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Research Paper

Ca-Al Layered Double Hydroxides Pillared $H_4[\alpha\text{-}PW_{12}O_{40}]\bullet nH_2O$ as Adsorbent Material for Cadmium (II) Removal from Aqueous Solution

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Abstract
Heavy metals in the environment can have a detrimental impact on human health. This study successfully used a new adsorbent material, specifically layered double hydroxide pillared with keggin polyoxometalate $H_4[\alpha\text{-}PW_{12}O_{40}]\bullet nH_2O$ (Ca-Al/POM), to effectively remove cadmium (II) from aqueous solution. The Ca-Al/POM adsorbent has been thoroughly analyzed using X-ray diffraction and FT-IR. The findings showed an increase in the maximum adsorption capacity for cadmium (II) when using Ca-Al LDH intercalated with POM. The study of equilibrium adsorption isotherms showed that the Ca-Al/POM adsorbent effectively removed cadmium (II) and fit the Freundlich isotherm model. In addition, the adsorption kinetics study showed that the adsorption of cadmium (II) on Ca-Al/POM followed a pseudo second-order kinetics model.

Keywords
Layered Double Hydroxides, POM, Adsorption, Cadmium

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1. INTRODUCTION

There has been a significant increase in the release of water contaminated with various heavy metal wastes (such as copper, lead, nickel, chromium, cadmium, arsenic, etc.) into the environment in recent years. This has resulted in significant problems commonly caused by various industries, including mining, metal smelting, alloy forming, pigments, biocides, and other sectors (Yuan et al., 2024). Human health and the environment are at serious risk due to environmental pollution and toxic metal contamination. It is known that heavy metals in the environment can pose a great threat to human health. With their non-degradable nature and ability to enter the food chain through various pathways, heavy metals can accumulate toxic levels in living organisms. The health effects of exposure to heavy metals can cause serious problems, including damage to the liver, lungs, bones and blood (Nkosi et al., 2024).

Various methods have been developed to remove heavy metal ions from industrial wastewater, such as membrane separation, adsorption, ion exchange, biological flocculation, and chemical precipitation (Dou et al., 2022; Palapa et al., 2023; Siregar et al., 2022; Xu et al., 2022; Zhang et al., 2019). However, among these methods, adsorption method is the most advanced and widely recognized in terms of its effectiveness to remove a variety of heavy metals and toxic substances from contaminated water sources (Abdelmonem et al., 2024).

Layered double hydroxide, also known as LDH, is a type of inorganic material that has a layered structure consisting of a positively charged metal surface layer (M^{2+}/M^{3+}) and an interlayer of anion that is negative charged to help maintain balance (Palapa and Wijaya, 2023). The ability of LDH to adsorb heavy and toxic metal ions certainly makes LDH has been frequently used (Li et al., 2024). However, LDHs with interlayers such as the natural anions nitrate (NO_3^-) and chloride (Cl^-) are known to have limitations in the removal of heavy metal contamination such as Cd (He et al., 2024). In addition, small inorganic anions such as nitrate (NO_3^-) usually exhibit small interlayer (basal) spacing which will affect the utilization of interlayer sites (Li et al., 2024). Therefore, performing the intercalation process by incorporating anions with larger size can increase the interlayer spacing of LDH and with more functional groups can help to improve the heavy metal adsorption efficiency significantly.

In this study, the anion in the interlayer was changed by intercalating with a larger anion, POM, to explore the changes observed in Ca-Al LDH. A new material, Ca-Al/POM, was prepared through the intercalation process, involving the keggin polyoxometalate compound $H_4[\alpha\text{-}PW_{12}O_{40}]\bullet nH_2O$. The successful preparation of the material was carried out by XRD and FT-IR analysis and was tested on cadmium (II) adsorption with various parameters such as time parameters (adsorption kinetics) and adsorption isotherms.

