Design of a Zwitter-Ionic Nanocomposite for Dyestuff Removal

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Abstract. Today, with the increasing awareness of environmental conservation, many scientists are directing their work on environmental improvements. In the textile industry, dyestuff load of wastewater increases, and improvements are made to reduce this load. As a contribution to these improvements, a nanocomposite is designed with clay, chitosan and its modifications, which are totally natural. As a preliminary study, the clay was modified and treated with dyestuff solutions to investigate the absorption properties of Methylene Blue with various clay types. According to the results obtained by UV visible spectrophotometer, Cloisite 30B, which is the clay with the best absorption property, has been determined as the reference material. With the lights of preliminary study, a nanocomposite was designed to adsorb dyestuffs from textile waste waters using modified clay and modified chitosan. With the anionic modification of chitosan, it can be converted into carboxymethylchitosan (CMCTS) and it can also have affinity to cationic structures. With this structure, colored composites are obtained while contributing to recycling and environment by providing adsorption of dyestuff. According to UV-vis and FT-IR results, CMCTS that is modified with Butanetetracarboxylic acid (BTCA) has better adsorption from textile wastewaters.

1. Introduction
Clay is accepted as the most used filling material thanks to its high visibility rate and its laminated morphology [1]. Economic value of clay is determined according to its mineral types and presence of non-clay material inside the clay. Clay minerals that have white, green, pink, grey and hues of brown colors can be found with different chemical compositions and at different contents, and pure clay mineral is rarely found in nature [2]. Due to their superior chemical and physical properties, easy accessibility in nature and having technologic properties such as plasticity, moisture adsorption, high strength, replacement with every kind of ions that are organic or inorganic, high adsorption amount and catalytic activity, currently more than 100 fields of production use clay as raw material [3].

Clay minerals are results of the alteration of the volcanic tuffs or hydration of the laminated silicates that have layer thickness of 1nm each and lateral diameter that is more than 100 nm.

Unless modification of clay surfaces is done, silicate layers cannot make good interaction with water repellent polymer matrices due to water absorbency of the layers. Many types of mechanisms can be used for modification of clay surfaces such as ion exchange using organic and inorganic cations, the attachment of organic and inorganic ions, getting into reaction with acids, burning, ultrasound, plasma etc. After modifications, clays are also used at removing organic pollutants from water, air and oil with adsorption, as rheological control factor and at dye and cosmetics fields [4].
Changeable cations in clay affect its physical structure. Organic and inorganic anions and cations that can penetrate into layers of clay are adsorbed by clay minerals and they are held in changeable state. When they are treated with ions in aqueous solutions, ions in changeable state can be replaced with new ones. The sum of changeable cations equivalent mass number (meg) at 100 grams of mineral is known as the cation exchange capacity (CEC) and it is an important parameter for selecting the most suitable clay type to use [5]. The surface polarity of the clay and the polarity of the polymers pairs increase and the middle layers of the clays enlarge when the organic onium ions that are located at the surface of the middle layer take the place of the inorganic changeable cations. Thus, polymers, dyestuffs and such matters can penetrate more properly when ions that have long alkali chains and organo-modified silicates (organoclays) are used [6]. According to their different element groups and orientations many organoclay types with many different characteristics are commercially available for using in polymer composites. However, Cloisite 30B has better absorbency, higher CEC and bigger gap values thanks to its long tallow ammonium chain. Also, previous study of the authors gives detailed information about clays and proves that among the commercially available modified clays Cloisite 30B is better one to use in this study [7].

Clay based nanocomposites are a good example of nanocomposites which are developed with high absorbency properties. They are preferred in dye removal applications due to their features such as having high aspect ratio, layered structure and providing good properties even at low add-on percentages. This structure provides a better and more environmentally friendly refining with natural absorbent structure by reducing the amount of chemical amounts and number of refining processes. Depending on the needs of the area of use, custom-made modifications of this nanocomposite are manufactured [8].

Further modifications can be done with intercalation of different polymers to clays. This polymer can be selected according to its characteristics and variety of nanocomposite structure can be increased by modification of polymer. In this study chitosan is selected but it is modified for adsorption of Methylene Blue dyestuff which is cationic.

