Adsorption of Methylene Blue onto Iron Oxide Magnetic Nanoparticles Coated with Sugarcane Bagasse

Siti Zuraida Razali¹, Mohd Yusmaidie Aziz²*, Hisham Atan Edinur³, Ahmad Razali Ishak¹
¹Center of Environmental Health & Safety, Faculty of Health Sciences, Universiti Teknologi MARA, Puncak Alam 42300, Selangor, Malaysia
²Integrative Medicine Cluster, Advanced Medical and Dental Institute, Universiti Sains Malaysia, 13200 Bertam, Kepala Batas, Penang, Malaysia
³School of Health Sciences, Universiti Sains Malaysia, Health Campus, 16150 Kubang Kerian, Kelantan, Malaysia

Email: mohd.yusmaidie@usm.my; ahmadr2772@uitm.edu.my

Abstract. The removal of dyes from coloured effluents, in particular from the textile industry, is currently one of the major environmental concerns. Current methods for removing dyes from wastewater are costly and cannot be used effectively to treat a wide range of such wastewaters. Thus, we investigated the removal of methylene blue dye from aqueous solution using iron oxide magnetic nanoparticles coated with sugarcane bagasse. This newly and low-cost adsorbent was analysed with Fourier Transform Infrared Spectrophotometer followed by optimisation of its physicochemical parameters such as contact time, initial dye concentration, adsorbent dosage, and pH of dye solution. The study showed that the adsorption of methylene blue was pH dependent and the highest removal (98%) was obtained at pH 7. The optimum conditions were also achieved by using 10 mg/L dye concentration, 0.6 gram dose of adsorbent and 60 minutes adsorption time. The results obtained followed the pseudo-second-order kinetics and the adsorption was fitted well to the Langmuir isotherm model where the maximum adsorption capacity (Qₘ) was 37.45 mg/g. It is suggested that iron oxide magnetic nanoparticles coated with sugarcane bagasse is a potential low-cost adsorbent for the dye removal from industrial wastewater.

1. Introduction

Water pollution has become critical environmental and economic problems worldwide due to industrialisation processes. One of the environmental pollutants that contributes to water pollution is synthetic dye. It is widely applied in textiles, leather, paper, fur, printed materials and cosmetics [1]. Synthetic dyes are relatively inexpensive and widely used in the textiles industry [2]. The presence of dye in water is a threat to both marine and human life. Dyes are essential recalcitrant that, when they stay in flowing water for a long time, they slow down photosynthetic process, inhibit the growth of
marine organisms by hindering sunlight and depletion of dissolved oxygen, and also reduce the recreation value of the stream [3].

It is very important to eliminate dye contaminants from wastewater effluents because even a little amount of dye in water is harmful and highly visible [4]. Various chemical processes to treat dyed wastewater can be applied such as ion exchange, membrane filtration, precipitation, flocculation, electro-kinetic coagulation, electro-flotation, electrochemical destruction, irradiation etc. However, these processes are not cost-effective, need to comply with a number of rules and are not available on the market for small wastewater treatment industries. Taking these factors into account, the adsorption process is more useful for wastewater treatment due to its lower cost, uncomplicated operation, less energy, no side effects of toxic substances and the absorption process is normally designed for coloured wastewater treatment [5].

Adsorption process is an effective method of removing dyes from the wastewater. Owing to its sludge free clean operation and full elimination of dyes from the diluted solution, the adsorption process has the advantage over the other processes. Thus, it is considered one of the best techniques for wastewater treatment. Activated carbon (powdered or granular) has been widely used as an adsorbent due to outstanding adsorption performance. Commercially available activated carbon is however very expensive and this has led to further studies of cheaper replacements [6]. One of the efforts is to produce green adsorbents using agro-industrial waste. An excellent green adsorbent is low cost and has acceptable adsorption properties and has the reuse opportunity. In the market nowadays, there are many low costs commercially available green adsorbents for removing dyes. However, with limited ability to remove pollutants and poor ability to separate, most of them are not fully effective [7]. On the other hand, the removal of pollutants by magnetic nanoparticles as adsorbents is an emerging field of water and wastewater treatment, particularly for the removal of magnetic contaminants [8]. Thus, in this study, we proposed iron oxide \((\text{Fe}_3\text{O}_4)\) magnetic nanoparticles coated with sugarcane bagasse as a potential low-cost adsorbent.

