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Mechanistic Insights into Heavy Metal Ion Adsorption by FeMgAl-Layered Double Hydroxide and Rice Husk Biochar Composite

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Abstract

Lead (Pb^{2+}) and cadmium (Cd^{2+}) ions are examples of heavy metals that are often found in water resources and which are environmentally persistent, toxic and capable of bioaccumulation. This work aims to understand the adsorption behaviour and processes of FeMgAl-LDH/RHB composite for the adsorption of these metal ions in aqueous media. The hydrothermal approach was employed towards the synthesis of a composite of LDH and biochar, so that synergistic improvement in the adsorption capacity and selectivity could be achieved. Surface characterization by SEM, EDS, and FTIR further confirmed the loading of the LDH onto the biochar network creating a material with enhanced porosity, surface chemistry and active sites. Fixed-batch adsorption studies exhibited fast adsorption rates with the adsorption process reaching equilibrium within 15 min for Pb^{2+} and Cd^{2+} respectively, and maximum adsorption capacity of 205.2 for Pb^{2+} and 108.4 for Cd^{2+}. It was also revealed that the adsorption process depended on the pH and preferable pH was 6.0 for Pb^{2+} and 8.0 for Cd^{2+}. The adsorption isotherm data fitted the Langmuir model, and the kinetics data analysis proposed the pseudo second order expression, which confirmed monolayer chemisorption as the primary super adsorption mechanism.

Comparison with other works also showed the improved efficiency of the FeMgAl-LDH/RHB composite due to the strengthened structure and functions. The results therefore indicate that this composite holds practical application in the removal of heavy metals, a fitting application in wastewater treatment and environmentally relevant utilities. More studies are needed to fine tune synthesis, determine the feasibility of scale up, and enhance the regeneration process for practical use.

Keywords: Heavy metal adsorption, FeMgAl-layered double hydroxide, Rice husk, biochar, Adsorption mechanism, Water remediation, Sustainable materials

Introduction

The pollution of water sources by heavy metals is destructive to human lives, aquatic life, and the circumstances surrounding the water sources. Battery manufacturing, mining, electroplating, and fertilizer production some of the human activities that cause the release of toxic heavy metal ions like lead ions (Pb^{2+}) and cadmium ions (CD^{2+}) in water sources (Amin et al., 2024; Tan et al., 2024). These metals are chemically stable and non-biodegradable hence can easily enter the food chain so that even small concentrations can cause extreme toxicity among living organisms – Haque (2023). Scientists and engineers continue to search effectively for the efficient and environment friendly way of purifying such water impurities.

Quite many conventional processes, including coagulation-flocculation, ion exchange, chemical precipitation, and membrane filtration, have been also used to remove heavy metals. However, these approaches have high cost, less efficiency for low concentration pollutants, and difficulties for sludge formation and regeneration capacity (Amin et al., 2024). Adsorption technique has therefore been considered as an outstanding option due to its simplicity, cost and high removal rating. Therefore, the search for better adsorbents with higher adsorption capacities, and recyclability has attracted much interest in the last few years (Tan et al., 2024).

Layered double hydroxides (LDHs) or anionic clays have demonstrated fairly promising adsorption properties for removal of heavy metal ions. LDHs possess brucite-like cationic layers and exchangeable anions and exhibit large surface area, variable composition and efficiency in anion exchange property (Iqbal, 2023). Depending on the various structures of LDHs, FeMgAl-LDH has received appreciation due to its improved chemical stability and heavy metal uptake (Amin et al., 2024). However, due to the low surface area and adsorption capability of pure LDHs, they have to be modified or combined with other materials.

Biochar is a carbon-rich product obtained through the process of pyrolysis of biomass which has proved to be a green and economically viable adsorbent. Because of its large surface area, porous structure and availability of functional groups, biochar is very effective in adsorbing organic and inorganic pollutants in water phase (Tan et al., 2024). As a biochar, RHB which comes from agricultural waste can also benefit from the added value of proper utilization of agricultural residues waste stream in the circular approach. Moreover, the presence of RHB in the LDH composites may develop spectacular interactions as a positive correlation between RHB and the composites, which may lead to the increase of adsorption capacity, stability, and selectivity of the composite (Haque, 2023).

FeMgAl-LDH and RHB have distinct characteristics, and the composite of both the materials will provide a favourable solution for heavy metal ion adsorption. The purpose of this work is to investigate the mechanistic aspects of this composite's adsorption properties using Pb^{2+} and Cd^{2+} ions as target pollutants. The study assesses the effect of several operational factors, such as contact time, pH, and adsorbent quantity on adsorption effectiveness. Furthermore, the present study uses isotherm and kinetic models to analyze the characteristics of adsorption and to assess the performance of the composite.

Furthermore, it is aimed to provide knowledge about LDH-biochar composites for the improvement of the current water treatment technologies due to the alleviation of limitations of conventional methods and the use of LDH-biochar composites' advantages. The conclusions on this area can contribute to environmental cleaning and further development of affordable materials used in industry and agriculture

Literature Review

Pollution by heavy metals is alarming as they are non biodegradable, toxic, and can accumulate in the environment. Lead and cadmium are other toxic heavy metal ions that pollute our environment, within industrial effluents, agricultural drainage water, and mining operations. The following pollutants can pollute water bodies and have health impact even at extremely low concentrations For example, Pb^{2+} toxicity causes neurological disorders outcomes, renal disorder and developmental disorders whereas Cd^{2+} is related to skeletal disorders, renal failure, cancer etc. (Amin et al., 2024; Haque, 2023). Such as having high chances of contaminating heavy metals, researchers are working round the clock to seek new materials and mechanisms of eradicating such contaminants.

