Synthesis of Chitosan-Silica Nanocomposite for Removal of Methyl Orange from Water: Composite Characterization and Adsorption Performance

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Abstract. Commercial chitosan (CH) was compositing with nanosilica prepared by the sol-gel method and was applied as an adsorbent for removal of Methyl-Orange (MO) dye from wastewater. Chitosan-Silica (CHS) was characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), atomic force microscopy (AFM), fourier transforms infrared spectroscopy (FTIR) and BET. The adsorption capacity of MO on CHS reached maximum 7.0mg.g⁻¹ on pH range 2.5 to 5, at equilibrium time 20 min. The effects of parameters, such as contact time, the adsorbent dosage of adsorbent, initial dye concentration on the removal of MO dye were examined. In general, the short time of MO dye removal, high adsorption capacity high, and dispensability in water, easy to remove by filtration suggests that CHS possesses high potential application for removal of MO from water, and can be considered as an eco-friendly adsorbent in water treatment processes.

Keywords: Adsorption, Nanocomposite, Chitosan, Silica, Water treatment, Biopolymer

1. Introduction

Dyes are widely used by several industries like textile rubber, plastics textile dyeing, textile lather dying factories, printing cosmetics, pharmaceutical and paper, these industries release large quantities of dyes in industrial effluents, it was estimated by the world bank that over 20% of world industrial water contamination source is the textile dyeing factories [1,2]. Dyes are stable and can disintegrate at temperatures above 200°C [3]. Therefore, they have negative effects on water resources, contaminated food, fish, and plants and then translate to humans and animals. Accordingly, dyes have been received extensive attention from researchers in the field of industrial water treatment. Many methods have been applied for dye removal from an aquatic environment, including physical, chemical and biological processes. Such methods are photocatalytic degradation biodegradation, flocculation, oxidation destruction via UV/ozone treatment membrane separation, and anaerobic biological treatment, sonolysis, but these methods suffer from several drawbacks including the formation of danger waste substance, high flow rates, ozone and free radicals, [4]. Applying the adsorption process has been found many advantages over other techniques. It is employed to produce natural or synthetic adsorbents used for adsorbed dyes chemically and physically in wastewater. The main advantage of adsorbent used is the availability, low cost, simplicity and, short time of treatment and no pollution as a side effect, by means of environmentally friendly. Thus considered as one of the most promising
processes for purification of impurities from wastewaters [5] to [8]. Chitosan and its derivatives are among the most low cost and plentiful biopolymer adsorbents and have a significant interest in the removal of organic and inorganic substances from wastewater due to their outstanding chelating behavior [9] to [12]. Chitosan as biomass has a high biodegradability, high chemical stability, non-toxicity, and environmental benignity is applied as a promising material in many fields for several years [9-11]. Also, the great deal towards the chitosan as an adsorbent is mainly due to the existence of hydroxyl and abundant amino groups in its structure [13] to [15].

Further improvement of chitosan to increase the active sites by compositing the chitosan with either organic or inorganic nanomaterial attract much research interest in a recent year [16]. was used a crossed linked chitosan/B-cyclodextrin composite for adsorption of methyl orange, the composite reveals high selectivity towards MO dye due to the attractive structure of cross-linked chitosan/B-cyclodextrin composite. Cross-linked quaternized chitosan/bentonite composite developed by Pan Huetal [17] and used for removal MO from wastewater. They are concluded that the possible pathways for MO adsorption may include the electrostatic interaction and hydrogen bonding between CHTCC/BT composite and MO with a monolayer adsorption capacity of 632.9mg/g. Ruihua Huang [18] was used protonated cross-linked chitosan in a batch system for adsorption of MO from aqueous solutions. Recent work has focused on magnetic chitosan composite to apply magnetic separation technology to avoid the drawback of chitosan lead to the blocking filters [19]. The objective of the present research was to synthesized and characterized new nanocomposite material utilizing chitosan as a cheap matrix phase and SiO$_2$ as a filler phase and examine the material as an adsorbent for removal of MO dye from industrial wastewater in batch experiment system.

