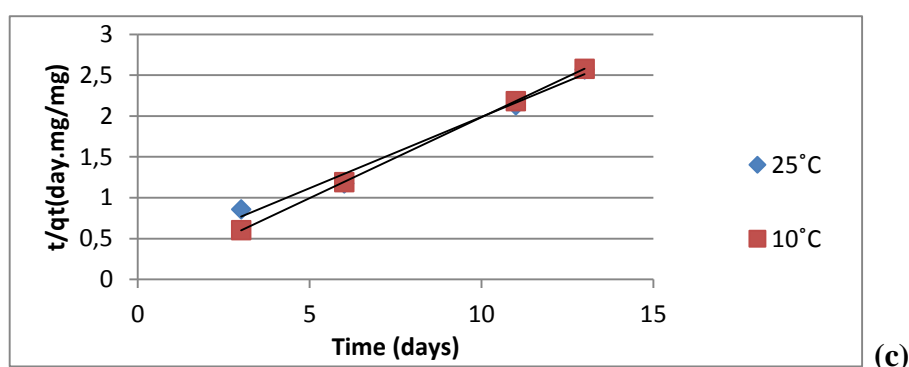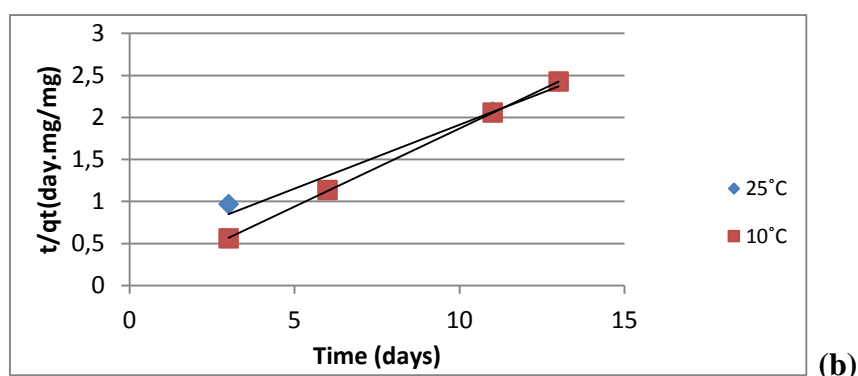

Figure 4.20 : Pseudo-second order rate equation for adsorption results of Chi-MMT composites with different temperature values (a) RB5 (b) RB221 (c) RR195 (Dye concentration=50 mg/L, pH=4,Adsorbent amount=1000mg/L).

For pseudo first order kinetic model, values of k_1, k_2, q_e, and R^2 are listed in Table 4.5.

Table 4.5 : Kinetic parameters of Chi-MMT composites for pseudo-first order model (Dye concentration=50 mg/L, pH=4).

Dye	Sample	k_1(day^{-1})	q_e(mg/mg)	R^2
Reactive Black 5	10˚C	0.029	0.135	0.810
	25˚C	0.33	2.89	0.705
Reactive Blue 221	10˚C	0.095	0.049	0.209
	25˚C	0.455	4.41	0.839
Reactive Red 195	10˚C	0.275	1.07	0.724
	25˚C	0.246	2.98	0.527

Kinetic parameters for pseudo second order model were given in Table 4.6.

Table 4.6 : Kinetic parameters of Chi-MMT composites for pseudo-second order model (Dye concentration=50 mg/L, pH=4).

Dye	Sample	k_1(mg/mg.day)	q_e(mg/mg)	R^2
Reactive Black 5	10˚C	6.733	4.97	1
	25˚C	0.029	7.09	0.894
Reactive Blue 221	10˚C	4.324	5.37	0.999
	25˚C	0.059	6.57	0.969
Reactive Red 195	10˚C	4.312	5.07	1
	25˚C	0.122	5.74	0.987

It can be seen from the tables that pseudo second order kinetic model have fit better for experimental values. Highest k_2 highest values are achieved with 10˚C. This can be explained by the fact that adsorption is exothermic and thus gives better results in low temperature.

