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Removal of Cationic Dye From Aqueous Solutions Using Chitosan

KEYWORDS: Adsorption; methylene blue; Chitosan , synthesized

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ABSTRACT *Adsorption of methylene blue (MB) from aqueous solution onto chitosan was investigated in a batch system. The effects of solution pH, initial dye concentration, and temperature were studied. Results indicated that chitosan could be used as a biosorbent to remove the cationic dyes from contaminated water. Synthesize of chitosan involved three main stages as preconditioning, demineralization, deproteinization, and deacetylation. Chitosan was characterized using Fourier Transform Infrared Spectroscopy (FTIR) and solubility in 1% acetic acid.*

1 Introduction

Synthetic dyes usually have a complex aromatic molecular structure, which possibly comes from coal-tar based hydrocarbons such as benzene, naphthalene, toluene, xylene, etc. The complex aromatic molecular structures of dyes make them more stable and more difficult to biodegrade. [1–3]. Textile, paper, plastics, and cosmetic industries use a wide variety of dyes to color their products and discharge large amount of effluents including dyes which are very toxic and could cause serious ecological problems. Therefore, dye pollution in water stream is a major environmental problem.[4].

The methods of dye removal from industrial wastewaters could require many processes such as biological treatment, coagulation, electrochemical techniques, adsorption, and oxidation. Among these methods, adsorption is considered an effective and economical method to remove dyes from wastewaters.[5-10]. It has been reported that many different types of adsorbents are effective in removing color from aqueous effluents. Natural polymeric materials are gaining more and more interest for application as adsorbents in wastewater treatment due to their biodegradable and non-toxic nature. Currently, the most common procedure involves the use of activated carbon [11]. Activated carbon is regarded as an effective but expensive adsorbent due to the high cost of manufacturing and regeneration. Because of its relatively high cost, there have been attempts to utilize low cost and naturally occurring adsorbents. There are many different studies on the use of low cost materials such as various agricultural wastes [12–14], Chitosan (CS) offers an interesting set of characteristics, including non-toxicity, biodegradability, biocompatibility, and bioactivity.

Chitosan and its derivatives have been extensively investigated as biosorbents for removal of heavy metals and dyes.[15-19]

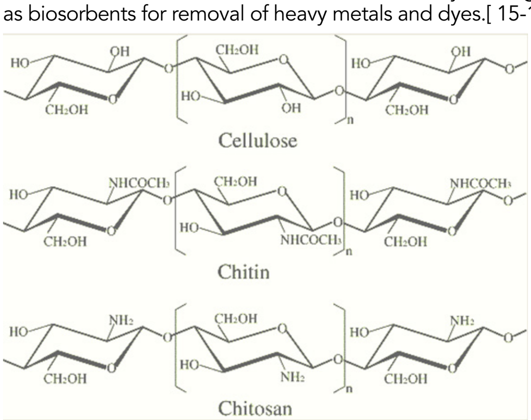

Figure 1. Chemical structures of chitin, chitosan and cellulose [21]

The overall objective of this study is to investigate the dye removal from wastewater by adsorption using chitosan. The specific objectives included; synthesize chitosan from fish shells and removal of methylene blue (MB) dye using as a bio-adsorption material.

2. Materials and methods

2.1. Preparation of Sorbent:

Traditional isolation of chitin consists of three traditional steps (Figure 2): demineralization (DM), deproteinization (DP), decolorization (DC), and deacetylation (DA).

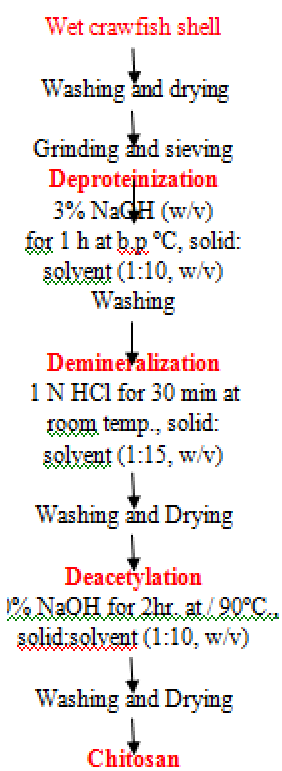

Figure 2. Traditional Chitosan Production [20].

2.2. Preparation of Adsorbent:

MB, a model of cationic dyes with a molecular formula of $C_{16}H_{18}N_3ClS$. The structure of MB is shown in Fig. 3. The MB used in the present study has a molecular weight of 319.85

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with its maximum absorbance at a wavelength of 665 nm. Distilled water was used for the preparation of dye solutions.

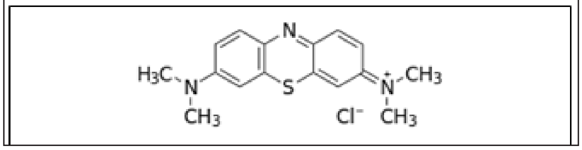

Figure (3); Chemical structure of MB dye.

The physiochemical properties of this dye can be shown in table(1)

Parameter	Value
Molecular formula	$C_{16}H_{18}N_3ClS$
Molecular weight	319.85
Maximum adsorption	665 nm
Nature	cationic dye

2.3. Batch adsorption experiments

A stock solution of MB (1.0 g/L) was prepared by dissolving 1 g of MB powder in 1 L of double distilled water. The desired concentrations ranging from 10 to 60 mg/L were obtained by dilution. For each adsorption experiment, 50 ml of the dye solution with a specified concentration was stirred at 100 rpm in a glass flask. The pH of solutions was adjusted to a desired value by adding 0.1 mol/L NaOH or HCl solution. Batch adsorption experiments were carried out using a thermostated shaker for a certain contact time at a determined temperature at 100 rpm. At predetermined time intervals, samples were withdrawn by a pipette and centrifuged at 4000 rpm. Then, the residual concentration was determined from a constructed calibration curve by measuring the absorbance at λ_{max} = 665 nm using UV-Vis spectrophotometer.

