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Synthesis of goethite-polyacrylate composite as a cationic and anionic adsorbent

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ABSTRACT

The use of powdered composites as an adsorbent of waste has been widely carried out but only focuses on one type of ion, which is cation or anion. This kind of composite was difficult to separate from the supernatant. This study aims to synthesize goethite-polyacrylate composite which is easy to separate from the supernatant and has the ability for cation and anion adsorption. The composite was synthesized by adding sodium polyacrylate to the formed goethite in thermal conditions. The synthesized composite was characterized by swelling, X-ray diffraction, and Fourier-transform infrared spectroscopy. The result of the study showed that the more sodium polyacrylate is added to goethite, the better the swelling ability of composites in water. In another hand, these composites can adsorb methylene blue and phosphate as cation and anion waste.

Keywords: Adsorbent; Multifunction; Polymer; Waste

1. Introduction

Environmental pollution, especially water pollution, is one of the current global problems. The need for global freshwater is around 6,000–7,000 km^3/y, while the groundwater reserve globally is about 70,000 km^3. This source of water was limited due to climate, vegetation cover, altitude, soil composition, vegetation cover, and water pollution. The pollutants come from urban, industrial, and agricultural drainage wastes [1]. Higher education is one of the institutions that use water for educational and research activities in laboratories. The water that has been used is disposed of in the form of chemical waste continuously for a long term. Even though the volume of waste produced is not as large as industrial waste, but from the type of waste produced and this becomes a long-term routine, it will make college waste one of an environmental problem. Laboratory waste that is disposed of carelessly will damage the environment. The waste will accumulate in living things through the food chain so that it can cause health problems. Nowadays, waste management in an educational institution is still not optimal due to a lack of awareness from the institutions [2], limited technology, and relatively expensive processing costs [3]. Therefore, special handling of laboratory waste is needed because the amount of waste is increasing along with the increasing number of students.

Laboratory waste is very diverse. It can be either organic or inorganic compounds which are usually soluble in water in ionic form. The adsorption method is often used as an alternative for handling ionic waste because it is more

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efficient and easily applied, so this method is very suitable for removing ions in laboratory wastes [4,5]. The use of goethite as an adsorbent material has been carried out to adsorb cations and anions because this material is stable and easily synthesized [6,7]. Goethite can adsorb cations and anions because it has a charge which is depended on pH. Goethite was used as an adsorbent in powdered form because its adsorption ability is strongly influenced by the particle size. This type of adsorbent is difficult to separate from the supernatant. Therefore, the development of a goethite-based composite is needed to improve its characteristics.

A composite is a composed material of two or more compounds that have different chemical and physical properties to obtain new properties [8]. Several studies have been carried out for the synthesis of goethite-based composites to adsorb cations and anions, but the form of this adsorbent is powder solids, so it is still difficult to separate from the supernatant [9,10]. The goethite-based composite synthesis continues to be developed to change its physical properties, but this adsorbent only adsorbs one type of ion, namely cations or anions [11,12]. In addition, the previous study reported that the composite of goethite-based was conducted by adding a crosslinking agent to combine the two precursors in a certain conditions. The adding of crosslinking caused the increase of waste in the rinsing process [11,13].

A simple method to synthesis a goethite-based composite that can be separated from the supernatant and can adsorb cations and anions is a novel idea that needs to be developed. The aim of this work is to synthesize a composite of goethite-polyacrylate with proper mechanical property and adsorption performance. In this study, sodium polyacrylate was used as a composited material with goethite. This is because polyacrylate has a high adsorption capacity, stable, and inexpensive hydrogel phase [14]. Hydrogel composites have better adsorption ability than dry composites because they have a porous structure and are hydrophilic [15]. The combination of goethite and polyacrylate gave two active sides of composite so that it can adsorb cationic and anionic waste.

2. Materials and methods

2.1. Materials

Sodium polyacrylate ($(C_3H_3NaO_2)^n$) was purchased from Sumitomo Seika. For the synthesis of goethite, ferric chloride ($FeCl_3$) and sodium hydroxide (NaOH) were purchased from Brataco Chemika Company with low-grade quality but economical to obtain low-cost adsorbent. Other chemicals, such as potassium dihydrogen phosphate (KH_2PO4), methylene blue ($C_{16}H_{18}C_1N_3S$), ascorbic acid ($C_6H_8O_6$), sulfuric acid (H_2SO_4), ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}$), antimony potassium tartrate ($C_8H_{10}K_2O_{15}Sb_2$) were purchased from Merck Company with analytical grade.

