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Intercalation of Zn/Al Layered Double Hydroxides with Keggin Ion as Adsorbent of Cadmium(II)

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Abstract. Layered double hydroxides containing Zn^{2+} and Al^{3+} ions with formula $[Zn_{1-x}Al_x(OH)_2]^{x+}[(NO_3^-)_{x/2}\times mH_2O]$ has been prepared using coprecipitation method at pH 10 to form Zn/Al layered double hydroxides (LDH). Zn/Al LDH then intercalated with Keggin ion of $[\alpha\text{-}PW_{12}O_{40}]^{3-}$ to form intercalated Zn/Al LDH. Materials were characterized using X-Ray and IR analyses. Zn/Al LDH and intercalated Zn/Al was applied as adsorbent of Cd(II) using batch system. Analysis of X-Ray and IR on Zn/Al LDH and intercalated Zn/Al with $[\alpha\text{-}PW_{12}O_{40}]^{3-}$ showed that synthesis of Zn/Al was successfully conducted which was indicated from diffraction at 11 deg and vibration at around 400-500 cm^{-1} for Zn-O and Al-O vibrations. Analysis of pH PZC on LDH showed that materials have pH PZC at 5. Adsorption of Cd(II) on Zn/Al LDH and intercalated Zn/Al LDH with $[\alpha\text{-}PW_{12}O_{40}]^{3-}$ at showed that intercalated Zn/Al LDH with Keggin ion of $[\alpha\text{-}PW_{12}O_{40}]^{3-}$ has higher adsorption capacity than Zn/Al LDH without intercalation.

INTRODUCTION

The use of many chemical substances in industrial processes resulted main product and by-products. By-products are produced in small amounts and caused accumulation in the environment. One of the important by-products are metal ions which was contamination in natural water, soil, and plant. Metal ions especially heavy metals are carcinogens causes various diseases. Therefore, treatment of metal ions is crucial for environmental security and human health.

Various methods have been developed to remove metal ions from solution such as adsorption [1-2], ion exchange [3], membrane material [4], and precipitation [5]. Adsorption is one of the simple and fast method for removal metal ions due to high efficiency and capacity [6]. The important things in the adsorption of metal ions is adsorbent. Adsorbent can be classified as organic and inorganic adsorbent with their advantages and disadvantages. Inorganic materials such as bentonite [7], kaolinite [8], zeolite [9], and also layered double hydroxides [10-12] were used to eliminate metal ions form solution.

Layered double hydroxides (LDH) with general formula $[M^{2+}_{(1-x)}M^{3+}_x(OH)_2][A^{m-}_{(x/m)}]\cdot nH_2O$ consists of divalent metal cation M^{2+}, trivalent metal cation M^{3+}, and anion A^{m-}. Structural investigation of LDH showed similarity with clay mineral and containing positive charge layer [13-14]. LDH is two-dimension low cost inorganic material with

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excellent anionic exchange capacity. Recently, the use of LDH is sharply increased for adsorbent, catalyst, and ion exchange.

LDH has effective adsorbent of dyes and metal ions. Several dyes such as congo red, procion red and methylene blue were efficiently removed from solution using Mg/Al [15], Ca/Al [16], and Zn/Al LDH [17]. Metal ion such as heavy metals also efficient removed using LDH as adsorbent. Copper and lead were adsorbed using Mg/Al LDH [18]. Mg/Al LDH was intercalated with organic acid anions in order to increase adsorption capacity of metal ions on LDH [19]. Intercalated LDH was also used as adsorbent to decrease heavy metal ions. Zn/Fe LDH intercalated with citrate anion showed efficient adsorption for lead(II) from solution and adsorption was fitted well with the pseudo-second order kinetic model and Langmuir isotherm model [20].

Recently the development of intercalated LDH is sharply increased due to flexibility of LDH with various anions. Inorganic and organic anions were widely used as pillaring agent for many LDH. Organic anions also amino acid [21] were successfully used for intercalant for LDH. On the other hand, inorganic anions such as chlorine, cyanide and sulfide were frequently used for intercalation of LDH [22-23]. Large sizes anion such as polyoxometalate were applied for intercalation of LDH including Keggin ions, Anderson ions, Dawson ions and also Lacunary type ions [24]. The gallery of LDH was increased significantly by using this anion due to increasing interlayer distance. Intercalated materials with polyoxometalate ions were also applied for adsorption of heavy metal ions form solutions [25].