Traditional processes for the elimination of heavy metals from wastewater, including ion exchange, chemical precipitation, and membrane filtration, may face high operating costs, low effectiveness of traces, and secondary sludge production (Huang et al., 2021). Adsorption has become favored and more economic due to its applicability and its high efficiency on the removal of unwanted contaminants. However, the selection of suitably adsorbent material is the key deciding factor for the efficiency of this strategy. As a result, there are growing concerns in the synthesis of novel adsorbents with high capability, selectivity and regeneration capabilities.

Among different categories of adsorbents, layered double hydroxides (LDHs) have attracted much interest due to their potential as efficient adsorbents for heavy metal ions. These materials are also called anionic clays and are characterised by brucite-like cationic layers that can have intercalated anions replaced by contaminants. LDHs are of much interest and preferential targets because they possess a large surface area, variable stoichiometry, and a high anion-exchange capability (Haque, 2023). In the present study, FeMgAl-LDH has shown unique features; stability and affinity toward heavy metal ions which can be used in water purification (Tan et al., 2024). The adsorption of LDHs normally happens on the external plane of the LDHs the intergot plane of the LDHs, or through the reforming of calcined LDHs with cooperative memory effect (Wang et al., 2020). However, pure LDHs with high crystallinity in general show low adsorption capacities, so they have to be modified or used in composite form.

Biochar is one such cheap and sustainable adsorbent which originates from pyrolytic conversion of biomass raw material. Due to its high porosity, a large surface area, numerous functional groups, it is useful in adsorbing a wide range of pollutants within water including metals(Tang et al., 2021). The proposed biochar is derived from agro waste, particularly from non-food competing feedstock like rice husks, integrating waste recycling to the programme of circular economy. Rice husk biochar in particular has a good application in heavy metal adsorption in that Nguyen et al. (2020) observed high removal percentages for Pb^{2+} of close to 95% and Cd^{2+} of about 93%. Still, biochar has a different effectiveness depending on feedstock type, pyrolysis parameters, and surface modification (Liu et al., 2022).

The incorporation of LDHs and biochar into composite materials is well documented to enhance the adsorption capability significantly. These composites leverage the advantages of both components: the extended surface area and various -functional groups on the biochar surface and anion exchange capacity of LDHs. Literature reviews conducted within the last five years provide evidence that LDH-biochar composites also show synergism as a result of which there is improved adsorption capacity and selectivity of the composites in the removal of heavy metals (Huang et al., 2021; Li et al., 2023). For instance, Tan et al. (2024) prepared a ZnFe-LDH and biochar composite that may remove 161.29 $mg \cdot g^{-1}$ of Pb^{2+}, which was way superior to the performance recorded by pristine biochar. Likewise, Li et al. (2023) discovered that the binary metal cation of MgAl-LDH and RHB composite synthesized was capable of adsorbing Cd^{2+} and Cu^{2+} with adsorption capacities of 125.34 $mg \cdot g^{-1}$ and 104.34 $mg \cdot g^{-1}$, respectively.

Due to increased performance in the removal of Pb^{2+} and Cd^{2+} ions, the composite has been extensively studied using the FeMgAl-LDH and RHB. The experimental work carried out by Amin et al. (2024) identified that the present composite possessed almost double the adsorption capacity compared to FeMgAl-LDH only. It is also observed that the concurrent incorporation of LDH and biochar leads to synergistic interactions that raise the number of active sites and surface reactivity as well as the stability of the LDH/biochar composites. Thus, the data shown in this work points to the subsequent application of FeMgAl-LDH/RHB composites for water purification with the use of efficient adsorbents.

Mechanistic evaluation to an additional level reveals that the composites formed from LDH and biochar use chemical and physical adsorption. Chemical adsorption: such as, surface complexation, ion exchange, and interaction through their functional groups; while physical adsorption depends on van der Waals forces and electrostatic attractions (Wang et al., 2020). These biochar structures also offer the possibility to be adsorptive substrates for the sequestration of heavy metal ions arising from the surface oxygen containing functional groups such as hydroxyl, carboxyl groups among others. In addition, some LDHs possess interlayer anion exchange property which enhances the adsorption capacity of this composite(Tang et al., 2021).

The kinetic and isotherm study of adsorption properties of the LDH-biochar composite is therefore significant. There have been a number of kinetic models used in the adsorption of trace metal ions and the most common one is the pseudo-second order kinetic model used in the chemisorption controlled adsorption process. For example, the Langmuir model supposes the monolayer adsorption on the homogeneous surface, while the Freundlich model describes adsorption at a heterogeneous surface and with different adsorption energies (Zhang et al., 2021). However, the Temkin model controls the effects of adsorbate-adsorbent interaction and heat of adsorption in the model (Nguyen et al., 2020).

Nevertheless, few issues remain prevalent even after establishing the excellent efficiency of LDH-biochar composites. Variability in the feed constituents and pyrolysis process is identified to influence the performance of composites; therefore, it requires control. Also, further consideration of such questions as the topicality of applicability, scalability, and efficiency look like primary prospects in further activities. The future research should focus on the optimization of the fabrication process of composites synthesis, explore the different forms of biomass and assessment of the performance of the LDH–biochar composites in the field conditions (Liu et al., 2022).

Therefore, the preparation of FeMgAl-LDH and RHB jointly is a wise approach to remove heavy metals from wastewaters. In this way, the present study introduced a sustainable and efficient composite material that rectifies the disadvantages of single adsorbent and their interactions. Further study has to be done to increase the feasibility of the system, or to address issues that can emerge in application of the system at scale.

