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RESEARCH PAPER

Synthesis and Characterization of Fe_3O_4- SiO_2 Nanoparticles as Adsorbent Material for Methyl Blue Dye Removal from Aqueous Solutions

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ABSTRACT
In this work, Fe_3O_4-SiO_2 nanoparticles were synthesized, characterized, and applied as adsorbent material to remove methyl blue stain from an aqueous solution. The prepared nanoparticles were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), and Brunauer–Emmett–Teller (BET) to determine the physical surface properties and correlate them to the adsorption efficiency. In addition, this study investigated the influence of several parameters on the removal percentage and adsorption capacity. Specifically, this study investigated the impact of changing the following parameters: pH (1 – 8), agitation speed (U_{speed}; 100 - 350 rpm), initial methyl blue (MB) concentration (1 - 100 mg/L), adsorbent dose (0.05 to 0.15 g), and contact time (10 - 100 min). The characterization study reveals that the prepared material has an excellent surface area (385 ± 5 m^2/g) and pore volume (0.31 cm^3/g) which enhances the adsorption capacity. In addition, the prepared material showed excellent efficiency where the removal percentage reached 99.0±1% at the optimal operating conditions and the maximum adsorption capacity was 40 mg/g. This study delivers a full elucidation of the adsorption of MB dye by Fe_3O_4-SiO_2 NPs which considers a promising inexpensive adsorbent. It also delivers important insight information about the adsorption process and the influence of each parameter, which fill the lack in this field.
Keywords: Adsorption; Stain; Nanomaterials; Magnetite; and Silica

INTRODUCTION

The pollution of water sources by organic and inorganic compounds has drawn high attention in the last decades because of the continuous increasing of the contamination level. There are different types of organic pollutants such as dyes and stains which are produced as wastes from various industries such as clothing industry (Kalash et al., 2020; Waisi et al., 2015). Diverse treatment methods have been investigated including membranes, ion exchange, extraction, and

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precipitation (Beauregard et al., 2020; Dixon et al., 2020; Kalash et al., 2019). However, adsorption is a very promising method due to its low cost, ease of operation, and high activity (Adda et al., 2020; Alalwan and Alminshid, 2020; Ungureanu et al., 2015). Researchers have suggested different adsorbent materials such as activated carbon (Chaudhary et al., 2021), agriculture waste (Alalwan et al., 2021b), and nanomaterials (Awad et al., 2020). Due to elevated price of preparing activated carbon and the low adsorption capacity of the agriculture waste, it is crucial to find inexpensive adsorbent with highly efficient.

Due to their attractive properties, nanomaterials have garnered increasing attention in different fields (Afluq et al., 2021; Alalwan et al., 2021a; Alminshid et al., 2021). Recently, nanomaterial adsorbents have attempted the researchers in water and wastewater treatment field due to their intense adsorption abilities for different pollutants such as organic and inorganic compounds. Several metal oxide adsorbents have been applied for wastewater treatment such as magnetite (Fe_3O_4), titanium dioxide (TiO_2), zinc oxide (ZnO), alumina oxide (Al_2O_3), magnesium oxide (MgO), and zirconium oxide (ZrO_2) (Fernández-Garcia and RODGRIGUEZ, 2007). Among them, magnetite nanoparticles (NPs) have attracted a lot of attention because of their valuable properties such as the magnetism property, high surface area, and intense adsorption bonding towards organic pollutants (Gutierrez et al., 2017). Magnetism property of magnetite expedites the removal and dispersion of the NPs in the aqueous solution when a source of an external magnetic field is applied. The few downsides of nanoparticles as adsorbent material are their running cost, garbage removal, and the low ability of their evacuation (Jasim and Walli, 2021). To overcome the losing of NP surface area due to the agglomeration problem which is the biggest issue that limits the practical use of metal oxide NP adsorbents for large scale applications, NPs can be uploaded to a larger mesoporous materials such as silicon dioxide (SiO_2), clay, zeolite, graphene, and polymers (Awad et al., 2020). SiO_2 has attracted a lot of attention in coating metal oxide NPs due to the high reactivity and thermal stability (Soares et al., 2016). It is worth to mention that Fe_3O_4-SiO_2 is well known for its high adsorption efficiency due to its law resistance to internal diffusion (Shariati-Rad et al., 2014).