2. EXPERIMENTAL SECTION

2.1 Materials

Various chemicals were used in this study including aluminum nitrate nonahydrate ($Al(NO_3)_3.9H_2O$), calcium nitrate tetrahydrate ($Ca(NO_3)_2.4H_2O$), sodium tungstate ($Na_2WO_4.2H_2O$), sodium phosphate ($NaHPO_4$), sodium hydroxide (NaOH), sodium chloride (NaCl), acetone (CH_3COCH_3), and cadmium sulfate okahydrate ($3CdSO_4.8H_2O$) from Merck Millipore. In addition, additional chemicals such as hydrochloric acid (HCl), nitric acid (HNO_3), sodium acetate trihydrate ($CH_3COONa.3H_2O$), and diethyl ether ($C_2H_5OC_2H_5$) were obtained from Sigma Aldrich.

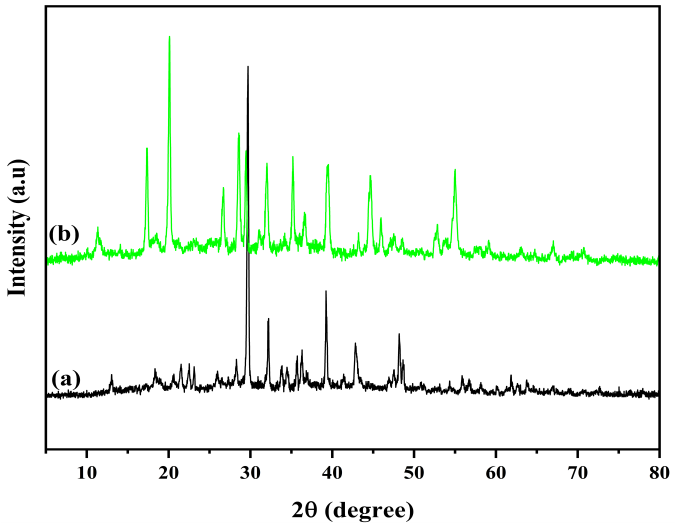

Figure 1. XRD Pattern of Ca-Al LDH (a) and Ca-Al/POM

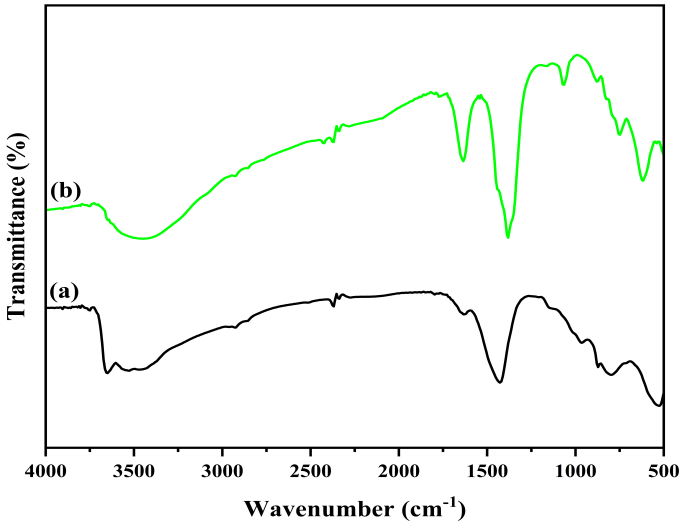

Figure 2. FT-IR Spectra of Ca-Al LDH (a) and Ca-Al/POM

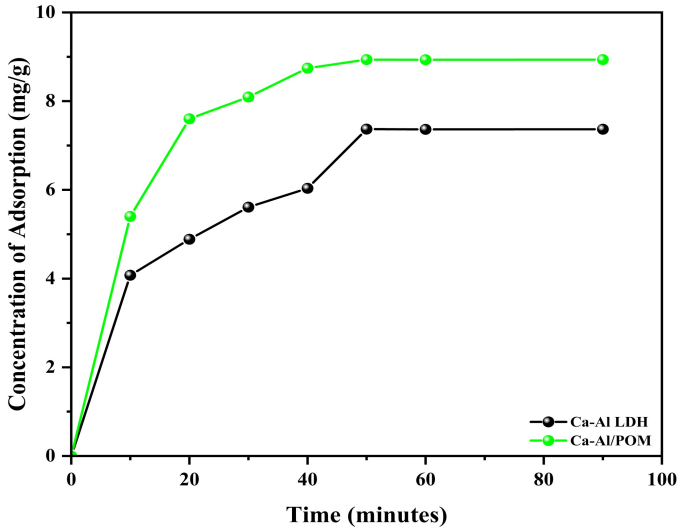

Figure 3. Effect of Contact Time on the Adsorption Efficiency of Cadmium (II) onto Ca-Al LDH and Ca-Al/POM