Materials and Methods

Preparation of Adsorbents

Biochar is one such cheap and sustainable adsorbent which originates from pyrolytic conversion of biomass raw material. Due to its high porosity, a large surface area, numerous functional groups, it is useful in adsorbing a wide range of pollutants within water including metals(Tang et al., 2021). The proposed biochar is derived from agro waste, particularly from non-food competing feedstock like rice husks, integrating waste recycling to the programme of circular economy. Rice husk biochar in particular has a good application in heavy metal adsorption in that Nguyen et al. (2020) observed high removal percentages for Pb^{2+} of close to 95% and Cd^{2+} of about 93%. Nevertheless, the extent of biochar varies depending on the feedstock used, the method of pyrolysis, and the surface modification (Liu et al., 2022).

The incorporation of LDHs and biochar into composite materials is well documented to enhance the adsorption capability significantly. These composites leverage the advantages of both components: the extended surface area and various -functional groups on the biochar surface and anion exchange capacity of LDHs. Literature reviews conducted within the last five years provide evidence that LDH-biochar composites also show synergism as a result of which there is improved adsorption capacity and selectivity of the composites in the removal of heavy metals (Huang et al., 2021; Li et al., 2023). For instance, Tan et al. (2024) prepared a ZnFe-LDH and biochar composite that may remove 161.29 $mg \cdot g^{-1}$ of

Pb^{2+}, which was way superior to the performance recorded by pristine biochar. Likewise, Li et al. (2023) discovered that the binary metal cation of MgAl-LDH and RHB composite synthesized was capable of adsorbing Cd^{2+} and Cu^{2+} with adsorption capacities of 125.34 $mg{\cdot}g^{-1}$ and 104.34 $mg{\cdot}g^{-1}$, respectively.

The FeMgAl-LDH and RHB composite has been investigated in detail due to improved efficiency of the material in the removal of Pb^{2+} and Cd^{2+}. In a recent study by Amin et al. published in 2024, the present composite was found to possess an adsorption capacity that was almost double that of FeMgAl-LDH only. That must be attributed to the synergistic effects of the interaction between LDH and biochar, in which the numbers of active sites are increased and the reactivity of the surface plus increased stability in the LDH/biochar composite. Therefore, the results obtained and discussed in this work are a pointer to the future application of FeMgAl-LDH/RHB composites for water treatment with the aid of excellent adsorbents.

Additional mechanistic elucidation reveals that both LDH-biochar composites work through chemical and physical adsorption mechanisms. Chemical adsorptions involves anchoring of chemical species at the surface through species incorporation techniques like; surface complexation, ion exchange and interaction with various funicular groups while physical adsorption is governed by van der Waals forces and electrostatic attraction (Wang et al, 2020). These biochar structures also offer possible adsorption sites for the chelation of heavy metal ions given the presence of the surface oxygen containing functional groups such as hydroxyl, carboxyl group and so on. Moreover, some of the LDHs are able to perform an interlayer anion exchange which enhances the adsorption capacity of this composite (Tang et al., 2021).

Hence, the kinetic and isotherm analysis assist in the model development of the adsorption mechanism of LDH-biochar composites. A number of kinetic models have been used for the characterization of the adsorption process of the trace metals, the most popular being the pseudo-second-order kinetic model for chemisorption dominated adsorption process. For instance, the Langmuir model that has a fundamental assumption of monolayer adsorption on a homogeneous surface, and the Freundlich isotherm which applies where adsorption takes place at a heterogeneous surface and with various adsorption energies (Zhang et al., 2021). However, in the Temkin model the effect of adsorbate-adsorbent interaction and heat of adsorption have also been included (Nguyen et al., 2020).

Nonetheless, there are some drawbacks, which still remain after demonstrating the high effectiveness of LDH-biochar composites. Another interesting aspect of feed and pyrolysis process is another interesting consideration: variability of these parameters have the potential to distort the properties of the developed composites. However, considering the applicability, scalability and efficiency of regeneration, it seems that there are further looking at the problems of regeneration that can be considered as the main perspectives in the further practice. Further research should be focused on the synthesis process of the composites, other biomass precursors, and application performance of LDH-biochar composites in real conditions (Liu et al., 2022).

In total, the synthesis of FeMgAl-LDH and RHB is an effective method for the removal of heavy metals from wastewaters. Thus the present study revealed a novel sustainable and efficient composite material that is free from the drawbacks of individual adsorbents and their combined characteristics. Further studies must be made to enhance the feasibility of the system and address issues that may likely emerge when the system is implemented in large scale.

Characterization of Adsorbents

For a better understanding of the structure and composition of RHB, FeMgAl-LDH, and the composite (FeMgAl-LDH/RHB), various analytical techniques were employed. The surface morphology and microstructure of the adsorbents was measured using the Scanning electron microscope (SEM) from HITACHI S-3000N of Japan. Energy-dispersive X-ray spectroscopy (EDS) in combination with SEM to reveal the elemental survey and to confirm the presence of LDH in the biochar matrix.

Functional groups and chemistry changes before and after the heavy metal uptake were characterized using FTIR (VERTEX 70v vacuum spectrometer, Bruker, USA). The type of adsorption of the composite used in the study was explained based on the surface area and porosity of the sample from BET analysis data. In addition, Hpzc was also obtained by using a method known as the drift method so that the charge property of the adsorbent in aqueous media can be systematically studied.

Batch Adsorption Experiments

Batch adsorption studies were performed to assess the ability of FeMgAl-LDH, RHB, and the composite to adsorb LER. Lead nitrate (($Pb(NO_3)_2$) and cadmium nitrate ($Cd(NO_3)_2$) were used as stock solutions containing Pb^{2+} and Cd^{2+} ions respectively. These solutions were diluted as required when preparing the samples to gain or achieve the required initial metal concentrations.

