Removal phospate-containing detergent wastewater by Mg–Al(NO3) layered double hydroxide

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Abstract. Detergent wastewater contains high phosphate concentrations, so that if the wastewater is directly disposed of into a ditch or river then the wastewater can cause water pollution and eutrophication. Layered double hydroxides (LDHs) are synthetic materials with positively charged pyruvate type coatings of mixed metal hydroxides by chemical precipitation method. The purpose of this study is to find out the efficiency of Mg–Al(NO_3) LDH on phosphate-containing detergent wastewater adsorption. The morphological structure of LDH by the SEM-EDS analysis method shows a loose lamellar structure with a particle size of about 1 μm, and the composition of Mg–Al(NO_3) LDH by the XRF analysis method shows that the Mg and Al elements dominate more than other elements. Batch adsorption experimental conducted for detergent wastewater, which is where in this study the phosphate content was of ca. 51.50 mg / L. The equilibrium time of the adsorption process using Mg–Al(NO_3) LDH is achieved after 60 minutes. The mole ratio of Mg : Al composition of LDH in the adsorption process has slightly affects the decrease in phosphate shown by a mole ratio of 1 : 1, 2 : 1 and 3 : 1 using Mg–Al (NO_3) LDH as adsorbent at dose of 1 g, stirring rate of 100 rpm, 60 minutes, and at room temperature that is equal to 4.15 mg/L, 4.14 mg/L and 4.08 mg/L, respectively. Mg–Al(NO_3) LDH is a promising adsorbent for phosphate removal in detergent wastewater.

1. Introduction

The laundry industry is one of the promising business opportunities in supporting the welfare of the family and regional economy. Laundry industry work processes are simple, namely mixing dirty clothes with detergent, whereas the laundry industry work process also produces detergent wastewater. Wastewater produced from this industry is detergent water which is usually directly discharged to the nearest aquatic environment without further processing. Detergent contain builders (50% by weight, approximately containing phosphate compounds), surfactants (as a detergent base around 15%), bleach (7%), enzymes (2%), soil anti-redeposition agents, foam

regulators, corrosion inhibitors, optical brighteners, dye transfer inhibitors, fragrances (as deodorizer), dyes, fillers and formulation aids [1]. Detergents are important compounds in numerous industrial processes with laundering industry being among their largest consumers. Due to their wide application, detergents are continuously developed to meet higher quality and environmental standards.

Detergent waste produced pollutes the environment, especially high phosphate content which can stimulate the growth of freshwater algal blooms so that it can cause eutrophication and reduce dissolved oxygen in waterways [2]. A large amount of used phosphate finally reaches water environment as diluted waste, which often leads to pollution of the water environment. It is of value to collect the finally disposed phosphates from effluents and drain water before further dispersion and dilution of them in the water environment. Phosphate is recognized as being one of the resources that will be lost in near future. A phosphate recovery processes should be incorporated with a phosphate removal system.

Coagulation–precipitation and biological methods are the most treatment methods for phosphate removal methods that are widely accepted at the industrial level. Extensive research has also been carried out to obtain simpler results and the efficiency of stable phosphate removal. Among these studies, many researchers have developed adsorbents with high selectivity and transfer capacity for phosphate adsorption. Adsorption or ion exchange with inorganic materials, such as layered double hydroxide (LDHs), has attracted intensive attention because of their high effectiveness and low cost operation [3].

Layered double hydroxides (LDHs) as an alternative adsorbent for the removal of anions have been used for phosphate adsorption. LDH is easily synthesized and shows good performance in removing phosphate. In addition, LDH can be easily regenerated [4]. However, studies for phosphate removal from detergent wastewater using LDH are rare because many people still do not know the efficiency and the effective of LDH. This research is to study the performance of Mg–Al (NO3) LDH as adsorbent onto phosphate removal from detergent wastewater. The Mg–Al (NO3) LDH was characterized, and phosphate adsorption by the LDH as a function of adsorbent dosage and molar composition of Mg:Al were subsequently studied.

2. Materials and Method

Detergent wastewater was taken from the equalization tank of laundry home industry in Banjarbaru, South Kalimantan. The detergent wastewater samples were preserved under 4°C to minimize the degradation of wastewater contents. The detergent wastewater was mainly containing high phosphate concentration around ca. 51.50 mg/L. The chemical used in this study including $Al(NO_3)_3.9H_2O$, $Mg(NO_3)_2.6H_2O$, NaOH, and HCl. All chemical used is analytical grade and no need further purification.

