



Removal of Lead from Aqueous Solution by Adsorption using Magnesium Aluminium Hydrogenphosphate Layered Double Hydroxides

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ABSTRACT

Layered double hydroxide with molar ratio of 4 (MAN 4) was synthesized by co-precipitation and followed by hydrothermal method. The compound was then later going through ion exchange with K_2HPO_4 for 48 hours to produce $MgAlHPO_4$ (MAHP 4). The solid produced were characterized using X-ray diffraction (XRD) and Fourier Transform Infrared spectroscopy (FTIR). Adsorption of lead solution by MAHP 4 was carried out using batch experiment by mixing the lead solution and the solid of layered double hydroxide. The effects of various parameters such as contact time, pH, adsorbent dosage and initial concentration were investigated. The optimum pH for lead removal was found to be at pH of 5 and the optimum time of lead removal was found at 2 hours. The isotherm data was analysed using Langmuir and the correlation coefficient of 0.998 was obtained. The maximum adsorption capacity, Q_0 (mg/g) of 500 mg/g was also recorded from the Langmuir isotherm. The remaining lead solution was determined by using EDXRF (Energy Dispersive X-Ray Fluorescence spectrometry) model MiniPal 4 (PAN analytical). The results in this study indicate that MAHP 4 was an interesting adsorbent for removing lead from aqueous solution.

| Layered Double Hydroxide (LDH) | adsorption | lead removal | anion exchange |

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1. INTRODUCTION

The term of heavy metals is refers to any metallic element that has a relatively high density and is toxic or poisonous at low concentration [1]. Heavy metals that are produced and released during domestic, agricultural and industrial activities can create a serious hazard to the environment [2]. Heavy metals discharged into the environment have been increased continuously as a result of the rapid development of various types' industrial activities and technologies; carry out direct or indirect impendence to environment and public health because of their toxicity and bioaccumulation in the food chain and persistence in the nature. Heavy metals can accumulate in living organism and causing disorders and various diseases which the like of chromium that can caused serious ailment [3].

The heavy metals like lead, copper, cadmium, zinc, nickel, chromium, mercury are among the most familiar pollutants found in industrial effluents and are non-biodegradable and harmful even at low concentration [4]. Lead is released into natural waters from various industrial activities such as oil refining, paint, metal plating, pigment producing and battery manufacturing. Lead can accumulates mainly in bones, brain, kidney and muscles and can causes serious disorders like anaemia, kidney diseases, nervous disorder and sickness even death [5].

Therefore, the removal of heavy metals from wastewater and water are important to protect a public health.

Heavy metals can be removed using several methods such as precipitation [6], coagulation, chemical precipitation, adsorption [7], ozonation, biological treatment [8], membrane filtration and reverse osmosis [9]. Recently, adsorption has becoming a widely used technique due its simplicity, potential to regeneration and sludge-free operation [10]. Moreover it can be attractive technique if the adsorbent that used can be made cheaply and readily used.

Layered double hydroxides also known as hydrotalcite-like compounds or anionic clays, have received much attention in the past decades due to their wide spread applicability. LDH have positively charged layers of metal hydroxides and the anions and water molecules are located between the layers. The positive charges that are produce from the isomorphous substitution of divalent cations and trivalent cations, are counter balanced by anions located between the layers [11]. LDHs have a general formula of $[M^{2+}_{1-x}M^{3+}_x(OH)_2][A^{n-}_{x/n}.mH_2O]$, where M^{2+} and M^{3+} are divalent and trivalent metal cations, respectively, A is the anions, and x is ratio $M^{3+}/(M^{2+} + M^{3+})$ [12]. The anions between the layers can be polymers, organic dyes, surfactants and organic acids [13].