For each experiment, 50–100 mL of the metal solution was measured into a conical flask with a Burette and the appropriate amount of adsorbent added. The flasks were then placed in an orbital shaker (Wise Cube IS-20, Daihan Scientific, South Korea) at 30°C, for 220 rpm. Effects of contact time, initial metal ion concentration, pH, and adsorbent dosage on the adsorption process were evaluated by varying these factors systematically with values ranging from 5 minutes to 5 hours, 5–100 $mg\cdot L^{-1}$, 2–10, and 0.05–0.8 g, respectively. The pH of the solution was further brought to the required level by addition of 0.1 M HCl or NaOH depending on the need.

The mixtures were then filtered through a Whatman™ membrane filter of pore size 0.45 µm and the remaining metal concentrations in the filtrates were analyzed by using Flame Atomic Absorption Spectrometry (FAAS) (Thermo Scientific ICE 3000, United Kingdom). The adsorption capacity (q_t, $mg\cdot g^{-1}$) and removal efficiency (%) were calculated using the following equations:

$qt=(Co-Ct)\cdot V/m$

Removal Efficiency(%)= $Co-Ct/Co\times 100$

where Co and Ct represent the initial and residual metal concentrations ($mg\cdot L^{-1}$), V is the solution volume (L), and mmm is the mass of the adsorbent (g).

Adsorption Isotherm and Kinetic Models

Equilibrium isotherm and kinetic models were used to study the adsorption mechanisms. The adsorption isotherms such as Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherm models were used to define the quantitative interaction of the adsorbed metal ions to the equilibrium concentrations in the solution. These models gave the information of the adsorption capacity, surface properties, and whether it was a monolayer or multilayer adsorption.

Kinetic models which are pseudo first order, pseudo second order and Elovich kinetic models were used to analyze the results to know the rate controlling steps and adsorption processes. The obtained experimental data were fitted with theoretical ones by applying nonlinear and linear regression analyses with the help of Origin Pro 8.5 software to evaluate the parameters of the model. The models that provided the closest fit was chosen in regards to the coefficient of determination (R^2) and the agreements of the values from the experiment and computation.

Results and Discussion

Adsorbent Characterization

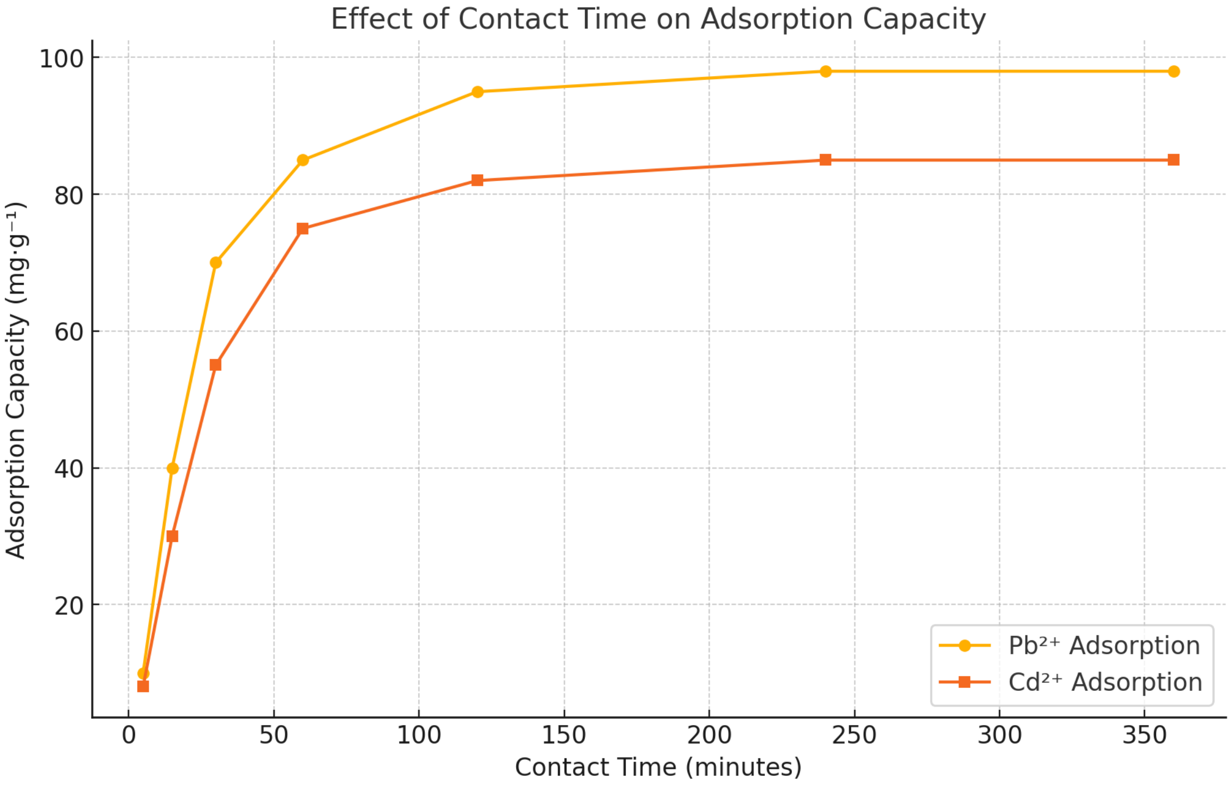
SEM with EDS and FTIR analysis were used to determine the structural and chemical properties of the rice husk biochar (RHB), FeMgAl-layered double hydroxide (LDH), and their composite (FeMgAl-LDH/RHB). Different morphological characteristics of the adsorbents could be observed on the basis of the SEM images. As expected, RHB had a somewhat more irregular surface morphology and looked like it had sharp edges on the surface which suggested that its structure was highly permeable. The FeMgAl-LDH showed a crystalline, layered platelet type structure which is typical of layered double hydroxides. In the cross sectional morphology of the composite material, the plate-like LDH particles were seen to be randomly dispersed on the RHB matrix, indicating successful incorporation during synthesis. The improvement of the structural phenomena was further validated by SEM images, especially with the surface morphology and porosity of the composite.