4.3.4 Application of pseudo second order rate equation for experiments with different pH values

Adsorption kinetic studies were applied for composites in different pH values with initial dye concentration of 50 mg/L, 25˚C and 1000 mg/L adsorbent. The results are presented in Figure 4.21. Kinetic parameters calculated applying pseudo first and second order kinetic model are given in Table 4.7 and 4.8.
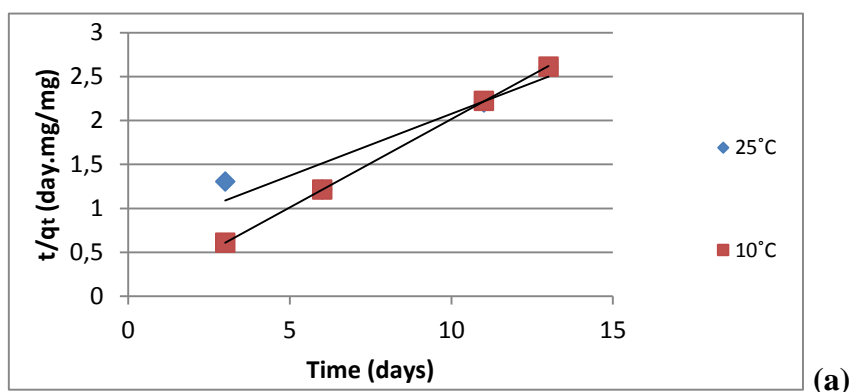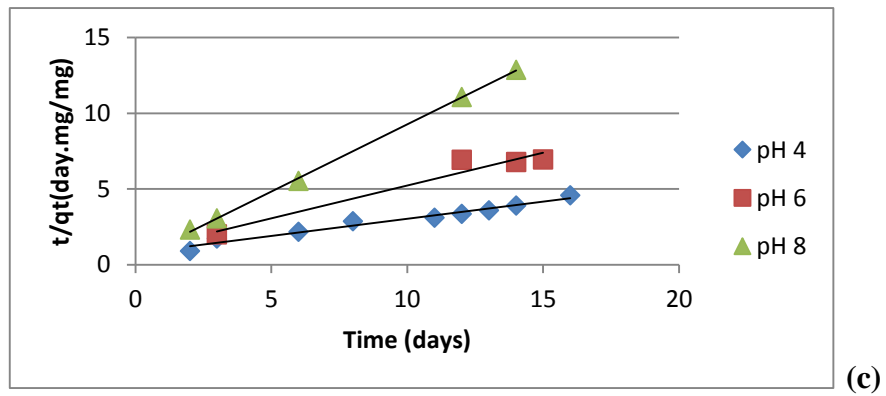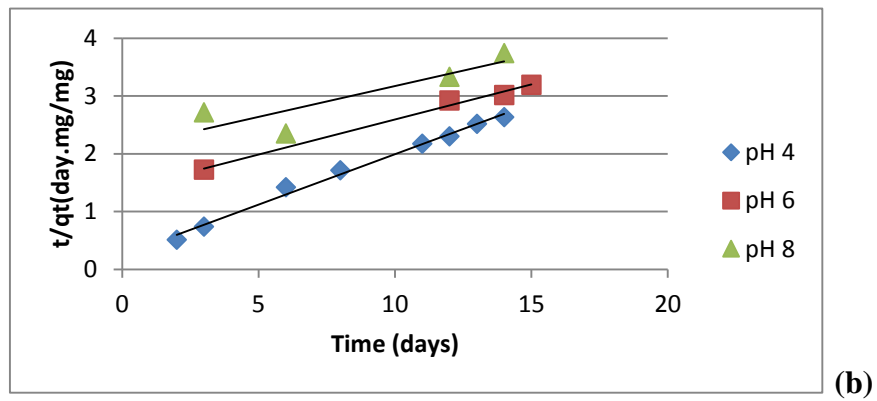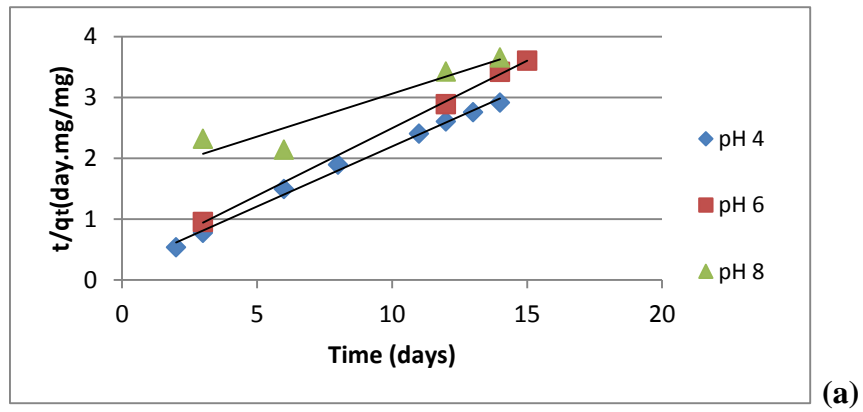
Figure 4.21 : Pseudo-second order rate equation for adsorption results of Chi-MMT composites with different pH values (a) RB5 (b) RB221 (c) RR195 (Dye concentration=50 mg/L, T=25˚C, Adsorbent amount=1000mg/L).