Many substances in effluents wastewater containing pollutants carry positive and negative charges. The LDH anion exchange ability, large surface area and regeneration ability ensures that this adsorbent can be effectively utilized in wastewater purification. Therefore, layered double

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hydroxide was used in our work to optimize the removal of lead from aqueous solution.

$$\frac{C_0 - C_t}{C_0} \times 100 \% \quad (1)$$

2. EXPERIMENTAL

2.1 Preparation of Layered Double Hydroxide

The co-precipitation method was used for the preparation of the nitrate precursors. In the preparation of Mg-AlNO₃, an aqueous solution of Mg (NO₃)₂·6H₂O (0.1M) was added to Al (NO₃)₃·9H₂O (0.025 M) to give Mg²⁺/Al³⁺ with a ratio of 4. An aqueous solution of NaOH (1M) was added to the mixture drop wise, with vigorous stirring at room temperature and the pH was adjusted simultaneous to 10.0 ± 0.02. The co-precipitation method was conducted under a stream of nitrogen gas to avoid, or at least minimize contamination by atmospheric carbon dioxide. The slurry was then aged at approximately 70°C for 24 hours in a thermostated oil bath shaker (hydrothermal method). The precipitate formed was cooled then filtered and washed with excess deionized water and dried at 70°C in an oven for 48 hours. The LDH was then ground by used of a mortar pestle and keep in sample bottles for further used and characterized

Preparation compound by used of anion exchange reactions were carried out at room temperature with approximately 1 gram of the LDH was suspended in a 0.1 M K₂HPO₄ solution and stirred for 48 hours at a pH 9. The solid was then filtered and washed several times with deionized water and then dried in an oven at 70°C for 24 hours.

2.2 Characterization of Layered Double Hydroxide

X-ray diffraction (XRD) pattern of the sample was characterized by using a Shimadzu XRD-6000 diffractometer, with Ni-filtered Cu-Kα radiation (λ = 1.54 Å) at 40 kV and 200 mA. Solid samples were mounted on alumina sample holder and basal spacing (d-spacing) was determined via powder technique. Samples scan were carried out at 10-60°, 2 θ/ min at 0.003° steps.

FTIR spectrum was obtained using a Perkin Elmer 1725X spectrometer where samples will be finely ground and mixed with KBr and pressed into a disc. Spectrums of samples were scanned at 2 cm⁻¹ resolution between 400 and 4000 cm⁻¹.

2.3 Batch Adsorption Experiment

Lead solution of 1000 ppm purchased from Merck was used for the adsorption experiment in this study. The batch experiments were carried out using 0.015 g sorbent dosage was put into 25 mL of 100-400 mg/L solutions of the lead. The amount of lead adsorbed onto the compounds (%) was calculated as:

Where C₀ is the initial lead concentration (mg/L), C_t is the concentration of lead (mg/L) at equilibrium time, t. The lead solution is filter through 0.45 μm micro fibre filter attached to a 10 ml syringe. The concentration of lead in the solution was measured using EDXRF (Energy Dispersive X-Ray Fluorescence Spectrometry). Adsorption isotherm was recorded over the concentration range between 100 mg/L and 400 mg/L of lead solutions in series of 100 ml Schott bottles containing 25 mL solution of each concentration. All the experiments were carried out in duplicates.

3. RESULTS & DISCUSSION

3.1 Characterization of Layered Double hydroxide

The XRD patterns of MAN 4 prepared by anion exchange method with phosphate are presented in Figure 1. As shown in the Figure 1, original MAN 4 indicate crystallinity with d-spacing of 7.9 Å and the interlayer spacing of compound recorded at 4.1 Å. The XRD pattern after anion exchange showed that the d-spacing and interlayer spacing were recorded at 7.8 Å and 3.8 Å, respectively. The crystallinity of MAHP 4 is lower than MAN 4 as shown by broadening of the lines and decrease in intensity. It was reported that LDHs with simple anions can have basal spacing in the range 7.4 - 8.2 Å and depend on the kind of anions [4].