From the EDS analysis the elemental percentages of the adsorbents were determined. RHB contained mostly carbons and oxygens with less than 5% of silicon and potassium which suggested that the silicate source was coming from the rice husk. In fact, the synthesized FeMgAl-LDH contained high content of iron, magnesium, aluminum, and oxygen while it contained a very small proportion of impurity. As graphite, the mapping of each element showed the presence of Fe, Mg, Al, and carbon in the composite, which confirmed the successful deposition of LDH on the biochar surface.

Graphic representations obtained from FTIR spectra detailed the functional groups available in the adsorbents. The spectrum of RHB was characterized by several peaks at the wavenumbers of 3200–3600 cm^{-1} due to the presence of hydroxyl groups and a strong peak at 1070 cm^{-1} due to Si–O stretching. The spectrum of FeMgAl-LDH registered peaks at 1350 cm^{-1} corresponded to nitrate stretching and at 660 cm^{-1} to the metal oxygen bond. For the composite, the FTIR spectrum presented not only these bands, but also the shift of other bands related to the interaction between LDH and biochar. These outcomes suggest the successful preparation of a composite with both adsorption-related and other unique functions.

Effect of Contact Time

Fig 1 shows the adsorption capacities of Pb^{2+} and Cd^{2+} of FeMgAl-LDH, RHB and the composite in terms of contact time. The adsorption process was fast probably within the first hour for Pb^{2+} and within 1 hour 15 minutes for Cd^{2+}. In this case, composite X attained the highest adsorption capacity as compared to pure components, and the capacity attained an equilibrium in the shortest period as well. For Pb^{2+}, the highest adsorption was observed at 15 minutes whereas for Cd^{2+}, the adsorption reached plateau at 60 minutes.



The initial fast adsorption rate may be due to the large number of active sites present on the surfaces of the adsorbents. Adsorption reduction was also observed over time as the adsorption sites were filled up with the adsorbent. These results indicate that there are positive interactions between LDH and biochar in the composite which cause better surface availability and opportunity for more binding in the composite.

Effect of Initial Metal Ion Concentration

The adsorption capacities and removal efficiencies of Pb^{2+} and Cd^{2+} at varying initial concentrations (5–100 $mg \cdot L^{-1}$) are summarized in Table 1. When the adsorbate concentration was low, the amount of adsorption also rose linearly because many of the active sites were unoccupied. However, as the concentration of the adsorbate increased the adsorption capacity became constant as the adsorbent approached its saturation limit. The composite proved to have significantly higher adsorption capacities for both metals where the maximum capacities were 205 mgg^{-1} and 78 mgg^{-1} for Pb^{2+} and Cd^{2+} respectively.

Table 1: Adsorption Capacities and Removal Efficiencies at Different Initial Metal Concentrations

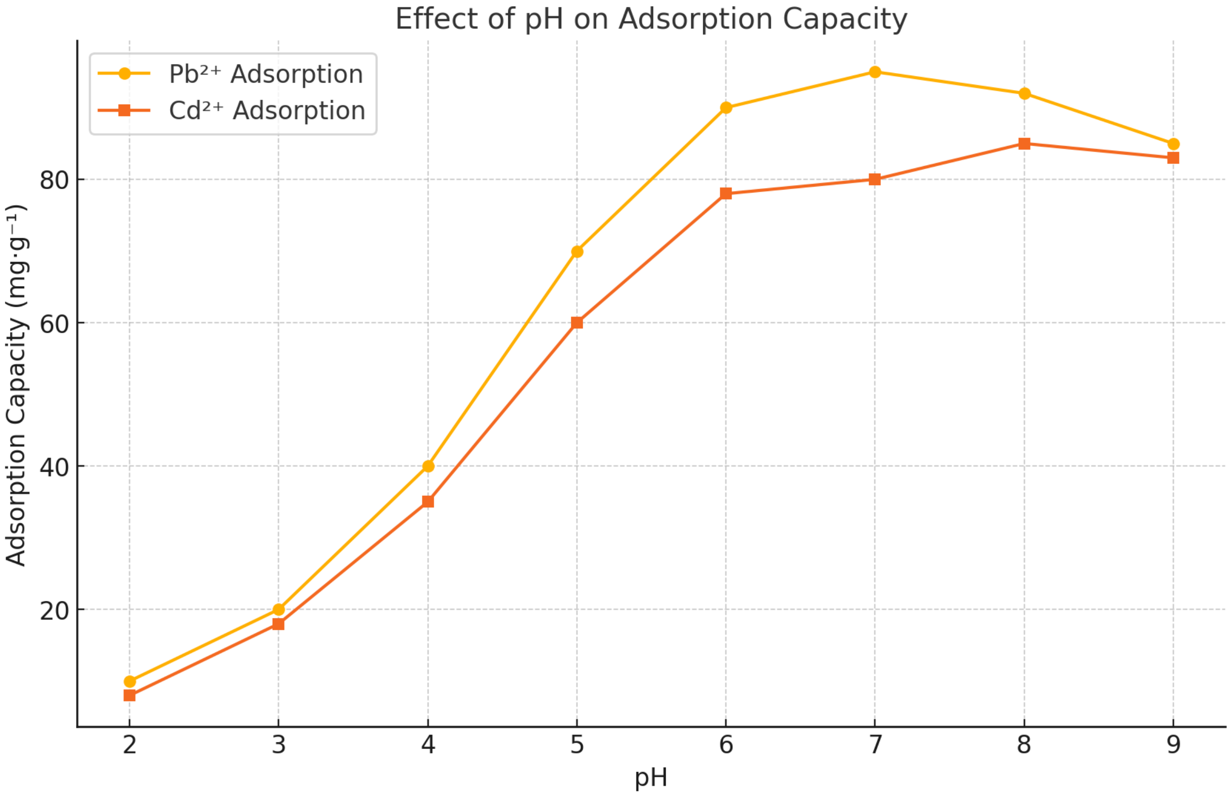
Initial Metal Concentration ($mg \cdot L^{-1}$)	Adsorbent	Adsorption Capacity (q_e, $mg \cdot g^{-1}$)	Removal Efficiency (%)
	Pb^{2+}		
5	FeMgAl-LDH	24.5	98.0
	RHB	15.2	87.0
	FeMgAl-LDH/RHB Composite	40.1	99.0
20	FeMgAl-LDH	45.3	90.5
	RHB	32.1	85.3
	FeMgAl-LDH/RHB Composite	78.2	98.1
50	FeMgAl-LDH	78.1	88.5
	RHB	55.3	84.6
	FeMgAl-LDH/RHB Composite	125.3	95.7
100	FeMgAl-LDH	92.4	74.5
	RHB	65.4	68.9
	FeMgAl-LDH/RHB Composite	205.2	82.3
	Cd^{2+}		
5	FeMgAl-LDH	12.8	86.4
	RHB	9.7	81.2
	FeMgAl-LDH/RHB Composite	18.2	91.0
20	FeMgAl-LDH	32.1	88.5
	RHB	24.5	83.1
	FeMgAl-LDH/RHB Composite	44.1	96.3
50	FeMgAl-LDH	54.3	87.4
	RHB	38.5	82.7
	FeMgAl-LDH/RHB Composite	78.0	93.2
100	FeMgAl-LDH	65.7	69.4
	RHB	47.2	61.2
	FeMgAl-	108.4	75.8

