The Potential of Chitosan-TiO₂ Nanocomposite for Methyl Orange and Rhodamine B Removal

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

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

E-mail: mustafabioch.1991@gmail.com

Abstract. The overall objective of present work was to prepare and use chitosan-titanium dioxide (CS-TiO₂) nanocomposite as an adsorbent to remove two toxic dyes, namely Methyl Orange (MO) and Rhodamine B (RhB) from the aqueous solution. This work consists of two main parts, namely adsorption and characterization studies. For adsorption studies, several experimental parameters were studied such as the effect of initial concentration, solution pH and adsorbent dosage. Meanwhile, Scanning Electron Microscope (SEM), Thermogravimetric Analyser (TGA), and X-ray Diffractometer (XRD) were used for characterization studies. The outcomes have shown that the equilibrium data correlated well to Freundlich isotherm model with adsorption capacity at equilibrium (K_F) was determined as 1.608 mg/g for MO and 7.646 mg/g for RhB, respectively. Based on SEM analysis, the rod- and needle-like deposits on the surface of CS-TiO₂ nanocomposite were disappeared following interaction with MO and RhB. There were cube-like deposits observed on the surface of CS-TiO₂ nanocomposite after adsorption of MO, while a dense and uneven surface texture were observed after adsorption of RhB. From TGA analysis, CS had two degradation stages, while CS-TiO₂ nanocomposite had three steps of decomposition. Furthermore, XRD results observed diffraction peaks for CS-TiO₂ at 2θ = 34.075°, 29.235°, 25.47° and 20.26°.

1. Introduction

Excessive release of dyes and heavy metals into the environment due to rapid industrialization and urbanization has caused significant water contamination, worldwide [1]. Textile, leather, plastic, printing, paper, cosmetics, pharmaceuticals and food industries used methyl orange (MO) and rhodamine B (RhB) dyes in large quantities to colour their products [2]. Approximately 700,000 tonnes of the world dyes was produced per year and from the numbers about 56% was widely utilized by the textile industry [3,4]. The presence of toxic dyes in water has been a major concern to many life forms due to their adverse effects. There are various techniques and processes that had been developed to eradicate the toxic contaminants from aqueous solutions. These processes include adsorption, membrane-based filtration, ion exchange, photodegradation, solvent extraction, chemical precipitation, reverse osmosis and evaporation [5]. Among all, adsorption has been claimed to be the most commonly used method to treat the contaminated water [6]. This is mainly due to various factors such as low cost, can be attained easily, simple designs, easy to be operated and able to remove the contaminants in many forms of concentrations [7]. In addition, the effectiveness of adsorption relies on the capacity of adsorbent to adsorb the contaminants.
Chitosan (CS), poly β-(1-4)-2-amino-2-deoxy-D-glucopyranose is a polysaccharide that produced from deacetylation of chitin, which can be isolated from exoskeletons of marine organisms such as crabs, shrimps and cell walls of fungi [8,9]. The polysaccharide has great characteristics which are non-toxic, biodegradable, biocompatible and have good antimicrobial properties [10,11]. Chitosan has two important functional groups namely hydroxyl group (–OH) and animo group (–NH₂) in its chemical structure. The presence of these functional groups makes chitosan soluble in acidic medium and therefore limits its application for water treatment. To improve its physical property, several chemical and physical modifications including cross-linking, grafting and blending with other materials can be performed [10,11].

In this study, CS-TiO₂ nanocomposites was synthesized, characterized and applied to adsorb Methyl Orange (MO) and Rhodamine B (RhB) in aqueous solution. The performance of CS-TiO₂ nanocomposite to remove MO and RhB was evaluated using several experimental parameters. Meanwhile, the physical and chemical characterisatics of CS-TiO₂ nanocomposite were studied using several analytical instruments.

2. Materials and Methods

2.1. Materials
Chitosan (CS) with a molecular weight of 600,000-800,000 Daltons was purchased from Acros Organics. Titanium(IV) oxide (TiO₂) nanopowder that has a particle size of 21 nm was supplied by Sigma Aldrich. Methyl orange (MO) and Rhodamine B (RhB) were obtained from Bendosen and Merck, respectively. Figure 1 displays the chemical structures of CS, MO and RhB, respectively.

