PH-DEPENDENT ADSORPTION/DESORPTION OF DYE MOLECULES USING MAGNETICALLY SEPARABLE QUARTZ SAND

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Abstract

Adsorption has been a feasible process to remove dye molecules from water resources. However, some of the proposed adsorbents required high temperature to be synthesized or hard to be separated towards the end of their applications. Realizing this, this study aims to fabricate Fe₃O₄-decorated sand that does not require high temperature in production. More importantly, the attached Fe₃O₄ nanoparticles provide intrinsic magnetic properties to ease the subsequent separation. The ability of this adsorbent to remove methylene blue (cationic dye), tartrazine (anionic dye), and disperse yellow 3 (non-ionic dye) at different medium pHs were investigated. Results showed that the Fe₃O₄-decorated sand performed better in dye removal as compared to the pure sand counterpart. In specific, sand doped with 5000 mg/L of Fe₃O₄ successfully removed 75.01 % of methylene blue, as compared to the 68.01 % achieved by using pure sand alone. It was also found that the effectiveness of dye adsorption and desorption strongly depends on the medium pH mostly due to the amphoteric nature of the Fe₃O₄ nanoparticles. The desorption of methylene blue, tartrazine, and disperse yellow 3 from the adsorbent best to be done using 30 % v/v acetone, 0.1 M NaOH, and 30 % v/v ethanol, respectively. Additionally, it was found that this adsorbent can be effectively separated using either high or low gradient magnetic fields.

Keywords: Adsorption, Magnetic Iron Oxide, Nanoparticles, Quartz Sand, Separation

Abstrak

Penjerapan merupakan proses yang sesuai digunakan untuk penyingkiran pewarna daripada sumber air. Namun begitu, bahan-bahan penjerap yang selalu dicadangkan memerlukan suhu sintesis yang tinggi atau sukar dipisahkan selepas aplikasinya. Selanjutnya, kajian yang dipaparkan ini bertujuan untuk menghasilkan pasir berhias nanopartikel Fe₃O₄ sebagai penjerap yang tidak memerlukan suhu sintesis yang tinggi dan mempunyai sifat magnetik untuk memudahkan proses pemisahan selepas aplikasinya. Keupayaan penjerap ini untuk menyingkiran metilena biru (pewarna kationik), tartrazin (pewarna anionik), dan bersurai kuning 3 (pewarna bukan ionik) daripada larutan dengan nilai pH yang berbeza telah dikaji. Hasil kajian menunjukkan bahawa pasir berhias Fe₃O₄ adalah lebih baik dalam penyingkiran pewarna apabila dibandingkan dengan pasir yang tidak berhias. Secara khususnya, pasir yang berhias dengan Fe₃O₄ berkepekatan 5000 mg/L dapat menyerap 75.01% metilena biru, dibandingkan dengan 68.01% yang dicapai apabila pasir yang tidak berhias digunakan. Turut dikesan, keberkesanan penjerap dan penyahjerapan dalam penyingkiran pewarna sangat bergantung pada nilai pH larutan yang digunakan akibat...
1.0 INTRODUCTION

Water contamination due to unintentional or intentional released of dyes has been one of the global concerns [1, 2]. Dye is mainly used in textile, paper, printing, pharmaceutical, and food industries. The presence of dye molecules in water resources is undesirable as some of the synthetic dyes are toxic and/or are difficult to be biodegraded [3-5]. Moreover, the coverage of dye molecules in the water medium may reduce light penetration; subsequently, the photosynthesis process of the aquatic plants will be retarded [3, 6]. In the effort to combat the dye pollution issue, several strategies have been developed which include ozonation, photo-catalytic degradation, coagulation/flocculation, membrane filtration, adsorption, and etc. Among all the proposed strategies, adsorption is recognized as an economic and effective method [7].

Synthetic adsorbents and activated carbon are the commonly used materials for dye adsorption [8-12]. In particular, activated carbon converted from biomass is a favored adsorbent as it has a highly porous structure and large internal surface area as adsorption sites [13]. However, the preparation of activated carbon involves high-temperature carbonization (300–900°C) [9, 12, 14] and activation steps. Such processes consume large amount of energy and are expected to release CO2 into the environment, subsequently, create additional challenges to the low carbon economy roadmap. Hence, there is a clear need to search for adsorbents that consumes lesser energy in production. Sand, an abundantly available matter, is a potential adsorbent.

