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Removal of Cd^{2+} from Aqueous Solution Using $MgAlCO_3$-Layered Double Hydroxide

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ABSTRACT

Anion clay hydrotalcite $MgAlCO_3$ *with a Mg/Al molar ratio of 3:1 was synthesized by co-precipitation at room temperature and pressure. The physicochemical properties were evaluated using Powder X-Ray Diffraction (PXRD), Fourier Transform Infrared (FTIR) spectroscopy and Thermogravimetric Analysis (TGA). The efficacy of anion clay hydrotalcite in the removal of* Cd^{2+} *from aqueous solutions was investigated with respect to contact time, initial concentration, pH, adsorbent dosage and temperature. The* Cd^{2+} *removal increased with the increased in contact time, adsorbent dosage, pH and initial concentration. Adsorption decreases with increasing initial concentration and temperature, for which the latter is indicative of an exothermic process. The equilibrium adsorption capacity of* $MgAlCO_3$ *was evaluated using linear Langmuir and Freundlich isotherms with respect to the separation factor,* R_L.

Keywords: *layered double hydroxide, cadmium,* R_L *factor, Langmuir isotherm, Freundlich isotherm*

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Introduction

Environmental pollution due to Cd(II) is of great concern due to its tendency to bioaccumulate and toxicity to many life forms. Cadmium is often detected in discharged wastewater from electroplating-, plastic-, battery- and zinc refining-industries [1]. Prolonged cadmium exposure can cause bone lesions, cancer, hypertension and inhibit lung and renal function [2], hence there is a crucial need to remove Cd(II) from municipal and industrial effluents before discharge.

A wide variety of techniques are available to remove heavy metals, including adsorption, electrochemical treatment and froth flotation. Adsorption is considered an attractive process due to its proven efficiency in the treatment of wastewater and ability to remove many different contaminants [3]. Layered double hydroxides (LDHs) are promising adsorbents due to their efficiency in removing large numbers of anionic species commonly found in aqueous effluents [4].

LDHs are an interesting class of layered compounds, also called hydrotalcites or anionic clays, which may be represented by the general formula $[M^{II}_{(1-x)}M^{III}_{x}(OH)_2]^{x+}(A_{x/n}^{n-}mH_2O)^{x-}$, where M^{II} = Mg, Ni, Co, Zn; M^{III} = Al, Fe, Cr, V; $A^{n-} = CO_3^{2-}$, Cl^-, and $x = 0.1 - 0.35$. The formula of the hydrotalcite used in this study is $Mg_6Al_2(OH)_{16}CO_3.4H_2O$ and is comprises of mixed hydroxide layers of Mg and Al in a brucite-like sheet [5-7]. Each magnesium ion is surrounded by six hydroxide ions in a regular octahedral manner connected through edge sharing to form infinite sheets. These sheets stacked one upon another yielding a layered network held together by hydrogen bonding. Anions and water molecules occupy these interspatial positions between the layers thereby maintaining electric neutrality. The interspatial positions are randomly located throughout the layered network and possess a high degree of mobility [8,9].

In the presented study, $MgAlCO_3$-layered double hydroxides with an M^{II}:M^{III} ratio of 3:1 were synthesized by co-precipitation under room temperature-pressure conditions. Physicochemical structural characterization of the synthesized hydrotalcite was performed using PXRD, FTIR spectroscopy and TGA. The adsorption efficiency was evaluated with respect to pH, temperature, contact time, adsorbent dosage and initial cadmium solution concentration.

Experimental

Synthesis of Carbonate-containing Mg-Al LDH

LDHs comprising of Mg-Al (3:1) layers with carbonates in the interspatial positions were prepared by co-precipitation under room temperature-pressure conditions as follows: A solution containing 1.000 mol of sodium hydroxide (NaOH) and 0.125 mol of sodium carbonate (Na_2CO_3) was added dropwise to 500 mℓ of an aqueous solution containing 0.300 mol of magnesium chloride hexahydrate ($MgCl_2.6H_2O$) and 0.100 mol of aluminium chloride hexahydrate ($AlCl_3.6H_2O$). The co-precipitation solution was maintained at pH 10 and the resultant suspension was aged in an oil batch set for 24 hours at 70 °C. After 24 hours, the mixed suspension was centrifuged and a white precipitate recovered. The solid was washed three times with distilled water and the suspension filtered and washed a further eight times. The resultant wet cake was dried in an oven for 24 hours at 80 °C.

