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

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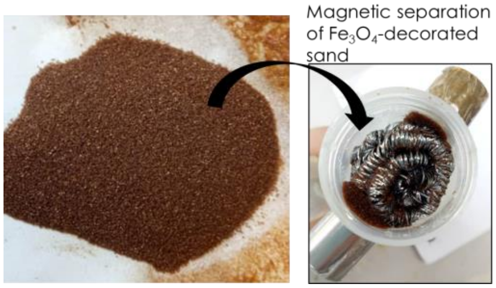
Graphical abstract



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 Fe_3O_4-decorated sand that does not require high temperature in production. More importantly, the attached Fe_3O_4 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 Fe_3O_4-decorated sand performed better in dye removal as compared to the pure sand counterpart. In specific, sand doped with 5000 mg/L of Fe_3O_4 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 Fe_3O_4 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 Fe_3O_4 sebagai penjerap yang tidak memerlukan suhu sintesis yang tinggi dan mempunyai sifat magnetik untuk memudahkan proses pemisahan selepas aplikasinya. Keupayaan penjerap ini untuk menyingkirkan metilena biru (pewarna kationik), tartrazin (pewarna anionik), dan bersurai kuning 3 (pewarna bukan ionic) daripada larutan dengan nilai pH yang berbeza telah dikaji. Hasil kajian menunjukkan bahawa pasir berhias Fe_3O_4 adalah lebih baik dalam penyingkiran pewarna apabila dibandingkan dengan pasir yang tidak berhias. Secara khususnya, pasir yang berhias dengan Fe_3O_4 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 daripada sifat amfoter yang dimiliki oleh nanopartikel Fe_3O_4. Penyahjerapan metilena biru, tartrazin, dan bersurai kuning 3 daripada pasir berhias Fe_3O_4 masing-masing paling tinggi dengan menggunakan 30 % v/v aseton, 1 M NaOH dan 30 % v/v etanol. Selain itu, kajian ini turut mendapati penjerap ini dapat dipisahkan dengan menggunakan medan magnetik kecerunan tinggi atau rendah.

Kata kunci: Penjerapan, Besi Oksida bermagnet, Nanopartikel, Pasir kuarsa, Pemisahan

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 CO_2 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 (SiO_2), 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 SiO_2, 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 (Fe_3O_4) 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 Fe_3O_4 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 Fe_3O_4-Decorated Sand

A stock solution of 1000 mg/L Fe_3O_4 suspension was prepared by dispersing 0.5 g of Fe_3O_4 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 Fe_3O_4 suspension and stirred for 2 hours at 300 rpm to promote mixing of the Fe_3O_4 nanoparticles and the sand. The Fe_3O_4-decorated sand was then separated from the excess Fe_3O_4 suspension and thoroughly washed with distilled water to remove any un-adsorbed Fe_3O_4. The Fe_3O_4-decorated sand was oven dried for 1 day before used for dye adsorption study. Note that the amount of Fe_3O_4 loaded onto the sand was varied from 1000 mg/L to 5000 mg/L to investigate the effect of Fe_3O_4 loading amount on dye adsorption efficiency. Figure 1 shows the look of the pure sand and the Fe_3O_4-decorated sand.


(a) (b)

Figure 1 Photo of the sand (a) before and (b) after decorated with Fe_3O_4 nanoparticles

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:

$$\varepsilon_{ADS}\ (\%) = \frac{C_o - C}{C_o} \times 100\ \% \qquad \text{(Equation 1)}$$

The second stage of the study aims to investigate the effect of Fe_3O_4 loading on dye adsorption efficiency. The same experimental procedure was used here, but with the sands decorated with different amounts of Fe_3O_4 nanoparticles.

To reveal the pH-dependent absorbability of the Fe_3O_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_3O_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_3O_4-Decorated Sand

Figure 2 shows that the surface of the quartz sand was successfully covered by Fe_3O_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_3O_4 (isoelectric point ~ pH 6.3 [28]). Note that the Fe_3O_4 nanoparticles appear in agglomeration form probably due to the high agglomeration tendency of bare Fe_3O_4 [29] and occurrence of multi-layer attachment. Despite that, the Fe_3O_4-decorated sand has an irregular structure which provides a large surface area for adsorption.