In this research Keggin ion of $[\alpha\text{-PW}_{12}O_{40}]^{3-}$ was used as intercalant of Zn/Al LDH under nitrogen condition. Intercalated Zn/Al LDH was used as adsorbent of cadmium(II). Several factor that influencing adsorption processes such as adsorption time, concentration of metal ion, and temperature were studied. Stability of Zn/Al LDH was performed using pH pzc analysis and effect of various pH on Zn/Al LDH.

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EXPERIMENTAL SECTION

Chemical and Instrumentations

Chemicals was used directly after purchased without further purification from Merck and Sigma Aldrich such as zinc nitrate, aluminum nitrate, sodium hydroxide, sodium carbonate, sodium tungstate, hydrochloric acid, diethyl ether, and disodium phosphate. Water was supplied from Integrated Research Laboratory, Universitas Sriwijaya using water system Purite® ion exchange pH 7. FTIR spectrophotometer was conducted using Shimadzu FTIR Prestige-21 using KBr disk and scanning was performed at wavenumber 400-4000 cm-1. XRD was performed using Rigaku Miniflex-600 and scanning was conducted at 0.1 deg min-1. Analysis of cadmium(II) was carried out using UV spectrophotometer double beam EMC-61PC after complexation using 1,10-phenanthroline.

Synthesis of Zn/Al LDH

Synthesis of Zn/Al layered double hydroxides was conducted according to K. Abderrazek et.al (2016) using co-precipitation method at pH 10 [26]. Solution of zinc nitrate (0.75 M, 10 mL) and aluminum nitrate (0.25 M, 10 mL) was mixed with slowly stirring. Sodium hydroxides (2 M, 10 mL) was added dropwise to form white gel. White gel was kept at 90 ^{o}C overnight then wash with water several times. Zn/Al LDH was obtained after kept white gel at 120 ^{o}C overnight. Characterization of Zn/Al LDH was performed using XRD powder analysis and IR spectroscopy.

Synthesis of $H_3[\alpha\text{-PW}_{12}O_{40}]\cdot nH_2O$

Synthesis of $H_3[\alpha\text{-PW}_{12}O_{40}]\cdot nH_2O$ was conducted as follow : A sodium tungstate (125 g) and 20 g of disodium phosphate were dissolved using 187.5 mL of boiling water. Hydrochloric acid (100 mL) was added slowly to solution with constant stirring and temperature was kept around 70 ^{o}C for 2 hours. Solution then kept at room temperature and solution was transferred to separation funnel. Diethyl ether (75 mL) was added to solution. After shaking, three layers remain and a little amount of water was added to dissolve the remaining of sodium chloride. The acid-ether complex in the lower layer was collected following the evaporation and recrystallization using water to produce $H_3[\alpha\text{-}PW_{12}O_{40}]$ [27]. Polyoxometalate was characterized using FT-IR spectroscopy and X-ray powder analysis.

Layered Double Hydroxides Intercalated Polyoxometalate

Intercalation of Zn/Al LDH with Keggin ion $[\alpha\text{-}PW_{12}O_{40}]^{3-}$ was carried out under nitrogen condition by ion exchange method. Zn/Al LDH was suspended with 1 M sodium hydroxide and Keggin ion was added by vigorous stirring under nitrogen atmosfer. The mixture was stirred overnight. Suspension was filtered to obtain solid bulky material and washed with water several times. Solid bulky material was dried at 110 °C for 3 days. Characterization of intercalated material was performed using XRD powder analysis and identification using FTIR spectrophotometer.

pH PZC analysis

pH point zero charge (pH PZC) was conducted using sodium chloride 0.1 M. pH solution of sodium chloride 0.1 M was adjusted from pH 1 to 10 by addition of sodium hydroxide or hydrochloric acid 0.1 M. in the series of sodium chloride solution with various pH, Zn/Al LDH was added. The mixtures were stirred for 24 hours then pH of filtrate was determined by pH meter. pH PZC was obtained by comparison initial and final pH solution.