2. Experimental

2.1. Chemicals

The tetraethylorthosilicate (TEOS), used as a source of silica with 99.9 % purity purchased from Merck. Chitosan powder (CS) or deacetylated chitin, poly (D-glucosamine) assay 99.5% purchased from, Suzhou Vitajoy Bio-Tech Co., Ltd., China, the acetic acid analytical reagent was from Chem-Supply Pty Ltd, (Australia), Ethanol solution (ETOH) 99.9% was from GCC, (UK). Deionized water (DW) (TDS=0) was from a local pharmaceutical company. The dye used in present work was a textile type methyl orange (MO) (Merk LTD) dye has a maximum absorption wavelength 460nm, molecular formula C$_{14}$H$_{14}$N$_3$NaO$_3$, molecular weight 327.33g.mol$^{-1}$, and its structure are illustrated in Figure 1. All the above chemicals used without further additive or purification.

![Chemical structure of methyl orange (MO).](image)

2.2. Characterization and measurements

The surface structure of the nanocomposite CHS was observed using scanning electron microscopy (SEM), JEOL, JSM-7000F, (Germany) operated at 15 kV and by AFM AA3000 scanning probe microscopy (USA). The surface area measurement was performed by using BET, ASAP 2020, Micromeritics, (Instrument Corp., USA), which used nitrogen for adsorption-desorption measurements. The standard diffractometric technique, LabX, XRD-6000 (Shimadzu, Japan) with a target Cu-K$\alpha$ was used to study the crystalline structure.
2.3. Preparation of Chitosan/SiO$_2$ (CHS)
The sol-gel method was used for synthesis CHS in this work. In a typical method, two solutions are prepared. The first solution contained 30 ml of ethanol added to 1 ml of distilled water (DW) and 0.5 ml hydrochloric acid. This mixture was later stirred for 10 min at 250 rpm at 28°C room temperature. After stirring was complete, 46.5 ml of tetraethylorthosilicate (TEOS) was added gradually and mixed carefully by a magnetic stirrer for 10 min at 250 rpm. The second solution contained 0.5 g of chitosan powder dissolved in 100 ml of 2% volume of acetic acid in a round bottom flask. This mixture was subsequently stirred for 2 hours after all of the chitosan had dissolved completely in the diluted acetic acid solution. To obtain CHS, the first mixture (sol 1) of TEOS solution was added dropwise into the second mixture of CS solution using a burette. After the solution was completely poured in, the reactant emulation was stirred at 200 rpm for 24 h. Next, the gel was kept for a week for crosslinking and dried in an oven at 60 °C. After the gel was dried, the calcination process was done at 500°C for 2 hours in a muffle furnace. After calcining, the powder obtained was crushed by using an alumina ball milling. The mill jar contained a ball-to-powder ratio of 10:1 at 200 rpm and was crushed to 225 mesh. The resultant powder was kept in a plastic closed bottle and labeled as CHS.

2.4. Dye adsorption procedure
Analytical grade MO dye was used to prepare a stock solution containing 1000mgL$^{-1}$ of MO which was diluted by deionized water to desired dye concentration. Briefly, a known amount (in weight percent) of (CHS) was added in a 250ml flask consisting 200 ml of MO solution of known concentration and pH was adjusted using 0.1 M HCl or 0.1M NaOH. The mixture was agitated with the speed of (250rpm) via magnetic stirrer at room temperature. After the equilibrate time passed, CHS was filtrated by filter paper the filtrate was analyzed using a UV-visible spectrometer (Gray 60) at maximum absorbency (460nm) of MO dye. Equation (1) bellow was used to calculate the amount of MO (q mg g$^{-1}$) adsorbed on CHS:

\[ q = \frac{C_0 - C_f}{M} V \]  