2.2 Methods

2.2.1 Synthesis of Ca-Al LDH

The synthesis of Ca-Al LDH was carried out by the coprecipitation method following the procedure described by De Sá et al. (2013). A solution of $Ca(NO_3)_2.4H_2O$ and $Al(NO_3)_3.9H_2O$ with a Ca/Al ratio of 2 (molar) was used to prepare Ca-Al LDH. Then, the solution was added slowly to 150 mL of 2 M NaOH with moderate stirring. The resulting white precipitate as the main product was then dried at 85°C for 18 hours. The product was then washed with distilled water to neutralize the pH and then dried at room temperature for 24 hours.

2.2.2 Preparation of Ca-Al LDH pillared $H_4[\alpha\text{-}PW_{12}O_{40}]\bullet n H_2O$ (Ca-Al/POM)

The $H_4[\alpha\text{-}PW_{12}O_{40}]\bullet nH_2O$ polyoxomethalate as the intercalant was prepared as follow. As much as 125 g of $Na_2WO_4.2H_2O$ and 20 g of $NaHPO_4$ was added into 187,5 mL of boiled water in a beaker flask. Afterward, 100 mL of HCl was added drop wisely into the solution then followed by continuous stirring until the entire solid was diluted. The phosfotungstate acid was separated in a half of HCl addition and eventually the clean solution was produced. The solution than cooled down in room temperature followed by addition of 75 mL diethyl ether. The mixture was extracted using separatory funnel then the bottom layer was evaporated until a white solid produced.

The CaAl LDH intercalated $H_4[\alpha\text{-}PW_{12}O_{40}]\bullet nH_2O$ was prepared by based on the ion exchanged method (Gardner et al., 1998). Solution A, 1 g of $H_4[\alpha\text{-}PW_{12}O_{40}]\bullet nH_2O$ diluted in 50 mL of distilled water, was added in to solution B (1 g of Ca-Al LDH diluted in 25 mL of 1 M NaOH). Both solution was agitated vigorously under N_2 atmosphere for 24 hours. Afterward, the solid was filtered and washed with distilled water for several times then dried at room temperature.

Table 1. Kinetics Parameters of Cadmium (II) Adsorption

Adsorbents	Qeexp (mg/g)	Pseudo First-Order			Pseudo Second-Order		
		q_{ecalc} (mg/g)	k_1 (min^{-1})	R^2	q_{ecalc} (mg/g)	k_2 ($g.mg^{-1}.min^{-1}$)	R^2
Ca-Al LDH	7.3701	6.048	0.041	0.9432	8.651	0.0085	0.9846
Ca-Al/POM	8.9356	9.084	0.091	0.9786	9.690	0.0178	0.9970