2.2. Synthesis of goethite and goethite-polyacrylate composite

Goethite was prepared by adding 90 mL of 2.5 M NaOH solution with continuous stirring to 50 mL of 0.5 M $FeCl_3$ solution in a beaker. The mixture was immediately diluted to 1 L with water and capped. The resulting precipitates were aged at 40°C for 7 and 21 d (the mixture was stirred every day). Then the content was washed with water and dried at 40°C for 24 h. 2 g of goethite was obtained [9].

To get 200 mg of goethite, 9 ml of 2.5 NaOH was added to 5 mL of 0.5 M $FeCl_3$ in 3 polyethylene flasks. The mixture dilutes to 100 mL distilled water, capped, and incubated at 40°C for 21 d. Sodium polyacrylates (50, 150, and 300 mg) were then added to each goethite respectively in the seventh day and incubated for 21 d. The contents were obtained as composites after they were washed and dried at 40°C for 24 h.

2.3. Characterization

Composite and goethite characteristics are known from the results of the Fourier-transform infrared spectroscopy (FTIR) spectrum (PerkinElmer Spectrum One, Massachusetts, USA) based on adsorption peaks at certain wavenumbers. To determine the degree of crystallinity, X-ray diffraction (XRD) (Bruker D8, Texas, USA) was used.

2.4. Degree of swelling (DS) determination

The degree of swelling is defined as a comparison between the weights of the swelled gels with dried gels. The degree of swelling can be determined by weighing about 5 mg of composites and dried until the constant weight was gained as dry weight (W_d). The composites were dissolved in distilled water and left for 24 h, then weighed as the swelling weight of composites (W_s). The degree of swelling was formulated as following equation [16].

$$\mathrm{DS} = \frac{W_s}{W_d} \tag{1}$$

2.5. Adsorption analysis

Analysis of phosphate ions as anions was carried out using a blue molybdate-ascorbate reagent. Dissolved as much as 0.176 g of ascorbic acid in 10 mL of water. To 10 mL of 2.5 M H_2SO_4, add 3 mL of ammonium heptamolybdate. Then 6 mL of ascorbic acid and 1 mL of antimony potassium tartrate were added. Analysis of phosphate ion adsorption was carried out by adding 0.03 g of the composite to 10 mL of KH_2PO_4 solution at a concentration of 200 ppm and left for 24 h. As much as 8 mL of the solution was transferred into a 10 mL measuring flask followed by the addition of a 1.6 mL reagent solution. Then distillate water is added until the volume of the solution was 10 mL. The solution is shaken and left for 10 min. The absorbance measurements were carried out at 890 nm wavelength using a UV-Vis spectrophotometer, then the adsorption capacity was calculated. The cation used in this analysis is methylene blue. For the adsorption reaction, 0.03 g of the composite was added to 10 ml of methylene blue solution at a concentration of 200 ppm, the mixture was then shaken. After 24 h, the absorbance is measured at a wavelength of 664 nm.

3. Results and discussion

3.1. Synthetic goethite

Goethite (αFeOOH) can be found in nature in the form of sediments and can be synthesized in the laboratory by reacting iron compounds with bases at certain temperature [9]. According to Kugbe et al. [9], synthesis of goethite was conducted by storing samples at 40°C for 3 weeks. But in this study, the synthesis times were 7 and 21 d, named GT7 and GT21 respectively. The XRD pattern of the two goethite samples has a typical diffractogram peak at 2θ = 18°, 21°, 26°, 33°, 35°, 37°, 40°, 41°, 53°, 57°, 59°, 59°, 61°, 64°. The results of the analysis showed that the GT7 and GT21 had the same diffractogram peak (Fig. 1a). These results are matched with databases in Match 3 software and are consistent with previous studies [17–19]. The degree of goethite crystallinity increases along with the length of sample incubation time. Goethite synthesized for 7 d had a crystallinity of 45.26%. Meanwhile, under the same conditions, the degree of crystallinity of goethite synthesized for 21 d was 56.03%. This is because the longer the synthesis time, the more goethite is formed. Differences in relative crystallinity can be observed from changes in peak width and height. A sharper peak and more indicates higher crystallinity.