Chitosan is soluble form of chitin which has the second biggest supply at the world as a polymer after cellulose and it produced when approximately 50% of deacetylation is done on chitin. This amount at the definition depends on the origin of the polymer which is a polysaccharide. Solubility of the Chitosan is seen when it is turned into polyelectrolyte form at acidic conditions and to make this protonation of \(-\text{NH}_2\) group of unit of D-glucosamine where the position of it is C-2 is done. It has many application areas including depollution and protein recovery as flocculent because of the specific property as being the only pseudonatural polymer which is cationic. Also the biggest reason for selecting Chitosan at different application areas with different forms from solution to fiber is its high solubility property [9].

Deacetylation of chitin is the main procedure of Chitosan production. With the usage of potassium/sodium hydroxide solutions or mixture of anhydrous hydrazine and hydrazine sulfate that produces an alkaline media, acetalated part of chitin is hydrolyzed and removed. Resultant Chitosan is yield when chitin is treated for 4-5 hours with 40–45 % (w/v) NaOH solution and the N-deacetylation reaction occurs at 90–120 °C [10-11].

Structure of Chitosan is semi crystalline when it is solid. If the low molecular-weight chitin is deacetylated totally, Chitosan with single crystals can be yield [12]. Degree of acetylation (DA), pH, protonation acid, ionic concentrations, acetyl group locations of Chitosan, drying and isolating conditions are the parameters that determines the final solubility. When DA is around 50% at neutral pH Chitosan becomes soluble. At pH 7- 7.1 and room temperature solution of Chitosan is stable, however when temperature is about 40° C it turns into gel form. Chitosan has two hydrogen bonds at its chain structure as first one is between O5 and OH3 and second one is between O of COO and OH6 [12].

Chitosan has many different classes according to its characteristics with different modifications as O-and N-Carboxymethlchitosans, Chitosan 6-O-sulfate, N-methylene phosphonic chitosans, Trimethylchitosan ammonium, Carbohydrate branched chitosans, Chitosan-grafted copolymers,
Alkylated chitosans and Cyclodextrin-linked chitosans. In this study, chitosan is modified as O-and N-Carboxymethylchitosan to adsorb cationic dyestuff. The most known type of Chitosan is Carboxymethylchitosan (CMCTS) which has amphoteric characteristic that means changing ionic character according to pH of the medium. When sodium hydroxide is present in the medium Chitosan gives O and N-carboxymethylation reaction with the help of sodium monochloracetate and forms O and N-CMCTS. pH range of being soluble is enlarged with the help of carboxymethylation reaction as pH>7, however its charges are balanced during the reaction, and this balancing causes phase separation between pH 2.5 and 6.5. Furthermore, when there is a reductive agent Chitosan reacts with glyoxyllic acid and forms N-CMCTS [13].

Nowadays, there are many applications of Chitosan at nanotechnology with different modifications of it in composites for different purposes and properties at cosmetics, biomedical engineering, biotechnology, ophthalmology, pharmaceuticals, agriculture, textiles, food processing nutrition etc. while application of chitin remains less. Chitosan is the only pseudo-natural polymer that has cationic character thanks to this property is inimitable. Together with this property, film forming capability brings more application areas to Chitosan. Properties are enhanced with modifications and combined at nanocomposites for needed products. Fibers, sponges, hydrogels, films and biomedical products can be manufactured from Chitosan since processability of it easier than that of chitin while its stability is less because of being hydrophilic and pH sensitive [9].

Nanocomposites of nanolayered silicates with Chitosan are the most popular method to enhance the characteristics physically, thermally, mechanically and chemically. Especially, utilization of montmorillonite is very popular as nanolayered silicates and enhanced properties vary according to harmony between Chitosan and montmorillonite and production processes [10]. When Chitosan is intercalated to Na+ montmorillonite for a nanocomposite, film forming tendency decreases which is resulted with resistant and stable products [14].