Sorbent Characterization

The as-synthesized hydrotalcite was evaluated using Powder XRD on an Xpert Pro PANalytcal diffractometer with Cu-K_{α} radiation (λ = 0.15406 nm) at 35 kV and 20 mA. FTIR spectra were obtained by pelletizing 25 mg of hydrotalcite with KBr and running on a Perkin Elmer BX 1600 Fourier Transform Infrared spectrometer. The thermal stability of the hydrotalcite was determined using a TGA 7 using a heating rate of 10 °C/min under nitrogen flowing at 35 mℓ/min from room temperature to 900 °C.

Adsorption Studies

Adsorbent-Cd(II) doped solutions of volume 50 mL were prepared by adding a predetermined mass of adsorbent to an agitated Cd(II) solution and allowed to attain adsorption equilibrium. The quantity of Cd(II) adsorbed was determined using ICP-AES spectrometry and evaluated with respect to adsorbent contact time, t, initial Cd(II) concentration, C_o, adsorbent dosage, initial solution pH and temperature. All the aforementioned experiments were performed in replicate for the purposes of reproducibility. The Cd(II) removal percentage (%) was determined according to the following equation:

$$\text{Cadmium removal (\%)} = \frac{(C_o - C_e)}{C_o} \times 100 \qquad (1)$$

where, C_o and C_e are the initial and equilibrium concentrations of Cd(II) (mg L^{-1}), respectively. The amount of cadmium adsorbed on the $MgAlCO_3$-LDH samples was determined according to:

$$q_e = \frac{(C_o - C_e)V}{m} \qquad (2)$$

where q_e is the quantity of Cd(II) adsorbed to the adsorbent (mg g^{-1}), V is Cd(II) solution volume (ℓ) and m is the adsorbent dosage (g).

Results and Discussion

Powder X-Ray Diffraction (PXRD)

The XRD pattern for the synthesized $MgAlCO_3$-LDH exhibits good crystallinity and is characteristic for layered materials with a hydrotalcite-like structure in the absence of $Mg(OH)_2$ and Al, Figure 1. The sharp peak at $d = 7.872$ Å ($2\theta = 11.5^o$) for the d_{003} plane (*hkl*) corresponds to a hydrotalcite structure with rhombohedral 3R layered packing [9]. The lattice parameters a and c have been calculated according to: $a = 2d_{110}$ and $c = 3d_{003}$ and correspond 3.063 Å and 23.616 Å, respectively, and are in good agreement with the values stated by Yang *et al.* in their work on carbonate-containing hydrotalcite materials [10]. The gallery spacing has been determined to be approximately 0.307 nm with respect to the thickness of the brucite layer which is 0.48 nm [11]. This gallery spacing is lower than the free CO_3^{2-} anion diameter (0.370 nm) [12], which implies strong interaction between the CO_3^{2-} anions and the brucite-like layer.

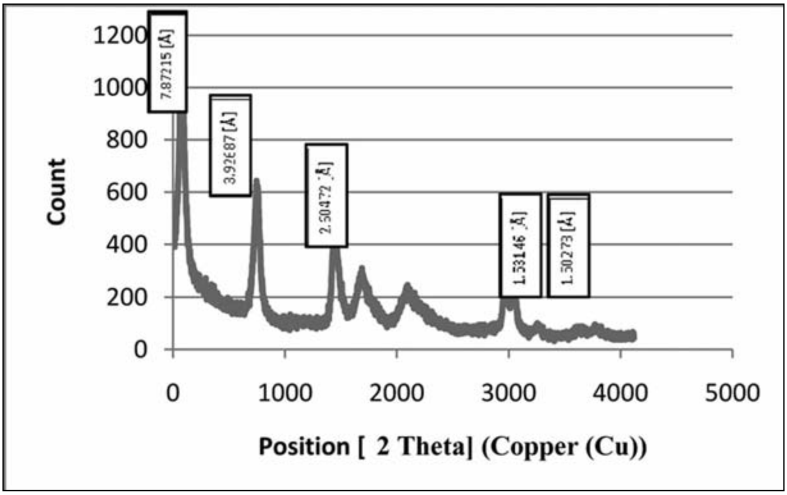

Figure 1: XRD pattern for the synthesized $MgAlCO_3$-LDH

Fourier Transform Infrared (FTIR)

Figure 2 presents the infrared spectrum for the $MgAlCO_3$-LDH over the range 400 – 4000 cm^{-1} and exhibits a broad band in the region 3464 cm^{-1}, which may be attributed to hydrogen bonding between water molecules in the interspatial positions. The band at 1650 cm^{-1} can be attributed to bending vibrations in the water molecules, whereas the band at 1375 cm^{-1} is characteristic of antisymmetric υ_3 vibrations in the carbonate anions. The medium band at 655.74 cm^{-1} is characteristic of magnesium and aluminium lattice vibrations within the octahedral sheet and provides evidence of crystallinity within the LDH phase. Table 1 summarizes the infrared frequencies for synthesized $MgAlCO_3$-LDH.