Dyes and stains removal have been investigated in deep using different adsorbent materials such as activated carbon and agriculture wastes (Saleh et al., 2020; Yagub et al., 2014). However, there is still lack in investigating the use of supported metal oxide NPs as adsorbent for methyl blue (MB) stain from wastewater. MB is classified under dyes and used in medication as well. It is a cationic stain that is widely used in biological fields and can cause supravital or intravital impacts and damaging nerve fibers (Nizamuddin et al., 2019). Thus, adsorption of MB stain using magnetite NPs coated by SiO_2 was investigated as innovative adsorbent material in a batch adsorption system. The optimum operating parameters, in specific, solution pH, adsorption time, MB initial concentration, agitation speed, and adsorbent dose were studied. Characterization of adsorbent NPs was done using XRD, SEM, TEM, and BET to determine the physicochemical properties, which enable to better understand the prepared NP adsorption behavior. This investigation delivers a full explanation of the adsorption of MB dye by Fe_3O_4-SiO_2 NPs, which is efficient and inexpensive adsorbent. The aim of this work is to provide a cost-effective adsorbent material to remove MB with high efficiency as well as identifying the optimum operating conditions for the adsorption process.

MATERIALS AND METHODS

The Fe_3O_4 NPs were synthesized as described in literature (Zhao et al., 2014). In general, 5.4

g of sodium acetate (NaAc; (Alfa Aesar (>99%)), 1.0 g of polyethylene glycol (PEG, Alfa Aesar), and 0.72 g of trisodium citrate ($Na_3C_6H_5O_7$; Fisher Scientific) were mixed with a 0.9 g of Ferric chloride hexahydrate ($FeCl_3.6H_2O$; Sigma-Aldrich (>98%)) solution and dissolved in 60 mL of ethylene glycol (EG; $C_2H_6O_2$; Sigma-Aldrich; anhydrous, >99.8%). Then the mixture was stirred for 25 min, and the suspension was sealed in a Teflon-lined stainless-steel autoclave. The mixture was kept at 185 ^oC for nine hours, and then left overnight to cool down to room temperature. The last step was washing the black precipitates by distilled water and ethanol (Sigma-Aldrich; 99%) four times, and then dried it in vacuum at 65 ^oC for ten hours. Fe_3O_4/SiO_2 NPs were synthesized through a modified Stöber method (Stöber et al., 1968). 0.2 g of Fe_3O_4 NPs were dissolved into a 250 mL mixture of ethanol and distilled water (V/V = 4:1) and 3 mL of ammonia ($NH_3.H_2O$, anhydrous; >99.9%) under ultrasonication. Then 2 mL of tetraethyl orthosilicate (TEOS; Na_2SiO_3; Sigma-Aldrich) was added very slowly into the mixture with stirred. The stirred of the mixture was kept for five hours. Then the prepared adsorbent was achieved by centrifugation and washed with deionized H_2O and ethanol for five times and dried in vacuum at 70 ^oC for six hours.

The bulk of the prepared adsorbent NPs was scanned by XRD using a Bruker D8 DaVinci system diffractometer. The surface morphology and particle sizes of the prepared adsorbent were determined using SEM (Hitachi S-4800) and TEM (JEOL 1230). BET adsorption isotherm technique using a Quantachrome NOVA 4200e Analyzer with nitrogen gas as the adsorbate was applied to identify the NP adsorbent surface area and pore volume, where the solid adsorbent was degassed for three hours at 374K. Then, the seven-point BET isotherm method was applied to determine the surface area. More details about the instruments used in this work are available elsewhere (Alalwan et al., 2021a). Sodium hydroxide (NaOH; Alfa-Aesar) and HCl (Sigma-Aldrich) were used to control the pH value of the aqueous solution. Methylene blue was purchased from Merck company's agent.