Characterization using FTIR was carried out to see the functional groups on goethite (Fig. 1b). The peaks found in the range 621–632 cm^{-1} indicate that there is an octahedral lattice of FeO. The peaks at 786–791 cm^{-1} show that there is a Fe–O–H vibration. The presence of a broad peak centered on 3,101–3,118 is in accordance with the goethite hydroxyl group. There are peaks in goethite in wavenumbers around 1,300–1,570 and 1,575–1,650 which indicate the possibility of the presence of the –C–NO_2 and amine groups as complementary material [19,20]. This is because the material used for the synthesis of goethite is a low-grade quality so that the purity level is low. The characterization data was obtained from a previous study [21].

3.2. Goethite-polyacrylate composite

The goethite-polyacrylate composite was synthesized by adding sodium polyacrylate on the seventh day of synthesizing goethite, with a variation of polyacrylate (Table 1). The formation of a goethite/polyacrylate composite can be simply explained by the illustration mechanism (Fig. 2). In this study, goethite was formed from $FeCl_3$ and NaOH bases, then sodium polyacrylate was used for the immobilization of goethite. The immobilization of goethite in sodium polyacrylate can be carried out by two possible mechanisms: (1) hydrogen interaction between the hydroxyl and carboxyl groups and (2) Fe atoms in goethite which is a Lewis acid that binds to the Lewis base in polyacrylate [12].

The characterization of the goethite-polyacrylate composite was determined using the infrared spectrum (Fig. 3). The carbonyl group (C–O) is observed in the range of 1,850–1,550 cm^{-1}. The spectrum of goethite is indicated by the band from 790 to 910 cm^{-1}, which indicates the Fe–O group, and about 3,000 cm^{-1} for the hydroxyl group [22]. Goethite-polyacrylate composites are characterized by a decrease in the intensity of Fe–O and C–O bands, compared to the goethite spectrum. The more polyacrylate added, the less the Fe–O band. This indicates the loss of goethite. The Fe–O

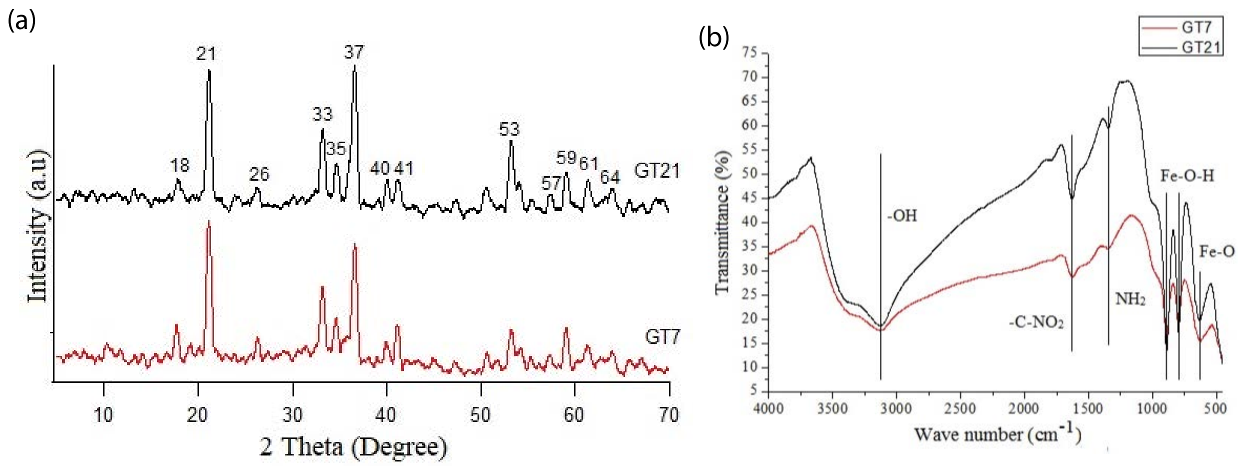

Fig. 1. (a) XRD diffractogram and (b) FTIR spectra of goethite.

