Removal of methylene blue and congo red by magnetic chitosan nanocomposite: Characterization and adsorption studies

J Jumadi, A Kamari, N A Rahim, S T S Wong, S N M Yusoff, S Ishak, M M Abdulrasool and S Kumaran

Department of Chemistry, Faculty of Science and Mathematics, Universiti Pendidikan Sultan Idris, 35900, Tanjung Malim, Perak, Malaysia.

E-mail: julianajumadi@gmail.com

Abstract. Dyes are stable organic pollutants that have been used in many industries and become one of the toxic contaminants for the environment. This research aimed at preparing a magnetic chitosan nanocomposite (MCN) as an effective adsorbent for cationic and anionic dye removal from aqueous solution. The MCN was synthesized using a coprecipitation method. The physical properties of MCN were characterized using elemental analysis (CHN-O), vibrating sample magnetometry (VSM), scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and X-ray diffractometry (XRD). The results confirm that chitosan has been embedded on the surface of magnetic material and shows superparamagnetic properties behavior. A series of adsorption were conducted to investigate dosage of adsorbent, contact time and initial dye concentration to obtain the optimum condition of adsorption for both methylene blue (MB) and congo red (CR) dyes. The experimental equilibrium adsorption were then analyzed by the Langmuir and Freundlich isotherm models. Based on the correlation coefficient ($R^2$) values, the equilibrium adsorption data were fitted to the Langmuir isotherm model. The maximum adsorption capacity ($q_m$) obtained from the Langmuir isotherm model for MB and CR onto MCN was 0.1308 and 1.8257 mg/g, respectively. Results highlight the potential of MCN application as an adsorbent for water contaminated by dyes.

1. Introduction

In this era of globalization, the rapidly growing of industries is in tandem with increasing of water demand that making water contamination become a serious problem in recent years. Textile industry is one of the industries that contribute to significant water pollution problems. It is known, textile production involves the use of many chemicals and dyes that are resistant to aerobic digestion due to their stability to light and oxidation [1]. In most situation, the wastewater from textile industry contain large amounts of suspended solids, oil and grease, high concentration of chemical oxygen demand (COD) and biochemical oxygen demand (BOD), organic and inorganic dyes and heavy metals that caused negative effects to the environment when discharged to the river without proper treatment [2]. Therefore, among a number of water treatment methods that are available to be applied for the removal of color from the wastewater, adsorption has been found to be the most effective in the elimination of color with cheap and simple method [3].

Chitosan is obtained from deacetylation of chitin and has reactive hydroxyl and amino group that makes chitosan received much attention as an excellent adsorbent for removal of dye as well as heavy metal [4,5]. To enhance the properties of the chitosan adsorption in term of separation of the adsorbent
from the solution after the treatment, the chitosan-magnetic Fe$_3$O$_4$ nanocomposite in the form core shell microsphere structure was studied. The adsorbent can be easily removed from the solution/effluent in a short time when the external magnetic fields are introduced [6]. The most important feature of magnetic chitosan nanocomposite adsorbent was it can be recyclable, high removal efficiency and low cost of production which economical for industry [7]. Although many researchers have been tested MCN to adsorb a number of dyes, there are no reports on preparing Fe$_3$O$_4$/chitosan hybrid nanocomposite with minimum ingredient using simple coprecipitation method to removal of dyes and characterization before and after the removal were also been studied.

Therefore, the target of this study was to prepare and characterize the magnetic chitosan nanoparticle for the removal of anionic congo red and cationic methylene blue from aqueous solution. Experiment was done on a series of adsorption test to figure out the optimum adsorbent dosage, contact time and initial dye concentration to achieve a maximum reduction of cationic and anionic dyes removal. Hybridization between chitosan and magnetic material is applicable and ease to be applying in dye removal by showing features such as good compatibility, low cost and easy operation.

2. Materials and methods

2.1. Preparation of magnetic chitosan nanocomposite (MCN)

Chitosan-coated magnetic Fe$_3$O$_4$ nanocomposite was synthesized using a technique suggested by Pham et al. [8] with some modifications. Basically, 2.0 g of sodium dodecyl sulfate (SDS) was dissolved in 400 mL of ionized water which then 0.25 g of iron oxide nanoparticles was added into the SDS solution with intensive stirring at room temperature. Subsequently, 100 mL chitosan solution (0.5 g) was added to obtain the MCN nanoparticle. The mixture was continuously stirred at a constant speed for one hour at room temperature. Then, the magnetic nanoparticle coated with chitosan obtained was magnetically separated from solution by using a magnet bar and thoroughly washed several times with deionized water and ethanol to remove any impurities. Finally, the synthesized MCN was then dried overnight at 60 °C. The ratio of expected MCN is 1:5 (w/w) of chitosan to Fe$_3$O$_4$ nanoparticle.

