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Methylene blue removal from water using H_2SO_4 crosslinked magnetic chitosan nanocomposite beads

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ABSTRACT

H_2SO_4 crosslinked magnetic chitosan nanocomposite beads had been prepared and applied as adsorbents for methylene blue removal. The nanocomposite beads were prepared with content variations of Fe_3O_4 and H_2SO_4. Nanosized Fe_3O_4 crystallite has been prepared and confirmed by XRD and SEM analysis. The Fe_3O_4 crystallite was used to synthesize H_2SO_4 crosslinked magnetic chitosan nanocomposite beads where their formation was confirmed by FTIR, XRD and SEM analysis. Adsorption experiments were conducted with several different contact times, pH values and initial concentrations of methylene blue. The equilibrium of methylene blue adsorption by H_2SO_4 crosslinked magnetic chitosan nanocomposite beads was reached at 25 min contact time. The adsorption capacity increased as the solution pH increased. Based on Langmuir isotherm model, the maximum adsorption capacity of H_2SO_4 crosslinked magnetic chitosan nanocomposite beads on methylene blue adsorption was 20.408 mg/g.

1. Introduction

Methylene blue is one of the most commonly used substances in the textile industry. Methylene blue can damages the balance of the ecosystem and adversely affect the environment [1–3]. The methylene blue compound is very easy to obtain because its cheap price and wide use in dyeing process [4]. The dye molecule is very stable, thus difficult to be decomposed under natural conditions. Therefore, it is necessary to remove the dye molecule before being discharged to the environment [5]. The removal technique of dyestuff has been widely studied including ion exchange, membrane filtration, coagulation-flocculation, flotation, electrochemical processes, reverse osmosis and adsorption [6–8]. Among all the processes, the adsorption process is the most frequently used [9]. The adsorption method is recognized as a relatively simple and an effective method [5,10].

There are many adsorbents that can remove dyestuff from wastewater, one of which is chitosan due to its advantages of being eco-friendly, highly effective, nontoxic and in expensive [11,12]. Chitosan as a chitin deacetylation product contains many amine and hydroxyl functional groups that can increase the adsorption capacity of the dyestuff and harmless to humans. Therefore, chitosan is often used as bio-adsorbent [13]. However, it still has limitations due to its weak mechanical properties, easily clumping or gel formation, high solubility in acids and difficulty to be separated from solution. Therefore, chitosan is often combined with other materials [14]. Chitosan was often modified by adding crosslinking agents in order to improve its mechanical performance such as glutaric dialdehyde, ethylene glycol diglycidyl ether, polyethylene glycol diglycidyl ether epichlorohydrin, sulfuric acid, and tripolyphospate [15–17]. Chitosan crosslinked with sulfuric acid exhibited the highest performance [17]. Therefore, in this study the properties of chitosan were improved by the addition of sulfuric acid as a crosslinking agent. Crosslinking process using H_2SO_4 produces chitosan chains that form strong anti-parallel structures and hydrogen bonds [18] which are chemically important modifications [19] because they can increase chitosan's adsorption capacity, stability and acid resistance [20], and reduce the crystallinity properties [18].

Integration of adsorbent with other materials forms the composite that has better adsorption properties than individual component. In order to improve adsorption properties and facilitate the separation after adsorption process, Fe_3O_4 particles was used on preparation of magnetic chitosan beads [21,22]. However, most of Fe_3O_4 particles used were commercial products resulting high cost adsorbent. Meanwhile, iron sand that contains Fe_3O_4 is easily found in Aceh, Indonesia. Therefore, the modification of chitosan in this work was conducted by using Fe_3O_4 particles isolated from local iron sand. The modified chitosan (H_2SO_4 crosslinked magnetic chitosan nanocomposite bead) was used as an adsorbent of methylene blue.