For pseudo first order kinetic model, values of k_1, k_2, q_e, and R^2 are listed in Table 4.7.

Table 4.7 : Kinetic parameters of Chi-MMT composites for pseudo-first order model (Dye concentration=50 mg/L, T=25˚C, Adsorbent amount=1000mg/L).

Dye	Sample	k_1(day^{-1})	q_e(mg/mg)	R^2
Reactive Black 5	pH 4	0.14	2.21	0.964
	pH 6	0.084	2.16	0.973
	pH 8	0.189	4.58	0.974
Reactive Blue 221	pH 4	0.122	2.49	0.938
	pH 6	0.104	2.69	0.972
	pH 8	0.254	6.04	0.999
Reactive Red 195	pH 4	0.154	2.47	0.733
	pH 6	0.035	2.12	0.337
	pH 8	0.066	0.64	0.250

Kinetic parameters for pseudo second order model were given in Table 4.8.

Table 4.8 : Kinetic parameters of Chi-MMT composites for pseudo-second order model (Dye concentration=50 mg/L, T=25˚C, Adsorbent amount=1000mg/L).

Dye	Sample	k_2(mg/mg.day)	q_e(mg/mg)	R^2
Reactive Black 5	pH 4	0.178	5.07	0.994
	pH 6	0.176	4.52	0.999
	pH 8	0.012	7.09	0.890
Reactive Blue 221	pH 4	0.121	5.74	0.992
	pH 6	0.010	8.26	0.991
	pH 8	0.005	9.43	0.773
Reactive Red 195	pH 4	0.065	4.42	0.966
	pH 6	0.208	2.30	0.946
	pH 8	1.933	1.12	0.999

It can be seen from the tables that pseudo second order kinetic model have fit better for experimental values. Highest k_2 values are achieved pH 4 value, except for Reactive Red 195. The highest q_e values are achieved with pH 4 value again, except for Reactive Red 195.

4.3.5 Application of pseudo second order rate equation for experiments with Chi-MMT-UF, Chi-MMT-UF2 and Chi-MMT-U

Adsorption kinetic studies were applied for composites of Chi-MMT-UF, Chi-MMT-UF2 and Chi-MMT-U with initial dye concentration of 50 mg/L, 25˚C and 1000 mg/L adsorbent. The results are presented in Figure 4.22. Kinetic parameters