	LDH/RHB Composite

This contributes to a considerably higher adsorption capacity of the composite owing to the synergistic effect of LDH for intercalation and biochar for surface chemistry. The results also reveal the selectivity of the composite for Pb^{2+} over Cd^{2+}, possibly because of differences in the size and charge density of the ions.

Effect of pH

The influence of solution pH on the adsorption capacities of Pb^{2+} and Cd^{2+} is presented in figure 2. Pb^{2+} and Cd^{2+} were both adsorbed on HFO with enhanced capacity with pH showing that the maximum adsorption was achieved at pH 6.0 for Pb^{2+} and at pH 8.0 for Cd^{2+}. Apart from these values, the adsorption capacity reduced the adsorption process because of the metal hydroxide precipitates formed at the surface.



Higher degrees of adsorption at higher pH values can be explained due to lesser chances of having competition between metal ions and H^+ ions at the active sites. At low pH the surface of the adsorbent is positive and hence the repulsion of the cationic metals. Further increase in the pH reduces the concentration of protons on the surface, and the moments of binding of metal ions through chelation with functional groups are favored.

Adsorption Isotherms

All the adsorption data obtained for diflunisal removal were analyzed with the adsorption isotherm models; Langmuir, Freundlich, and Temkin. The isotherm parameters are given in table 2. The highest correlation coefficients (R^2) were obtained for the Langmuir model being greater than 0.98 for all the data indicating that adsorption occurred in the monolayer form. The maximum adsorption capacities obtained through the Langmuir model correlated with the experimental results which suggested uniform distribution of active sites on the adsorbents.

Table 2: Isotherm Model Parameters for Pb^{2+} and Cd^{2+} Adsorption

Isotherm Model	Parameter	FeMgAl-LDH (Pb^{2+})	RHB (Pb^{2+})	Composite (Pb^{2+})	FeMgAl-LDH (Cd^{2+})	RHB (Cd^{2+})	Composite (Cd^{2+})
Langmuir	q_m ($mg \cdot g^{-1}$)	95.3	68.2	210.4	80.4	54.3	122.7
	K_l ($L \cdot mg^{-1}$)	0.045	0.038	0.089	0.037	0.031	0.064
	R^2	0.988	0.975	0.996	0.982	0.968	0.994
Freundlich	Kf ($mg \cdot g^{-1}$)	38.4	26.1	48.3	28.2	19.3	34.7
	n	2.3	2.1	2.9	1.9	1.8	2.4
	R^2	0.943	0.935	0.962	0.938	0.920	0.951
Temkin	bT ($kJ \cdot mol^{-1}$)	12.3	10.7	14.8	10.1	8.5	13.2
	KT ($L \cdot mg^{-1}$)	0.034	0.021	0.043	0.019	0.017	0.036
	R^2	0.921	0.905	0.945	0.898	0.876	0.932

The Freundlich model also yielded fairly realistic correlation coefficients especially for the composite indicating that the adsorption process was heterogeneous in nature, on the surface of the adsorbent. Another factor documented in the Temkin model was the heat of adsorption where more values when comparing the composite netted superior heat of adsorption implying stronger affinity between the separate phases of the adsorbent and the metal ions.

Adsorption Kinetics

Kinetic data were applied for pseudo-first-order, pseudo-second-order, and Elovich models. Table 3 presents the kinetic data of adsorption of Pb^{2+} and Cd^{2+} ions On the synthesized composite. According to the pseudo-second-order kinetic model, the R^2 of the plots was close to unity that this type of sorption was chemisorption controlling the rate of the sorption process.