The major constituent of the sand is mineral quartz composed of silica (SiO2), while the minor constituents are aluminium, iron bearing, and feldspar minerals [15]. The macro-porous and mesoporous structure of the sand making it to have a large surface area; coincidentally, pores lead to high selectivity on reaction and adsorption interactions [16-18]. Hence, sand is a suitable natural sorbent for the removal of heavy metals [19] and dyes [5, 20].

While it composes mainly of SiO2, there are many negative surface sites on the sand. This makes it feasible to adsorb positively-charged dye (via electrostatic attraction) [21]. The present work aims to further modify the sand surface with magnetite nanoparticles (Fe3O4) to make it magnetically responsive. This is to ease the subsequent step whereby the spent adsorbents are to be isolated from the treated water using magnetic field [22, 23]. Also, the attached Fe3O4 may add value by imposing amphoteric property on the adsorbent. To prove this, pH-dependent absorbability/desorbability of this magnetically separable sand was tested on cationic, anionic, and non-ionic dye molecules.

2.0 METHODOLOGY

2.1 Preparation of Sand

The quartz sand (supplied by Sigma-Aldrich) was subjected to a few times of washing using distilled water before drying up for subsequent usage. This washing step was done to clean the sand surface.

2.2 Preparation of Fe3O4-Decorated Sand

A stock solution of 1000 mg/L Fe3O4 suspension was prepared by dispersing 0.5 g of Fe3O4 nanoparticles (Nanostructured & Amorphous Materials, Inc, USA) in 500 ml of distilled water, followed by an hour of sonication in a bath sonicator. Later on, 10 g of sand was added in 20 ml of the Fe3O4 suspension and stirred for 2 hours at 300 rpm to promote mixing of the Fe3O4 nanoparticles and the sand. The Fe3O4-decorated sand was then separated from the excess Fe3O4 suspension and thoroughly washed with distilled water to remove any un-adsorbed Fe3O4. The Fe3O4-decorated sand was oven dried for 1 day before used for dye adsorption study. Note that the amount of Fe3O4 loaded onto the sand was varied from 1000 mg/L to 5000 mg/L to investigate the effect of Fe3O4 loading amount on dye adsorption efficiency. Figure 1 shows the look of the pure sand and the Fe3O4-decorated sand.
2.3 Dye Adsorption Study

The adsorption study was conducted in batch mode. Briefly, 50 mg/L of different dye solutions were prepared by dissolving a known amount of dye powder in distilled water. For every set of experiments, a total of 50 ml dye solution was used as the study volume. Three different types of dye solutions were investigated here, namely methylene blue (a cationic dye), tartrazine (an anionic dye), and disperse yellow 3 (a non-ionic dye). The chemical structures of these dyes are shown in Figure S1.

To study the effect of sand quantity on dye removal, methylene blue solution at pH 6 was added with different amounts of pure sand (ranging from 1 g to 20 g). The mixture was stirred at 300 rpm for 1 hour. After 1 hour, the sand was separated and the supernatant (un-adsorbed methylene blue) was analyzed by UV-Vis spectrometry at the wavelength of 668 nm [24]. The absorbance obtained from the spectrometry measurement was converted to concentration (mg/L) using a calibration curve. Later on, the corresponding adsorption efficiency (%) was calculated using Equation 1:

\[ \epsilon_{\text{ADS}} (\%) = \frac{C_0 - C}{C_0} \times 100 \% \quad \text{(Equation 1)} \]

The second stage of the study aims to investigate the effect of Fe\textsubscript{3}O\textsubscript{4} loading on dye adsorption efficiency. The same experimental procedure was used here, but with the sands decorated with different amounts of Fe\textsubscript{3}O\textsubscript{4} nanoparticles.

To reveal the pH-dependent absorbability of the Fe\textsubscript{3}O\textsubscript{4}-decorated sand, the next experiment was conducted using all three types of dyes. The dye solution was adjusted from pH 2 to pH 10 (using 0.1 M HCl or NaOH) as solution pH will affect the surface charge of dye molecules, sand, and Fe\textsubscript{3}O\textsubscript{4}. Note that the spectrometry wavelength used to analyze tartrazine and disperse yellow was 426 nm [25] and 402 nm [26], respectively.