The FTIR patterns of MAN 4 prepared by anion exchange with phosphate are presented in Figure 2. As shown in the Figure 2, original MAN 4 compound showed very intense band located approximately around 1383 cm⁻¹ which attributed to NO₃⁻ vibration groups [14]. The band at 3440 cm⁻¹, 1625 cm⁻¹ and 825 cm⁻¹, are corresponds to vibration of hydroxyl groups, vibration of water and vibration of planar lattice hydroxyl group, respectively. FTIR pattern for the compound prepared by used of anion exchange with phosphate showed a new bands related to phosphate groups at 1220 cm⁻¹, 1050 cm⁻¹, 870 cm⁻¹ and 550 cm⁻¹ which attributed to the orthophosphate of (P-OH) and PO₄³⁻, vibration respectively [15]. Layer charge compensation was completed by a small amount of NO₃⁻ anions, as confirmed by the weak band at 1383 cm⁻¹. The broadening and dissymmetry of the band was also observed due to the characteristic of hydroxyl groups. The broadening of the band is due to the establishment of hydrogen bond between the phosphate groups and water molecules of the interlayer space [16].

3.2 Calibration of Lead Using EDXRF

The calibration graph for lead solution was measured using EDXRF (Energy Dispersive X-Ray Fluorescence spectrometry) model MiniPal 4 (30 kV and 0.150 mA) in the range between 20 ppm to 400 ppm. 5 ml of sample was

measured using pipette and placed in cup holder by used of 6.5 μm thin Mylar film. The reading from XRF used was count per second (cps) unit. From the data, the CPS was plotted against concentration of lead solutions. The correlation coefficient value for the calibration graph is 0.998. The detector used in this study is high-resolution Si drift detector. Generally, this technique may improve the

low atomic elements intensities such as beryllium until high atomic elements like uranium. The MiniPal4 consist 2048 multi-channel analyzer was used to determine the present of elements in the sample. EDXRF is non-destructive method and it's suitable for used with solid, liquid or powdered samples. The analyzing process was fast and highly accurate.