MB adsorption process was performed in a batch system for different initial concentrations of MB solutions using the prepared NP powder in an orbital water bath shaker (JULABO) at different operating conditions. The procedure was started by supplying a specific Fe_3O_4-SiO_2 NP amount to 50 ml of the MB solution at the desired concentration in a 125 ml conical flask. The agitation speed was set at the required value and the aqueous mixture was agitated for the desired time. After the adsorption process was done, the adsorbent was separated using a magnet. The concentration of MB stain remained in the solution after the adsorption process was identified by UV-Spectrophotometer (double beam; V-TECH) where the calibration curve of MB stain using UV-Spectrophotometer is shown in Figure 1. The adsorption study investigated the impact of changing the following parameters: pH (1 – 8), agitation speed (U_{speed}; 100 - 350 rpm), initial MB concentration (1 - 100 mg/L), adsorbent dose (0.05 to 0.15 g), and contact time (10 - 100 min). All experiments were performed at room temperature. The ranges of operation's parameters were chosen based on other works reported in the literature (Tan et al., 2015; Yao et al., 2012; Yimin et al., 2018). 0.1 M of NaOH or HCl was applied to adjust the pH value of the mixture to the desired value. The procedure was duplicated for accuracy and good reproducibility was observed and the average values were considered. The adsorption efficiency (R%) was determined using equation (1).

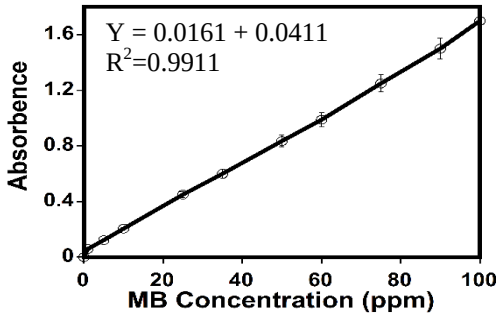

Fig 1. Calibration curve of MB stain using UV-Spectrophotometer

$$R\% = \left(1 - \frac{C_o}{C_i}\right) \times 100 \quad \ldots (1)$$

Where: R is adsorption efficiency, C_i MB initial concentration, and C_o MB remaining concentration.

RESULTS AND DISCUSSION

Figure 2 shows the characterization of the prepared NPs. Specifically, Figure 2-a shows the XRD analysis of the prepared adsorbent, and it confirms the existence of amorphous phase of SiO_2 which identified by the wide peak at 2Θ equals to 22°, while the other peaks were assigned to Fe_3O_4 (Alalwan et al., 2018). Figure 2-b shows the SEM image of the prepared adsorbent, and it shows tiny SiO_2 NPs cover the Fe_3O_4 NPs. TEM images (Figure 2-c as an example) of the prepared adsorbent were used to calculate the average particle diameter and it was found to be 25 ± 5 nm. The BET surface area and pore volume size were found to be 385 ± 5 m^2/g and 0.30 cm^3/g, respectively. The high surface area is very appreciable criteria in the adsorption process, while the measured pore volume indicates that the prepared material has small diffusion resistance which will increase its removal efficiency.

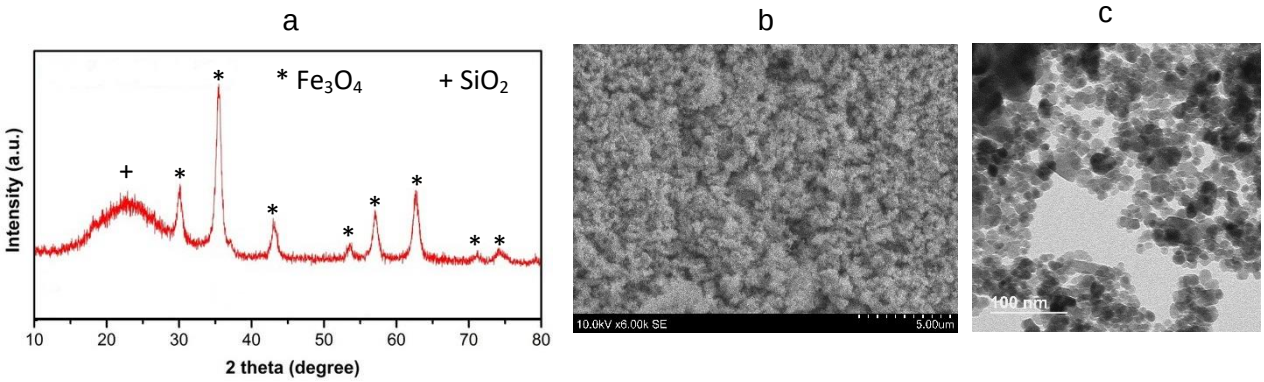

Fig 2. Characterization of synthesized Fe_3O_4-SiO_2. a) XRD, b) SEM, and c) TEM

The first experiment set was used to identify the optimum pH by varying the pH value between one to eight with keeping the values of the other parameters constant at a speed, MB concentration, NP amount, and adsorbing time of 350 rpm, 100 mg/L, 0.05 g, and 100 min, respectively. The influence of changing the pH on the adsorption efficiency of NP is shown in Figure 3-a. Rising the pH value from one to three slowly enhances the uptake percentage from 4.0 % to 15.25%, but the further increasing to the value of six rapidly increases the removal