2.4 Dye Desorption Study

The dye-adsorbed adsorbents were rinsed with a minimum amount of distilled water (to remove any weakly-attached dye molecule), dried for 1 hour before proceeded to desorption study. 0.6 g of the dye-adsorbed adsorbents was put in contact with 20 ml of desorbing agent for 4 hours [27]. Four types of desorbing agents were employed here, namely 0.1 M HCl, 0.1 M NaOH, 30 % v/v ethanol, and 30 % v/v acetone. The desorbing agents were selected in the way that the acid and base tested the effect of pH on desorption; while acetone and ethanol explored the effect of hydrophobicity on desorption. The desorbed dye was analyzed by UV-Vis spectrometer for its' absorbance value.

3.0 RESULTS AND DISCUSSION

3.1 Characterization of Fe\textsubscript{3}O\textsubscript{4}-Decorated Sand

Figure 2 shows that the surface of the quartz sand was successfully covered by Fe\textsubscript{3}O\textsubscript{4} nanoparticles. It is anticipated that such success of decoration was driven by the electrostatic attraction between the negatively charged sand surface and the positively charged Fe\textsubscript{3}O\textsubscript{4} (isoelectric point ~ pH 6.3 [28]). Note that the Fe\textsubscript{3}O\textsubscript{4} nanoparticles appear in agglomeration form probably due to the high agglomeration tendency of bare Fe\textsubscript{3}O\textsubscript{4} [29] and occurrence of multi-layer attachment. Despite that, the Fe\textsubscript{3}O\textsubscript{4}-decorated sand has an irregular structure which provides a large surface area for adsorption.

3.2 Role of Pure Sand Amount on Dye Removal Efficiency

In the first stage of this study, the effectiveness of using pure sand for dye removal was evaluated. Here, the amount of pure sand used as adsorbent was varied from 1 g to 20 g. Result depicted that the pure sand is a good adsorbent for methylene blue in which the removal efficiency was successfully improved by increasing the amount of pure sand (see Figure 3a). The removal efficiency was rather low (25.73 %) when only 1 g of pure sand was used,
and it improved remarkably to 68.01 % when the pure sand amount was increased by ten times. The adsorption of methylene blue onto the pure sand was expected to be triggered by electrostatic attraction between the positively charged methylene blue and the negatively charged sand surface [21]. Thus, the more sand added, the more negative sites available to adsorb the methylene blue. This hypothesis was further proven as the removal efficiency continuously enhanced with the addition of pure sand amount up to 15 g. At 15 g, about 95.28 % of methylene blue removal efficiency was achieved.

Nevertheless, pure sand has no magnetic properties; hence, in the next stage, the sand was surface decorated with Fe$_3$O$_4$ nanoparticles. To ensure the effects of adding Fe$_3$O$_4$ nanoparticles on dye removal can be clearly seen, 10 g of pure sand (which induced 68.01 % removal) was employed as the control sample.

### 3.3 Role of Fe$_3$O$_4$ Concentration on Dye Removal Efficiency

Various concentrations of Fe$_3$O$_4$ nanoparticles (i.e. 1000 mg/L, 2000 mg/L, 3000 mg/L, 4000 mg/L, and 5000 mg/L) were decorated onto 10 g of pure sand to produce Fe$_3$O$_4$-decorated sand. The formed adsorbent was used for methylene blue removal. As shown in Figure 3b, the dye removal efficiencies attained by 1000 and 2000 mg/L Fe$_3$O$_4$-decorated sand were 53.48 % and 53.62 % respectively; these values are lower than the removal efficiency of the pure sand (without surface decoration). This might be a consequence of blockage of the substrate’s pore by the nanoparticles [30-33]. However, the dye removal efficiency was found to increase back to 60.36 %, 74.10 %, and 75.01 % when 3000, 4000, and 5000 mg/L of Fe$_3$O$_4$ nanoparticles were used for the decoration, respectively. Such observation implies creation of new adsorption sites by the extra-loaded Fe$_3$O$_4$ nanoparticles. Considering the dye removal efficiency was merely improved by ~ 1 % despite the concentration of Fe$_3$O$_4$ nanoparticles has been largely increased from 4000 mg/L to 5000 mg/L, there was no further increment of Fe$_3$O$_4$ nanoparticles (i.e. to a concentration above 5000 mg/L) performed in this study. The 5000 mg/L Fe$_3$O$_4$-decorated sand was chosen to be further synthesized and used as the adsorbent for the rest of the study.