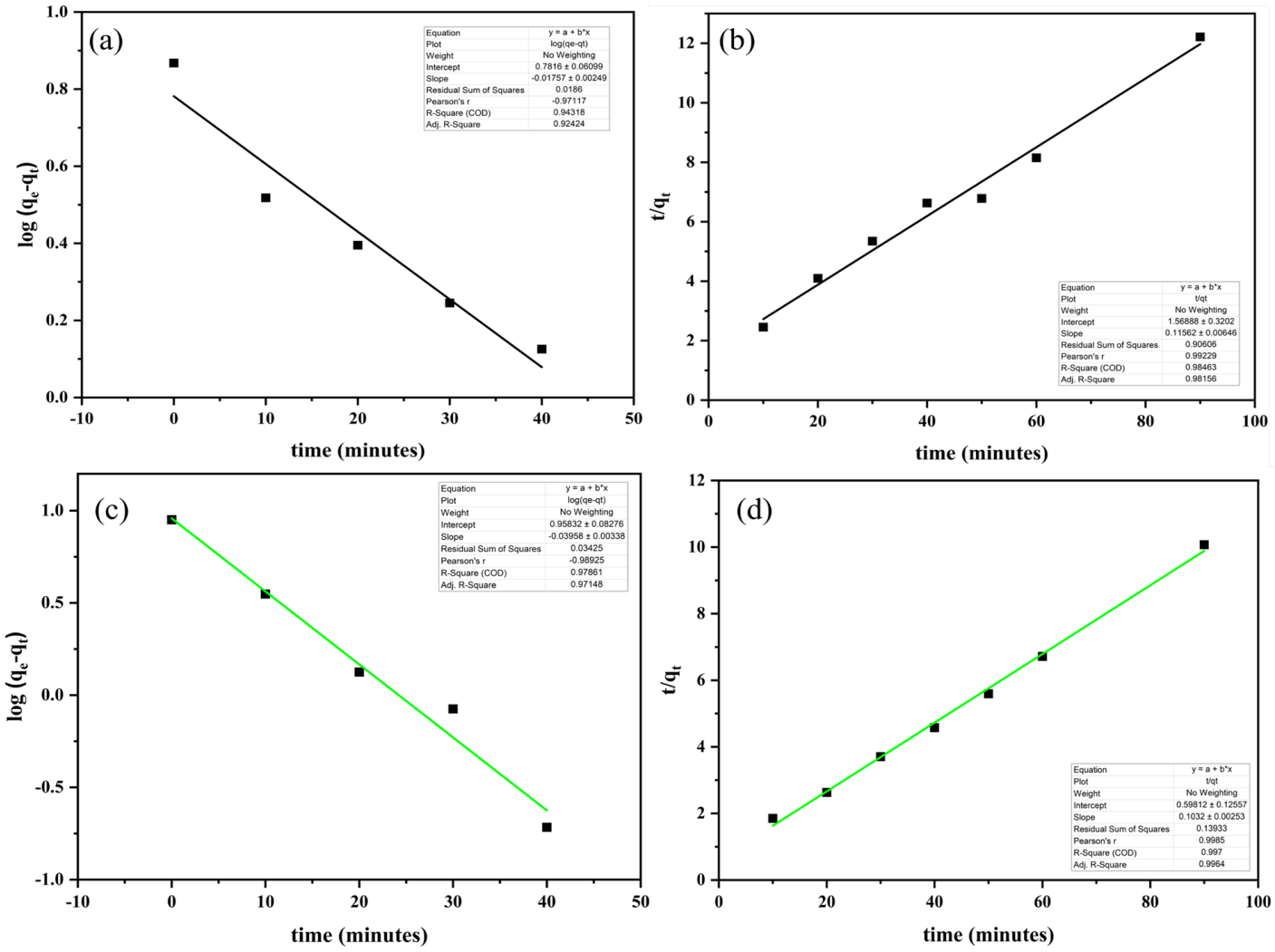

Figure 4. Plot of the Cadmium (II) Adsorption Data on the Pseudo-First-Order Model Ca-Al LDH (a), Pseudo-Second-Order Model Ca-Al LDH (b), Pseudo-First-Order Model Ca-Al/POM (c), and Pseudo-Second-Order Model Ca-Al/POM (d)

2.3 Material Characterization

The properties of the adsorbent material were characterized using x-ray diffraction (XRD) and infra-red spectrometry (FT-IR). XRD analysis was conducted using XRD Rigaku model Miniflex 600 diffractometer in scanning range 5o to 80° with CuKα radiation at 40 kV and 30 mA. The FTIR spectra of the adsorbent were recorded using Shimadzu FTIR spectrometer model Prestige-21 using KBr pellet method at wavenumber range 400 to 400 cm^{-1}.