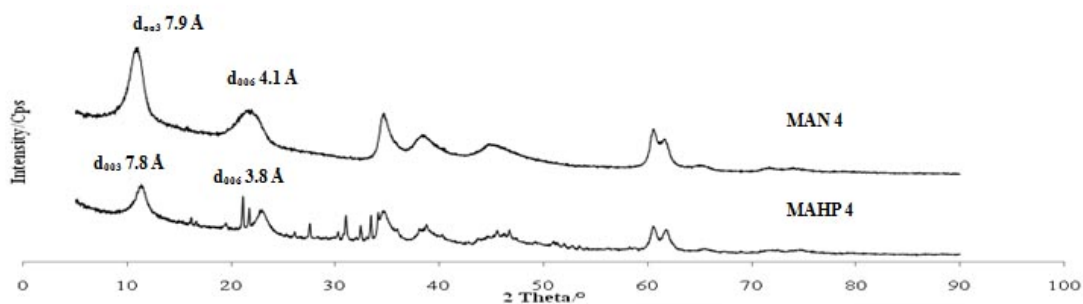


Fig. 1 XRD pattern of MAN 4 and MAHP 4

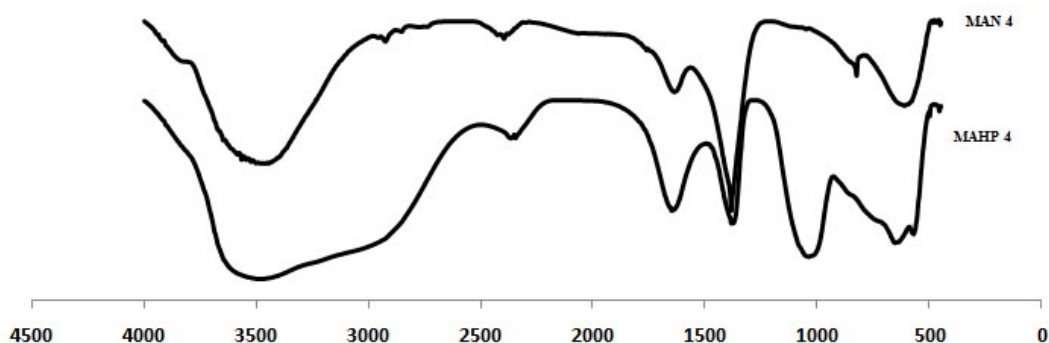


Fig. 2 FTIR pattern of MAN 4 and MAHP 4

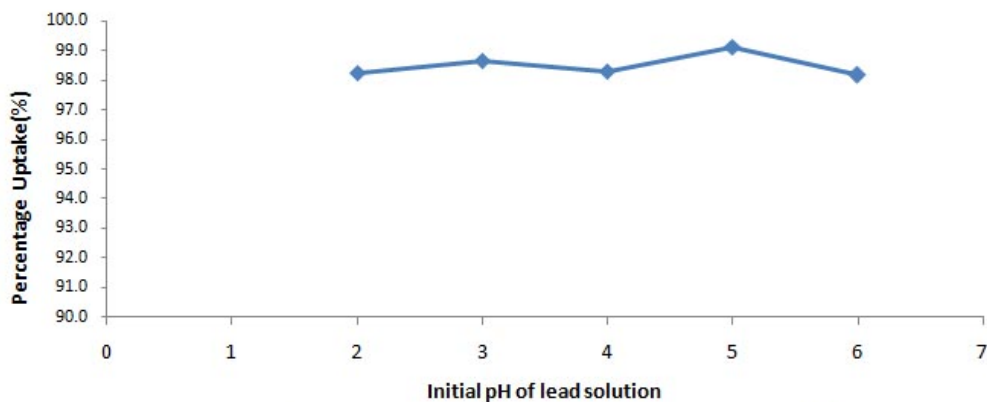


Fig. 3 The effect of pH on the removal of lead solution using MAHP 4

3.3 Effect of pH

The effect of pH on the removal of lead was carried out at a fixed initial concentration of lead (100 ppm) and LDH dosage of 0.03 g for 2 hours of contact time. The range of pH between 2 and 6 were prepared in this study. The range was selected because the lead will be precipitated at high pH [17]. At the pH values which is higher than 6.0, both ion exchange and aqueous metal hydroxide formation may become significant mechanism in the removal process of metal [18]. As shown in the Figure 3, it can be observed that the maximum percentage of lead removal from aqueous solution optimized at pH of 5. The percentage removal at this point is 99.1 %. The removal of lead increased with increasing pH from pH 2 to pH 5 and began to decrease at pH 6 is 98.2 %. When pH of the solution is low, the increase of pH is related to the slight dissolution of LDHs. When the pH of solution is high, the decrease of pH is related to the direct sorption of OH^- from the solution on LDHs samples [19]. The pH solution of 5 subsequently selected for other optimization experiments in this study.

3.4 Effect of Contact Time

The adsorption experiments to evaluate the contact time effect on removal of lead using MAHP 4 was carried out ranging from 15 minutes to 6 hours. The experiments were conducted under the standard conditions of: temperature; 298K, pH 5.0 and the concentration lead solution; 100 ppm and 200 ppm. As shown in Figure 4, the amounts of lead removed increased rapidly within 30

minutes and remained constant after 2 hours indicating attained an equilibrium state. At the contact time of 2 hours, the lead removal (%) for 100 ppm and 200 ppm are 98.9 % and 99.7 %, respectively. In addition, the MAHP-LDH compound has two types of adsorption sites that are available. Firstly, the external surface which lead to surface adsorption formation lead hydroxide results [20] and secondly within the interlayer which the formation of lead phosphate is believed to occur. The contact times of 2 hours subsequently selected for other optimization experiments in this study.

3.5 Effect of Adsorbent Dosage

The adsorption study with different adsorbent dosage at a fixed pH of 5, temperature of 298K, a contact time of 2 hours and different concentration of lead solution (100 ppm, 150 ppm, 250 ppm, 350 ppm and 400 ppm) were carried out. The dosages were selected from 0.01 g to 0.03 g. The effect of adsorbent dosage on lead removal is presented in Figure 5. From the graph, it can be seen that the removal of lead increased with increased in adsorbent dosage. It was found that dosage of 0.025 g, obtained the percentage removal of 100% for all different concentrations of lead. With 0.01 g of the dosage, the percentage removal for lead concentration of 100 ppm, 150 ppm, 250 ppm, 350 ppm and 400 ppm were 100 %, 97.7 %, 83.2 %, 63.7 % and 59.3% respectively. The increased in dosage provided more surface and adsorption site, hence increased adsorbent adsorption [21].