2. Materials and Methods

2.1. Sugarcane Bagasse and methylene blue standard

Sugarcane bagasse was collected from a local night market in Klang, Selangor. The sugarcane bagasse was dried under sunlight, followed by drying in an oven at 100°C for 24 hours. The dried sugarcane bagasse was then crushed mechanically to provide a smaller particle to increase the surface area of the size of the adsorbent and were sieved afterwards to obtain a particle size between 0.3-1.0mm. Methylene blue standard was purchased from Merck (Darmstadt, Germany).

2.2. Synthesis \(\text{Fe}_3\text{O}_4\) Magnetic Nanoparticles coated with Sugarcane Bagasse

Magnetic particles were synthesized by dissolving 4.58 g of \(\text{FeCl}_2\cdot4\text{H}_2\text{O}\) and 8.93 g of \(\text{FeCl}_3\cdot6\text{H}_2\text{O}\) in 80mL distilled water with intense stirring (1000 rpm). Approximately 10mL (25%) of ammonium hydroxide solution was applied to the solution as it was heated to 80°C. Then, 10g of sugarcane bagasse powder was added to the solution, and the reaction was allowed to carry out for 30 minutes at 80°C under constant stirring to ensure the maximum growth of nanoparticle crystals. The samples were cooled down to room temperature after 30 minutes, and washed regularly with distilled water to eliminate unreacted chemicals. The iron oxide nanoparticles coated with sugarcane bagasse (\(\text{Fe}_3\text{O}_4\) MNP-SCB) was then filtered and dried in an oven at 105°C before use.
2.3. Characterization of Fe$_3$O$_4$ Magnetic Nanoparticles Sugarcane Bagasse

Fe$_3$O$_4$ MNP-SCB was characterized using Fourier Transform Infrared Spectroscopy (FTIR). The spectra were recorded at ambient temperature using a KBr disc method on the Perkin Elmer spectrophotometer (RX-IFTIR, USA). The disk was prepared from 0.001 g of the sample finely ground with 0.3g of fine grade KBr and then scanned at the wavelength range of 400 - 4000 cm$^{-1}$.

2.4. Batch Absorption Study

The batch experiment was carried out to determine the optimum experimental conditions (pH, dosage, contact time and initial dye concentration) for removal of methylene blue. The known concentration of dye was prepared by adding ultra-pure water from a stock solution. The dye solution pH was then adjusted to the desired value for optimization. For a defined period the mixture has been stirred at 200rpm. The filtering method was applied after a certain amount of stirring to separate the solid from liquid. Calculation of the adsorption potential and adsorption performance as follows:

$$\text{Adsorption Efficiency (\%)} = \frac{C_0 - C_e}{C_0} \times 100$$  

(1)

Where Co and Ce are the initial and final concentration of methylene blue respectively (mg/L).

$$\text{Adsorption Capacity (mg/g), } q_e = \frac{C_0 - C_e}{W} \times V$$  

(2)

Where W is the weight of adsorbent (g), and V is the volume of the solution (L).

The results from the study were also used to determine the type of kinetics and isotherm models which fitted to the adsorption condition. Two type of kinetics models namely pseudo first-order and pseudo second-order were tested meanwhile for isotherms, Langmuir and Freundlich models were used.

3. Results and Discussion

3.1 Fourier Transform Infrared (FTIR) characterization

FTIR analysis was carried out to determine the functional group present in magnetic nanoparticles (MNP) and magnetic nanoparticles coated with sugarcane bagasse (MNP-SCB) and we can affirm the binding between the other groups (Figure 3.1). The appearance of bands between 3000 to 3500 cm$^{-1}$ and the band around 2800- 2900 cm$^{-1}$ for both compounds could be attributed to O-H group of cellulose and the CH$_2$ groups respectively. The band at 559 cm$^{-1}$ and 538 cm$^{-1}$ relate to Fe–O bond. The absorption band at 1605 cm$^{-1}$ contribute to the deformation vibration of O-H group. The presence of absorption band at 1025 cm$^{-1}$ for MNP-SCB is related to the C–OH stretching vibration. Results indicated that sugarcane bagasse was coated to the magnetic Fe$_3$O$_4$ nanoparticles successfully.
3.2 Batch Adsorption Study - Effect of pH, dosage, contact time and initial concentration on dye removal