calculated applying pseudo first and second order kinetic model are given in Tables 4.9 and 4.10.
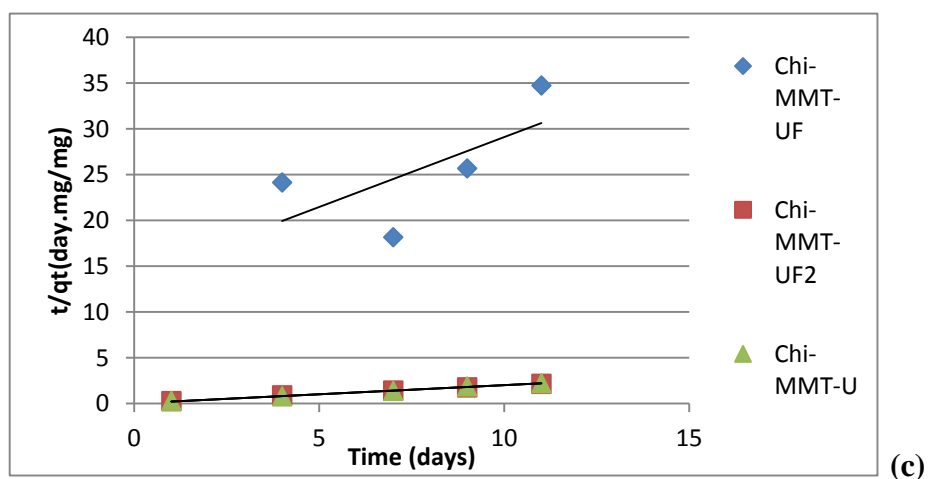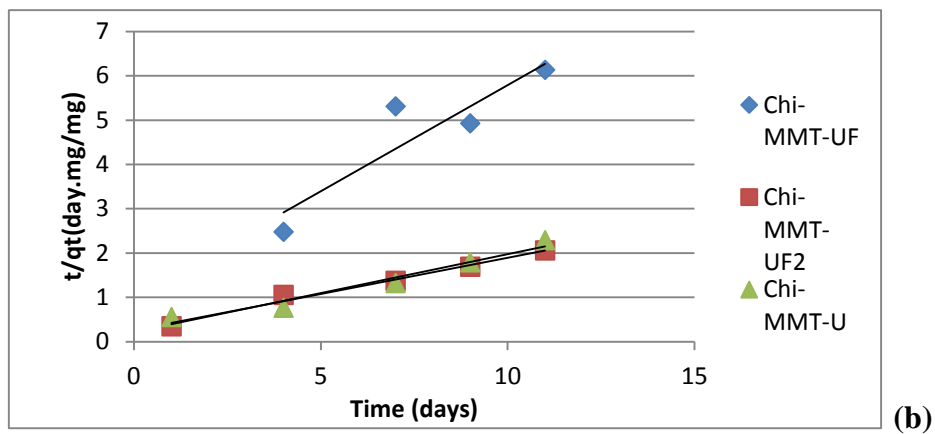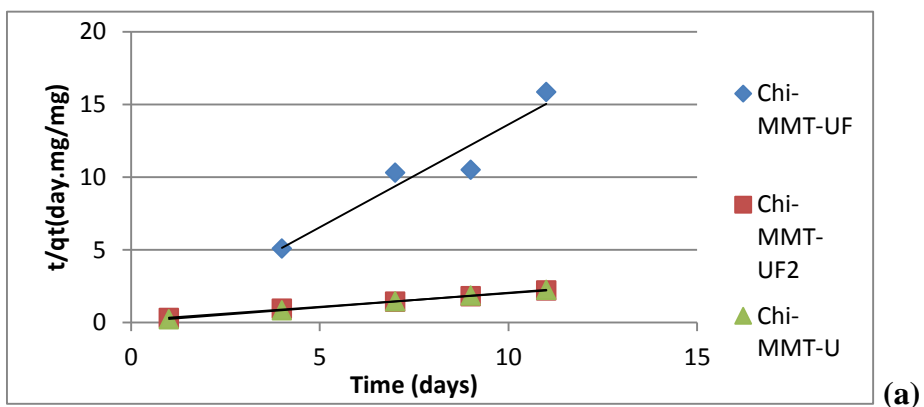

Figure 4.22 : Pseudo-second order rate equation for adsorption results of Chi-MMT-UF, Chi-MMT-UF2 and Chi-MMT-U composites (a) RB5 (b) RB221 (c) RR195 (Dye concentration=50 mg/L, T=25˚C, Adsorbent amount=1000mg/L).

For pseudo first order kinetic model, values of k_1, k_2, q_e, and R^2 are listed in Table 4.9.

Table 4.9 : Kinetic parameters of composites for pseudo-first order model (Dye concentration=50 mg/L, T=25˚C, Adsorbent amount=1000mg/L).

Dye	Sample	$k_1(day^{-1})$	$q_e(mg/mg)$	R^2
Reactive Black 5	Chi-MMT-UF	0.013	0.16	0.006
	Chi-MMT-UF2	0.239	2.34	0.955
	Chi-MMT-U	0.07	0.69	0.288
Reactive Blue 221	Chi-MMT-UF	0.178	1.03	0.476
	Chi-MMT-UF2	0.264	3.81	0.947
	Chi-MMT-U	0.132	1.51	0.242
Reactive Red 195	Chi-MMT-UF	0.03	0.29	0.056
	Chi-MMT-UF2	0.242	1.99	0.979
	Chi-MMT-U	0.099	0.81	0.236

Kinetic parameters for pseudo second order model were given in Table 4.10.