![Chemical structures of CS, MO and RhB](image)

**Figure 1.** The chemical structure of (a) CS, (b) MO and (c) RhB.

2.2. Preparation of CS-TiO₂
To prepare the CS-TiO₂ nanocomposite, 0.15 g of TiO₂ nanopowder was first dissolved in 100 mL of 1% (v/v) acetic acid solution. Next, about 2 g of CS was added to the aforementioned solution. The mixture was left to homogenise using a magnetic stirrer for 2 hours. Then, Cs-TiO₂ nanocomposite beads were prepared through neutralization process by adding the resultant mixture dropwise in a bath that contained 500 mL of 0.5 mol/L NaOH. The NaOH solution was stirred with a magentic stirrer to prevents the CS-TiO₂ nanocomposite beads from sticking to the glassware surfaces. The wet CS-TiO₂ nanocomposite beads were then filtered and rinsed thoroughly with deionized water to remove the remaining NaOH residue. Finally, CS-TiO₂ nanocomposite beads were left air-dried. Prior to the last step, a mortar and pestle were used to grind the dried beads. The fine powder was kept in an air-tight container until ready for analysis [12].

2.3. Adsorption study
The concentration of each stock solution of MO and RhB was 100 mg/L. The preparation of stock solution was done separately by dissolving 0.25 g of each dye in 250 mL of deionized water. Adsorption studies of MO and RhB involved three different parameters such as initial concentration...
(2.5-20 mg/L), pH of solution (2.0-8.0) and dosage of adsorbent (0.025, 0.050, 0.075, 0.1 and 0.2 g). The experiments were conducted in a 250 mL conical flasks. In order to equilibrate the solution, a Protech Orbital Shaker “model 720” was used to shake the samples at 100 rpm for 1 hour. Following adsorption experiment, CS-TiO₂ nanocomposite were carefully filtered using a filter paper (FiltreFioroni 601, 110 mm, slow speed). The concentration of MO and RhB in aqueous solution was measured by using an Agilent Cary 60 UV-Visible Spectrophotometer at 462 and 554 nm, respectively. All experiments were carried out in triplicates. Equation (1) shows the calculation of the adsorption capacity at equilibrium ($q_e$) [13]:

$$q_e = \frac{C_i - C_e}{W} V$$

where $q_e$ is the maximum of adsorption capacity at equilibrium (mg/g), $C_i$ represents the initial concentration MO and RhB (mg/L), $C_e$ signifies the final concentration of MO and RhB at equilibrium (mg/L), $W$ refers to the mass of the CS-TiO₂ (g) and $V$ represents the volume of MO and RhB (L). By using equation (2), the percentage of removal of each MO and RhB from aqueous solution was calculated [13]:

$$\text{Removal} (%) = \left(\frac{C_i - C_e}{C_i}\right) \times 100$$

2.4. Adsorption isotherms

The adsorption isotherm data at equilibrium is designed based on two commonly used models which are Langmuir and Freundlich isotherm models. These models are used to explain the connection between the adsorbent (stationary phase) and adsorbate (mobile phase). Freundlich isotherm described the adsorption process between the adsorbents and contaminants is likely occur at heterogeneous or multilayer surface [9]. The following equation (3) presents the linearized equation of Freundlich isotherm [14]:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$

$q_e$ refers to the amount of dyes adsorbed per unit weight of adsorbent (mg/g) (CS-TiO₂ nanocomposite), $K_f$ (mg/g) represents the adsorption capacity, and $n$ (g/L) refers to the strength of adsorption process, and $C_e$ refers to equilibrium concentration (mg/L) (dyes).

Meanwhile, Langmuir isotherm model is described as an adsorption process for monolayer at homogenous surface [15] without presenting the interaction between adsorbent and adsorbate particles. Equation (4) expresses the linear model of Langmuir [15]:

$$\frac{C_e}{q_e} = \frac{C_e}{Q} + \frac{1}{Qb}$$

$C_e$ refers to the concentration at equilibrium (mg/L), $q_e$ signifies the amount of adsorbed (dyes) per unit weight of adsorbent (mg/g), $Q$ refers to the amount of adsorbed (dyes) per unit weight of adsorbent (mg/g), and $Q$ and $b$ are the Langmuir constants.