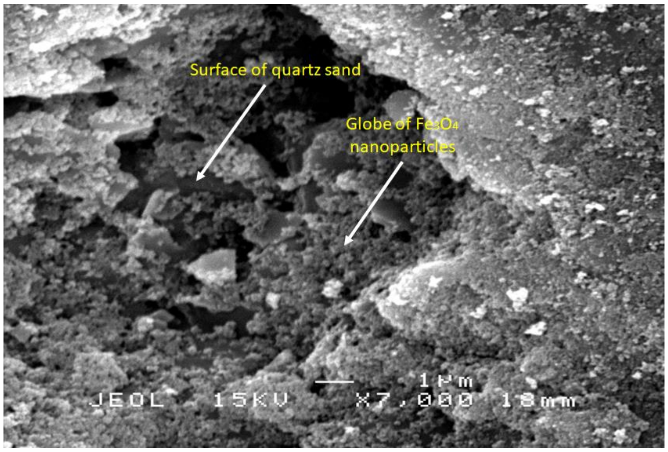


Figure 2 SEM micrograph of Fe_3O_4-decorated sand

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_3O_4 nanoparticles. To ensure the effects of adding Fe_3O_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_3O_4 Concentration on Dye Removal Efficiency

Various concentrations of Fe_3O_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_3O_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_3O_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_3O_4 nanoparticles were used for the decoration, respectively. Such observation implies creation of new adsorption sites by the extra-loaded Fe_3O_4 nanoparticles. Considering the dye removal efficiency was merely improved by ~ 1 % despite the concentration of Fe_3O_4 nanoparticles has been largely increased from 4000 mg/L to 5000 mg/L, there was no further increment of Fe_3O_4 nanoparticles (i.e. to a concentration above 5000 mg/L) performed in this study. The 5000 mg/L Fe_3O_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_3O_4 nanoparticles, it is proposed that the surface charge of Fe_3O_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.

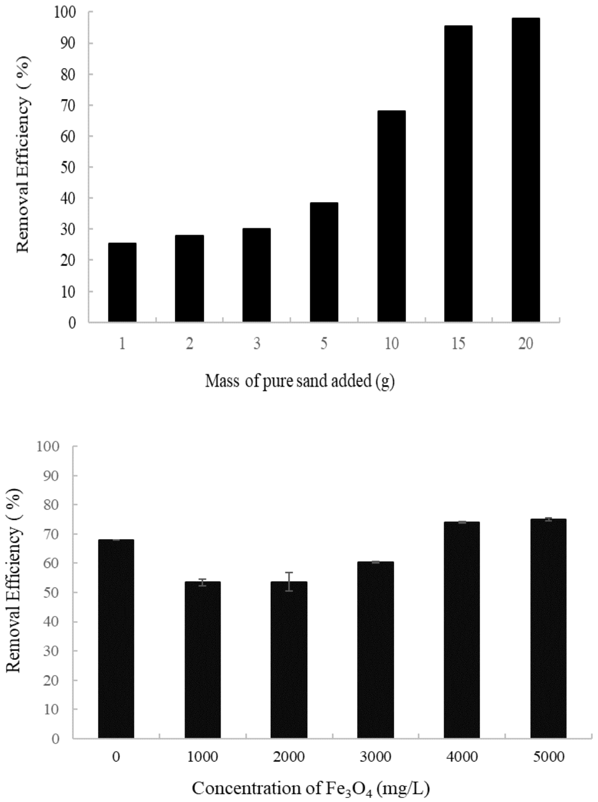


Figure 3 (a) Methylene blue removal efficiency (%) with respect to the amount of pure sand used (b) Methylene blue removal efficiency (%) with respect to the concentration of Fe_3O_4 being decorated onto the sand [Condition: Sand amount = 10 g, medium pH = pH 6).