Table 4.10 : Kinetic parameters of composites for pseudo-second order model (Dye concentration=50 mg/L, T=25˚C, Adsorbent amount=1000mg/L).

Dye	Sample	$k_2(mg/mg.day)$	$q_e(mg/mg)$	R^2
Reactive Black 5	Chi-MMT-UF	0.304	1.08	0.868
	Chi-MMT-UF2	1.063	4.97	1
	Chi-MMT-U	0.339	5.37	0. 997
Reactive Blue 221	Chi-MMT-UF	0.019	4.06	0.926
	Chi-MMT-UF2	0.143	5.68	0.958
	Chi-MMT-U	0.102	6.13	0.983
Reactive Red 195	Chi-MMT-UF	0.168	0.65	0.542
	Chi-MMT-UF2	1.237	5.02	0.996
	Chi-MMT-U	0.302	5.43	0.998

It can be seen from the tables that for k_2 highest values are achieved with Chi-MMT-UF2. Furthermore, highest q_e values were obtained with Chi-MMT-U. Similar trends were obtained with all of the dyes.

4.3.6 Application of pseudo second order rate equation for experiments with optimum conditions

Adsorption kinetic studies were applied for optimum conditions of pH 4, 10 ˚C and Chi-MMT flakes for initial dye concentration of 50 mg/L, and 1000 mg/L adsorbent. The results are presented in Figure 4.23.

(a)

(b)

(c)

Figure 4.23 : Pseudo-second order rate equation for adsorption results of Chi-MMT flakes (a) RB5 (b) RB221 (c) RR195 (Dye concentration=50 mg/L, T=10˚C, Adsorbent amount=1000mg/L).

Another experiment was performed by increasing dye amount and the same experiment was repeated at 10 ˚C and pH 4 with 1000 mg/L adsorbent in 100 ml dye