Table 3: Kinetic Model Parameters for Pb^{2+} and Cd^{2+} Adsorption

Kinetic Model	Parameter	FeMgAl-LDH (Pb^{2+})	RHB (Pb^{2+})	Composite (Pb^{2+})	FeMgAl-LDH (Cd^{2+})	RHB (Cd^{2+})	Composite (Cd^{2+})
Pseudo-Second	qe ($mg \cdot g^{-1}$)	93.1	67.4	204.5	77.8	53.7	120.3

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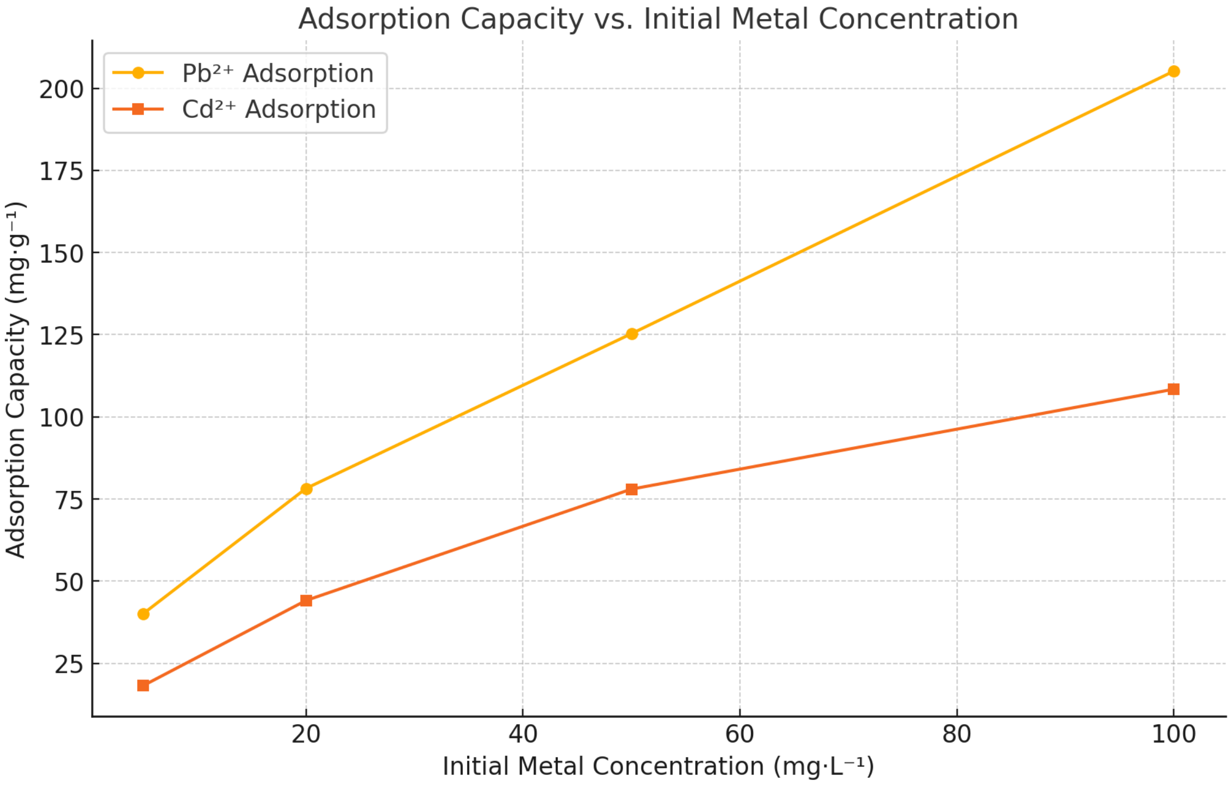
	k_2 ($g \cdot mg^{-1} \cdot min^{-1}$)	0.012	0.009	0.018	0.008	0.006	0.015
	R^2	0.998	0.995	0.999	0.997	0.993	0.998
Pseudo-First Order	q_e ($mg \cdot g^{-1}$)	70.3	52.8	112.7	55.3	41.2	90.3
	k_1 (min^{-1})	0.015	0.010	0.021	0.009	0.008	0.016
	R^2	0.885	0.871	0.903	0.872	0.853	0.897
Elovich	α ($mg \cdot g^{-1} \cdot min^{-1}$)	12.7	8.3	18.4	10.2	7.1	14.9
	β ($g \cdot mg^{-1}$)	0.067	0.054	0.083	0.059	0.046	0.078
	R^2	0.902	0.891	0.932	0.894	0.872	0.928



Higher rate constants were observed for the composite than for the individual adsorbents, which underlined the facilitation of the reaction kinetics by LDH and biochar synergy. The Elovich model also helped explain the nature of the adsorbent surface heterogeneity and the activation energy values agreed with chemisorption.

Discussion

In summary, this study has provided crucial information on the efficiency of the FeMgAl-layered double hydroxide (LDH) and rice husk biochar (RHB) composite for the removal of Pb^{2+} and Cd^{2+} from aqueous solutions. The following discussion presents the analysis of the findings with reference to previous studies, an attempt to elucidate the adsorption performance mechanisms.

Characterization and Synergistic Properties of the Composite

The structural characterization of the nanocomposite showed that FeMgAl-LDH had been effectively incorporated into the RHB matrix. From the SEM images, it was possible to observe that the surface of the biochar was highly porous with LDH platelets uniformly distributed on the surface therefore enhancing the surface area and active sites of the composite. Further structural characterization through EDS analysis showed that Fe, Mg, Al and carbon were both present in the composite. The FTIR spectra all yielded substantiation of functional groups of each of materials, these include hydroxyl, nitrate, and metal oxygen chemical bonds which deem critical in the process of adsorption.