2.2. Characterization study

Elemental analye was carried out by using Thermo-Finnigan Flash EA 1112 Elemental Analyzer. The magnetic property was measured on a LakeShore-7404 vibrating sample magnetometer at room temperature for 5 to 25 min. Surface morphology of nanocomposite was examined on a Hitachi SU 8020 UHR FESEM and elemental composition by using Horiba EDX Spectrometer. Thermal behavior of nanocomposite was performed with a TGA/DSC 1 Mettler Toledo that carried out under argon atmosphere in the range of heating temperature 25-1000°C with a 20 mL/min of flow rate. The structure phases of the sample before and after the adsorption were investigated by Rigaku Miniflex II in the range of 3 - 90° with 2° per min of rate.

2.3. Adsorption study

A series of adsorption experiment was carried out in order to determine the adsorption efficiency of magnetic chitosan nanocomposite. The adsorption experiments were conducted by adding 50 mg of MCN into 50 mL of required dye solution in Erlenmeyer flask followed by mechanically agitating by using a Protech Orbital shaker model 720 at 100 rpm for 1 hour. The test was performed at ambient temperature. The external magnet was used to separate adsorbent from the supernatant and then small amount of sample were collected. Finally, the concentration of dyes in the supernatant after magnetic separation was determined using an Agilent Cary 60 UV-Visible Spectrophotometer at the maximum wavelength ($\lambda_{max}$) of 498 nm and 665 nm for CR and MB, respectively. The adsorption experiments were conducted as a function of three operational parameters namely, dose of adsorbent, contact time and initial dye concentration. The percentage of dyed uptake onto MCN was calculated using equation (1) [18]:

\[ \text{Percentage of Dyed Uptake} = \frac{C_{initial} - C_{final}}{C_{initial}} \times 100 \]
where $C_i$ is an initial concentration of dyes and $C_e$ are the concentrations of dye solution at time $t$ (mg/L).

3. Results and discussion

3.1. Characterization of MCN

Elemental analysis: The percentage of elemental composition analysis of carbon (C), hydrogen (H), nitrogen (N) and oxygen (O) for chitosan and MCN are presented in Table 1.

| Sample  | Weight percent (%) | Experimental value | Theoretical value |
|---------|--------------------|--------------------|-------------------|
|         | C                  | H                  | N                  | O                  |
| Chitosan| 45.22 ± 0.8        | 7.81 ± 0.2         | 7.37 ± 0.8         | 38.85 ± 0.3        |
| MCN     | 29.16 ± 0.3        | 4.95 ± 0.6         | 5.68 ± 0.5         | 36.82 ± 0.2        |

*values represent mean ± standard deviation from three replicates.

The experimental value for elemental composition was in the coherence to the theoretical values with difference within ± 0.4% for both chitosan and MCN. For that reason, it may be concluded that with small difference elemental analysis results proved that the MCN was successfully synthesized.

Magnetic properties analysis: Vibrating sample magnetometry was used to identify the magnetic properties of the magnetite and MCN, as shown in Figure 1(a). From the results, both samples exhibited superparamagnetic properties with zero remanence and coercivity at room temperature was observed in the hysteresis loop. The saturation magnetization values (Ms) of the Fe$_3$O$_4$ and MCN were 46.901 and 9.2315 emu/g, respectively. The decreased of saturation magnetization of MCN due to the presence of the chitosan coated onto the surface of Fe$_3$O$_4$ nanoparticles or due to decrease in particle size of nanocomposite [8,9].

![Magnetization hysteresis loop of Fe$_3$O$_4$ and MCN at room temperature](image)

**Figure 1.** (a) Magnetization hysteresis loop of Fe$_3$O$_4$ and MCN at room temperature, and (b) SEM image of (i) chitosan and (ii) MCN at 50,000x magnifications.

SEM analysis: The morphology of pristine chitosan and synthesized magnetic chitosan nanoparticle are presented in Figures 1(b) i and 1(b) ii, respectively. SEM image of chitosan shows a nonporous and flat surface while MCN image shows the spherical shape represents the Fe$_3$O$_4$ nanoparticle which illustrates a high degree of agglomeration caused by the dipole-dipole interaction [10]. It was observed
that after coating of chitosan at the surface of magnetic particle, the small cluster was formed within the spherical shape due to the presence of chitosan layer on the surface of magnetic material. On the other hand, the EDX spectra has confirmed the formation MCN (Figure 2(a)), where displays three sharp peaks at the energy values of 0.3, 0.5 and 6.4 KeV, which assigned as carbon, oxygen and iron element, respectively.