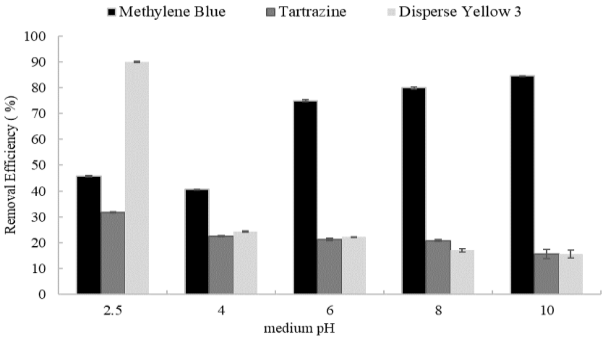


Figure 4 Methylene blue, tartrazine and disperse yellow 3 removal efficiency (%) at different medium pHs

As shown in Figure 4, the Fe_3O_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_3O_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 Fe_3O_4 alone [35] or other types of bare Fe_3O_4-decorated adsorbents [6, 36-38]. Hence, it is proposed that the adsorption of dye molecules onto Fe_3O_4-decorated sand was mainly controlled by the Fe_3O_4 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 Fe_3O_4 nanoparticles to positive charge ($-OH_2^+$) [39, 40]; thus, promoted electrostatic attraction towards the anionic groups of tartrazine ($R-SO_3^-$ and $R-COO^-$). Similarly, Zandipak and Sobhanardakani [41] reported that better removal of anionic dyes (eg. tartrazine, sunset yellow, and Eriochrome Blank T) by $NiFe_2O_4$ 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–) 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 Fe_3O_4-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 amphipathic 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 Fe_3O_4-decorated sand. Once the Fe_3O_4-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 Fe_3O_4-decorated sand [27].

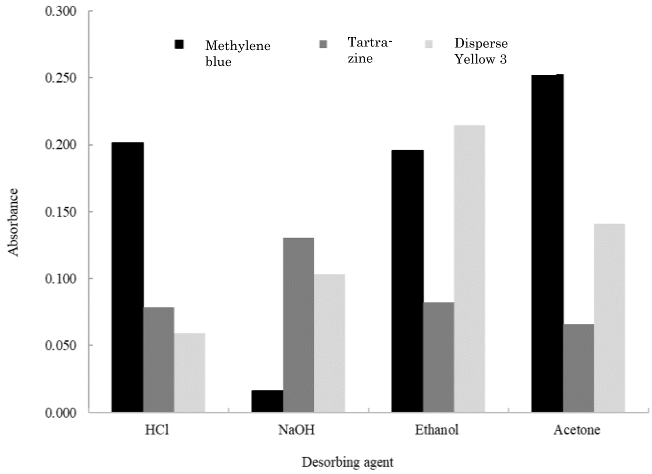


Figure 5 Desorption of methylene blue, tartrazine and disperse yellow 3 in different types of desorbing agents

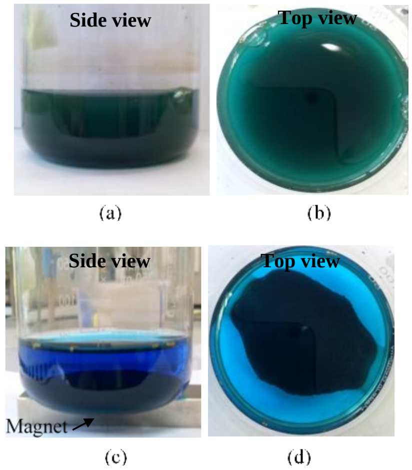
The pH-dependent desorption of dye molecules from the Fe_3O_4-decorated sand was affirmed when better desorption of tartrazine was achieved using NaOH than HCl. The addition of NaOH turns the Fe_3O_4-decorated sand negative. Once the Fe_3O_4-decorated sand lost its' positivity, the affinity towards the 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 amphipathic nature, whereby they contain hydrophilic (-OH, C=O) and hydrophobic group (CH_3CH_2-, $-CH_3$). 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 Fe_3O_4-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).