The initial pH value of the solution has significant influence as the pH of the dye solution affects the properties of the adsorbent such as the dye chemistry, surface charge and its degree of ionization. It could be assumed that the electrostatic attraction, ionic properties and structure of adsorbent and dye molecules under different pH values play important role in removal efficiency [9]. pH region between 5 and 9 was chosen because most of practical applications are within this range. As shown in Figure 2a, the lowest percentage for dye concentration removal was 67% at pH 5.0 while highest percentage for dye concentration removal was 98% at pH 7.0 with 0.5882 value of adsorption capacity. Increasing of the solution pH increases the number of hydroxyl groups, thus increase the number of negative charges and enlarges the attraction between dye and the adsorbent surface. It was attributed that the presence of more negative charges adhering to positive charges of methylene blue which resulted to higher methylene blue adsorption process [10].

The result from figure 2b shows that the removal efficiency is ranged between 92-96% regardless the adsorbent dose. The adsorbent capacity was also in the range of 0.55-0.58 mg/g. The higher percentage of dye removal with the adsorbent dose studied can be attributed to the availability of more adsorption sites and the adsorbent surface area. The effect of contact time on the removal of dye concentrations increased with increased contact time as shown in Figure 2c. At 60 minutes, the equilibrium had reached where the methylene blue removal was the highest at 98.03%. Initially, the methylene blue molecules reach the boundary of the layer during the first phase before being diffused to the adsorbent surface. At the later stage, the molecules were diffused into the porous structure of the adsorbent. This phenomenon will therefore take a relatively longer time [11].

Adsorption studies of Fe₃O₄ magnetic nanoparticles of sugarcane bagasse show that the percentage of dye removal efficiency was higher at a higher concentration of methylene blue (Figure 2d). The maximum removal efficiency was at 94.40 % at 10 mg/L of methylene blue solution. This removal efficiency probably due to increased contact of adsorbate with available sites of adsorbent. This can be
due to the fact that the increase of the initial adsorbent concentration is a driving force to resolve the resistance of the dye to mass transfer between the aqueous and solid phases [12].

![Graphs](image)

**Figure 2.** Effect of a) pH, b) absorbent dosage, c) contact time and d) initial concentration on dye removal using Fe₃O₄ magnetic nanoparticles of sugarcane bagasse

3.3 Adsorption Kinetics and Isotherm

The adsorption kinetic models such as the pseudo-first-order and pseudo-second-order are useful for determining behaviour of adsorption process; physical or chemical. In this study, the kinetics of removal of methylene blue follows the pseudo-second order kinetics ($R^2 = 0.99$) which indicate the adsorption process was more inclined towards chemisorption (Figure 3a).
Figure 3. a) Pseudo second-order kinetic b) Langmuir sorption isotherm for removal of methylene blue using Fe$_3$O$_4$ magnetic nanoparticles of sugarcane bagasse.

The pseudo second-order model is explicitly explained in equation 3 and 4.

$$\frac{Dq_t}{dt} = K2(qe - qt)^2$$  \hspace{1cm} (3)

Where $K2$ (min$^{-1}$) is the rate constant of pseudo-second order adsorption, $q_e$ and $q_t$ denote the amount of methylene blue adsorption (mg/g) and the amount of methylene blue adsorption (mg/g) at equilibrium and at time (t) in minutes respectively. Integrating equation 3 and applying initial condition gives:

$$\frac{t}{q} = \frac{1}{K2qe^2} + \frac{t}{qe}$$  \hspace{1cm} (4)

The isotherm model was simulated to describe the mechanisms of interaction between the adsorbent and the adsorbate. Modelling of the equilibrium data is a very important way to predict the adsorption mechanisms of various adsorption systems. In this study, the adsorption isotherm of methylene blue was better fitted into Langmuir model as shown in Figure 3b ($R^2 = 0.99$). The Langmuir isotherm assumes monolayer adsorption to a surface containing a finite number of adsorption sites with no transmigration of adsorbent in the surface of the plane. If a site has been filled up, there can be no further sorption at that site. This means that the surface reaches a point of saturation at which the optimum surface adsorption is achieved [13]. The linear form of the Langmuir equation is expressed as follow:

$$\frac{Ce}{qe} = \frac{1}{bQm} + \frac{Ce}{Qm}$$  \hspace{1cm} (5)