solutions in 200 mg/L dye concentration. Highest q_e values were obtained with this experiment since amount of dye for each mg of adsorbent has been increased. The results are presented in Figure 4.24.
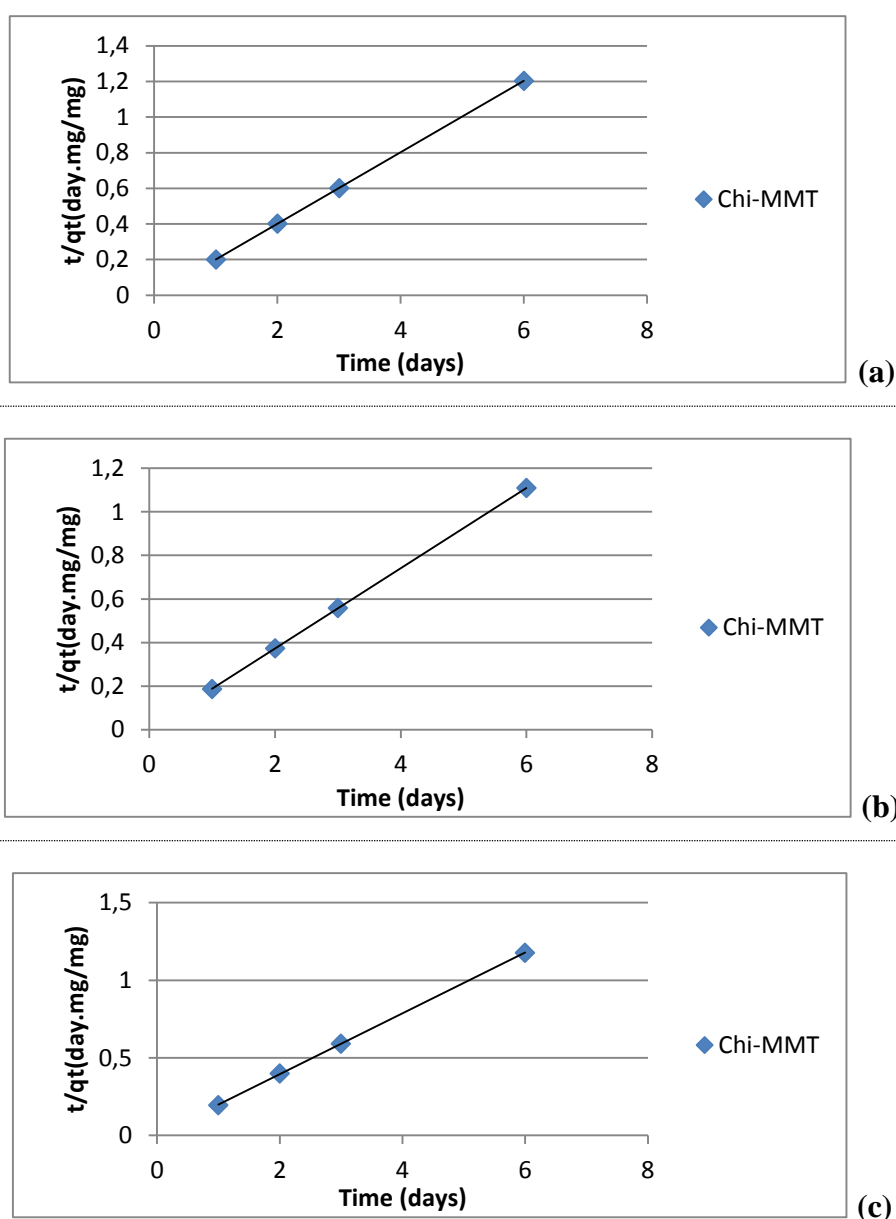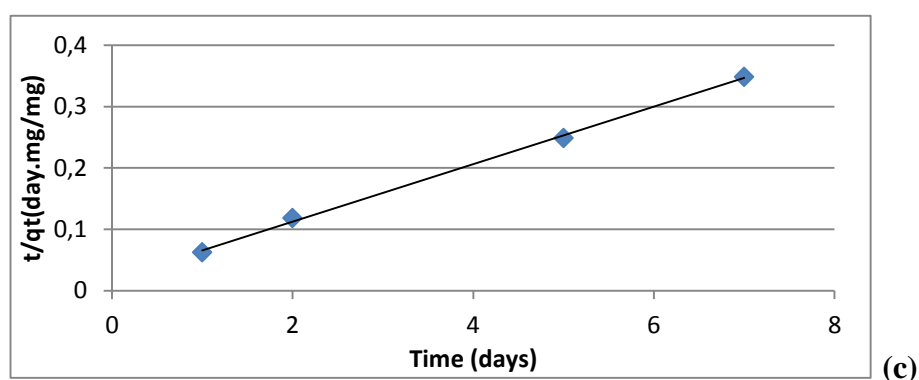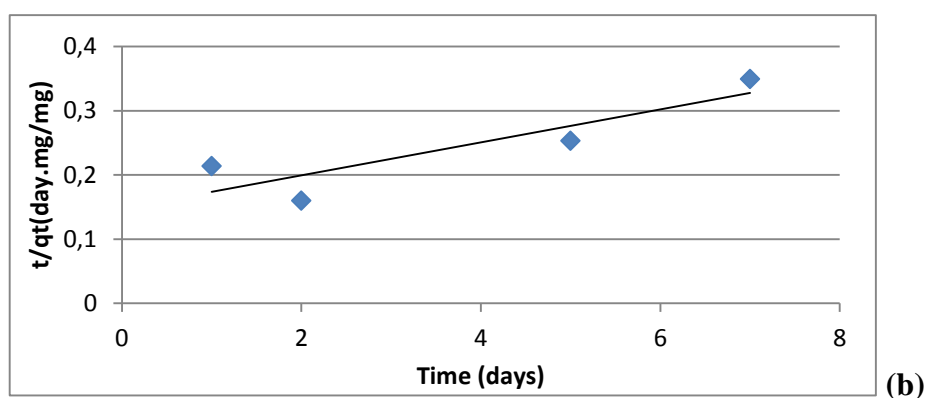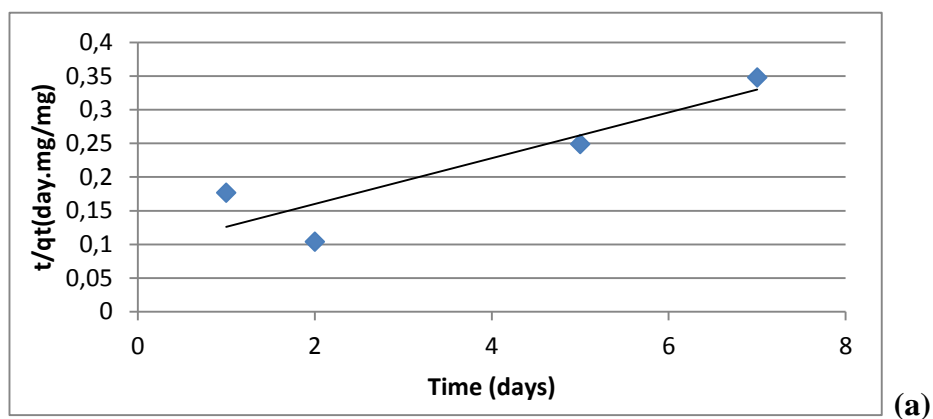