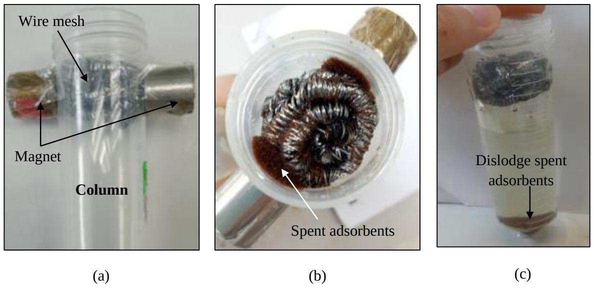


(a) (b)

(c) (d)

Figure 6 Photos showing the treated dye solution (a,b) in the absence of permanent magnet and (c,d) in the presence of permanent magnet

The same demonstration was carried out using a high gradient magnetic field (HGMF). Here, a packed column consisted of wire mesh was customized and connected to two permanent magnets (see Figure 7a). The permanent magnets magnetized the wire matrices and created a highly localized magnetic field [28]. As shown in Figure 7b, the Fe_3O_4-decorated sand was retained inside the column when being poured across the magnetized wire matrices. These captured sands can be dislodged easily by water rinsing once the wire matrices were demagnetized (Figure 7c).



(a) (b) (c)

Figure 7 Photos showing (a) the customized HGMF separation column, (b) the retention of adsorbents on the wire matrices, and (c) the dislodge of the captured adsorbents upon removal of external magnets

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. Fe_3O_4-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 Fe_3O_4 nanoparticles appeared in an agglomeration form and turned the quartz sand's surface rougher. The Fe_3O_4-decorated sand performed better than the pure sand when the concentration of Fe_3O_4 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 Fe_3O_4-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

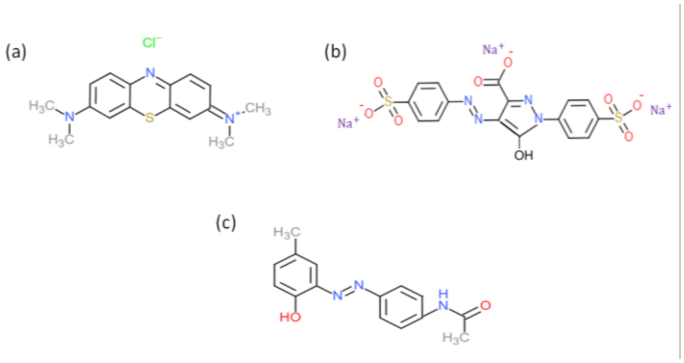

Figure S1 Chemical structures of (a) methylene blue, (b) tartrazine, and (c) disperse yellow 3

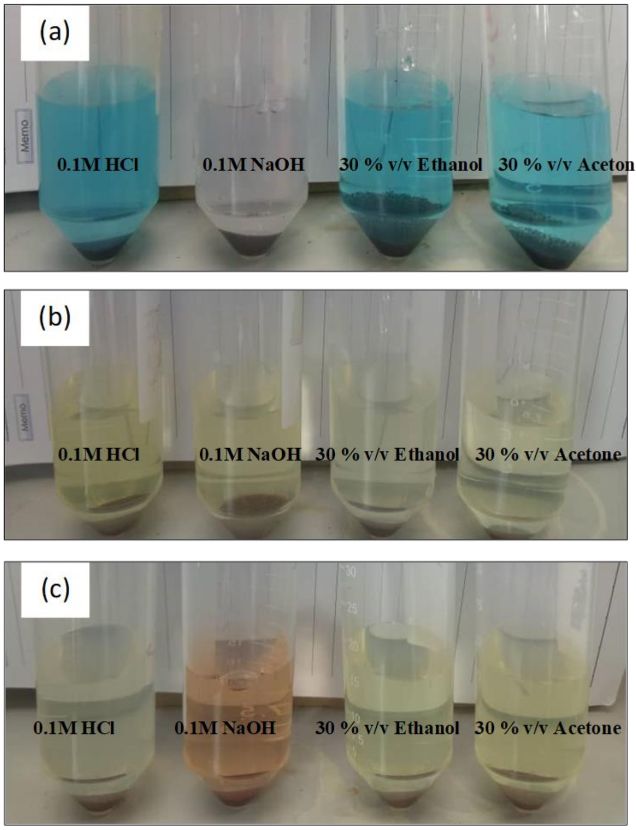

Figure S2 Photo showing the desorbed (a) methylene blue, (b) tartrazine, and (c) disperse yellow 3 after subjected to 4 hours of immersion in various desorbing agents

References

[1] David Noel, S., Raja,n M. R. 2014. Impact of Dyeing Industry Effluent on Groundwater Quality by Water Quality Index and Correlation Analysis. *Journal of Pollution Effects & Control*. 2: 1000126.