2.1. Syntheses of Mg–Al (NO_3) LDH

The Mg–Al (NO_3) LDH with various molar ratio of Mg^{2+}/Al^{3+} is synthesized by using coprecipitation method [5]. Mixed solution of ca. 700 mL containing 0.1 mol of Mg $(NO_3)_2.6H_2O$ and 0.1 mol Al $(NO_3)_3.9H_2O$ (i.e. of molar ratio of Mg^{2+}/Al^{3+} was 1) was added dropwise under vigorous magnetic stirring of 200 rpm into 1500 mL 2 M NaOH solution until well-mixed solution, while heated with temperature of 45±2°C during this process. After that, slurry obtained was reheating at 85°C±2°C for 2 hours under slow mixing of 50 rpm. The slurry was kept in room temperature for around 12 hours, then separated the top solution and bottom solid by using a pipette volume. The solid products were separated by centrifugation and washed with deionized water

several times until the pH reaches constant of 8–9 and the conductivity is constant. The Mg–Al (NO3) LDH was formed were dried at 60°C for 24 hours then were crushed and sieved to the size of 100 mesh for further experiment as adsorbent in adsorption experimental.

2.2. Batch experimental adsorption of phosphate-containing detergent wastewater

Detergent wastewater solution (containing phosphate of ca. 51.50±2 mg/L) is put into a 250 mL plastic bottle. An amount of Mg–Al (NO_3) LDH is added to the solution. The mixture solution is shaker with magnetic stirrer at 100 rpm, room temperature with the specified time. Then the mixed solution is filtered. Finally, the filtrate and residue are collected and stored and then analyzed further.

2.3. Analytical approach

The efficiency phosphate removal (R, %) and the phosphate removal capacity (q_e, mg/g) were calculated from the following equations:

$$R(\%) = \frac{(C_o - C_o)}{C_o} x\ 100 \quad (1)$$

$$q_e = \frac{(C_o - C_o).V}{m} \quad (2)$$

where C_O and C_e is the initial and equilibrium (or residual) concentration of phosphate as P (mg/L), V is the volume of the sample solution (L), and m is the mass of Mg–Al (NO_3) LDH as adsorbent (dry weight, g). All experiments were duplicated to make sure the data reproducibility in this study. The structure morphology properties, thermal behaviour and chemical composition properties of Mg–Al (NO3) LDH have been characterized using scanning electron microscopy (SEM) and X-ray fluorescence (XRF). The surface morphology of the Mg–Al (NO3) LDHs were observed by Scanning electron microscopy (SEM, JOEL JSM-6500F) with energy-dispersive X-ray spectroscopy (EDAX), and Elemental Analysis by Energy Dispersive X-ray Fluorescence (PANalytical's MiniPal 4 energy-dispersive EDXRF bench-top spectrometer) to conclude the identity and quantities of the elements in samples. Moreover, the data from experiment were fitting and figure out by Sigma Plot® version 10 of software. The maximum variation of each adsorption experiment was 5%.

3. Results and Discussion

3.1. Characterization of Mg–Al (NO_3) LDH

The synthesized LDHs were characterized for their chemical composition by XRF analysis, surface area and morphology by SEM analysis. The results of XRF measurements from Mg–Al (NO_3) LDH samples in a ratio of 1 : 1 shows that the dominance of the Mg and Al elements in the sample is the same shown in Table 1. This value is approximately equal to the ratio used for preparing the starting solution (Mg/Al = 2), thus the synthesis process was efficient. Molar ratio of metal in LDHs structure influences ion exchange process. The XRF measurement results from the Mg–Al (NO_3) LDH sample with a ratio of 2: 1 and 3 : 1 shows that the Mg element is more dominant than the Al element in the sample. However, increase in starting Mg/Al ratio did not resulted in dramatic enhancement in final Mg/Al ratio in product, especially the Mg/Al ratio above 3. Shown in Table 1, representatively, final Mg/Al ratio of 1 was 1, ratio of 2 was 1.57 and ratio of 3 was 2.14.

Table 1. Elemental analysis of Various Mg-Al Mol Ratio measured by XRF

Composition of Mg/Al	Component (Conc. Unit %)				
	MgO	Al_2O_3	P_2O_5	CaO	Fe_2O_3
1 : 1	47	47	2,7	0,85	0,33
2 : 1	58	37	2,7	0,94	0,33
3 : 1	64	30	3,3	1,10	0,23

The result of observations with SEM analysis in Figure 1 shows that Mg–Al (NO_3) LDH is loose lamellar-shaped structure. This structure would be better for ions to diffuse and penetrate into the inside of each adsorbent particle and be trapped in LDH [6]. Figure 1 shows that Mg-Al (NO_3) LDH has an irregular sheet shape with a particle size of about 10 µm. This result is almost in accordance with the average size of LDH particles is 9.24 µm [5]. LDHs with higher Mg/Al molar ratio have more positive sites (Mg^{2+} ions) in the layers and a larger concentration of interlayer anion is required.