Adsorption Studies

Adsorption of cadmium(II) was performed using intercalated material and Zn/Al LDH as control. Adsorption was studied through effect of pH, adsorption times, initial concentration of cadmium(II), and temperatures. pH of adsorption system was studied by addition of sodium hydroxide or hydrochloric acid to adsorption system. pH was adjusted at 1, 3 4, 5, 7, and 9. Analysis of filtrate after adsorption was carried out using UV at wavenumber 326 nm.

Kinetic parameter was calculated based on data of adsorption time. Adsorption time was conducted at 10, 20, 30, 40,50, 60, and 90 minutes. Thermodynamic parameter was calculated based on data of initial concentration of cadmium(II) and temperatures. Initial concentration of cadmium(II) was 0,5, 1, 2, 3, 5, 7, and 10 mg/L and variation of temperatures was 30, 40, 50, 60, and 70 °C.

RESULTS AND DISCUSSION

XRD powder pattern of Zn/Al LDH, $[\alpha\text{-}PW_{12}O_{40}]^{3-}$ Keggin ion, and intercalated Zn/Al LDH are shown in Fig. 1. Fig. 1a shows specific diffraction of Zn/Al LDH. The interlayer material of Zn/Al was identified at diffraction 11 deg. Other diffractions of LDH was detected at 2θ X, 31, 37, 46, 60, and 61 deg, which are attributed to diffraction of Zn and Al oxides [28].

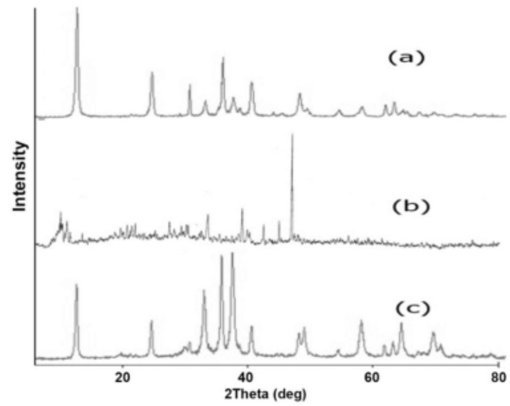

FIGURE 1. XRD powder patterns of ZnAl LDH (A), Keggin type polyoxometalate $K_3[\alpha\text{-}PW_{12}O_{40}]$ (B), and intercalated ZnAl with Keggin ion (C).

Diffraction of Keggin ion $[\alpha\text{-}PW_{12}O_{40}]^{3-}$ was appeared with sharp diffraction at 5-7 deg and that is assigned as unique diffraction of Keggin ion. Intercalated Zn/Al LDH with $[\alpha\text{-}PW_{12}O_{40}]^{3-}$ ion showed that characteristic vibrations at 35-38 deg and 58 deg. Interlayer gallery of Zn/Al LDH intercalated with $[\alpha\text{-}PW_{12}O_{40}]^{3-}$ was increased 0.06 Å at 38 deg. Probably lower increasing of interlayer space is due to horizontal position of Keggin ion toward Zn/Al LDH. If position of Keggin ion in interlayer Zn/Al about >3 Å than vertical position of intercalation was achieved. These diffractions are indicated that Keggin ion was successfully intercalated into Zn/Al LDH in horizaontal position. FTIR spectrum of Zn/Al LDH, $[\alpha\text{-}PW_{12}O_{40}]^{3-}$ Keggin ion, and intercalated Zn/Al LDH are presented in Fig. 2.

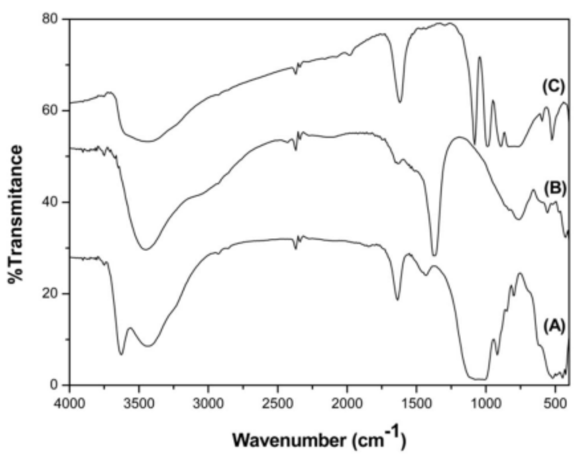

FIGURE 2. FTIR Spectrum of intercalated ZnAl with Keggin ion (A), ZnAl LDH (B), and Keggin type polyoxometalate $K_3[\alpha\text{-}PW_{12}O_{40}]$ (C).