Chitosan become a good material of many studies at the literature whether used alone or with a clay combination. Firstly, Chitosan was used alone in adsorption of anionic dyestuff and sulphonated azo dyestuff by coagulation of Chitosan [15,16]. In case of combination of Chitosan with clay, N, O-Carboxymethyl Chitosan/ Montmorillonite with 5:1 weight ratio is used for anionic dyestuff removal and it shows an increased the dye adsorption with decreasing of pH [17]. Secondly, bentonite filled with chitosan and acrylic copolymer is used to remove synthetic dyes from waters and examined for effects of co-monomers [18]. Also crosslinked Chitosan and Bentonite is used for cationic dyestuff and anionic azo dyestuff removal [19,20]. Chitosan and CTAB modified bentonite is used for removing of dyestuff while magnetic carboxymethyl chitosan-g-poly(acrylamide)/laponite RD with improved dye adsorption capacity is produced for use at acidic media [21,22].

With the light of all these information, the purpose of the project is to create a nanocomposite from nanoclays that is chemically activated, having more branched structure with intercalation of Chitosan and Carboxymethyl Chitosan (CMCTS) and removing dyestuff from waste water with its enhanced absorbency for textile industry.
2. Materials and method

2.1. Materials

In this study, alkyl ammonium based organoclay (Cloisite 30B) which is supplied by Southern Clay Company, is used. Chitosan with medium molecular weight is bought from Sigma Aldrich to produce nanocomposite with clay. Chloroacetic acid is an organochlorine compound which has a molecular formula of CICH₂CO₂H. It has a molecular weight of 94.49702 g/mol and it is used as a modifier to modify Chitosan to produce CMCTS. 1,2,3,4-Butanetetracarboxylic acid is an organic compound which has a molecular formula of C₈H₁₀O₈. It has a molecular weight of 234.16 g/mol and it is used as a modifier to modify Chitosan to produce CMCTS. Sodium Hydroxide (NaOH), which has a molecular weight of 39.99 g/mol and ethanol (ethyl alcohol), which has a molecular formula of C₂H₅OH are used to modify Chitosan. At the experiment nanocomposites are used to adsorb Methylene Blue (C.I 52015) which is a standard basic dyestuff with a molecular formula of C₁₆H₁₈N₃SCl. It has a molecular weight of 319.85 g/mol. 60% (v/v) Perchloric acid (HClO₄) which has a density of 1.764 g/mL, is used to protonate Methylene Blue dyestuff solution. Dichloromethane is an organic compound which has a general formula of CH₂Cl₂. It is used as dissolver material of Methylene Blue dyestuff solution.

2.2. Method

2.2.1. Modification of Chitosan (Preparation of CMCTS). 5 g Chitosan is soaked into 50 mL NaOH solution (20 wt%) for 12 hours and mixture is filtered. Filtered Chitosan is soaked into 50mL ethyl alcohol at volumetric flask and stirred for 30 minutes. While stirring continues 4 g butanetetracarboxylic acid (BTCA) or chloroacetic acid is added and stirring is continued for 30 minutes more. Then mixture is cooled to 20°C and kept at the temperature for 1 hour. Finally, treated sample is filtered, dissolved in distilled water and pH value is set as 7.0 by adding acetic acid. The mixture is poured into ethyl alcohol for precipitation as foam gel and the white precipitate is taken into petri dishes by separating with pouring. It is washed three times by using ethanol/water mixture with ratio of 70%/30% (volume on volume) and one more time by using pure ethyl alcohol. Samples in petri dishes are placed into oven at 80°C for drying of the CMCTS. Finally, CMCTS is scraped off from the petri dishes and it is turned into powder form by mechanical milling. FT-IR analysis is done to CMCTS sample and resultant peaks are compared with those presented in the literature [17].

2.2.2. Combination of Modified Chitosan and Clay. Firstly, swelling of 1 g clay is done at 100 mL distilled water. Secondly, CMCTS solutions are prepared separately by dissolving CMCTS at distilled water which refers to 5:1 weight ratio at nanocomposite. After that, CMCTS solution is added to clay suspension slowly and stirred at 60°C for 6 hours. Then until the supernatant becomes pH 7.0 nanocomposites are washed by using distilled water and placed in oven at 60°C for 12 hours. Finally, CMCTS-clay nanocomposite is scraped off and turned into powder form by mechanical milling [17]. Chitosan (CTS)-clay combination is produced following the same procedure with the exception of preparing CTS solution with water instead of CMCTS.