efficiency to reach 40% which is the maximum value observed under these conditions. The adsorption capacity under these conditions was found to be 40.0 mg/g which is higher than some other adsorption materials reported in the literature (Awad et al., 2020). Then, any further increasing of pH value decreases the removal efficiency. The point of zero charge (pHpzc) for Fe_3O_4/SiO_2 is 3.8 (Wang et al., 2016) which means that the surface charge of NPs is negative at pH bigger than 3.8 and positive at pH lower than that. Thus, rising the pH value enhances the hydroxyl ion concentration, which in turn enhances the negative surface adsorption sites and promotes adsorption of the MB positive charged molecules (Bahgat et al., 2013). The decreasing of removal efficiency above pH value of six suggests increasing in the repulsive forces between the MB molecules and the NP surface probably due to the deprotonation of surface hydroxyl (Wang et al., 2016). Thus, the optimum pH value of six was used in the subsequent experiments.

The second experiment set was used to determine the preferred agitation speed (U_{speed}), where the same former conditions were considered but at the pH value of six. The impact of changing the U_{speed} from 100 to 350 rpm is shown in Figure 3-b. Increasing the U_{speed} up to 250 rpm resulted in enhancing the removal efficiency from 25% to 40%. This behavior is probably due to increase the turbulent flow which resulted in better contacting between MB molecules and the NPs which raise the removal rate. Further raising of the U_{speed} did not show any obvious change which indicates that the U_{speed} reached its steady state.

Next, the influence of the MB initial concentration from 1 to 100 mg/L on the uptake efficiency was examined with considering the previous determined optimum values for a period of 90 minutes as shown in Figure 3-c. Generally, and as expected, low initial MB concentrations show better uptake efficiency due to the availability of plenty adsorbing sites and few MB molecules. However, this case is accompanied by low adsorption capacity, while increasing the initial MB concentration or minimizing the NP dose resulted in a higher adsorption capacity due to minimizing the adsorption sites with increasing the MB molecules. Increase the MB molecules comparing to the available adsorption sites resulted in increasing the driving force for moving the molecules from the liquid solution to the solid surface. High adsorption capacity is preferable in industrial applications because of economic reasons. Therefore, an initial concentration of 100 mg/L was considered in the subsequent experiments due to the highest adsorption capacity achieved at this concentration.

Figure 3-d shows the influence of rising the adsorbent amount from 0.05 to 0.15 g. As explained previously, rising the NP amount enhances the removal percentage because of increasing of available sorption sites. On the other hand, increasing the NP dose causes a decreasing in the sorption capacity which is a crucial parameter for a practical industrial application. At the lowest adsorbent dose, the highest sorption capacity with a value of 40 mg/g was recorded. On the other hand, at the highest adsorbent dose, the removal efficiency reached its maximum value which was 99.0±1%. Therefore, 0.15 g of NP adsorbent was considered in the rest of the experiments.

As shown in Figure 3-e**,** the influence of contact time was studied at the optimum values and at room temperature by raising the adsorption time from 10 to 100 minutes. Increasing the adsorption time between the NPs and MB solution enhances the removal efficiency in general. Specifically, increasing the period from 10 to 80 min enhanced the adsorption efficiency from 60.0±4% to 99.0±1% because of supplying sufficient time for the MB molecules to transfer from the solution to the empty sorption sites on NPs surface. Increase the adsorption time to 100 minutes did not result in any obvious change in the removal efficiency which indicates that 80 minutes is the optimal value, and it was considered in the rest of the experiments.