[2] Hussain, S., Khan, N., Gul, S., Khan, S., Khan, H. 2019. Contamination of Water Resources by Food Dyes and Its Removal Technologies, in: Eyvaz, M., Yüksel, E. (Eds.). Water Chemistry. IntechOpen.

[3] Gita, S., Hussan, A., Choudhury, T. G. 2017. Impact of Textile Dyes Waste on Aquatic Environments and its Treatment. *Environment & Ecology*. 35: 2349-2353.

[4] Kant, R. 2012. Textile Dyeing Industry an Environmental Hazard. *Natural Science*. 4(1): 5.

[5] Bello, O. S., Bello, I. A., Adegoke, K. A. 2013. Adsorption of Dyes Using Different Types of Sand: A Review. *South African Journal of Chemistry*. 66: 117-129.

[6] Tan, K. A., Morad, N., Teng, T. T., Norli, I., Panneerselvam, P. 2012. Removal of Cationic Dye by Magnetic Nanoparticle (Fe_3O_4) Impregnated onto Activated Maize Cob Powder and Kinetic Study of Dye Waste Adsorption. *APCBEE Procedia*. 1: 83-89.

[7] Crini, G. 2005. Recent Developments in Polysaccharide-based Materials Used as Adsorbents in Wastewater Treatment. *Progress in Polymer Science*. 30: 38-70.

[8 Vijayalakshmi, G., Ramkumar, B., Mohan, S. C. 2019. Isotherm and Kinetic Studies of Methylene Blue Adsorption Using Activated Carbon Prepared from Teak Wood Waste Biomass. *Journal of Applied Sciences*. 19: 827-836.

[9] Malik, P. K. 2004. Dye Removal from Wastewater Using Activated Carbon Developed from Sawdust: Adsorption Equilibrium and Kinetics. *Journal of Hazardous Materials*. 113: 81-88.

[10] Foo, K. Y., Hameed, B. H. 2010. An Overview of Dye Removal via Activated Carbon Adsorption Process. *Desalination and Water Treatment*. 19: 255-274.

[11] Hilal, N. M., Badawy, N. A., Mostafa, O. I., Elrefay, H. M. 2019. Synthetic and Application of a Novel Resin from Waste Foam Packing for Adsorption of Acid Orange 67 from Aqueous Solution. *Bulletin of the National Research Centre*. 43: 58.

[12] Nizam, N. U. M., Hanafiah, M. M., Mahmoudi, E., Halim, A. A., Mohammad, A. W. 2021. The Removal of Anionic and Cationic Dyes from an Aqueous Solution using Biomass-based Activated Carbon. *Scientific Reports*. 11: 8623.

[13] Henning, K-D. 2019. Solvent Recycling, Removal, and Degradation. In: Wypych, G. (Ed.). Handbook of Solvents. Third Edition. ChemTec Publishingpp. 1635-1727.

[14] Contescu, C. I., Adhikari, S. P., Gallego, N. C., Evans, N. D., Biss, B. E. 2018. Activated Carbons Derived from High-Temperature Pyrolysis of Lignocellulosic Biomass. *C-Journal of Carbon Research*. 4: 51.

[15] Duvuna, G. A., Ayuba, A. 2015. A Study on Silica Sand Quality in Yazaram and Mugulbu Deposits for Glass Making. *Nigerian Journal of Technology*. 34: 109-112.

[16] Haryanto, B., Siswarni, M. Z., Chang, C. H., Kuo, A. T., Singh, W. B. 2018. Interaction Models on Sand Surface of Natural Adsorbent with Adsorbate Cd^{+2}metal Ions in Solution with Batch Operation. *IOP Conference Series: Materials Science and Engineering*. 308: 012020.

[17] Chen, H., Wang, J., ur Rahman, Z., Worden, J. G., Liu, X., Dai, Q., Huo, Q. 2007. Beach Sand from Cancun Mexico: A Natural Macro- and Mesoporous Material. *Journal of Materials Science*. 42: 6018-6026.

[18] Kaneko, K. 1994. Determination of Pore Size and Pore Size Distribution: 1. Adsorbents and Catalysts. *Journal of Membrane Science*. 96: 59-89.