2.4 Adsorption Experiments

The adsorption behavior of Cadmium (II) on modified Ca-Al LDH has systematically studied in batch process. The ability of modified Ca-Al LDH was evaluated by various parameters such as contact time variation (adsorption kinetics) and adsorption isotherm. Typically, the adsorption process was conducted by adding a certain amount of modified Ca-Al LDH into 50 mL of Cd solution in a canonical flask. The mixture than agitated under mild stirring for a predetermined time. After finished, amount

Table 2. Isoterm Parameters of Cadmium (II) Adsorption

Adsorbent	T (°C)	Langmuir			Freundlich		
		q_{max}	k_L	R^2	n	k_F	R^2
Ca-Al LDH	30	0.848	0.267	0.697	0.579	2.547	0.899
Ca-Al/POM	30	1.457	0.435	0.764	0.695	1.182	0.965

of the Cd remain in the solution was measured using UV-Vis spectrophotometer with phenotroline method.

3. RESULTS AND DISCUSSION

3.1 Adsorbent Characterization

The peaks observed in the Ca-Al LDH material (Figure 1(a)) correspond to specific indices. These indices closely match the reference pattern of JCPDS No. 89-6723. The observed peaks are located at approximately 11°, 22.45°, 32.15°, 36.17°, 39.25°, 42.82°, 46.8°, 48.6°, 55.87°, 56.79°, and 62.63°, which are assigned to (002), (004), (110), (106), (018), (114), (116), (108), (206), (300), (1010), and (113), respectively (Noorani Khomeyrani et al., 2022). In Figure 1(b), following the intercalation of Ca-Al LDH using POM, a noticeable shift in diffraction angles towards smaller values can be observed, particularly in the (002), (004), and (110) planes. Furthermore, following the intercalation of Ca-Al LDH, there was an observed increase in the basal spacing in the (004) and (110) planes, with values of 4.4107 and 2.8825 Å, respectively, compared to the initial measurements of 3.958 and 2.7814 Å (AitAghzzaf et al., 2024).

Figure 2(a) displays the FT-IR spectra of the Ca-Al layered double hydroxide. The wavenumbers 3649 and 3471 cm^{-1} correspond to the O−H stretching vibrations. There is a weak band observed at 1635 cm^{-1}, which suggests the bending vibrations of water molecules between layers (Zhang et al., 2022). Additionally, there is a peak at 1427 cm^{-1}, indicating the presence of nitrate anions. The 794 band is indicative of lattice vibrations involving M−O or M−OH, with M representing either Ca or Al metal (Wang et al., 2023). After Ca-Al LDH was intercalated with POM, there was a significant decrease in the wave number of the nitrate anion peak (Figure 2(b)). The peak that was previously at 1427 cm^{-1}, shifted to wavenumber 1381 cm^{-1} . This is possible due to the presence of POM anion in the interlayer that occurs in this event (Lesbani et al., 2020). In addition, the emergence of a new absorption band at 1064 cm^{-1} indicates the presence of strain vibrations associated with (Si−O) which is characteristic of POM (Rezvani et al., 2024).

3.2 Adsorption Studies

3.2.1 Effect of Contact Time

Figure 3 shows the effect of time on the adsorption process of Cadmium (II) using Ca-Al LDH and Ca-Al/POM materials. This treatment was carried out for 90 minutes. Based on the results obtained, it is clear that the adsorbed concentration of Cadmium (II) increases with time and reaches its peak at the 60^{th} minute. After exceeding the 60^{th} minute, both materials showed less increase in adsorption capacity or remained constant. This is due to having reached equilibrium due to saturated adsorption sites (Allaoui et al., 2024).

Several kinetic models have been observed in the adsorption process of cadmium (II) on both materials, including the pseudo first-order and pseudo second-order kinetic models. Figure 4 illustrates that both materials prioritize adherence to the pseudo second-order kinetic model. This is supported by the strong correlation coefficient (R^2) value, which is very close to 1. Furthermore, Table 1 reveals that the equilibrium capacity value (q_e calculation) in the pseudo-second order kinetics model is more closely aligned with the equilibrium capacity value (q_e experiment) compared to the pseudo-first order kinetics model.