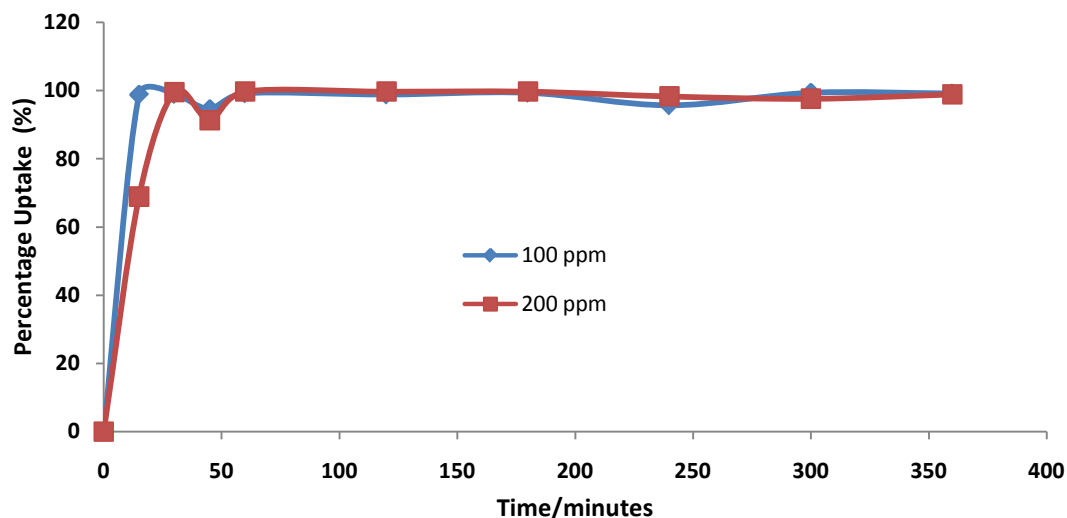


Fig. 4 The effect of contact time on the removal of lead solution using MAHP 4

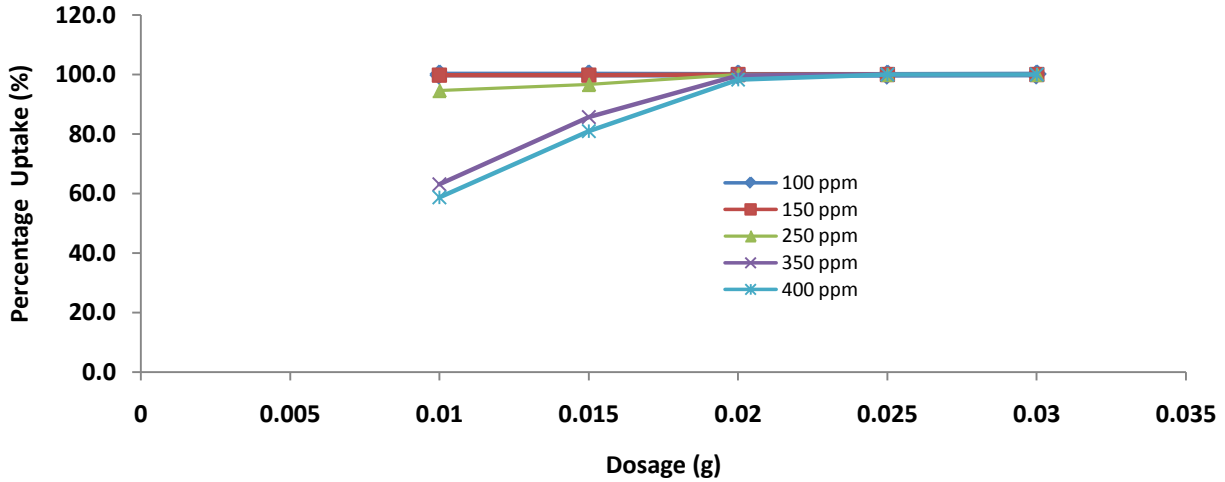


Fig. 5 The effect of adsorbent dosage time on the removal of lead solution using MAHP 4