Figure 2. (a) EDX spectra of MCN and (b) TGA thermograms of uncoated Fe$_3$O$_4$, MCN, MCN-CR and MCN-MB.

TGA analysis: Figure 2(b) presents the TGA thermograms pattern of Fe$_3$O$_4$, MCN and MCNs after interaction with MB and CR dyes denoted as MCN-MB and MCN-CR that were used to identify the stability of the four particles at high temperature. It was observed that the uncoated Fe$_3$O$_4$ shows refractory material properties that can resist heat at high temperature were no significant change in weight loss or stable up to 1000 °C. On the other hand, MCN shown that about 4% of weight loss from uncoated Fe$_3$O$_4$ may be due to the loss of physically adsorbed moisture or OH group on chitosan was adsorbed onto the Fe$_3$O$_4$ surface [8]. In addition, the weight loss found around 380-425 °C of 4.5% for samples MCN-MB and MCN-CR related to the presence of organic compound of dye. These result of electrostatic interaction or hydrogen bonding interaction and chemical reaction of protonated dyes molecule attach on the surface of MCN [15].

Figure 3. XRD patterns of uncoated Fe$_3$O$_4$ and MCN before and after dyes adsorption.

XRD analysis: The crystal structures of Fe$_3$O$_4$, MCN and MCNs before and after adsorption of dyes were examined, and are shown in Figure 2(a). The X-ray diffraction patterns for the uncoated Fe$_3$O$_4$ shows six main sharp peaks at 30.02, 35.58, 42.95, 53.37, 57.00 and 62.82° which matched with the standard Fe$_3$O$_4$ (ICSD, file n° 01-086-1340) [16]. The narrow and sharp peaks indicated that the Fe$_3$O$_4$ particles were associated with cubic crystalline magnetite structure and patterns peaks observed in all MCN, MCN-CR and MCN-MB nanoparticle showed the crystalline structure of magnetite. The average crystallite size Fe$_3$O$_4$, MCN, MCN-MB and MCN-CR were calculated using the Scherrer’s equation was 31.12, 28.38, 28.07 and 27.73 nm, respectively.
3.2. Adsorption Studies

Effect of dosage on adsorption: The adsorbent dose is the most essential parameter in adsorption studies to evaluate the effect of the amount of adsorbent at the minimum value on the adsorption efficiency for removal of dyes. Figures 4(a) and (b) show the adsorption removal of MB and CR, respectively, onto chitosan, Fe₃O₄, and MCN at the various dosage of adsorbent from 20-100 mg at dye initial concentration 10 mg/L. According to the result, it was clearly seen that with increasing amount of three types of adsorbent, removal of both dyes percentage was also increase. It may be due to available surface area of the adsorbent that has more vacant adsorption sites on its surface to penetrate the dyes. Fe₃O₄ has the lowest removal efficiency on MB and CR with maximum removal is less than 3% and 30% at 80 and 100 mg dose of adsorbent, respectively. The pristine chitosan shows the higher adsorption in all different dosage for both MB and CR removal compared to MCN adsorbent. The sorption of MCN is lower may be because no hydrogen/electrostatic bonding was formed between negatively charged iron oxide nanoparticle with the protonated MB and CR dyes molecules that do not contain a hydroxyl group in the structure, which lead to less adsorption efficiency [14].

![Figure 4. Effect of adsorbent dosage for the adsorption of (a) MB and (b) CR onto MCN (initial concentration: 10 mg/L in 50 mL of dyes solution, at 26 ± 2 °C).](image)

Effect of contact time on adsorption: Effect of contact time is also a vital parameter for determining the maximum time consumed for the outstanding dyes adsorption onto adsorbent especially in industry perceptive. For the evaluation of adsorption as a function of time, graph adsorption efficiency for the removal of MB and CR against contact time was plotted as presented in Figures 5(a) and 5(b). The dye removal percentage increased with the increase in contact time. As time progress the surface coverage of the adsorbent is high and furthers no adsorption take place. The decreased adsorption rate indicates the possible monolayer formation of dyes on the adsorbent surface caused by lacking active site for further adsorption [12]. As for MCN, by increasing the contact time the adsorption of both dyes was keep increase which shows the availability of the MCN surface to interact with the dyes molecule.