Fig. 2A shows intercalated Zn/Al LDH has broad vibration at 1000-1100 cm^{-1} due to mix Zn-Al-O vibrations. Keggin ion was intercalated into Zn/Al LDH was identified through vibration of Keggin ions around 800-900 cm^{-1}. Zn/Al LDH in Fig. 2B has vibration at 470.6 cm^{-1} and 424 cm^{-1} which were assigned as vibration of Al-O and Zn-O. Water of crystallization was identified at 3448.7 cm^{-1} [29]. Fig. 2C showed that vibration of Keggin ion P-O, W=O and W-O-W were appeared at 1080, 987, and 894 cm^{-1}, respectively.

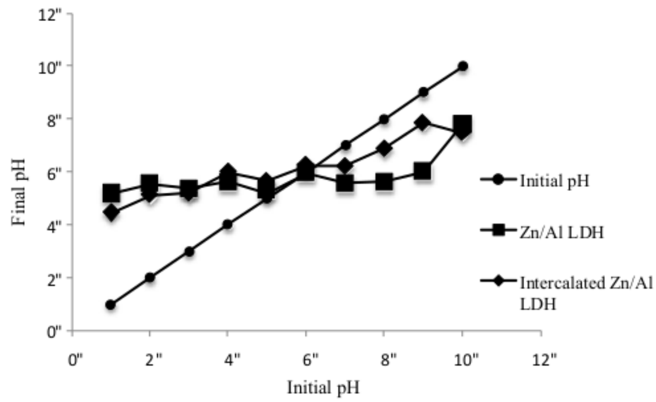

FIGURE 3. pH PZC graph

Determination pH PZC of Zn/Al LDH was resulted graph with joining three point at pH 6. The properties of Zn/Al LDH at pH before 6 indicated positive charge material was dominated on Zn/Al LDH. On the other hand, negative charge was dominated at pH above 6. Adsorption using Zn/Al LDH was performed at pH 6. At that point, adsorption was expected on surface material of Zn/Al LDH. Adsorption of Cd(II) on Zn/Al LDH was conducted at various adsorption time as shown in Fig. 4.

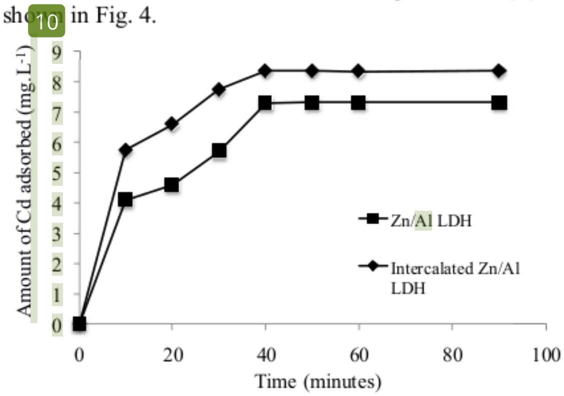

FIGURE 4. Effect of adsorption time on adsorption Cd(II) using ZnAl LDH and intercalated ZnAl

Adsorbent for Cd(II) was Zn/Al intercalated Keggin ion and Zn/Al LDH as control. Fig.1 showed that both adsorbents reach optimum adsorption after 50 minutes. Adsorption of Cd(II) on Zn/Al LDH and intercalated Zn/AL before 50 minutes' almost increase by increasing adsorption time. Fig. 4 also shows intercalated material has higher adsorption amount than material before intercalation. The data of adsorption in Fig. 4 was calculated to obtain kinetic parameter using Langmuir Heinselwood equation [30-31] to produce adsorption rate constant as shown in Table 1.

TABLE 1. Kinetic parameter

Adsorbent	Adsorption Rate Constant (min^{-1})	R^2
Zn/Al LDH	0.0164	0.8045
Intercalated Zn/Al	0.0479	0.8841

The data in Table 1 showed that intercalated Zn/Al LDH with Keggin ion of $[\alpha\text{-}PW_{12}O_{40}]^{3-}$ was faster than Zn/Al LDH. Interlayer space after intercalation was increased and resulted adsorption was occurred not only on surface material but also on interlayer intercalated material.