Figure 4.24 : Pseudo-second order rate equation for adsorption results of Chi-MMT flakes (a) RB5 (b) RB221 (c) RR195 (Dye concentration=200 mg/L, T=10°C, Adsorbent amount=1000mg/L).

For pseudo first order kinetic model, values of k_1, k_2, q_e, and R^2 are listed in Table 4.11.

Table 4.11 : Kinetic parameters of Chi-MMT composites for pseudo-first order model (Adsorbent concentration=1000 mg/L, pH=4, T=25˚C).

Dye	Sample	$k_1(day^{-1})$	$q_e(mg/mg)$	R^2
Reactive Black 5	50 mg/L	0.019	0.18	0.658
	200 mg/L	0.93	14.64	0.892
Reactive Blue 221	50 mg/L	0.570	10.91	0.857
	200 mg/L	0.821	35.26	0.992
Reactive Red 195	50 mg/L	0.347	0.16	0.942
	200 mg/L	0.805	9.68	0.881

Kinetic parameters for pseudo second order model were given in Table 4.12.

Table 4.12 : Kinetic parameters of Chi-MMT composites for pseudo-second order model (Adsorbent concentration=1000 mg/L, pH=4, T=25˚C).

Dye	Sample	$k_1(mg/mg.day)$	$q_e(mg/mg)$	R^2
Reactive Black 5	50 mg/L	40	5	1
	200 mg/L	0.012	29.41	0.809
Reactive Blue 221	50 mg/L	11.28	5.43	1
	200 mg/L	0.004	40	0.783
Reactive Red 195	50 mg/L	19.20	5.10	0.999
	200 mg/L	0.117	21.73	0.998

It can be seen from the tables that for optimum conditions very fast adsorption is obtained. Similar trends were obtained with all of the dyes.

CONCLUSIONS AND RECOMMENDATIONS

The objection of this thesis is the adsorption of textile dyes from water by chitosan derivatives and determining optimum conditions for rapid and effective color removal. Chitosan-montmorillonite composites, and composites of Chi-MMT with urea and urea-formaldehyde were formed for this study.

FTIR analysis was performed for characterization of composite samples and respective peaks were examined. Furthermore, SEM analysis was performed for the determination of morphology of the composites. With the help of UV/Visible spectroscopy, adsorption data of every experiment and adsorption capacities and adsorption rate were determined. Optimum values for rapid adsorption was investigated with performed experiments and it was found that best results were obtained with low pH (pH 4), low temperature and Chi-MMT flakes. Effect of even short periods of stirring is undeniable in every adsorption experiment, by the help of stirring dye molecules and adsorbent particles were able to come across and adsorption period was much more shorter. Even though experiments were performed without stirring dye solutions, it was observed that in the optimum conditions adsorption was completed in a matter of hours by adding stirring into process.

In conclusion, chitosan-montmorillonite composites gave good results when used for adsorption of textile dyes and due to their rapid adsorption and simple handling properties, they can be used for wastewater treatment for color removal.

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CURRICULUM VITAE

Name Surname:	**Zeynep Ceren BUMİNOĞLU**
Place and Date of Birth:	**Kadıköy – 04/10/1986**
Address:	**Korkut Sok. No:21/25 Kozyatağı / ISTANBUL**
E-Mail:	**cerenbuminoglu@hotmail.com**
B.Sc.:	**ITU, Department of Chemical Engineering**