2.2.3. Dyestuff Adsorption of Clay and its Combinations. Sivathasan J.’s study which comprises dissolving of 2 g Cloisite 15A at 200 mL dichloromethane (DCM) and adding 2mmol cationic dyestuff with 5 mL HCl solution with ratio of 70% is taken as reference to determine the solution ingredients [23]. Firstly, 200 mL of DCM is put into each flask. Secondly, combined clays are treated with the certain dyestuff solution to examine the adsorbed amount and comparisons are made. 2 g per each sample with weight ratios as Chitosan 5:1, CMCTS 5:1 that gives the best adsorption result is used. Then, 5.83 mL perchloric acid with ratio of 60% is added to each flask for protonation. Finally, 0.6397 g Methylene Blue (equivalent of 2 mmol dyestuff) is added to mixtures at each flask and each mixture stirred by magnetic stirrer at 60 rpm for 12 hours. After stirring they are let to precipitate for 24 hours.
3. Results and Discussion

With this final structure, a colored composite will be obtained while contributing to recycling and environment by providing adsorption of dyestuff. FT-IR for characterization of the nanocomposite and UV-vis spectrophotometer for dyestuff adsorption results are used. Methylene Blue dyestuff solution.

3.1. UV-Visible Spectrophotometer (UV-vis)

The formula below is used to calculate the removal rate of dyestuff from the solutions by using UV-vis results. At the formula, R is removal percentage, \( c_0 \) (mg L\(^{-1}\)) is the initial concentration and \( c_t \) (mg L\(^{-1}\)) is the final concentration of adsorbate by adsorbents [24].

\[
R = \frac{c_0 - c_t}{c_0} \times 100\%
\]  

(1)

According to UV-vis results, Chitosan and clay composites decrease the amount of dyestuff in waste water but modified ones adsorb more dyestuff on themselves thanks to highly anionic characteristics. BTCA works more than Chloroacetic acid (CAA) in modification, thus BTCA- CMCTS has best removal capacity as 67.77%. This phenomenon is probably due to higher number of available reactive side groups BTCA has when compared to those offered by CAA.
Table 1. Removal Percentage of Nanocomposites

| Sample                              | Absorbance (AU) | Number of Peaks | Removal Percentage (%) |
|-------------------------------------|-----------------|-----------------|------------------------|
| Dyestuff Solution                   | 9.0             | too many        | -                      |
| Chitosan-Clay                       | 3.6             | 4               | 60.00                  |
| CMCTS with Chloroacetic Acid-Clay   | 3.1             | 3               | 65.55                  |
| CMCTS with BTCA-clay                | 2.9             | 3               | 67.77                  |

3.2. Fourier Transform Infrared Spectrophotometer (FT-IR)

As it can be seen from the FT-IR graph, Chitosan makes peaks at 1090 cm\(^{-1}\), 3336 cm\(^{-1}\), 1597 cm\(^{-1}\), 879.88 cm\(^{-1}\) and at 1355 cm\(^{-1}\). At 1090 cm\(^{-1}\), bending of C-O bonds occur, at 3336 cm\(^{-1}\), bending vibration of -OH and amine bonds occur, at 1597 cm\(^{-1}\), NH2 bonding occurs and lastly at 1355 cm\(^{-1}\), amide III bonds are observed. When these peaks are compared with those of Chitosan which is modified with Butanetetracarboxylic acid, at BTCA/Chitosan, the 1597 cm\(^{-1}\), 879.88 cm\(^{-1}\) and 1355 cm\(^{-1}\) shifted to 1565 cm\(^{-1}\), 865 cm\(^{-1}\) and 1399 cm\(^{-1}\), respectively and two of the peaks which are 1090 cm\(^{-1}\), 3336 cm\(^{-1}\) disappeared but two new peaks at 1216 cm\(^{-1}\) and 622 cm\(^{-1}\) are formed which can be the characteristics of BTCA.