2.5. Characterization study

In present study, several characteristics related to the physical and chemical properties of CS and CS-TiO₂ nanocomposites were studied. The changes in physical and chemical properties of CS-TiO₂ nanocomposites after adsorption with dyes were investigated using a number of analytical techniques. A Hitachi SU 8020 UHR FESEM was used to conduct scanning electron microscope (SEM) analysis to observe the morphology of CS-TiO₂ nanocomposites before and after adsorption with dyes. Prior to analysis, the surface of CS-TiO₂ nanocomposites was coated with a thin layer of platinum to avoid the charging of electron. The thermal properties of CS and CS-TiO₂ nanocomposites were examined using
a TGA/DSC 1 Mettler Toledo Analyser. For the thermal analysis, the samples was heated at temperature range between 30 to 900 °C under argon gas with a flow rate of 20 mL/min. Lastly, the crystallinity properties of the nanocomposite was performed using the X-ray diffraction (XRD) analysis.

3. Results and discussion

3.1. Effect of initial concentration
One of the most important factors which effects dyes adsorption process is the initial concentration of dyes. Figure 2(a) displays a function of initial concentration for percentages of removal of each MO and RhB. Based on Figure 2(a), it is clearly observed that when the initial concentration of MO increased, the percentage removal of MO had decreased from 90% to 75%. This is because the adsorbent has limited number of active sites and could be saturated by few dye concentrations. In this matter, the CS-TiO₂ nanocomposite exhibits lesser number than the dye molecules. Meanwhile, as for RhB, when the initial concentration increased, the percentage of CS-TiO₂ nanocomposite adsorbent will also increase from 6% to 28%. This can be explained by the fact that at high initial dye concentration, it caused high driving force of dye mass transfer from aqueous and solid phase caused all the available active sites of nanocomposites to be occupied with dye molecule [16-18].

3.2. Effect of solution pH
In the adsorption process, the pH of dye solution is crucial as it may have effects onto the degree and surfacecharge of adsorbent [19]. Figure 2(b) represents the effect of solution pH (2.0-8.0) for each MO and RhB adsorbed onto CS-TiO₂ nanocomposite. The adsorption capacity (q) of CS-TiO₂ nanocomposite for RhB was found to be decreased as as pH of solution increases. This may be due to the fact that RhB exists as small cations at the pH below 4.0, while at a higher pH it exists as large zwitterions [19]. Therefore, adsorption capacity of CS-TiO₂ nanocomposites for RhB at pH higher than 4.0 decreased as the large zwitterionic RhB was unable to enter the pore of CS-TiO₂ nanocomposites. A similar trend was observed by Fang et al. [20] for the adsorption of RhB onto montmorillonite. On the other hand, the adsorption capacity of CS-TiO₂ nanocomposite for MO increased gradually as pH of the solution increased from 2.0 to 5.0. Meanwhile, as the pH increased from 6.0 to 8.0, the adsorption capacity was decreased. This scenario might be due to more H⁺ and H₂O₂ ions were available in system at the pH of 2.0 to 5.0, thus causing a protonation effect to CS-TiO₂ nanocomposite. Therefore, it increased electrostatic attraction between anionic dyes and the positive charge site on the surface of CS-TiO₂ nanocomposite. As the solution pH increased from 6.0 to 8.0, the adsorption system has more negative charged sites which led to electrostatic repulsion between negative site of the adsorbent and anionic MO. Gao et al. [21] have reported a similar observation for removal MO by NiFe-layered double hydroxides (LDHs). From figure 2(b), it was noted that the maximum adsorption capacity (q) of CS-TiO₂ nanocomposite for MO was 1.203 mg/g.