Where:
CO: The initial MO concentration (mg.L$^{-1}$)
Cf: The final MO concentration at equilibrium time capacity (mg.L$^{-1}$)
M (g): The mass of CHS adsorbent (kg)
V (L): The initial volume of MO dye solution.
The removal efficiency (R %) of the MO dye by CHS adsorbent was calculated using equation (2):

\[ R(\%) = \frac{C_0 - C_f}{C_0} \times 100 \]  

3. Result and Discussion
3.1. Characterization of absorbent
The structure of chitosan-silica CHS nanocomposite was analyzed by SEM and atomic force microscopy (AFM) as shown in Figures 2 and 3 respectively. SEM of CHS samples reveals a particulate structure of original natural chitosan, which seems to be fused decorated by SiO$_2$ nanoparticles (white particles) as shown in Figure 2. Some of the SiO$_2$ nanoparticles embedded within the structure of the chitosan matrix and other particles are dispersed onto their surface. The average particles size of nanocomposite powder 68.33nm as measured by AFM from the particle size distribution.
The AFM 3D topographic image of Figure 3 shows that the CHS nanocomposite sample calcined at 500°C exhibits a rough moderated flat texture with a granular nanostructure surface, and clear interstices can be observed between the particles/aggregates. The results show that it is possible to obtain a material with a highly developed surface. Such a surface structure creates a high porosity, which plays a beneficial influence on pollutants removal from aqueous solutions. This result is well agreed with the result obtained by Ruchi Nandanwar et al. [20]. The Brunauer–Emmett–Teller (BET)
surface area of CHS was measured as 389.3 m$^2$.g$^{-1}$ and the adsorption pore volumes were reported as 0.208 cm$^3$.g$^{-1}$, and pore size was 2.195 nm, using Barret–Joyner–Halenda (BJH) analysis [21].

Figure 2. Scanning electron micrograph (SEM) of nanocomposite CHS that are synthesized from SiO$_2$ nanoparticles and chitosan, (a) Chitosan (CH), (b) Chitosan-SiO$_2$ nanocomposite (CHS).

Figure 3. Atomic force micrograph of CHS sample. SiO$_2$ nanoparticles with average size particles 68.33nm as measured by AFM.

The XRD pattern in Figure 4 of the CHS showed the powder samples obtained from sol ultrafine in dimensions. The result shows the amorphous structure rather than a crystalline structure. The crystalline structure was supposed to be obtained as a result of the heat treatment of the sample at high calcination temperature (i.e. 500˚C). This may suggest the presence of HCl enhances the acidic reaction in the solution [20], which means crystalline particles having random structure and amorphous structure has been obtained of the material. This type of structure is suitable for application in catalytic purposes and adsorption processes [21].

Powder samples obtained from sol-gel was ultrafine in dimensions. The result shows the amorphous structure rather than a crystalline structure. The crystalline structure with a sharp silica peak was supposed to be obtained as a result of the heat treatment of the sample at high calcination temperature (i.e. 500˚C). This may be attributed to the presence of HCl enhances the acidic reaction in the solution.
[22], which means crystalline particles having random structure and amorphous structure has been obtained, such materials can be used for catalytic purposes and adsorption processes [23]. The FTIR spectra of the SiO$_2$ nanopowder, chitosan and CHS nanocomposite sample are shown in Figure 5. Chitosan observed rich structure in functional groups, transmission peaks at 1656 cm$^{-1}$ which may correspond to the C=O stretching of the amide I band, while the peak at 1422 cm$^{-1}$ was corresponding to C-H bending and the peak at 1154 cm$^{-1}$ was assigned for antisymmetric stretching of (C–O–C) bridge. Some of these groups disappeared after compositing chitosan with SiO$_2$ nanoparticles as shown in the FTIR spectrum of CHS due to SiO$_2$ embedded in the matrix. However, the transmission band at 3446 cm$^{-1}$ for SiO$_2$ and CH sample and 3453 cm$^{-1}$ for CHS sample refers to water present in the samples are attributed to the OH groups stretching vibration or to free H$_2$O. The peak near 460 cm$^{-1}$ shown in SiO$_2$ and CHS. FTIR spectrums are nomination is Si-O-Si which is out of the bends plane and stretching modes, these results provide evidence of a successful composite structure between SiO$_2$ and chitosan. The peaks vibration of SiO$_2$ groups which are assigned to symmetric and asymmetric stretching modes (1104 and 806 cm$^{-1}$) and bending mode at 464 cm$^{-1}$.