### 3.4 Effect of pH on Cationic, Anionic and Non-Ionic Dyes Removal

Medium pH has a direct effect on dye adsorption as it will alter the surface charge of an adsorbent. While the outermost layer of this adsorbent is Fe$_3$O$_4$ nanoparticles, it is proposed that the surface charge of Fe$_3$O$_4$ nanoparticles plays the dominant role in dye adsorption. In the following study, the dye removal efficiency was conducted at different medium pH (i.e. pH 2, 4, 6, 8, and 10) for three different types of dyes. The experimental results are depicted in Figure 4.

![Figure 3](image1.png)  (a) Methylene blue removal efficiency (%) with respect to the amount of pure sand used  (b) Methylene blue removal efficiency (%) with respect to the concentration of Fe$_3$O$_4$ being decorated onto the sand [Condition: Sand amount = 10 g, medium pH = pH 6].

![Figure 4](image2.png) Methylene blue, tartrazine and disperse yellow 3 removal efficiency (%) at different medium pHs

As shown in Figure 4, the Fe$_3$O$_4$-decorated sand best to remove methylene blue at alkaline pH. In particular, the removal efficiency increased to 84.62 % at pH 10. Under the alkaline condition, both the quartz sand (isoelectric point ~ pH 2.44 [21, 34]) and Fe$_3$O$_4$ nanoparticles were in negative charge (isoelectric point ~ pH 6.30). Thus, it favors to the attraction of cationic dye electrostatically. This answered the observed trend whereby the higher
the medium pH, the higher the methylene blue removal efficiency. A similar outcome has been observed for methylene blue removal using bare Fe₃O₄ alone [35] or other types of bare Fe₃O₄-decorated adsorbents [6, 36-38]. Hence, it is proposed that the adsorption of dye molecules onto Fe₃O₄-decorated sand was mainly controlled by the Fe₃O₄ nanoparticles which stay at the outermost layer.

Nevertheless, a reverse trend was seen for tartrazine dye. Here, the removal efficiency was found to decrease from 31.69 % to 15.50 % when the medium pH shifted from acidic (pH 2.5) to alkaline (pH 10). The higher adsorption achieved in the acidic medium can be ascribed to protonation of the Fe₃O₄ nanoparticles to positive charge (–OH₂⁺) [39, 40]; thus, promoted electrostatic attraction towards the anionic groups of tartrazine (R-SO₃⁻ and R-COO⁻). Similarly, Zandipak and Sobhanardakani [41] reported that better removal of anionic dyes (e.g. tartrazine, sunset yellow, and Eriochrome Blank T) by NiFe₂O₄ nanoparticles was observed in an acidic medium.

For disperse yellow 3, it was recorded that the highest removal efficiency (90.05 %) was obtained at pH 2.5. However, the removal efficiency reduced along with the increase in medium pH. At pH 10, only 15.60 % of dye removal was achieved. Since disperse yellow 3 contains secondary amide group (–C(=O)N–J in the structure and exists mainly in neutral form due to its charge properties, electrostatic interaction might not be the main contributor to its’ adsorption onto the adsorbent; instead, hydrogen bonding would have occurred between the hydroxyl surface groups of the adsorbent and the N atom or aromatic ring of the dye [42, 43]. Moreover, the protonation of Fe₃O₄-decorated sand provides more H-atom for hydrogen bonding formation [42]. This may serve as one of the reasons for the removal efficiency of disperse yellow 3 to be higher in acidic medium.