Table 1
Goethite-polyacrylate product composition

Fe^{3+} concentration (M)	NaOH concentration (M)	Mass of polyacrylate (mg)	Label
0.5	2.5	50	K50
0.5	2.5	150	K150
0.5	2.5	300	K300

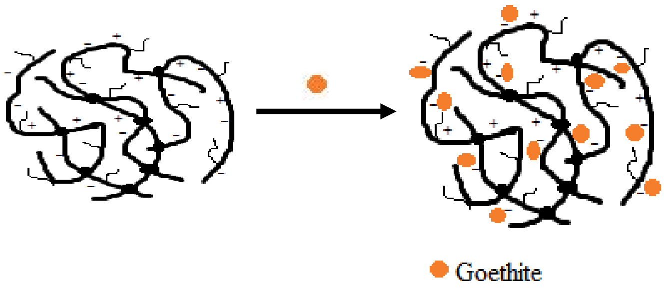

Fig. 2. Illustration mechanism of goethite-polyacrylate composite formation.

band disappears along with the appearance of the C–O band in the numbers 1,850–1,550 cm^{-1}.

The XRD pattern of composite samples with the addition of 150 and 50 polyacrylates still show a goethite peak with high intensity at 2θ = 18°, 21°, 26°, 33°, 35°, 37°, 40°, 41°, 53°, 57°, 59°, 59°, 61°, 64°. The crystallinity degree of K50 and K150 was 77.27% and 88.37% respectively. This is because there is a residual of goethite that does not bind to the group in polyacrylate. Meanwhile, K300 composites have low intensity and degree of crystallinity (45.78%) because almost all goethites are bound to polyacrylate (Fig. 4).

3.3. Swelling ability

Composite swelling ability is influenced by the mass ratio between goethite and polyacrylate. The K300 composite still can swell even though it is very small compared to its initial precursor, sodium polyacrylate. This is because there is an active side of polyacrylate (–COO– group) which does not interact with goethite (Fig. 5). Composite swelling ability decreases along with the reduced of added polyacrylate, namely K150 (1.53 mg/mg) and K50 (0.95 mg/mg) composites. The more polyacrylate added, the more groups that are not bonded with goethite, so that they can still interact with water [23]. The swelling equilibrium of composite and polyacrylate was achieved at 12 h.

3.4. Adsorption of cations (blue methylene) and anions (phosphates)

There is a difference in the cation and anion adsorption capacity of goethite, sodium polyacrylate, and composites (Fig. 6b). Goethite still has cation and anion adsorption capabilities because it has a variable charge, a charge that depends on pH. In an acidic solution, goethite has an active side of $–Fe–OH^{2+}$ which changes to Fe–OH in an alkaline solution [24]. In contrast to goethite, polyacrylate can adsorb cations through the carboxyl group (–COO–) at alkaline pH. Polyacrylate is difficult to adsorb anion because at acidic pH the active side will be protonated to –COONa. The polyacrylate cation adsorption capacity is higher than goethite because it has more active side [25]. Using a similar volume of adsorbate, the mass of the polyacrylate adsorbent used is half of the goethite mass. This is because sodium polyacrylate (SPA) has a high swelling ability (Fig. 6a).

The two active sides of goethite and polyacrylate are used to adsorb cations and anions in the composite.

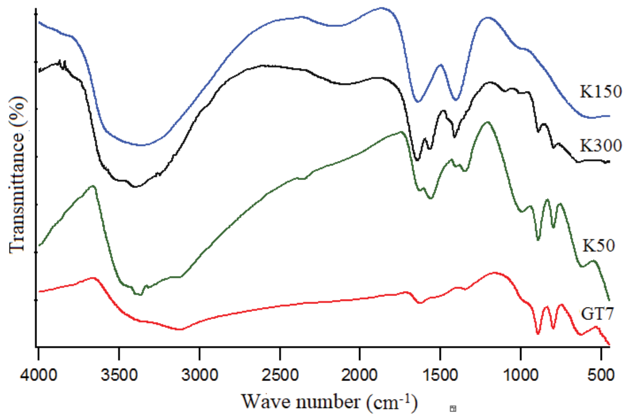

Fig. 3. FTIR spectra of composite.