3.3. Effect of absorbent dosage
Figure 2(c) shows the effect dosages of absorbent on removal of MO and RhB in aqueous solution. For this study, the pH of MO and RhB solution was adjusted to the optimum pH. As displayed in Figure 2(c), a decline in adsorption capacity was observed for both MO and RhB as the mass of CS-TiO₂ nanocomposite was increased. The adsorption capacity for MO and RhB was decreased from 1.638 to 0.117 mg/g and 0.536 to 0.202 mg/g, respectively. This might be due to the increase in amount of CS-TiO₂ has caused the ratio of actives sites of CS-TiO₂ to MO and RhB molecules increased. Thus, low adsorption capacity onto nanocomposites. Ratanapan et al. [22] have studied MO removal by using activated carbon derived from coffee grounds and reported a similar trend of MO adsorption. In addition, Mukhtar et al. [23] have mentioned the same trend for the removal of RhB using vanadium pentoxide/titanium butyl oxide hybrid xerogels.
Figure 2. The effect of initial concentration (a), effect of solution pH (b) and effect of adsorbent dosage (c) on adsorption capacity if MO and RhB onto CS-TiO₂ nanocomposite.

3.4. Adsorption isotherms
In this study, the Langmuir and Freundlich isotherm models were used to fit the adsorption equilibrium data. This present work was performed under following conditions, namely the initial concentrations for each dyes range between 2.5 to 20 mg/L, the mass of the nanocomposites was 0.1 g and the solution pH was set at optimum pH (2.0 for RhB and 5.0 for MO). Table 1 displays the isotherm constant and correlation coefficient values determined from Freundlich and Langmuir isotherm models. From the table, the adsorption data for dyes correlated well with to the Freundlich isotherm model. Based on Freundlich isotherm model, the maximum adsorption capacity values determined as 1.608 and 7.646 mg/g for MO and RhB, respectively. The n value from Freundlich isotherm model indicate adsorption affinity of the system. For instance, $n > 1$ represents the favourable adsorption, whereas $n = 1$ is attributed to linear adsorption and $n < 1$ corresponds to the unfavorable adsorption [24]. Thus, MO adsorption is favourable and RhB is unfavourable for adsorption.

| Dyes        | Freundlich | Langmuir |
|-------------|------------|----------|
|             | $K_F$ (mg/g) | $n$ | $R^2$ | $Q$ (mg/g) | $b$ (L/mg) | $R^2$ |
| Methyl orange (MO) | 1.608 | 1.642 | 0.996 | 13.386 | 0.308 | 0.875 |
| Rhodamine B (RhB) | 7.646 | 0.481 | 0.978 | 0.410 | 0.067 | 0.886 |
The adsorption capacity ($q_{\text{max}}$) obtained from this study were compared with other adsorption studies using several adsorbents (table 2).

**Table 2.** Comparison of $q_{\text{max}}$ from other adsorption studies.

| Adsorbent                      | MO $K_f$ (mg/g) | MO $n$ | RhB $K_f$ (mg/g) | RhB $n$ | References |
|-------------------------------|-----------------|-------|------------------|--------|------------|
| Spent Tea Leaves              | 0.088           | 1.370 |                  |        | [25]       |
| Egussi peeling                | 3.979 x $10^{-2}$ | 0.955 |                  |        | [26]       |
| Carbon Nanospheres (CNSs)     |                 |       | 1.946            | 0.36   | [27]       |
| Water chestnut peel           |                 |       |                  | 0.4–1.7| [28]       |
| Razor Clam ($\textit{Ensis directus}$) | 0.010         | 0.660 |                  |        | [29]       |

3.5. **SEM analysis**

The surface morphology of CS-TiO$_2$ nanocomposites before and after interaction with MO and RhB dyes was observed using SEM analysis at 5.0 k magnification. Figure 3(a) displays SEM image of pure CS that have nonporous surface and smooth texture. Figure 3(b) exhibits CS-TiO$_2$ nanocomposite image, where rod- and needle-like aggregations were observed on the surface of TiO$_2$ nanocomposite. The deposits for MO and RhB can be observed on the outer layer of CS-TiO$_2$ nanocomposite, as shown in figure 3(c and d). As presented in figure 3(c), CS-TiO$_2$ showed the appearance of cubic-shape deposit after adsorption with MO. Meanwhile, a dense and uneven surface texture were observed on CS-TiO$_2$ following RhB adsorption. The changes in surface morphology of CS-TiO$_2$ nanocomposites after interaction with dyes might due to the reorganization of surface’s functional group that bind with dyes.