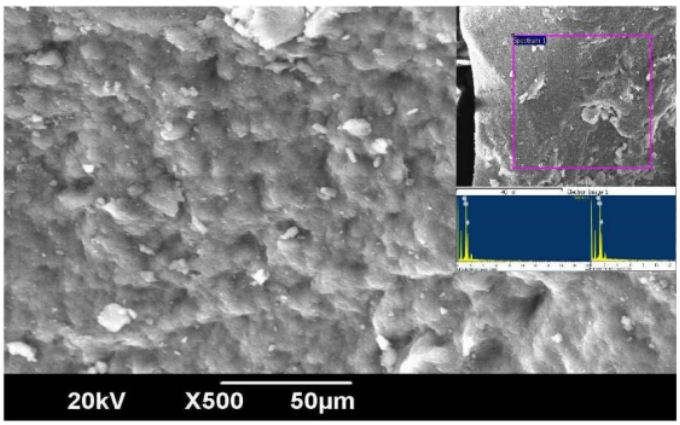

Figure 1. SEM images of Mg/Al LDH (C_O P = 51.50 mg/L; pHe = 8.0 ± 0.2; LDHs dose = 1 g/L, room temperature, Mg/Al ratio of 3)

3.2. Batch adsorption using Mg-Al (NO_3) LDH as adsorbent

3.2.1. Effect of contact time

Figure 2 can be seen that the ability of adsorbents to adsorb phosphate content in detergent wastewater is higher with the length of contact time, the longer the contact time, the more phosphate concentration is adsorbed. However, this phenomenon is limited by the saturation state, where the Mg–Al (NO_3) LDH surface has been blocked by impurities or adsorbates, thus decreasing the adsorbing power. Detergent waste phosphate content is 51.50 mg/L. While the phosphate levels for LDH with a mole ratio of 1 : 1, 2 : 1 and 3 : 1 within the first of 30 minutes. The fast adsorption in the beginning due to the active site of the LDH was vacant and the abundant protonated active sites combined with the highly ordered porous matrix of LDH adsorbent. In addition, the phosphate anions

can easily interact with the surface adsorption sites adequately and diffuse from bulk solution into the internal of adsorbent surface [7].

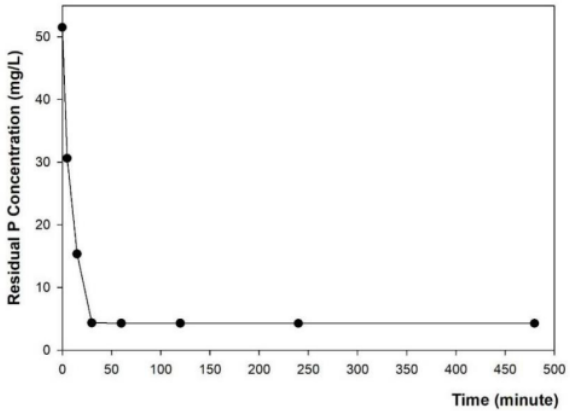

Figure 2. Equilibrium time determination (C_O P = 51.50 mg/L; pHe = 8.0 ± 0.2; LDHs dose = 1 g/L, room temperature, Mg/Al ratio of 3)

Afterward, the adsorption rate was slow and gradually saturated by the adsorbed. However, the adsorption equilibrium was achieved by 60 minutes, then the 60 minutes time was selected for determining the maximum adsorption capacity for the next experiment. Based on the data obtained the most optimum results are shown in Mg–Al ratio was 3 : 1 within a mixing time of 60 minutes. LDH in a ratio of 3 : 1 with contact time of less than 1 hour can adsorb up to 90% with the residual phosphate concentration of ca. 4.08 mg/L. Phosphate uptake in LDH will increase with increasing time and reach equilibrium in less than 1 hour [8]. In general, it can be concluded that LDH is able to adsorb phosphate content in detergent wastewater.

3.2.2. Effect of Mg/Al ratio composition

Based on Figure 3 it can be seen that the decrease in phosphate levels is increasing along with the increasing molar ratio of Mg–Al (NO_3) LDH as an adsorbent. The highest adsorption capacity of phosphate is obtained at a 3: 1 mole ratio and at 60 minutes with an adsorption capacity of 11.84 mg/g. Metal ratio considered important as it could determine surface charge for on phosphate uptake because it interacts with negatively charge. As mention, the content of divalent/trivalent metal would determine positive charge density of LDH [9]. In addition, the 3 : 1 mole ratio shows greater adsorption capacity, because phosphate can be adsorbed on the external and interlayer surfaces [10]. Increase of Mg/Al ratio also would increase the interlayer spacing and adsorption capacity, since the interlayer spacing was the critical parameters for anions adsorption [11, 12].