3.6 Adsorption Isotherm

Adsorption isotherm study is important to study in order to understand the interactions between adsorbent and adsorbate. The isotherm is normally obtained at a constant temperature with fix adsorbent dosage by measuring the change of concentration at different initial concentration of lead solutions after equilibrium has been attained. The Langmuir model is based on assumption that uptake occurs on a homogenous surface by monolayer sorption without interaction between adsorbed molecules [22]. It is expressed as:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 \cdot b} + \frac{C_e}{Q_0} \quad (2)$$

Where, q_e is the amount of lead adsorbed per unit mass of adsorbent (mg/g); C_e is the equilibrium lead concentration (mg/L); and Q_0 and b are the Langmuir constants representing the monolayer adsorption capacity (mg/g) and the energy of adsorption (L/mg), respectively.

The plot of C_e/q_e versus C_e gives a straight line with a slope of $1/Q_0$ and an intercept of $1/Q_0 \cdot b$.

The isotherm study of lead removal was generated in batch experiments using different initial concentrations range from 100 ppm to 400 ppm at constant temperature of 298 K, a pH of 5 and 0.015 g dosage of MAHP 4. The isotherm is presented in Figure 6 and from the figure it can be concluded that equilibrium data fitted with the Langmuir Isotherm with high correlation coefficient value of 0.998. The calculated Langmuir isotherm constant for the maximum capacity of lead removal, Q_0 (mg/g) was 500 mg/g.

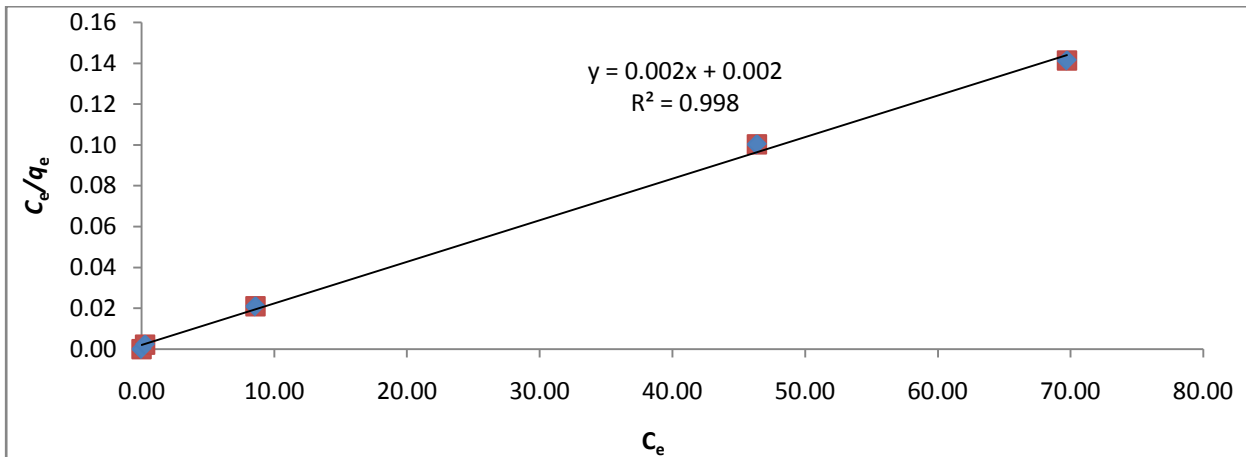


Figure 6: Langmuir Isotherm plot for the removal of lead solution using MAHP 4

4. CONCLUSION

The present study shows that MAHP (layered double hydroxide) is suitable adsorbents for the removal of lead from aqueous solution. The removal of lead was shown to be dependent on pH, contact time, adsorbent dosage and initial concentration. The experimental data well fitted to Langmuir equation confirming the monolayer coverage of lead solution onto layered double hydroxide adsorbents.

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