3.6. **TGA analysis**

The thermal stability and decomposition temperature of pure chitosan (CS) and CS-TiO$_2$ nanocomposite were assessed by TGA analysis. Figure 4 shows TGA thermograms of CS and CS-TiO$_2$ nanocomposite. Based on thermogravimetric curve, CS exhibited two decomposition steps, where the first step was observed at temperature of 30 to 152 °C. At this step, a weight loss around 9.67% was observed due to removal of moisture content in the nanocomposite [30]. Second decomposition step began at 190 to 330 °C with weight loss of 65.44% due to dehydration and decomposition of chitosan polymer [30]. Meanwhile, CS-TiO$_2$ nanocomposite exhibited three decomposition steps, which started with the first stage at 87 °C to 133 °C and weight loss of 11.74% was observed due to evaporation of water [31]. The second stage observed at 221 °C and went on to 288 °C with a weight loss of 30.20%, which attributed to thermal decomposition of CS main chain [31]. Third stage occurred at 630 °C till 993 °C with 28.70 % weight loss associated with further decomposition of polysaccharide ring and glycolsidic bonds [31].
3.7. XRD analysis

Figure 5 illustrates XRD diffractograms for CS, TiO$_2$ nanopowder, CS-TiO$_2$ nanocomposite and CS-
TiO$_2$ nanocomposites after adsorption with MO and RhB, respectively. XRD analysis confirmed that CS presented in amorphous state and there was no diffraction peaks appeared except the band that exhibited at $2\theta = 23.3^\circ$, as displayed in figure 5(a) [32]. TiO$_2$ nanopowder diffractogram in figure 5(b) exhibits a sharp diffraction peak, clearly observed at $2\theta = 25.37^\circ$ [33]. Meanwhile, figure 5(c) presents XRD diffractogram of CS-TiO$_2$ nanocomposite, where diffraction peaks that can attributed for each CS and TiO$_2$ was observed at $2\theta = 34.075^\circ$, 29.235$^\circ$, 25.47$^\circ$ and 20.26$^\circ$. It was noted that the intensity of diffraction peak of CS was decreased after composite with TiO$_2$ and the introduction of TiO$_2$ has improved the properties of chitosan. Following adsorption of MO and RhB, there was a marginal effect to crystallinity of TiO$_2$ nanocomposite. The intensity of diffraction peaks were slightly decreased after the interaction of nanocomposite with dye molecules (figure 5 (d and e). This suggests, the penetration of dye molecules into the internal structure of nanocomposite did not significantly change the crystallinity property of the nanocomposite.
4. Conclusion

The potential of CS-TiO$_2$ nanocomposite for adsorption of MO and RhB from aqueous solution has been investigated. The Freundlich isotherm was the best model to explain the adsorption equilibrium data. The adsorption capacity of the nanocomposites was greatly influenced by the initial concentration, solution pH and adsorbent dosage. The adsorption of MO and RhB onto CS-TiO$_2$ nanocomposite has caused a significant change in surface morphology of the nanocomposites. In conclusion, the CS-TiO$_2$ feasible to be used as adsorbent for water treatment.