![Figure 5. Effect of contact time for the adsorption of (a) MB and (b) CR onto MCN at different contact time (initial concentration: 10 mg/L in 50 mL of dyes solution, at 26 ± 2 °C).](image)
Effect of initial concentration on adsorption: The effect of the initial dye concentration factor depends on the immediate relation between the dye concentration and the available sites on the adsorbent surface. The effect of the initial MB and CR concentration, on the adsorption efficiency is shown in Figure 6(a) and (b). This may be attributed to the fact that at low concentration of dyes solution the number of vacant active sites adsorbent is higher and hence all dye molecules may interact with the adsorbent. It might be explained that during the preliminary stage, an abundant number of vacant surface sites of MCN was available for dyes adsorption. However, with longer the adsorption time, the remaining vacant surface sites were difficult to be occupied due to steric barrier between MB adsorbed on the surface of MCN and solution phase [11]. The adsorption efficiency increased with increase in the initial dye concentration for MB due to the increasing in the driving force for mass transfer.

3.3 Adsorption Isotherm

Langmuir isotherm: The Langmuir model assumes that the possible monolayer adsorptions of the dyes occur at homogeneous sites on the chitosan, Fe₃O₄ and MCN surface until equilibrium adsorption takes place [17]. The linear form of saturated monolayer isotherm represented by the equation (2) and can be expressed in terms of dimensionless equilibrium parameter called equilibrium parameter (Rₑ) as equation (3):

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

\[ R_L = \frac{1}{1 + K_L C_e} \]
where $C_e$ is the equilibrium concentration of dyes (mg/L), $q_e$ is the amount of dye adsorbed per unit mass of MCN (mg/g), $q_m$ is the maximum adsorption efficiency (mg/g) and $K_L$ is Langmuir constant (L/mg).

Value of Langmuir parameter and correlation coefficients are summarized in Table 2. The Langmuir plot of $C_e/q_e$ against $C_e$ give a $R^2$ value of CR adsorption for three adsorbents are very close to 1 compared to adsorption on MB, considering that the adsorption isotherm of CR is better described in Langmuir model than MB. Thus, these results show that both dyes were adsorbed onto MCN by a monolayer adsorption process. On the other hand, the $R_L$ value of all adsorbent in MB and CR system was found between 0 and 1 which indicate the adsorption of the dyes on to adsorbent is favorable. Based on another researcher at low concentration of adsorbate, the surface of adsorbent becomes homogeneous that make the system difficult to obey the Langmuir model due to the energetic heterogeneity of adsorption sites [13].

### Table 2. Langmuir and Freundlich Isotherm Models for the Adsorption of MB and CR onto MCN, Fe$_3$O$_4$ and Chitosan.

| Dye | Adsorbent | Langmuir | | Freundlich | |
|-----|-----------|----------|---|------------|---|
|     |           | $q_m$ (mg/g) | $K_L$ (L/mg) | $R_L$ | $R^2$ | $K_F$ (mg/g) | $n$ | $R^2$ |
| MB  | MCN       | 0.1308   | 0.3316 | 0.2868 | 0.8805 | 0.6354 | 2.4310 | 0.0699 |
|     | Fe$_3$O$_4$ | 0.0351   | 0.1976 | 0.4029 | 0.7986 | 1.3409 | 0.8610 | 0.7180 |
|     | Chitosan  | 0.0088   | 0.2154 | 0.3823 | 0.6803 | 1.4796 | 0.621  | 0.7257 |
| CR  | MCN       | 1.8257   | 13.906 | 0.0095 | 0.9919 | 1.6429 | 20.756 | 0.0569 |
|     | Fe$_3$O$_4$ | 1.1091   | 0.7420 | 0.1523 | 0.9032 | 1.6989 | 16.765 | 0.2140 |
|     | Chitosan  | 12.466   | 18.859 | 0.0072 | 0.9968 | 12.012 | 4.0178 | 0.9678 |

*Freundlich isotherm:* The Freundlich model equation indicates the empirical relationship between the loadings of adsorbent on the heterogeneous surface to the concentration of dye that involved in not uniform adsorption energies of each site [17]. The logarithmic form Freundlich equation is expressed as equation (4):

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$

where $q_e$ and $C_e$ same meaning as in Langmuir equation, $K_F$ is a Freundlich adsorption capacity constant (mg/g) and $n$ is an intensity of adsorption. Table 2 shows the Freundlich adsorption of the MB and CR dye onto the three adsorbents by linear analysis. The experimental data of $n$ value for dyes adsorption onto MCN less than 1 indicating chemical process was occur in adsorption while $n$ value more than 1 point out physical process which represent good adsorption due to a distribution of surface sites or any factor that causes a decrease in adsorbent-adsorbate interaction with increasing surface density [16]. However, the $R^2$ for all adsorbent in MB and CR in Freundlich is lower than Langmuir. The extremely lower $R^2$ is at MB and CR adsorption onto MCN at 0.0699 and 0.0569, respectively which worst fitting agreement in the isotherm model.