[19] Selim, K. A., El-Tawil, R. S., Rostom, M. 2018. Utilization of Surface Modified Phyllosilicate Mineral for Heavy Metals Removal from Aqueous Solutions. *Egyptian Journal of Petroleum*. 27: 393-401.

[20] Marghzari, S., Sasani, M., Kaykhaii, M., Sargazi, M., Hashemi, M. 2018. Simultaneous Elimination of Malachite Green, Rhodamine B and Cresol Red from Aqueous Sample with Sistan Sand, Optimized by Taguchi L16 and Plackett–Burman Experiment Design Methods. *Chemistry Central Journal*. 12: 116.

[21] Jada, A., Ait Akbour, R. 2014. Adsorption and Removal of Organic Dye at Quartz Sand-Water Interface. *Oil & Gas Science and Technology – Rev. IFP Energies Nouvelles*. 69: 405-413.

[22] Che, H. X., Yeap, S. P., Osman, M. S., Ahmad, A. L., Lim, J. 2014. Directed Assembly of Bifunctional Silica–Iron Oxide Nanocomposite with Open Shell Structure. *ACS Applied Materials & Interfaces*. 6: 16508-16518.

[23] Nicola, R., Costişor, O., Ciopec, M., Negrea, A., Lazău, R., Ianăşi, C., Picioruş, E-M., Len, A., Almásy, L., Szerb El, Putz A-M. 2020. Silica-coated Magnetic Nanocomposites for Pb^{2+} Removal from Aqueous Solution. *Applied Sciences*. 10: 2726.

[24] Whang, T-J., Huang, H-Y., Hsieh, M-T., Chen, J-J. 2009. Laser-induced Silver Nanoparticles on Titanium Oxide for Photocatalytic Degradation of Methylene Blue. *International Journal of Molecular Sciences*. 10: 4707-4718.

[25] Vaiano, V., Iervolino, G., D. S. 2016. Photocatalytic Removal of Tartrazine Dye from Aqueous Samples on $LaFeO_3$/ZnO Photocatalysts. *Chemical Engineering Transactions*. 52: 847-852.

[26] Robertson, J. R. 1978. The Products of Biodegradation of Selected Carpet Dyes and Dyeing Auxiliaries, School of Textile Engineering, Georgia Institute of Technology, Atlanta, Georgia. 125.

[27] Navarro, A. E., Elliot, S. C., Paul, C., Soo, Y. Y., Angela, M. 2013. Separation of Dyes from Aqueous Solutions by Magnetic Alginate Beads. *Trends in Chromatography*. 8: 31-41.

[28] Yeap, S. P., Ahmad, A. L., Ooi, B. S., Lim, J. 2012. Electrosteric Stabilization and Its Role in Cooperative Magnetophoresis of Colloidal Magnetic Nanoparticles. *Langmuir*. 28: 14878-14891.

[29] Yeap, S. P., Leong, S. S., Ahmad, A. L., Ooi, B. S., Lim, J. 2014. On Size Fractionation of Iron Oxide Nanoclusters by Low Magnetic Field Gradient. *The Journal of Physical Chemistry C*. 118: 24042-24054.

[30] Luo, S., Shen, M. N., Wang, F., Zeng, Q. R., Shao, J. H., Gu, J. D. 2016. Synthesis of Fe_3O_4-Loaded Porous Carbons Developed from Rice Husk for Removal of Arsenate from Aqueous Solution. *International Journal of Environmental Science and Technology*. 13: 1137-1148.

[31] Ho, M. Y., Khiew, P. S., Isa, D., Tan, T. K., Chiu, W. S., Chia, C. H., Hamid, M. A. A., Shamsudin, R. 2014. Nano Fe_3O_4-Activated Carbon Composites for Aqueous Supercapacitors. *Sains Malaysiana*. 43: 885-894.

[32] Jiang, Y., Xie, Q., Zhang, Y., Geng, C., Yu, B., Chi, J. 2019. Preparation of Magnetically Separable Mesoporous Activated Carbons from Brown Coal with Fe_3O_4. *International Journal of Mining Science and Technology*. 29: 513-519.