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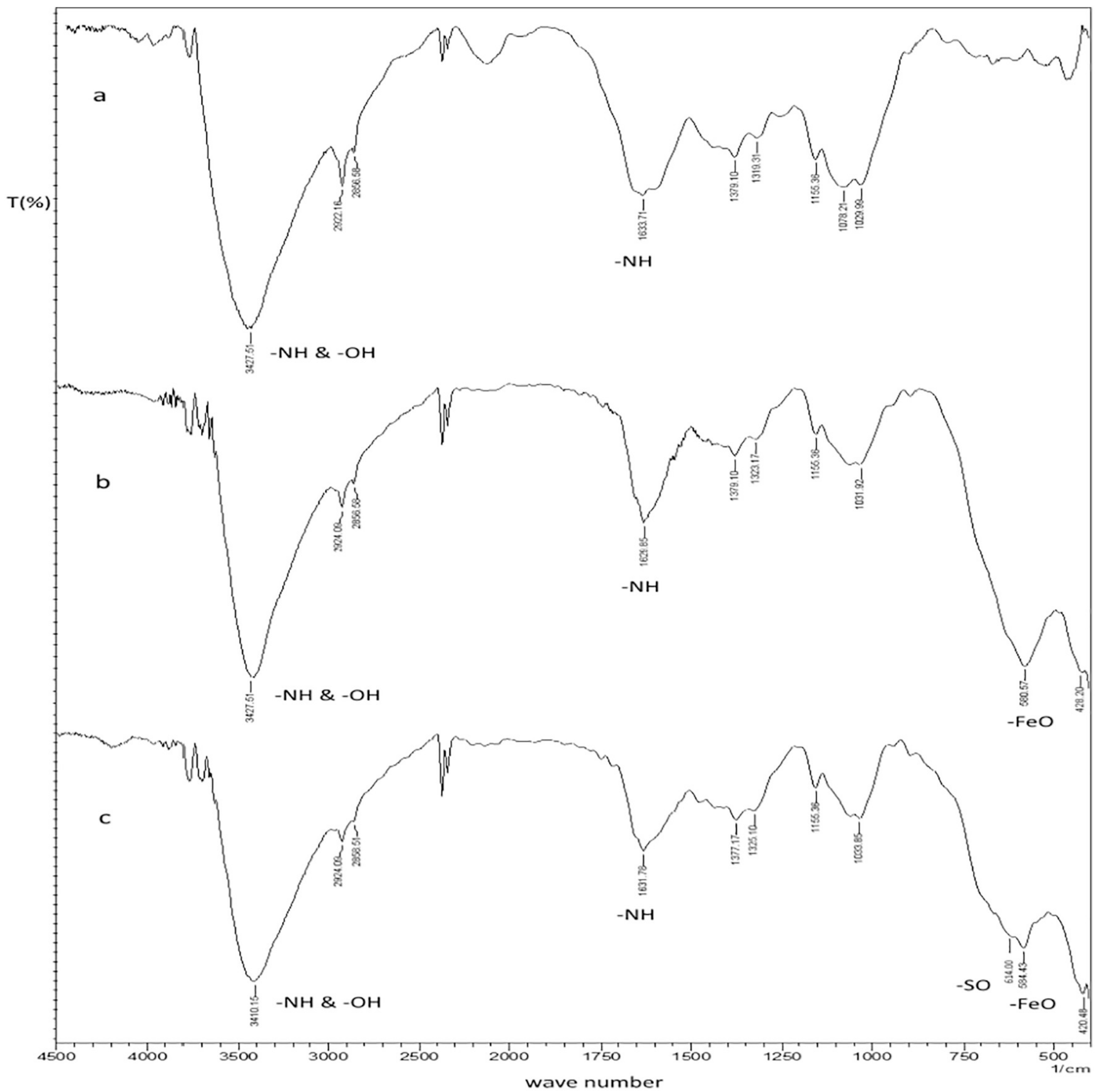

Fig. 1. FTIR Spectra of chitosan beads (a), magnetic chitosan nanocomposite beads (b) and H_2SO_4 crosslinked magnetic chitosan nanocomposite beads (c).

2. Experimental

2.1. Materials

Iron sand was collected from Aceh, Indonesia. Chitosan (obtained from shrimp shell where deacetylation degree was 75.0–85.0%) was purchased from Tokyo Chemical Industry Co., Ltd. Japan with code number C0831. All other chemicals were obtained from Sigma-Aldrich and used as received without further purification.

2.2. Isolation of Fe_3O_4 particles

Fe_3O_4 particles were isolated from local iron sand. The experiment was conducted according to procedure reported by Taufiq [23].

2.3. Preparation of H_2SO_4 crosslinked magnetic chitosan nanocomposite beads

H_2SO_4 crosslinked magnetic chitosan nanocomposite beads were prepared by mixing 0.35 g of chitosan into 20 mL of acetic acid (2%) and stirred using a magnetic stirrer for 2 h. H_2SO_4 was added with several concentrations (0.02, 0.06 and 0.08 M) to the chitosan solution and stirred using a magnetic stirrer for 2 h. Then the H_2SO_4 crosslinked chitosan was added with Fe_3O_4 particles with various amounts (0.1, 0.2, 0.3, 0.4, 0.5, 0.6 and 0.7 g) and stirred for 1 h. Afterwards the dope solution was dropped into NaOH 3 M solution in order to form the beads and then washed with distilled water until the pH neutral was reached and dried.

2.4. Adsorption experimental

Investigation of methylene blue adsorption onto H_2SO_4 crosslinked magnetic chitosan nanocomposite beads was carried out in batch experiments. 0,1 g of the nanocomposite beads was added into Erlenmeyer flask containing 10 mL methylene blue solution. The mixture was shaked at 150 rpm for 25 min. The adsorbent was separated from the mixture by using permanent magnet and the absorbance of methylene blue was determined by UV–Vis spectrophotometer. Methylene blue adsorption capacity (q, mg/g) was determined using Eq. (1) [24]:

$$q = \frac{(Co - C)V}{w} \tag{1}$$

where C_0 (mg/g) and C (mg/L) are the initial and final methylene blue concentration, respectively. V (L) is the volume of methylene blue solution and w (g) is the mass of the nanocomposite. UV–Vis