Batch adsorption experiments were carried out to examine effects of adsorbent dosage, initial dye concentration, solution pH, and time on the adsorption of MB on chitosan.

The amount of MB adsorbed on chitosan (at a predetermined time t), qt (in mg/g), was determined using the mass balance equation:

$qt = (C_o - Ct) \times m / v$ ………. (1)

The decolorization rate (η) of MB was calculated by the following equation:

$\mu = (C_o - Ct) / C_o \times 100\%$ ………. (2)

where C_0 is the initial concentration of MB (in mg/L), Ct (in mg/L) is the instant concentration of MB at a predetermined time t, V is the volume of the solution (in L), and m is the mass chitosan (in g).

3. Results and discussion

3.1.Effect of adsorbent dosage

The effect of adsorbent dosage (varied from 0.025 to 0.25 gm) on the percentage removal of 50 mg/L MB solution is shown in Fig. 4. The percentage removal of MB from the solution increased from 26% to 88% as the adsorbent dosage increased from 0.025 to 0.25 gm. This result is expected because of the increased adsorbent surface area and availability of more adsorption sites caused by increasing adsorbent dosage [21,22]

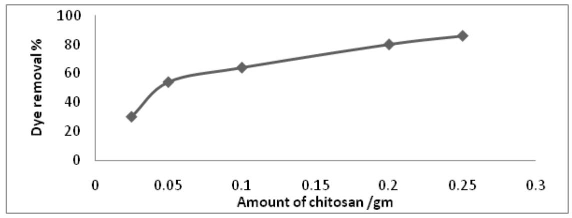

Figure 4. Effect of adsorbent dosage in MB removal.

3.2. Effect of solution pH

The pH of the dye solution affects the surface charge of the adsorbent, the degree of ionization of the materials, and the dissociation of functional groups on the active sites of the adsorbent. As well, it affects the structure of the dye molecule[23]. The percentage removal of MB at different pH values is plotted in Fig. 5. The percentage removal increased from 25.27% to 89.45% when pH was increased from 2 to 8. This was because of the molecular nature of MB (cationic molecule). meaning that the adsorbent's surface was positively charged at solution pHs below 5. This causes competition between protons and MB formed cations for adsorption locations [24,25] as well as the repulsion of cationic MB molecules, resulting in the reduction of dye adsorption.

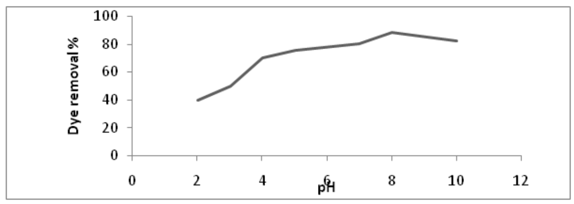

Figure 5. Adsorption of MB by chitosan as a function of pH at initial concentration of 50mg/L and adsorbent dosage 0.1 g .

3.3. Effect of contact time

A 50ml of 50mg/L of MB dye was taken in conical flasks and treated with 0.1 gm chitosan (adsorbent) at several times (20, 40, 60, 80, 100, 120 and 140 min.). the variation in percent removal of dye with the time was shown in figure 6. The percentage removal increased from 31.41% to 80.60% when time was increased from 20 to 140 min., this due to saturation of active sites which do not allow further adsorption to take place[26].

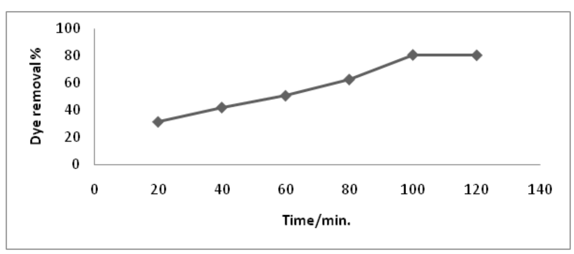

Figure 6. Effect of contact time on MB adsorption(50mg/L) by 0.1gm chitosan.

3.4. Effect of initial MB concentration

The effect of initial MB concentration on the percentage removal of the dye is shown in figure 6. The initial MB concentration was varied from 10 to 60 mg/L. A rapid initial adsorption of MB took place within the first 20 min, after which the adsorption slowed down and then almost reached equilibrium at 120 min. The percentage of MB removal evidently decreased with increasing initial dye concentration. The percentage removal was 82.05% for 10 mg/L initial concentration, and only 30.26% for 60 mg/L after 120 min of adsorption (figure 7). This was caused by an increase in the mass

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gradient pressure between the solution and adsorbent. The gradient acted as the force that drove the transfer of the dye molecules from the bulk solution to the particle surface[21] .

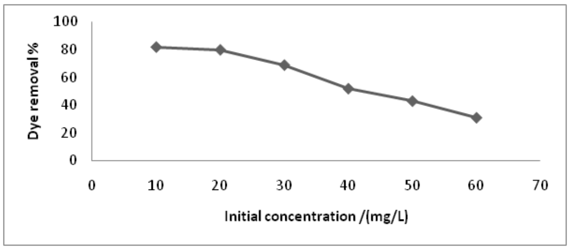

Figure 7. Effect of different initial MB concentration on dye removal.

4. Conclusions

The synthesize of chitosan involved three main stages demineralization, deproteinization, and deacetylation., it characterized by using Fourier Transform Infrared Spectroscopy (FTIR) and solubility in 1% acetic acid. MB adsorption onto the chitosan depended highly on adsorbent dosage, initial dye concentration, solution pH and time.

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