3.2.2 Adsorption Isotherm

Adsorption isotherm models are commonly employed to explain and comprehend the adsorption process of substances on solid surfaces once equilibrium conditions are attained (Cevallos-Mendoza et al., 2024). Table 2 demonstrates clearly that both materials show a strong correspondence to the Freundlich isotherm model. This is because the correlation coefficient (R^2) of the Freundlich isotherm is more than/greater than the correlation coefficient (R^2) of the Langmuir isotherm. The Freundlich isotherm model indicates that adsorption occurs on the surface of the adsorbent which is characterized by its heterogeneous and multilayered nature (Debnath and Das, 2023).

4. CONCLUSIONS

In general, the synthesis of Ca-Al/POM materials has shown significant efficacy in the removal of cadmium (II) from water. As part of this study, POM was used instead of nitrate anion (NO_3^-) in the Ca-Al LDH intercalated anion. This substitution resulted in a significant increase in the interlayer spacing. Based on the investigation of adsorption kinetics and isotherm matching studies, it is clear that both materials exhibit characteristics consistent with the pseudo second-order kinetics model and the Freunlich isotherm. The results obtained also show that the intercalation process can significantly improve the ability of cadmium (II) to adsorb onto the surface.

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REFERENCES

Abdelmonem, H. A., T. F. Hassanein, H. E. Sharafeldin, H. Gomaa, A. S. A. Ahmed, A. M. Abdel-lateef, and A. H. Tilp (2024). Cellulose-Embedded Polyacrylonitrile/Amidoxime for the Removal of Cadmium (II) from Wastewater: Adsorption Performance and Proposed Mechanism. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **684**; 133081

AitAghzzaf, A., Y. Zarki, B. Rhouta, A. Khalil, D. Veys-Renaux, H. Majdoub, and E. Rocca (2024). Intercalation of Decanoate Anions (C_{10}) in Layered Double Hydroxide Mg-Al and Its Application as Controlled-Release Corrosion Inhibitor of Steel. *Surface and Coatings Technology*, **489**; 131055

Allaoui, I., M. El Mourabit, B. Arfoy, M. Hadri, A. Barhoun, and K. Draoui (2024). Adsorption Equilibrium, Kinetic, and Thermodynamic Studies on the Removal of Paracetamol from Wastewater Using Natural and HDTMA-Modified Clay. *Desalination and Water Treatment*, **318**; 100345

Cevallos-Mendoza, J. E., J. S. Cedeño-Muñoz, J. M. Navia-Mendoza, F. Figueira, C. G. Amorim, J. M. Rodríguez-Díaz, and M. C. B. S. M. Montenegro (2024). Development of Hybrid MIL$-_{53}$(Al)@*CBS* for Ternary Adsorption of Tetracyclines Antibiotics in Water: Physical Interpretation of the Adsorption Mechanism. *Bioresource Technology*, **396**

De Sá, F. P., B. N. Cunha, and L. M. Nunes (2013). Effect of pH on the Adsorption of Sunset Yellow FCF Food Dye into a Layered Double Hydroxide (CaAl$-$LDH$-$$NO_3$). *Chemical Engineering Journal*, **215–216**; 122–127

Debnath, S. and R. Das (2023). Strong Adsorption of CV Dye by Ni Ferrite Nanoparticles for Waste Water Purification: Fits Well the Pseudo Second Order Kinetic and Freundlich Isotherm Model. *Ceramics International*, **49**(10); 16199–16215

Dou, D., D. Wei, X. Guan, Z. Liang, L. Lan, X. Lan, and P. Lan (2022). Adsorption of Copper (II) and Cadmium (II) Ions by In Situ Doped Nano-Calcium Carbonate High-Intensity Chitin Hydrogels. *Journal of Hazardous Materials*, **423**; 127137

Gardner, E. A., S. K. Yun, T. Kwon, and T. J. Pinnavaia (1998). Layered Double Hydroxides Pillared by Macropolyoxometalates. *Applied Clay Science*, **13**(5–6); 479–494

He, L., Y. Wang, C. Ding, G. Huang, X. Tu, Z. Zhou, and S. Zheng (2024). Selective and Efficient Immobilization of Cadmium in Soil by Layered Double Hydroxides Intercalated with the Mercaptosuccinic Acid. *Science of the Total Environment*, **937**; 173473