![Figure 4. The XRD pattern of the CHS and SiO$_2$ nanoparticles.](image)

3.2. Adsorption
3.2.1. Effect of pH
To understand the mechanism of pH of the solution on the adsorption process one should identify the role played by the pH which has a great effect on changing the surface charges of the adsorbent. [24]. Figure 6 shows the effect of pH over the range of pH (2-8) on the adsorption of MO dye on CHS sample. The amount of adsorbent (0.05g, contact time 20min) dye concentration 50mg.L$^{-1}$ and temperature 25$^\circ$C were kept constant during the experiment. The maximum removal efficiency was over the range 85% at the pH range 2-5.5and exhibit maximum efficiency at the initial of the pH range. The sharp decrease in pH was recorded at pH of 5.5 reaches the minimum value at pH 8. At low pH (in the acidic region), the amino groups belonging to the adsorbent has a protonated and they interact with the anionic group of dye molecules, given favoring adsorption. The decrease in the amount adsorption at pH>5.5 may due to the lack of positive charge on the surface of the CHS sample [25].
3.2.2. The effect of contact time

Figure 7 shows the contact time effect on the adsorption capacity of MO dye by the nanocomposite CHS throughout 2 hours in a batch experiment. The amount of adsorbent was 0.05 g, initial concentration 50 mg L\(^{-1}\), pH of the solution was 4 and temperature was 25\(^\circ\)C. Adsorption of MO by CHS increases rapidly with time and then reaches the adsorption equilibrium in about 20 mins. This can be attributed to numerous sites on the surface area available for adsorption at an early stage of treatment followed by less available sites due to repulsive forces between the MO dye and CHS phases [26]. At equilibrium time there is an active site on the CHS. This indicated an enhancement of separation in practical application.
3.2.3. Effect of initial dye concentration

Figure 8 shows the effect of initial MO dye concentration on removal efficiencies of CHS. The removal efficiency (R%) decreases with increasing MO dye concentration from 25 to 200 mg.L$^{-1}$. The maximum removal efficiency at the initial concentration of dye 25mg.L$^{-1}$ was found to be 98% but decreased to 44% at 200mg.L$^{-1}$ of dye concentration. A large number of sites on the surface are activated when initial dye concentration by the existence of CHS sorbent which is a boost to transport from liquid to solid phase, then after most of the active sites on CHS become saturated and the excess dye remains in solution.

3.2.4. Effect of CHS Dosage

Figure 9 shows the sorption of the MO dye onto the CHS sample as a function of CHS dose (M). The removal efficiency (R%) of MO was increased with increasing the dose of sorbent until reaching (89.5%) at 0.40 g (in 50mL of 50mg.L$^{-1}$ dye solution at pH 4 and 20min contact time) of CHS. The increase in removal efficiency with the CHS dosage attributed to the availability of large amounts of active sites of the CHS adsorbent [27].
### 3.2.5. Adsorption Isotherm:
The data obtained from adsorption experiments for CHS was fitted into Langmuir and Freundlich models. The linear form of the Langmuir model [28]:

\[
\frac{C_e}{q} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}
\]  

(3)

Where \( q, C_e, q_m, \) and \( K_L \) are the amount of MO dye adsorbed at equilibrium (mg.g\(^{-1}\)), the equilibrium concentration of dye (adsorbate) (mg L\(^{-1}\)), maximum adsorption capacity (mg.g\(^{-1}\)) and Langmuir constant (Lm.g\(^{-1}\)), respectively. \( q_m \) and \( K_L \) Langmuir constants were determined from the linear plots of \( \frac{C_e}{q} \) versus \( C_e \), respectively, as illustrated in Figure10. The Langmuir maximum adsorption capacity for the CHS sample was found to be 7.0. The Langmuir model shows better fitting with coefficients of correlation \( (R^2 > 0.99) \).

