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The influence of Fe_3O_4 on Magnetic Chitosan composite preparation for Methylene blue removal from water

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The influence of Fe_3O_4 on Magnetic Chitosan composite preparation for Methylene blue removal from water

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Abstract. The influence of Fe_3O_4 on magnetic chitosan composite preparation for methylene blue removal from water had been studied. Fe_3O_4 was loaded on chitosan with various content. The prepared magnetic chitosan composites were characterized by Fourier Transform Infrared (FT-IR), Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) analysis. Results showed Fe_3O_4 loading on magnetic chitosan composites preparation improved methylene blue adsorption capacity of chitosan. The best ratio of chitosan/Fe_3O_4 obtained in this work was 0.35g/0.5g. The methylene blue adsorption capacity of the magnetic chitosan composite was higher than pure chitosan. Magnetic composite can be used as potential adsorbent for methylene blue removal from water.

1. Introduction

Waste is an increasingly crucial environmental problem as technology develops and changes in the times. One of the wastes that become environmental problems is dye. Staining products in various industries such as textiles, varnishes, leather and plastics generally produce toxic waste andhighly carcinogenic. They give mutagenic effects on humans and aquatic animals [1]. Methylene blue is a harmful dyestuff used by the textile industry. Methylene blue can cause irritation of the digestive tract, cyanosis and skin irritation. This compound is quite stable so it is difficult to degrade in nature and harmful to the environment. In high concentrations, methylene blue can increase COD (Chemical Oxygen Demand) and can damage the balance of environmental ecosystems characterized by the death of aquatic organisms around the waste disposal site [2]. Therefore, further treatment for dyestuff waste before disposal to the environment is necessary.

Treatments for wastewater have been widely used, one of which is adsorption [3]. The adsorption process is the best alternative because it is able to eliminate the polluting dye effectively by using adsorbents that have high absorption capacity. Currently, the development of waste-based adsorbents such as chitosan derived from shrimp shells waste with high adsorption capacity and biodegradation [4]. The ability of chitosan in adsorption is still limited due to its weakness as easily coagulated and easily soluble in acid and difficult to separate from the solution. Therefore, chitosan was often combined with other materials [5] such as the use of Fe_3O_4 to facilitate chitosan separation from solution after adsorption [1].

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In this work, chitosan was combined with Fe_3O_4 obtained from coastal sand of Syiah Kuala, Aceh. Magnetic material is an appropriate solution for the combination of chitosan where insoluble and paramagnetic properties allow separation to be more efficient [6].

2. Experimental

2.1. Materials
Chitosan was purchased from Tokyo Chemical Industry Co., Ltd. Japan (obtained from shrimp shell where deacetylation degree was 75.0-85.0%). Iron sand were collected from coastal sand of Syiah Kuala, Aceh. HCl, NH_4OH, NaOH, acetic acid and methylene blue.

2.2. Isolation of Fe_3O_4 particles
Fe_3O_4 particles were isolated by coprecipitation method. The iron sand was dissolved into 35 mL HCl at a temperature of 70^0C and stirred for 30 minutes using a magnetic stirrer. The solution was filtered with filter paper. After 30 minutes the NH_4OH was added to the solution while stirring with a magnetic stirrer and heated at a temperature of 70^0C for 30 minutes. The obtained precipitate was washed with distilled water until neutral pH was reached. Then the precipitate was dried in the oven at 70^0C for 2 hours [7,8].

2.3. Preparation of magnetic chitosan composite
Magnetic chitosan was prepared by mixing 0.35 g of chitosan into 20 mL of 2% acetic acid and stirred using a magnetic stirrer for 2 h. Fe_3O_4 particles were then added to the chitosan solution with several compositions (0.1, 0.2, 0.3, 0.4, 0.5, 0.6 and 0.7 grams) and stirred manually for 1 hour. Afterwards the dope solution was dropped into 3M NaOH solution to form the microsphere and then washed with distilled water until the pH neutral reached and dried. Each magnetic chitosan composites obtained were examined their adsorption capacity on methylene blue adsorption. The magnetic chitosan composite with highest adsorption capacity of methylene blue was then characterized by using Fourier Transform Infra Red (FTIR), X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM).