### 4. Conclusion

In this research, the hybrid Fe$_3$O$_4$/chitosan nanocomposite was prepared with a simple coprecipitation method. The characterization using several analysis instruments revealed that the chitosan successfully coated to the Fe$_3$O$_4$ surface and exhibited superparamagnetic behavior. The removal efficiency of the MB and CR dyes was increased as the adsorbent dosage and contact time increased at 14 and 36 %,
respectively, at an initial adsorbent dosage of 100 mg. The adsorption process was best described by the Langmuir isotherm model which indicated the dyes occur at monolayer surface of MCN. CR had greater affinity towards adsorbents as compared to MB. The maximum adsorption capacities ($q_m$) of MCN, Fe$_3$O$_4$ and chitosan for CR were determined as 1.8257, 1.1091 and 12.466 mg/g, respectively. The MCN has great potential to be used as an environmentally friendly and cost-effective adsorbent. The influence of chitosan to magnetite ratio in the production of MCN on adsorption capacity of MCN for cationic and anionic dyes is being studied.

References
[1] Mohan D, Singh K P, Singh G and Kumar K 2001 Ind. Eng. Chem. Res. 41 3688-3695
[2] Liang C-Z, Sun S-P, Zhao B-W and Chung T-S 2015 Ind. Eng. Chem. Res. 54 11159-11166
[3] Cheng M, Zheng G, Huang D, Lai C, Liu Y, Zhang C, Wang R, Qin L, Xue W, Song B, Ye S and Yi H 2018 J. Colloid Interface Sci. 515 232-239
[4] Zhang Lei, Zeng Y and Cheng Z 2016 J. Mol. Liq. 214 175-191
[5] Wan Ngah W S, Teong L C and Hanafiah M A K M 2011 Carbohyd. Polym. 83 1446-1456
[6] Reddy D H K and Lee S-M 2013 Adv. Colloid. Interfac. 201-202 68-93
[7] Liu X, Hu Q, Fang Z, Zhang X and Zhang B 2009 Langmuir 25 3-8
[8] Pham X N, Nguyen T P, Pham T N, Tran T T N T and Tran T V T 2016 Adv. Nat. Sci.: Nanosci. Nanotechnol. 7 045010
[9] Malwal D and Gopinath P 2017 Colloid Interfac. Sci. Commun. 19 14-19
[10] Shete P B, Patil R M, Thorat N D, Prasad A, Ningthoujam R S, Ghosh S J and Pawar S H 2014 Appl. Surf. Sci. 288 149-157
[11] Shi H, Li W, Zhong L and Xu C 2014 J Ind. Eng. Chem. 53 1108-1118
[12] Pathania D, Sharma S and Singh P 2017 Arab. J. Chem. 10 S1445-S1451
[13] Bhatt A, Sakaria P L, Vasudevan M, Pawar R R, Sudheesh N, Bajaj H C and Mody H M 2012 RSC Adv. 2 8663.
[14] Saha B, Das S, Saikia J and Das G 2011 J. Phys. Chem. C 115 8024-8033
[15] Wang P, Yan T and Wang L 2013 Bioresources 8 6026-6043
[16] Freire T M, Dutra L M U, Quiriz D C, Ricordi N M P S, Barreto K, Denardin J C, Wurm F R, Sousa C P, Correia A N, Lima-Neto P D and Fechine P B A 2016 Carbohydr. Polym. 151 760-769
[17] Robita D, Mirza B, Rajabi M, Moradi O, Tyagi I, Agarwal S and Gupta V K 2016 Chem. Eng. J. 284 687-697
[18] Aljeboree A M, Alshirifi A N and Alkaim A F 2017 Arab. J. Chem. 10 S3381-S3393

Acknowledgement
The authors would like to express their sincere gratitude to Department of Chemistry, Faculty of Science and Mathematics, Universiti Pendidikan Sultan Idris for providing the instrumentation services for this research.