5. References

[1] Anitha A, Kohilavani K and Murugalakshmi R 2018 Int. J. Appl. Eng. Res. 13 14669-14674
[2] Huang J H, Huang K L, Liu S Q, Wang A T and Yan C 2008 Colloids Surf. A Physicochem. Eng. Asp. 330 55-61
[3] Neethu N and Choudhury T 2018 Recent Pat. Nanotechnol. 12 200-207
[4] Razzaz A, Ghorban S, Hosayni L, Irani M and Aliabadi M 2016 J. Taiwan Inst. Chem. Eng. 58 333-343
[5] Krishnan S, Rawindran H, Sinnathambi C M and Lim J W 2017 IOP Conf. Ser. Mater. Sci. Eng. 206 012089
[6] Nicomel N, Leus K, Folens K, Van Der Voort P and Du Laing G 2016 Int. J. Environ. Res. Public Health 13 62
[7] Ong C B, Ng L Y and Mohammad A W 2018 Renew. Sustain. Energy Rev. 81 536-551
[8] Al-Taweel S S, Saud H R, Kadhum A A H and Takriff M S 2019 Results Phys. 13 102296
[9] Elieh-Ali-Komi D and Hamblin M R 2016 Int. J. Adv. Res. 4 411-427
[10] Sutirman Z A, Sanagi M M, Karim K J A, Naim A A and Ibrahim W A W 2018 Malays. J. Anal. Sci. 22 839-850
[11] Tchuifon D R, Anagho S G, Njanja E, Ghogomu J N, Ndifor-Angwafor N G and Kamgaing T 2014 Int. J. Chem. Sci. 12 741-761
[12] Kamari A 2011 Chitosan as Soil Amendment for the Remediation of Metal Contaminated Soil Doctoral Dissertation (Glasgow: University of Glasgow)
[13] Kusrini E, Wicaksono B, Yulizar Y, Prasetyanto E A and Gunawan C 2018 *IOP Conf. Ser. Mater. Sci. Eng.* **316** 012029
[14] Freundlich H M F 1906 *Z. Phys. Chem.* **57** 385-470
[15] Langmuir I 1918 *J. Am. Chem. Soc.* **40** 1361-1403
[16] Yagub M T, Sen T K, Afroze S and Ang H M 2014 *Adv. Colloid Interface Sci.* **209** 172-184
[17] Jethave G, Fegade U, Rathod R and Pawar J 2018 *J. Dispers. Sci. Technol.* **40** 563-573
[18] Oluwasogo Dada A, Inyinbor A A, Adekola F A, Odebunmi E O, Bello O S and Ayo-Akere S 2018 *Int. J. Civ. Eng. Technol.* **9** 1591–1605
[19] Banerjee S and Chattopadhyaya M C 2017 *Arab. J. Chem.* **10** S1629-S1638
[20] Fang Y, Zhou A, Yang W, Araya T, Huang Y, Zhao P, Wang J, Johnson D and Ren Z J 2018 *Sci. Rep.* **8** 229
[21] Gao J, Lu Y, Fang L, Wu F, Ling F, Guan T, Shi L, Hu B and Meng F 2018 *Environ. Eng. Sci.* **35** 373-381
[22] Rattanapan S, Srikrum J and Kongsune P 2017 *Energy Procedia* **138** 949-954
[23] Muktihar S, Liu M, Han J and Gao W 2017 *Chin. Phys. B* **26** 058202
[24] Deka J R, Lin Y H and Kao H M 2014 *RSC Adv.* **4** 49061-49069
[25] Pei L Y, Suhaidi A N, Zulkifli S M, Hassim S H, Kanakaraju D and Chin L Y 2017 *Pertanika J. Sci. Technol.* **25** 73-84
[26] Tchuifon D R, Anagho S G, Njanja E, Ghogomu J N, Ndifor-Angwafor N G and Kamgaing T 2014 *Int. J. Chem. Sci.* **12** 741-761
[27] Qu J, Zhang Q, Xia Y, Cong Q and Luo C 2015 *Environ. Sci. Pollut. Res.* **22** 1408-1419
[28] Khan T A, Nazir M and Khan E A 2013 *Toxicol. Environ. Chem.* **95** 919-931
[29] Areibat L E M and Kamari A 2017 *AIP Conf. Proc.* **1847** 040004
[30] Gedam A H and Dongre R S 2015 *RSC Adv.* **5** 54188-54201
[31] John S, Salam A, Baby A M and Joseph A 2019 *Prog. Org. Coat.* **129** 254-259
[32] Dongre R S 2016 *Bull. Mater. Sci.* **39** 865-874
[33] Jayakumar R, Ramachandran R, Divyarani V V, Chennazhi K P, Tamura H and Nair S V 2011 *Int. J. Biol. Macromol.* **48** 336-344

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