2.4. Adsorption studies
Methylene blue adsorption onto the composite was performed in batch experiments. 0,1 g of the composite was placed into erlenmeyer flasks containing 10 mL methylene blue solution. The mixture was shaken at room temperature, 150 rpm for 25 minutes. The mixture was separated by using permanent magnet and the absorbance of methylene blue in the solution was determined by using UV-Visible spectrometer. Methylene blue adsorption capacity (q, mg/g) and removal efficiency (R,%) were calculated using the following equations:

$$q = \frac{(Co-Ct)V}{m} \tag{1}$$

$$R(\%) = \frac{Co-Ct}{Co} \times 100 \tag{2}$$

Where C_0 (mg/g) and C_t(mg/L) are the initial methylene blue concentration and final concentration of methylene blue after contacting with the composite for certain time, t (min). V (L) is the volume of methylene blue and m (g) is the mass of the composite. UV-Visible spectrometry analysis was carried out at 655 nm. Calibration curve was obtained by using methylene blue concentrations of 1, 2, 3, 4, 5, 6 and 7 ppm.

3. Result and discussion

3.1. Characterization

The chemical structures of the raw materials and magnetic chitosan composite were studied by FTIR spectroscopy. FTIR spectra of chitosan, and magnetic chitosan composite are shown in Fig. 1.

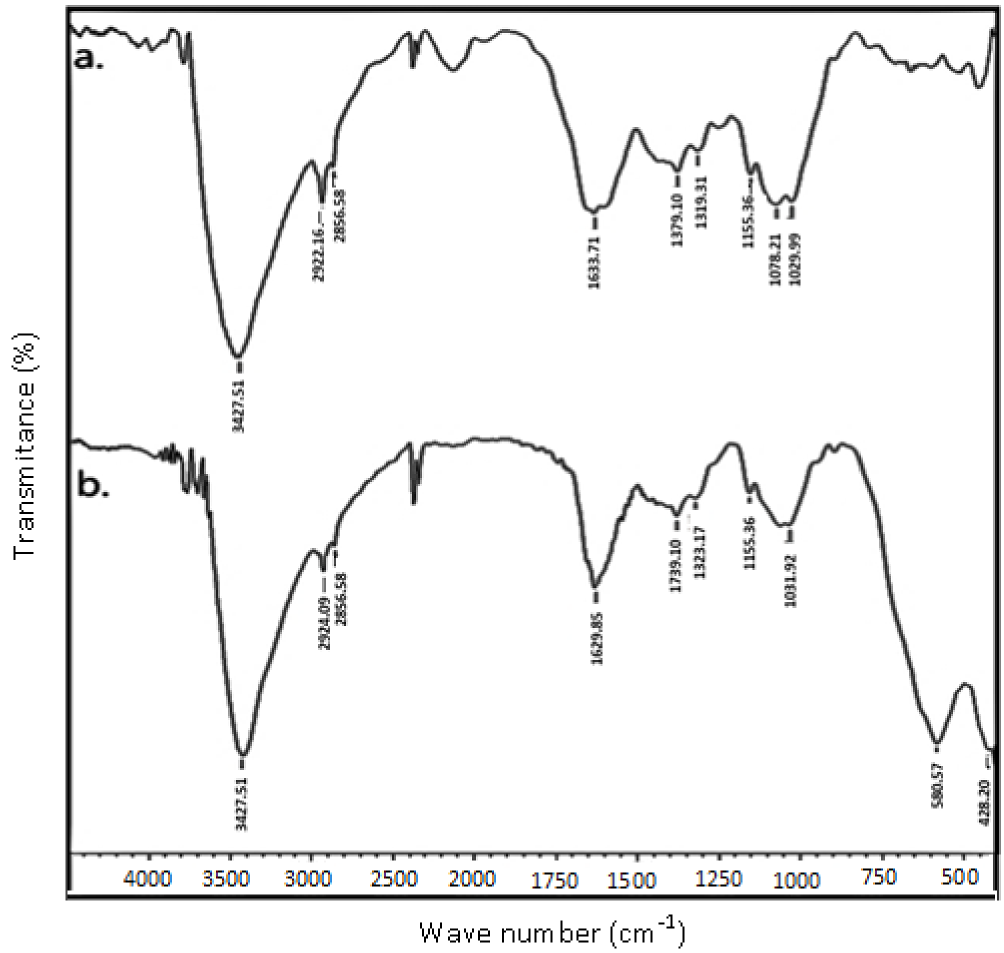

Figure 1. Spectra of chitosan (a) and magnetic chitosan composite (b)