After the modification of Chitosan, the BTCA/Chitosan polymer is combined with Cloisite 30B and its characterization showed the characteristics of both BTCA/Chitosan and Cloisite 30B. The formed nano composite gives peaks at 463.87 cm\(^{-1}\), 527 cm\(^{-1}\), 618 cm\(^{-1}\), 665 cm\(^{-1}\), 1034 cm\(^{-1}\), 1212 cm\(^{-1}\), 1399 cm\(^{-1}\) and 1561 cm\(^{-1}\). The 618 cm\(^{-1}\), 1212 cm\(^{-1}\), 1399 cm\(^{-1}\) and 1561 cm\(^{-1}\) peaks are derived from the peaks of the BTCA modifier and Chitosan which are respectively 622 cm\(^{-1}\) and 1216 cm\(^{-1}\) from the modifier and 1355 cm\(^{-1}\) and 1597 cm\(^{-1}\) from Chitosan. The other peaks are derived from the structure of Cloisite 30B which were 515 cm\(^{-1}\), 630 cm\(^{-1}\), 689 cm\(^{-1}\) and 1125 cm\(^{-1}\). With the peaks of 622 cm\(^{-1}\) from Chitosan and 630 cm\(^{-1}\) at the nanocomposite the peak at 618 cm\(^{-1}\) strengthened.

![Figure 5. FT-IR result of clay and chitosan based composites after dyestuff removal stage](image-url)

Lastly, the nanocomposite is treated with Methylene Blue dyestuff and the formed structure has the peaks of both the nanocomposite and the Methylene Blue dyestuff. The dyestuff treated nanocomposite has new peaks formed that are at 3509 cm\(^{-1}\), 1625 cm\(^{-1}\) and at 1264 cm\(^{-1}\) and it can be the characteristic of the Methylene Blue dyestuff. Instead of these points the peaks of dyestuff-treated
nanocomposite are parallel to those of un-dyed one but 1561 cm\(^{-1}\), 1034 cm\(^{-1}\) and 618 cm\(^{-1}\) peaks are shifted to 1625 cm\(^{-1}\), 1061 cm\(^{-1}\) and 619 cm\(^{-1}\).

When combination of Clay-Chitosan modified with Chloroacetic acid graph is examined it is seen that 1050.3 cm\(^{-1}\) comes from clay component referring stretching of Si-O-Si bonding, 3364.4 cm\(^{-1}\) referring to bending vibration of -OH and amine bonds and 1549.5 cm\(^{-1}\) referring to NH\(_2\) bonding comes from Chitosan. Peaks at 1640.6 cm\(^{-1}\), 1406.8 cm\(^{-1}\) and 1260.2 cm\(^{-1}\) appeared at this sample and they can be coming from chloroacetic acid. In case of dyestuff-treated form of the sample, dyestuff peaks which are 3498.67 cm\(^{-1}\), 1625.70 cm\(^{-1}\) and 1264.80 cm\(^{-1}\) appear while 1549.5 cm\(^{-1}\) and 1406.8 cm\(^{-1}\) disappear. Peaks of clay component are preserved and peak at 1060.06 cm\(^{-1}\) is strengthened.

Results achieved from both CMCTS appear to be similar but CMCTS modified with chloroacetic acid could not make the peak at 702.43 cm\(^{-1}\) which means there is less bonding therefore CMCTS modified with BTCA offered better results. FT-IR results show that BTCA- CMCTS makes higher number of bonding with dyestuff than other composites, therefore it refines more precisely.

4. Conclusion
Textile industry needs a refinement for wastewater that includes dyestuff, and easier and shorter refinement processes gain an importance in case of economy and time consumption. Clay combinations are examples of natural refining chemicals with enhancing characteristics. Within this study, clay combinations are prepared with Chitosan, and Chitosan that has cationic characteristic is modified anionically to produce an attraction for adsorption of a standard cationic dyestuff, namely Methylene Blue. This modification is done by using two different chemicals, BTCA and Chloroacetic acid, and dyestuff adsorption potentials of such modified products are compared with each other, and with that of ordinary Chitosan. Results of yield nanocomposites show that anionic modification is maintained properly with both chemicals and thanks to carboxymethylation cationic dyestuff adsorption capacities are significantly increased. However, BTCA-CMCTS-clay combination is more precise option among them as a result of making more bonds with dyestuff. With regards to its unique structure, the composite has a potential to get different chemicals from a single refining bath thus to decrease refining process steps and chemicals that are used to refine until the quality of wastewater becomes within waste management standard limits.

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