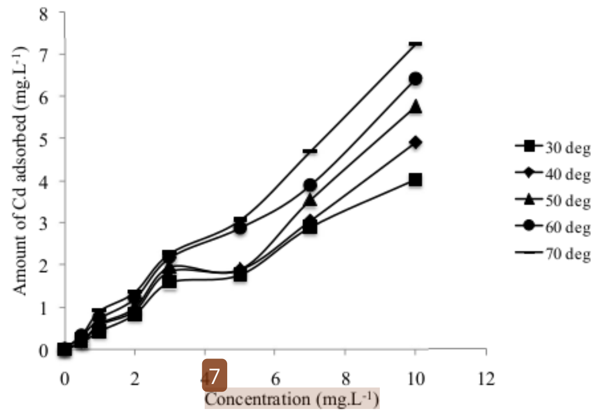

FIGURE 5. Effect of initial concentration and temperature on adsorption of Cd(II) using ZnAl LDH

Adsorption of Cd(II) on Zn/Al LDH and Zn/Al intercalated $[\alpha\text{-}PW_{12}O_{40}]^{3-}$ were carried out at various concentration of Cd(II) and temperatures. The results are shown in Fig. 5 and Fig. 6.

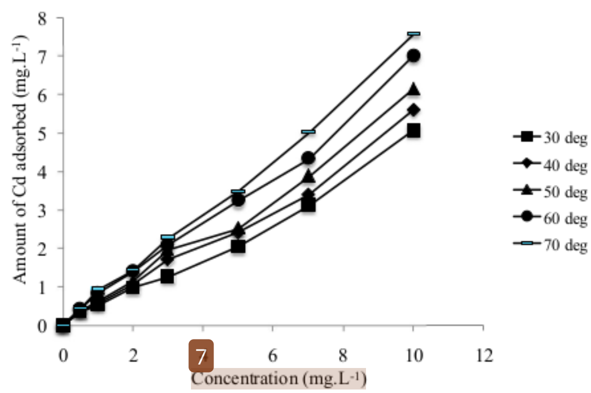

FIGURE 6. Effect of initial concentration and temperature on adsorption of Cd(II) using intercalated Zn/Al LDH

Fig. 5 and Fig. 6 showed that by increasing temperature will increase the amount of Cd(II) adsorbed onto materials. Zn/Al LDH intercalated with $[\alpha\text{-}PW_{12}O_{40}]^{3-}$ has slightly higher adsorption capacity than Zn/Al LDH without intercalation at the same temperature.

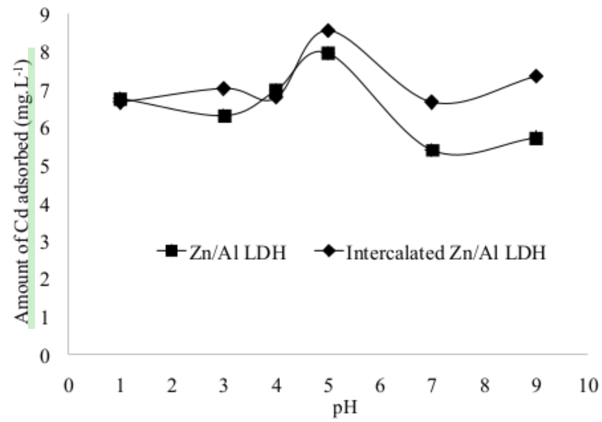

FIGURE 7. Effect of pH on adsorption of Cd(II)

Effect of pH of adsorption of Cd(II) on Zn/Al LDH and intercalated Zn/Al are shown in Fig. 7. Data in Fig. 7 showed that both materials Zn/Al LDH and intercalated Zn/Al have optimum adsorption pH at 5. That point was similar with point of pH PZC. Optimum adsorption was achieved because materials have no charge and physical adsorption was occurred in this research.

CONCLUSION

Effect of pH of adsorption of Cd(II) on Zn/Al LDH and intercalated Zn/Al are shown in Fig. 7. Data in Fig. 7 showed that both materials Zn/Al LDH and intercalated Zn/Al have optimum adsorption pH at 5. That point was similar with point of pH PZC. Optimum adsorption was achieved because materials have no charge and physical adsorption was occurred in this research.

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