Figure 1a exhibits typical FTIR spectrum of chitosan, where $-NH_2$ stretching vibration band appears at wave number 3427.51 cm^{-1} and amide stretching vibration at wave number 1633.71 cm^{-1}. Compared with FTIR spectrum of chitosan, FTIR spectrum of magnetic chitosan composite shows some differences. Band at wave number 2922,16 cm^{-1} of chitosan spectrum shifts to wave number 2924,09 cm^{-1} on magnetic chitosan composite spectrum. Band at wave number 1029.99 cm^{-1} shifts to wave number 1031,92 cm-^{1}. New bands, typical bands of FeO, are found at wave numbers 580.57 cm^{-1} and 428.20 cm^{-1} on magnetic chitosan composite spectrum. These results show interaction between chitosan and Fe_3O_4 in the composite.

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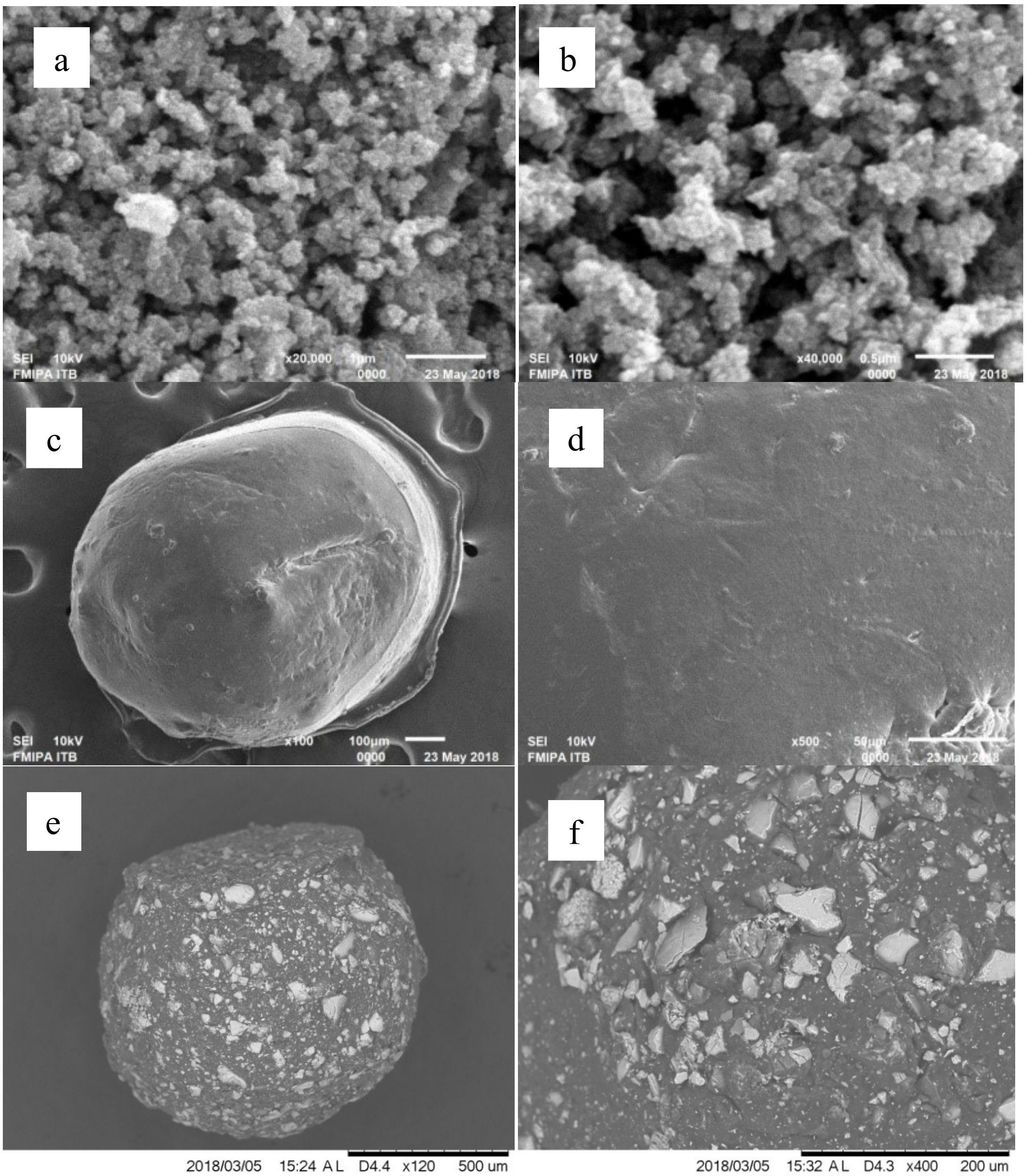

Figure 2. SEM images of Fe_3O_4 (a,b), bead chitosan (c,d) and magnetic chitosan composite (e,f).