![Figure 9. CHS mass on removal efficiency of MO dye (C_0=50, pH=4, time=20min).](image)

![Figure 10. Langmuir isotherm plot for adsorption of MO dye on CHS adsorbent.](image)

The values of \( q_m, K_L \) and \( R^2 \) are listed in table 1. To identify the nature of adsorption process a dimensionless constant \( R_L \) can be used and can be defined by the following expression [26]:

\[
R_L = \frac{1}{1+K_L C_0}
\]  

(4)
Where; $C_0$ is the initial MO concentration (mgL$^{-1}$). The characteristic of the adsorption process is either favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$), unfavorable ($R_L > 1$), linear ($R_L = 1$). The values of the RL factor were found to be (0.19) or $R_L < 1$, indicate the favorable sorption.

The experimental data for MO adsorbed by CHS (mg·g$^{-1}$) could also be approximated by Freundlich’s model [28]:

$$
\log (q) = \log (K_F) + \frac{1}{n} \log (C_e)
$$

(5)

Where; $K_F$ and $n$ are Freundlich constants.

The plot between $\log (C_e)$ versus $\log (q)$ is shown in **Figure 11**. It is employed to calculate $K_F$ (from intercept) and $n$ from the slope $(1/n)$.

![Figure 11. Freundlich isotherm plot for adsorption of MO on CHS sample.](image)

The results are listed in Table 1. The better fit exhibited $R^2 = 0.98$ for the CHS sample. As we can be gathered from the result that the obtained adsorption capacity was low, this may due to the diminished of some functional groups related to chitosan after combination with silica as observed by FTIR result, but the resulting CHS sample, practically shows high dispensability in water, easily for removal by filtration and have a high stability during the adsorption process, this may be due to the good combination between SiO$_2$ and CH within the composite structure.

| Model  | Langmuir data | Freundlich data |
|--------|---------------|-----------------|
| Variable | $q_m$ | $K_L$ | $R^2$ | $n$ | $K_f$ | $R^2$ |
| CHS    | 6.99 | 0.082 | 0.99 | 4.46 | 2.23 | 0.98 |

### 4. Conclusions

The synthesized Chitosan-Silica (CHS) Nanocomposite was characterized and applied in a batch experiment process for removal of MO dye from wastewater. The adsorbent properties of chitosan are improved after compositing with Silica which made chitosan more stable and suitable for MO dye removal. The experiments showed that the removal efficiency of MO enhanced with the increase in the contact time and CHS dosage and decreases with an increase in initial MO concentration. The maximum removal efficiency was over the range 85% in the acidic part of pH range and decrease at a minimum in the base region, this was attributed to the protonated of the amino group of adsorbent at low pH and to the interaction of amino groups with the anionic dye molecules groups given favoring adsorption. The maximum adsorption capacity of MO calculated by Langmuir model is 7.0 mg·g$^{-1}$ with CHS at an initial concentration of MO day with a range of 20-200mgL$^{-1}$ and at equilibrium...
contact time 20min. The study of adsorption isotherms suggested that the adsorption processes are better fitted by the Langmuir isotherm model. In general, the adsorption of MO, onto CHS increase in pH range 2.5-5 and reach a minimum at pH=8. CHS sample showed high speed in the water, easy to remove by filtration and high stability during the adsorption process, this may be attributed to the good compositing between SiO$_2$ and CH. The good properties of CHS nanocomposite may make them useful in many application and especially in water treatment because it is environmentally friendly.

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