Lesbani, A., T. Taher, N. R. Palapa, R. Mohadi, A. Rachmat, and Mardiyanto (2020). Preparation and Utilization of Keggin-Type Polyoxometalate Intercalated Ni–Fe Layered Double Hydroxides for Enhanced Adsorptive Removal of Cationic Dye. *SN Applied Sciences*, **2**(3); 1–4

Li, Y., S. Wang, X. F. Ouyang, Z. Dang, and H. Yin (2024). Acetate Anions Intercalated Fe/Mg-Layered Double Hydroxides Modified Biochar for Efficient Adsorption of Anionic and Cationic Heavy Metal Ions from Polluted Water. *Chemosphere*, **362**; 142652

Nkosi, N., N. D. Shooto, P. Nyamukamba, and P. M. Thabede (2024). Binary Adsorption of Toxic Nickel (II) and Cadmium (II) Ions from Aqueous Solution by Acid Modified Chilli Peppers. *Energy Nexus*, **15**; 100313

Noorani Khomeyrani, S. F., B. Ghalami-Choobar, M. H. Ahmadi Azqhandi, and M. Foroughi (2022). An Enhanced Removal of Para-Nitrophenol (PNP) from Water Media Using CaAl-Layered Double Hydroxide-Loaded Magnetic g-CN Nanocomposite. *Journal of Water Process Engineering*, **46**; 102516

Palapa, N. R. and A. Wijaya (2023). Layered Double Hydroxide Coated by Carbon-Based Material for Environmental Dye Pollutant. *Indonesian Journal of Material Research*, **1**(3); 84–90

Palapa, N. R., A. Wijaya, P. M. S. B. N. Siregar, A. Amri, N. Ahmad, T. Taher, and A. Lesbani (2023). Adsorption of Fe(II) by Layered Double Hydroxide Composite with Carbon-Based Material (Biochar and Graphite): Reusability and Thermodynamic Properties. *Indonesian Journal of Chemistry*, **23**(1); 101–112

Rezvani, M. A., A. Hemmatzadeh, M. S. Seyed Dorraji, N. Nourbakhsh, and G. Oroumi (2024). New Magnetic Nanocomposites Based on Hexaferrite and Keggin-Type Heteropolyanions: Synthesized and Characterized for Removal of Environmental Pollutants. *Heliyon*, **10**(9); e30289

Siregar, P. M. S. B. N., A. Wijaya, Amri, J. P. Nduru, N. Hidayati, A. Lesbani, and R. Mohadi (2022). Layered Double Hydroxide/C (C=Humic Acid; Hydrochar) As Adsorbents of Cr(VI) Patimah. *Science and Technology Indonesia*, **7**(1); 41–48

Wang, H., Y. Gao, W. Hu, Q. Wu, X. Zhong, B. Huang, and C. Wu (2023). Health Management of Cd-Contaminated Soil Using Ca$-$Al Layered Double Hydroxide: Response of Different Vegetables. *Agriculture, Ecosystems and Environment*, **356**; 108631

Xu, Y., H. Xia, Q. Zhang, G. Jiang, W. Cai, and W. Hu (2022). Adsorption of Cadmium (II) in Wastewater by Magnesium Oxide Modified Biochar. *Arabian Journal of Chemistry*, **15**(9); 104059

Yuan, X., S. Ma, C. Zhao, X. Chen, Y. Zhou, S. Xi, and S. Liu (2024). Cadmium (II) Ion Adsorption of an Industrial Liquid Waste-Derived Ferric Oxide Loaded with Chitosan: Parameters Optimization, Isotherms, Kinetics and Thermodynamics. *Desalination and Water Treatment*, **319**; 100578

Zhang, S., Y. Chen, J. Li, Y. Li, W. Song, X. Li, and H. Yu (2022). Highly Efficient Removal of Aqueous Cu(II) and Cd(II) by Hydrothermal Synthesized CaAl-Layered Double Hydroxide. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **641**; 128584

Zhang, Y., X. Yue, W. Xu, H. Zhang, and F. Li (2019). Amino Modification of Rice Straw-Derived Biochar for Enhancing Its Cadmium (II) Ions Adsorption from Water. *Journal of Hazardous Materials*, **379**; 120783