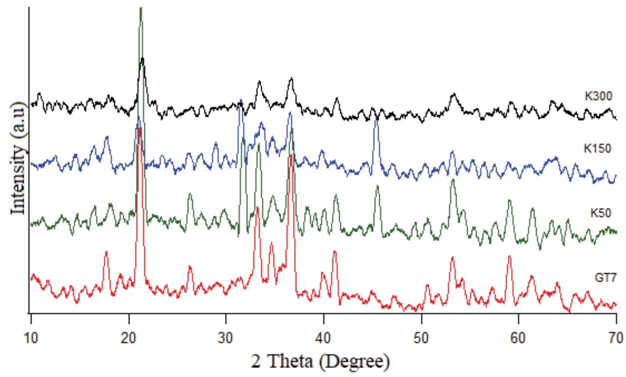

Fig. 4. XRD pattern of goethite and composite.

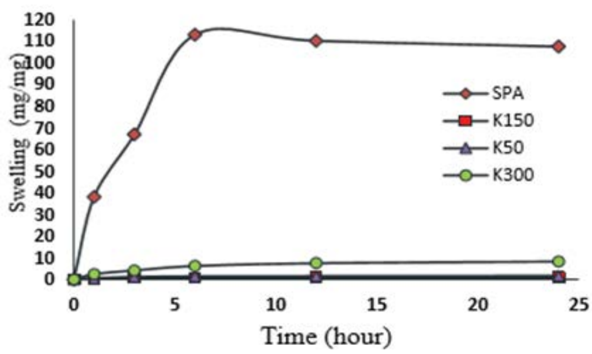

Fig. 5. Composites swelling ability.

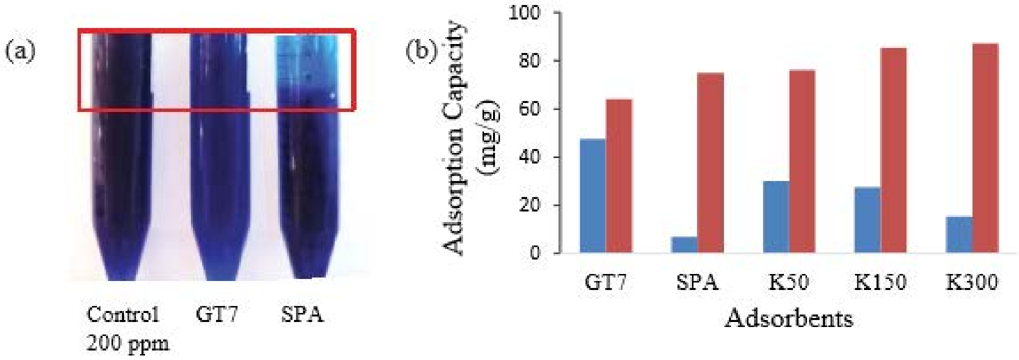

Fig. 6. (a) Adsorption ability of GT7 and SPA and (b) anion and cation adsorption capacity of adsorbents for 24 h.

The composite will adsorb the methylene blue cation on the active side of polyacrylate (–COO–), which is not bound to goethite and adsorbs the phosphate anion through the active side of $-Fe-OH^{2+}$ in an acidic solution. Composites with higher amounts of polyacrylate have a higher ability to adsorb methylene blue. This is related to the –COO– group which will be bound to the goethite. The more polyacrylate is used, the more the –COO– groups are free, so this increases the adsorption of methylene blue cations, and vice versa [26]. The more the amount of polyacrylate, the less the phosphate is adsorbed because of more bonds with goethite, so that the group of $-Fe-OH^{2+}$ is less.

4. Conclusion

The formation of goethite-polyacrylate composite was attributed to hydrogen bonding between goethite and hydroxyl groups of polyacrylate and the Lewis interaction. Goethite-polyacrylate composites can be synthesized using iron and alkaline precursors for 7 d. The K300 composite still has swelling ability compared to K150 and K50 composites, this is due to the more free hydrophilic functional groups to absorb water at low content of goethite, and vice versa. The ratio of goethite and polyacrylate in the composite directly affected the adsorption capacity. The analysis showed that the less polyacrylate is, the better the adsorption of phosphate is, but the amount of polyacrylate will increase the adsorption of methylene blue. This is because the active site of polyacrylate and goethite interacted with positive charges of methylene blue while almost of phosphate anion is only chemically adsorbed on the active side of goethite.

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