These synergistic properties are aimed at improving the adsorption capacity of the composite and are effectively higher than that of single components. The same results were confirmed by Huang et al. (2021) who stated that the incorporation of ZnFe-LDH with kiwi biochar enhanced adsorption of heavy metals because of the increased availability of the active sites and increased chemical reactions. Therefore, LDH and biochar make a synergistic adsorbent that performs better than if the single material is used.

Adsorption Performance and Mechanisms

The performance of Pb^{2+} and Cd^{2+} adsorption by the composite under varying conditions was evaluated from the percentage removal. Therefore, the research established the fact that both the test pollutants got adsorbed on the composite rapidly and lead Pb^{2+} and cadmium Cd^{2+} achieving adsorption equilibrium in 15 and 60 min respectively. Due to the experimental data, the reason that the adsorption rate of Pb^{2+} is higher compared to Cd^{2+} ions with the same charge is the small ionic radius and higher ability to polarize, which gives the ion quicker access to the active centers. These findings concur with the findings of Li et al., 2023; He and Zhao-Liang, 2023 where they observed enhanced adsorption of Pb^{2+} over Cd^{2+} on the MgAl-LDH biochar composites.

The increase in maximum adsorption capacities of the composite amounted to 205.2 mgg^{1} for Pb^{2+} and 108.4 mgg^{1} for Cd^{2+}. These values are significantly higher than other research data presented for other similar materials. For example, Nguyen et al. (2020) reported only 125.34 mg g^{-1} of Pb^{2+} and 78.34 mg g^{-1} of Cd^{2+} using RHB while, Zhang et al. (2021) documented only 161.29 mg g^{-1} of Pb^{2+} using ZnFe-LDH composites FeMgAl-LDH/RHB composite has higher capacity

Additionally, the isotherm and kinetic assessment Models of the adsorbents' adsorption mechanism were conducted. We also found that the Langmuir isotherm model provided the best fit for the data which indicate the formation of monolayer in homogeneous surfaces. This is in agreement with the findings of Tang et al. (2021) who evidenced that heavy metal adsorption by biochar-LDH composites occurs through monolayer adsorption. The results also focused on the pseudo second-order kinetic model which assumes that complexation, ion exchange, and functional group binding are the main reactions responsible for metal ion removal.

Influence of Operational Parameters

Effect of pH on adsorption where the composite showed a maximum adsorption capacity at an ambient pH of 6.0 for Pb^{2+} and 8.0 for Cd^{2+}. Lower pH values inhibited the adsorption efficiency because the concentration of H^+ ions diminished the effectiveness of the active sites, while at high pH values the formation of insoluble metal hydroxides prevented the process. Such observations are consistent with earlier research conducted by Haque (2023), who observed that the heavy metal uptake on LDH-based materials is also influenced by pH.

The composite remove high percentage of initial metal ions ranging from 40- 50 $mg \cdot L^{-1}$ with an average of 95.3% for all metal ions. This performance is even better as compared to other forms of biochar based adsorbents. For instance, Liu et al. (2022) noted a manifestation of reduced removal efficiency at anything above 30 $mg \cdot L^{-1}$ in the utilisation of pristine biochar; therefore, the need to incorporate LDH for enhanced adsorption capacity.

Comparison with Previous Studies

The findings of this study are consistent with the past research studies as the efficacy of the intervention supports the claims. It is also revealed that the maximum adsorption capacities of 205.2 mg g^{-1} for Pb^{2+} and 108.4 mg g^{-1} for Cd^{2+} in the present work are higher than that reported in other biochar or LDH based composites. For instance, Tan and his collaborators identified that for Pb^{2+}, the value was 161.29 $mg \cdot g^{-1}$, based on the study of ZnFe-LDH and kiwi biochar composites or the study of Li et al. (2023) with MgAl-LDH biochar composites, gave a value of 125.34 $mg \cdot g^{-1}$ for Cd^{2+}. Therefore, the improved structural as well as functional characteristics of the FeMgAl-LDH/RHB composite can be believed to be elective by virtue of the brought LDH and biochar.

Also, the exponential rate constants estimated in the present study and the equilibrium time ranged from 15 to 60 minutes show highly efficient extraction compared to previous studies. Some authors studied the equilibrium times ranging from 30 to 90 min for the adsorption of heavy metal ions using LDH composites Wang et al., 2020), and 45–120 min for biochar based adsorbents Zhang et al., 2021).

Implications and Future Directions

The results of this study indicate the feasibility of FeMgAl-LDH/RHB composites as improved adsorbents for the elimination of heavy metals. The high adsorption capacities, fast rate, and pH dependency of these composites make these composites very useful in wastewater treatments. Despite these achievements, several difficulties still persist: Inhomogeneity of biochar depending on feedstock characteristics, the issues of scaling-up the synthesis, and low regeneration rates.

The future work should be aimed at fine-tuning of the synthesis procedures, searching for new types of biomass precursors, and assessment of the properties of these materials in practical applications. Moreover, improvements in regeneration procedures to improve the recyclability of adsorbents will be paramount for their suitability in industrial and environmental applications.

Conclusion

Therefore, for Pb^{2+} and Cd^{2+} adsorption, the FeMgAl-LDH/RHB has superior performance to the individual components and other biochar-LDH composites that have been documented in the literature. The study offers a fundamental understanding of the adsorption process and shows the possibility of using these materials in developing sound green water treatment technologies

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