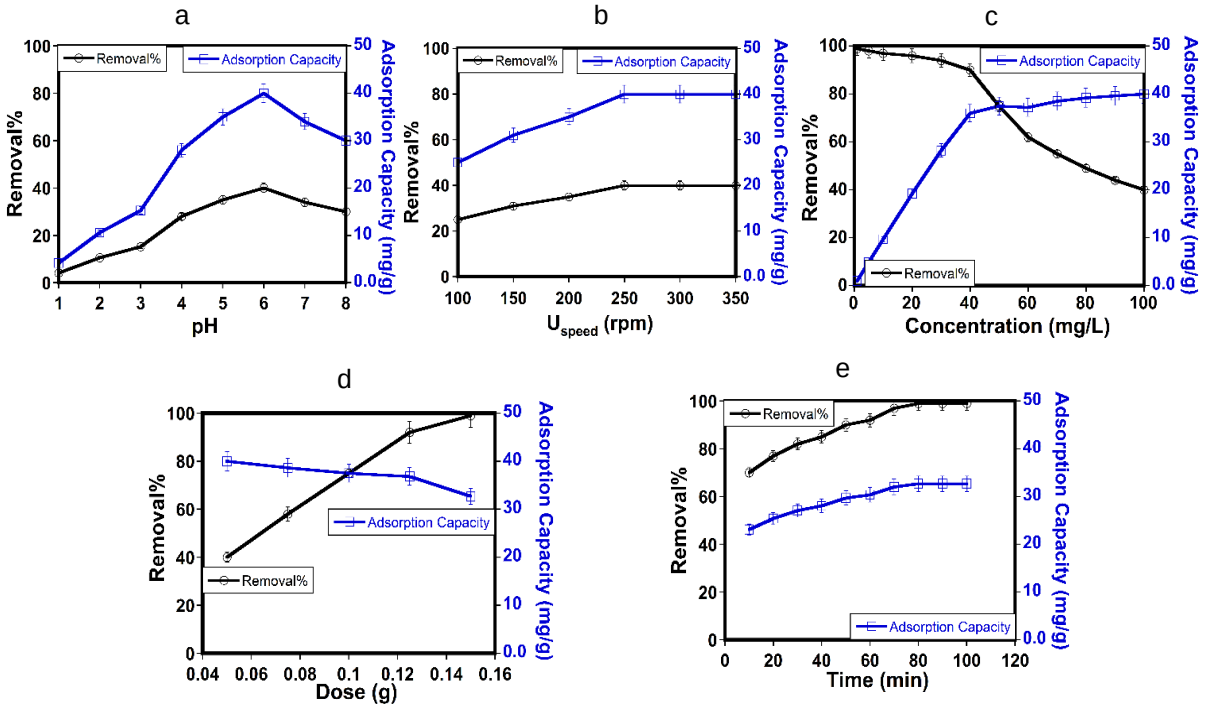

Fig 3. The impact of sorption conditions on the uptake percentage of MB dye from aqueous solution using Fe_3O_4/SiO_2 NPs as adsorbent and the the adsorption maximum capacity of the adsorbent, a) pH value, b) agitation speed, c) initial MB concentration, d) NP amount, and e) adsorption time.

CONCLUSIONS

The results of this study correlate the physical surface properties of the prepared NP adsorbent to the removal efficiency. The excellent removal efficiency observed in this investigation is assigned to the high surface area of the adsorbent NPs. In addition, the pore volume of the prepared NPs minimizes the diffusion resistance which in turn enhances the adsorption efficiency. Furthermore, this study provides insight information about the influence of some parameters on the adsorption efficiency. Specifically, it was found that increasing the pH value up to the pHpzc of Fe_3O_4/SiO_2 resulted in slow improvement in the removal efficiency, while the further rising of the pH to the value of six rapidly enhances the removal efficiency. Increasing the removal percentage with speeding the agitation indicates the need of good interaction between the adsorbent and adsorbate materials.

Using low initial concentration of MB or high dose of Fe_3O_4/SiO_2 resulted in excellent removal of MB from the solution. This superior efficiency is attributed to the availability of plenty sorption sites in compared to the initial MB molecules in both cases. However, the opposite situation resulted in lower removal efficiency, but with higher adsorption capacity. Increasing the contact time increases the removal efficiency which indicates the need to provide sufficient time for the MB molecules to reach the sorption sites.

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The present research did not receive any financial support.

CONFLICT OF INTEREST

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent,

misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

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