3.5 Desorption Studies

In the subsequent study, desorption was conducted using four types of desorbing agents, namely 0.1 M HCl, 0.1 M NaOH, 30 % v/v ethanol, and 30 % v/v acetone. The experiment results are presented quantitatively (Figure 5) and qualitatively (Figure S2). As shown in Figure 5, methylene blue best desorbed in acetone with the desorbed solution having an absorbance value 0.252. Similarly, ethanol (an amphiphatic solvent) is effective in desorbing methylene blue. In fact, the ability of ethanol or acetone to desorb methylene blue has been reported elsewhere [44-46]. Other than that, 0.1 M HCl was also effective in desorbing methylene blue; here, the lowering of medium pH by HCl will protonate the Fe₃O₄-decorated sand. Once the Fe₃O₄-decorated sand was protonated, an electrostatic repulsion force will be created between the adsorbent and the cationic adsorbate which lead to desorption. This also explained the observation where methylene blue was less effectively desorbed in 0.1 M NaOH (absorbance of the desorbed solution = 0.016). The very mild desorption of methylene blue in 0.1 M NaOH might be ascribed to the competition of sodium ion (Na⁺) with cationic dyes onto the negatively charged Fe₃O₄-decorated sand [27].

The pH-dependent desorption of dye molecules from the Fe₃O₄-decorated sand was affirmed when better desorption of tartrazine was achieved using NaOH than HCl. The addition of NaOH turns the Fe₃O₄-decorated sand negative. Once the Fe₃O₄-decorated sand lost its’ positivity, the affinity towards the tartrazine dye is expected to decrease dramatically. Hence, NaOH favored to desorption of anionic dye but unfavored to desorption of cationic dye.

Besides NaOH and HCl, both acetone and ethanol were found to provide a considerable desorption capability. For instance, desorption of disperse yellow 3 was found to be the most effective by using ethanol (absorbance of the desorbed solution = 0.215). This was followed by acetone, NaOH, and lastly, HCl. The good dye desorbability shown by ethanol and acetone can be ascribed to their amphiphatic nature, whereby they contain hydrophilic (–OH, C=O) and hydrophobic group (CH₃CH₂-, -CH₃). Xing et al. [47] reported that the hydrophobic/hydrophilic group of a desorbing agent plays an influencing role in dye desorption. It was proposed that the hydrophobic part of the desorbing agent will adsorb onto the hydrophobic part of the adsorbent; while its’ hydrophilic part will interact with the hydrophilic part of the adsorbent, leading to dye desorption.

3.6 Demonstrating Magnetic Separability of the Spent Adsorbent

This section aims to demonstrate the separability of the spent adsorbents by using a permanent magnet.
As shown in Figure 6a&b, a portion of the Fe₃O₄-decorated sand had settled down upon the cease of stirring. Nevertheless, the solution remains cloudy as there was no permanent magnet to further separate the unsettled adsorbents. Upon exposure to a permanent magnet, the unsettled adsorbent immediately moved to the bottom and accumulated at the location where the permanent magnet was positioned (see Figure 6c&d). This result indicated that the separation of this adsorbent has been effective even by just using a low gradient magnetic field (LGMF).

4.0 CONCLUSION

This study is part of the effort to address sustainable development goals 6 (Clean Water) by reducing water pollution imposed by dye released from the textile industry. Fe₃O₄-decorated sand with amphoteric and magnetic bi-functionalities was successfully produced for methylene blue (cationic dye), tartrazine (anionic dye) and disperse yellow 3 (non-ionic dye) removal. The surface morphology study showed that the Fe₃O₄ nanoparticles appeared in an agglomeration form and turned the quartz sand’s surface rougher. The Fe₃O₄-decorated sand performed better than the pure sand when the concentration of Fe₃O₄ nanoparticles was above 4000 mg/L. Further investigation showed that medium pH had a stronger effect on dye removal efficiency. In particular, the optimum pH for removal of methylene blue, tartrazine, and disperse yellow 3 were pH 10, pH 2.5, and pH 2.5, respectively. The pH-dependent desorption of dye molecules was observed for methylene blue and tartrazine. Other than that, amphipathic solvents are effective for desorption too; the desorption of methylene blue, tartrazine, and disperse yellow 3 from the Fe₃O₄-decorated sand best to be done using 30% v/v acetone, 0.1 M NaOH, and 30% v/v ethanol, respectively. The spent adsorbents were separable by either low or high gradient magnetic field; such characteristic eases the subsequent recycling of adsorbent.

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SUPPLEMENTARY INFORMATION

Figure S1 Chemical structures of (a) methylene blue, (b) tartrazine, and (c) disperse yellow 3.
Figure S2 Photo showing the desorbed (a) methylene blue, (b) tartrazine, and (c) disperse yellow 3 after subjected to 4 hours of immersion in various desorbing agents

References


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