Particle size and morphology of materials are studied by SEM. The SEM images of Fe_3O_4, chitosan bead and magnetic chitosan composite bead are shown in Figure 2. Figure 2a and 2b are SEM images of Fe_3O_4 particles with different magnification. Figure 2c and 2d are SEM images of chitosan bead. The surface of chitosan bead is smoother than the surface of magnetic chitosan composite bead (Figure 2e and Figure 2f). The difference of surface morphology of chitosan bead and magnetic chitosan composite bead is due to the Fe_3O_4 distribution on the surface magnetic chitosan composite bead.

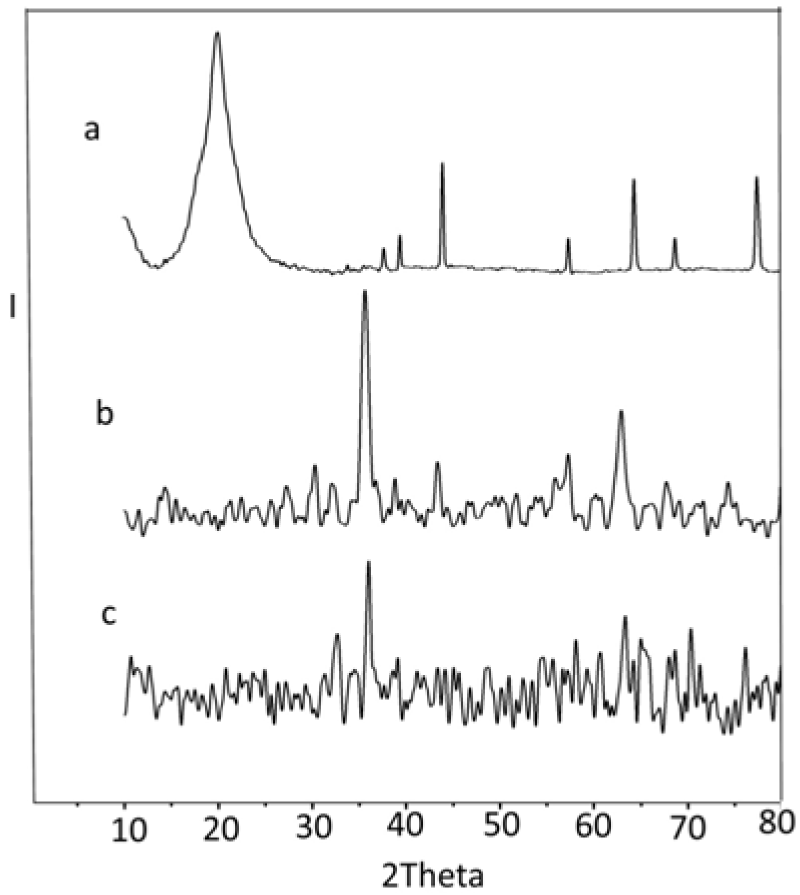

Figure 3. XRD patterns of chitosan (a), Fe_3O_4 (b) and magnetic chitosan composite (c).

Figure 3 shows the XRD pattern of chitosan (Figure3a), Fe_3O_4 (Figure3b) and magnetic chitosan composite (Figure 3c). Chitosan peak (Figure 3a) in this study shows 2θ at 19.5°. XRD pattern of chitosan exhibits 2θ=19.5°. Karimi [9] and Ge [10] reported that chitosan has typical peak at 2θ=19°-20°. Figure. 3b shows the typical XRD pattern of Fe_3O_4 at *2θ*=30,10°, 35,44° and 62,59°. XRD pattern of Fe_3O_4 (Figure.3b) shows that Fe_3O_4 has nano size particle with size 0.0587 nm. It was obtained by Scherrer formula, the crystallite size D is given by [11].

$$D = \frac{0{,}9\lambda}{B(\cos\frac{2\vartheta}{2})} \qquad (3)$$

Where 0.9 is a correction factor used for the determination of the full width half maximum (FWHM), the wavelength λ is 0.5418 Å, B is the FWHM, and $\cos\frac{2\vartheta}{2}$ is the cosine of the angle.