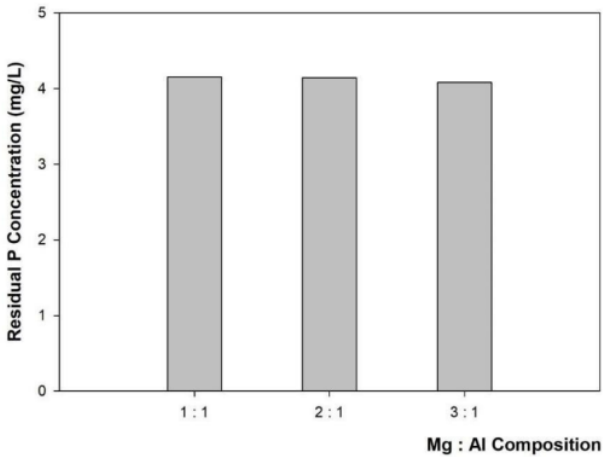

Figure 3. Mg/Al mole composition onto P adsorption (C_o P = 51.50 mg/L; pHe = 8.0 ± 0.2; LDHs dose = 1 g/L, room temperature)

3.2.3. Effect of adsorbent doses of Mg-Al (NO3) LDH

The increasing dose of adsorbent used as shown in Figure 4, the adsorption capacity will also increase. This is due to the increased surface area of adsorption along with the weight of the adsorbent so as to produce a greater adsorption capacity [13]. A finer size adsorbent will have more surface area and after activation the pores will open more so that pollutants will be absorbed into the adsorbent which causes phosphate levels to decrease. LDH has a loose lamellar structure (flattened) so that the contact area of large particles that are capable of metal ions can diffuse and penetrate into the inside of each adsorbent particle and are trapped in LDH [6]. Slightly increasing Mg–Al (NO_3) LDH adsorbent dosage after 1 g/L was related to maximum saturated adsorption of active sites during the adsorption process. Using Mg–Al (NO_3) LDH as adsorbent at dose of 1 g, stirring rate of 100 rpm, 60 minutes, and at room temperature the residual phosphate concentration is equal to 4.08 mg/L (around 91% phosphate removal).

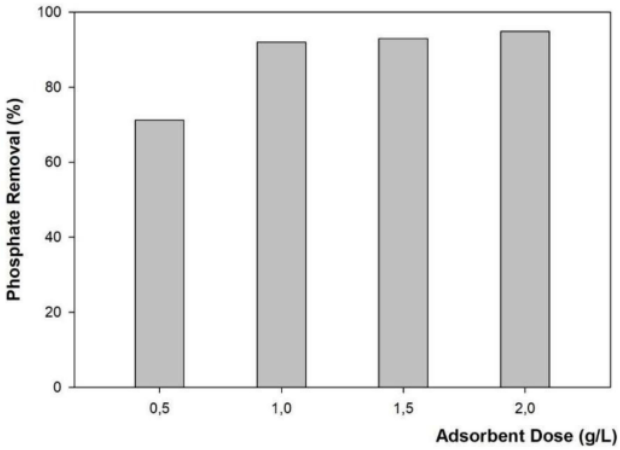

Figure 4. The effect of LDH adsorbent dosage on phosphate removal (C_O P = 51.50 mg/L; pH_e = 8.5±0.2; stirring rate of 100 rpm; room temperature, Mg/Al ratio of 3)

4. Conclusions

Mg–Al (NO_3) LDH with different molar ratio of Mg/Al were well synthesized by co-precipitation method. SEM analysis results obtained loose lamellar Mg–Al (NO_3) LDH structure (flat) in which this structure will be good for metal ions can diffuse and penetrate into the inside of each adsorbent particle and trapped in Mg–Al (NO_3) LDH. The XRF measurement results from the Mg–Al (NO_3) LDH in a ratio of 2 : 1 and 3 : 1 indicate that the Mg element is more dominant than the Al element in the sample. Mg–Al (NO_3) LDH showed up high efficiency (more than 90%) in removing phosphate from detergent wastewater. The optimum pH for phosphate removal process was around 8.5±0.2. The process of phosphate adsorption by LDH with a ratio of Mg–Al (NO_3) LDH 3 : 1 is the most optimum because it has decreased phosphate levels to 4.08 mg/L within equilibrium time of 60 minutes. The results demonstrated that Mg–Al (NO_3) LDH as potential adsorbent for phosphate removal and expand the application of LDH technology.

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