[33] Juang, R-S., Yei, Y-C., Liao, C-S., Lin, K-S., Lu, H-C., Wang, S-F., Sun, A-C. 2018. Synthesis of Magnetic Fe_3O_4/activated Carbon Nanocomposites with High Surface Area as Recoverable Adsorbents. *Journal of the Taiwan Institute of Chemical Engineers*. 90: 51-60.

[34] Li, Z., Liu, Y., Wang, D., Wang, P., Xu, R., Xie, D. 2019. Characterizing Surface Electrochemical Properties of Simulated Bulk Soil In Situ by Streaming Potential Measurements. *European Journal of Soil Science*. 70: 1063-1072.

[35] Yirga, G., Ananda, Murthy, H. C., Bekele, E. 2019. Synthesis and Characterization of Humic Acid-coated Fe_3O_4 Nanoparticles for Methylene Blue Adsorption Activity. *Advanced Materials Letters*. 10: 715-723.

[36] Ebrahimian Pirbazari, A., Saberikhah, E., Habibzadeh Kozani, S. S. 2014. Fe_3O_4–wheat Straw: Preparation, Characterization and Its Application for Methylene Blue Adsorption. *Water Resources and Industry*. 7-8: 23-37.

[37] Li, Y., Zimmerman, A. R., He, F., Chen, J., Han, L., Chen, H., Hu, X., Gao, B. 2020. Solvent-free Synthesis of Magnetic Biochar and Activated Carbon through Ball-mill Extrusion with Fe_3O_4 Nanoparticles for Enhancing Adsorption of Methylene Blue. *Science of The Total Environment*. 722: 137972.

[38] Lawagon, C. P., Amon, R. E. C. 2020. Magnetic Rice Husk Ash 'Cleanser' as Efficient Methylene Blue Adsorbent. *Environmental Engineering Research*. 25: 685-692.

[39] Xu, X. Q., Shen, H., Xu, J. R., Xie, M. Q., Li, X. J. 2006. The Colloidal Stability and Core-shell Structure of Magnetite Nanoparticles Coated with Alginate. *Applied Surface Science*. 253: 2158-2164.

[40] Toh, P. Y., Ng, B. W., Ahmad, A. L., Chieh, D. C. J., Lim, J. 2014. Magnetophoretic Separation of Chlorella sp.: Role of Cationic Polymer Binder. *Process Safety and Environmental Protection*. 92: 515-521.

[41] Zandipak, R., Sobhanardakani, S. 2016. Synthesis of NiFe2O4 Nanoparticles for Removal of Anionic Dyes from Aqueous Solution. *Desalination and Water Treatment*. 57: 11348-11360.

[42] Konicki, W., Cendrowski, K., Bazarko, G., Mijowska, E. 2015. Study on Efficient Removal of Anionic, Cationic and Nonionic Dyes from Aqueous Solutions by Means of Mesoporous Carbon Nanospheres with Empty Cavity. *Chemical Engineering Research and Design*. 94: 242-253.

[43] Ahmad, T., Danish, M., Rafatullah, M., Ghazali, A., Sulaiman, O., Hashim, R., Ibrahim, M. N. M. 2012. The Use of Date Palm as a Potential Adsorbent for Wastewater Treatment: A Review. *Environmental Science and Pollution Research*. 19: 1464-1484.

[44] Momina, Mohammad, Sx., Suzylawati, I. 2020. Study of the Adsorption/desorption of MB Dye Solution Using Bentonite Adsorbent Coating. *Journal of Water Process Engineering*. 34: 101155.

[45] Momina, Rafatullah, M., Ismail, S., Ahmad, A. 2019. Optimization Study for the Desorption of Methylene Blue Dye from Clay Based Adsorbent Coating. *Water*. 11: 1304.

[46] Wang, J., Xu, J., Wu, N. 2017. Kinetics and Equilibrium Studies of Methylene Blue Adsorption on 2D Nanolamellar Fe_3O_4. *Journal of Experimental Nanoscience*. 12: 297-307.

[47] Xing, X., Qu, H., Shao, R., Wang, Q., Xie, H. 2017. Mechanism and Kinetics of Dye Desorption from Dye-loaded Carbon (XC-72) with Alcohol-water System as Desorbent. *Water Science and Technology*. 76: 1243-1250.