The XRD pattern of magnetic chitosan composite (Figure 3c) shows the loss of chitosan crystallinity at 2θ=19,5°. Associated with that, there is a low Fe_3O_4 diffraction pattern at 2θ 35.42°, 43.05° and 62.5°. The combination of chitosan and Fe_3O_4 (magnetic chitosan composite) forms amorphous material.

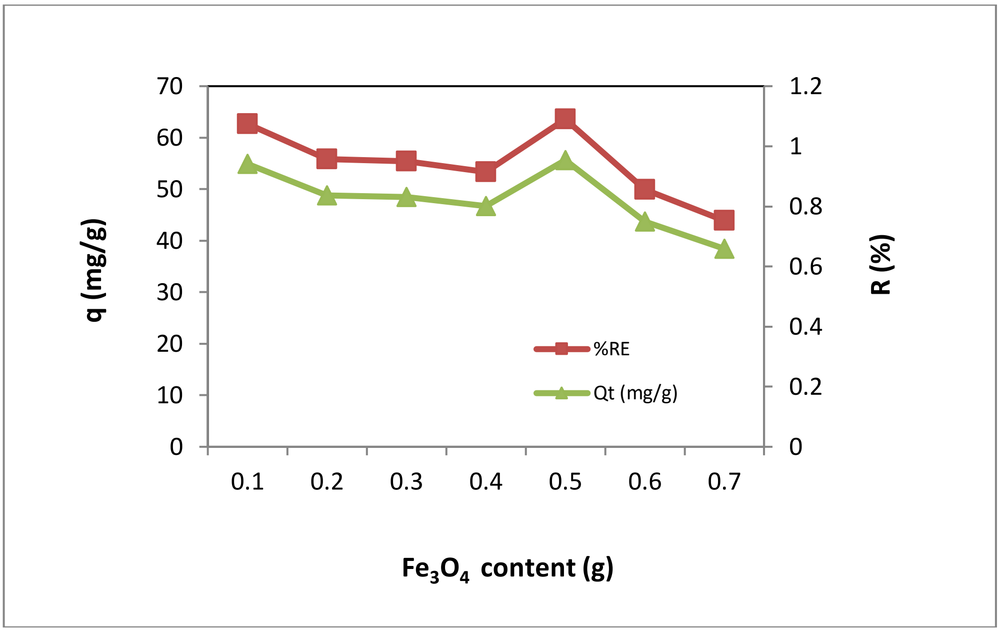

Figure 4. Adsorption capacity of methylene blue onto magnetic chitosan composites with different content of Fe_3O_4 particles

Figure 4 shows methylene blue adsorption capacity of magnetic chitosan composites with different content of Fe_3O_4 particles. Adsorption capacity of magnetic chitosan composites that contain Fe_3O_4 particles more and less than 0.5 gram are lower than adsorption capacity of magnetic chitosan composite that contain 0.5 gram of Fe_3O_4 particles. In low content of Fe_3O_4 particles the main component of adsorben is chitosan where Fe_3O_4 particles were covered by polymer chains of chitosan. By increasing Fe_3O_4 particles content, the adsorption capacity decrease. However, when Fe_3O_4 particles content is 0.5 gram, chitosan can not totally cover the Fe_3O_4 particles that lead interaction between methylene blue and Fe_3O_4 particles resulting in increasing in adsorption capacity. In high content of Fe_3O_4 particles, chitosan content decrease and its ability to cover Fe_3O_4 particles also decrease. The main component of adsorbent is Fe_3O_4 particles that has lower adsortion capacity than chitosan. Therefore, the best magnetic chitosan composite is obtained at Fe_3O_4 particles content of 0.5 gram where it shows the high adsorption capacity (62,7%). The magnetic chitosan composite at Fe_3O_4 particles content of 0.1 gram also shows high adsorption capacity (63,6%), however it was not easily separated from solution by magnet permanent due to low content of Fe_3O_4.

4. Conclusions

Adsorption capacity of chitosan can be improved by Fe_3O_4 loading on magnetic chitosan composites preparation. The ratio of magnetic chitosan composites preparation was obtained 0.35g/0.5g (chitosan/Fe_3O_4) where it showed the highest adsorption capacity (63,6%). This result showed the methylene blue adsorption capacity of the magnetic chitosan was higher than pure chitosan.

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