Where $Q_m$ is the maximum adsorption capacity (maximum quantity of adsorbate required to form a single monolayer on unit mass of adsorbent), $b$ is adsorption equilibrium constant, $q_e$ is the amount adsorbed on unit mass of the adsorbent and $Ce$ is the concentration of adsorbate at equilibrium. In this study, the maximum adsorption capacity $Q_m$ for Fe$_3$O$_4$ magnetic nanoparticles material coated with sugarcane bagasse was 37.45 mg/g.
4 Conclusion

This study revealed that Fe$_3$O$_4$ magnetic nanoparticles material coated with sugarcane bagasse prepared through chemical co-precipitation method could be successfully employed as an alternative low-cost adsorbent for the removal of methylene blue dye. The effects of pH, initial concentration, contact time and dosage of magnetic field intensity on the methylene blue dye adsorption were optimised and confirmed by pseudo-second order adsorption kinetics and Langmuir adsorption isotherm models. To recommend, this newly Fe$_3$O$_4$ magnetic nanoparticles – sugarcane bagasse adsorbent shall be applied for dye removal in real wastewater samples. However, before testing in the real samples, we propose for further characterization study to confirm the nano-composite materials using Ultraviolet-visible spectroscopy (UV-VIS), X-ray fluorescence (XRF), X-ray diffraction (XRD), Scanning electron microscopy (SEM) and Thermo gravimetric analysis (TGA).

References

[1] El Harfi S and El Harfi A 2017 Classifications, properties and applications of textile dyes: A review Applied Journal of Environmental Engineering Science 3 00000-3 N° 3 (2017) 311-320
[2] Yaseen D and Scholz M 2019 Textile dye wastewater characteristics and constituents of synthetic effluents: a critical review International journal of environmental science and technology 16 1193-226
[3] Tkaczyk A, Mitrowska K and Posyniak A 2020 Synthetic organic dyes as contaminants of the aquatic environment and their implications for ecosystems: A review Science of The Total Environment 717 137222
[4] Ismail M, Akhtar K, Khan M, Kamal T, Khan M A, M Asiri A, Seo J and Khan S B 2019 Pollution, toxicity and carcinogenicity of organic dyes and their catalytic bio-remediation Current Pharmaceutical Design 25 3645-63
[5] Leal T W, Lourenço L A, Scheibe A S, de Souza S M G U and de Souza A A U 2018 Textile wastewater treatment using low-cost adsorbent aiming the water reuse in dyeing process Journal of Environmental Chemical Engineering 6 2705-12
[6] Razi M A M, Hishammudin M N A M and Hamdan R 2017 Factor affecting textile dye removal using adsorbent from activated carbon: A review. In: MATEC Web of Conferences: EDP Sciences) p 06015
[7] Rajabi A A, Yamini Y, Faraji M and Nourmohammadian F 2016 Modified magnetite nanoparticles with cetyltrimethylammonium bromide as superior adsorbent for rapid removal of the disperse dyes from wastewater of textile companies Nanochemistry Research 1 49-56
[8] Mahmoodi N M, Abdi J and Bastani D 2014 Direct dyes removal using modified magnetic ferrite nanoparticle Journal of Environmental Health Science and Engineering 12 96
[9] Rezaei H, Haghsenasfard M and Moheb A 2017 Optimization of dye adsorption using Fe3O4 nanoparticles encapsulated with alginate beads by Taguchi method Adsorption Science & Technology 35 55-71
[10] Albroomi H, Elsayed M, Baraka A and Abdelmaged M 2015 Factors affecting the removal of a basic and azo dye from artificial solutions by adsorption using activated carbon J. Turk. Chem. Soc 2 17-33
[11] Khodaie M, Ghasemi N, Moradi B and Rahimi M 2013 Removal of methylene blue from wastewater by adsorption onto ZnCl2 activated corn husk carbon equilibrium studies Journal of Chemistry 2013
[12] El-Wakil A, El-Maaty A W and Oudah A A A-R 2015 Methylene blue dye removal from aqueous solution using several solid stationary phases prepared from Papyrus plant Journal of Analytical & Bioanalytical Techniques 1
[13] Desta M B 2013 Batch sorption experiments: Langmuir and Freundlich isotherm studies for the adsorption of textile metal ions onto teff straw (Eragrostis tef) agricultural waste *Journal of thermodynamics* 2013