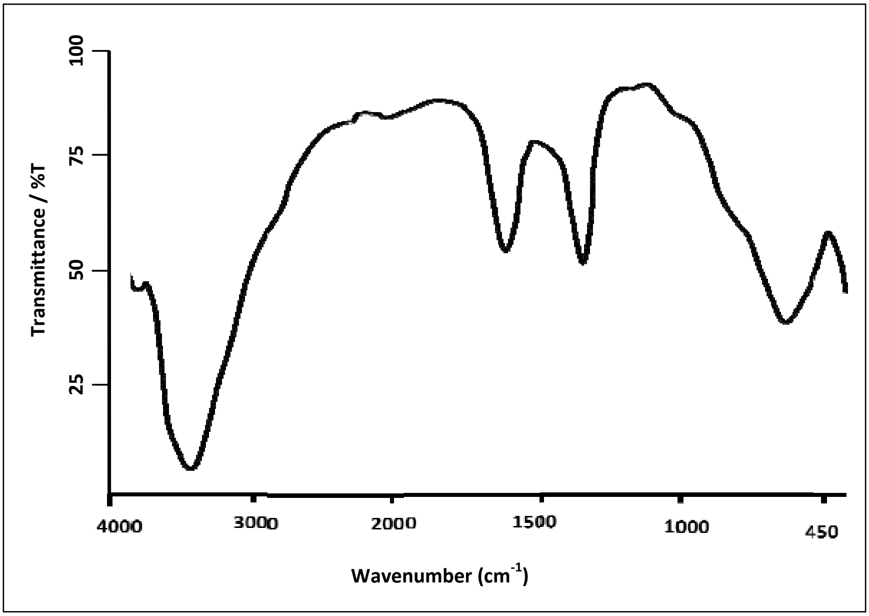

Figure 2: FTIR spectra for the synthesized MgAlCO$_3$-LDH

Table 1: Wavenumber (cm^{-1}) summary for the synthesized MgAlCO$_3$-LDH

Vibration type	Wavenumber (cm^{-1})
O-H	3464.59
H_2O	1650.76
CO_3^{2-}	1375.32
Mg-O, Al-O	655.74

Thermogravimetric Analysis

Thermograms for the synthesized MgAlCO$_3$-LDH indicate two significant stages of weight loss, Figure 3. The first weight loss occurs in the range 80–250 °C, which corresponds to an endothermic process and may be attributed to the removal water in the interspatial positions in the MgAlCO$_3$-LDH. The second significant weight loss occurs in the range 260 – 600 °C and may be attributed to the loss of hydroxyl groups from the brucite-like layer containing the carboxylate anions achieved through dehydroxylation and decarboxylation reactions.

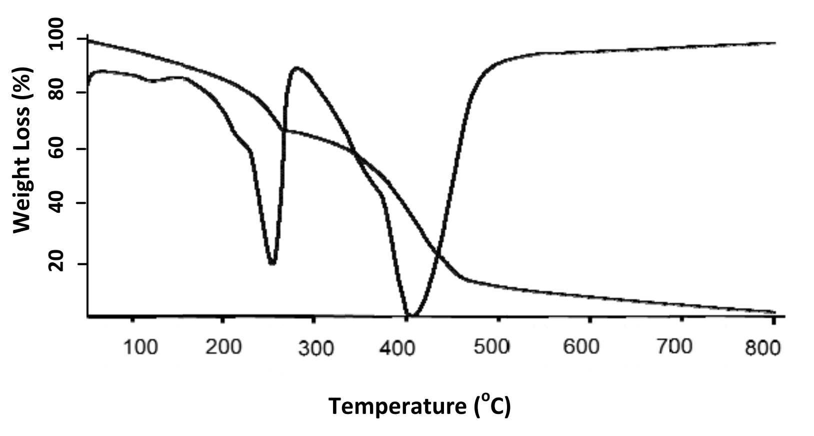

Figure 3: TGA (DSC) profile for the synthesized $MgAlCO_3$-LDH

Adsorption Studies

Effect of Contact Time

The effect of contact time on percentage uptake is presented in Figure 4, which indicates that maximum Cd(II) uptake is attained at 3 hours. Adsorption increases from 48.48 % for one hour of exposure up to 70.74 % for three hours after which the adsorption percentage asymptotes. The increase in cadmium uptake can be attributed to the large number of vacant adsorption sites initially available on the $MgAlCO_3$-LDH surface, which become progressively occupied until saturation is attained in accordance with the work of Meena *et al.*, [13].

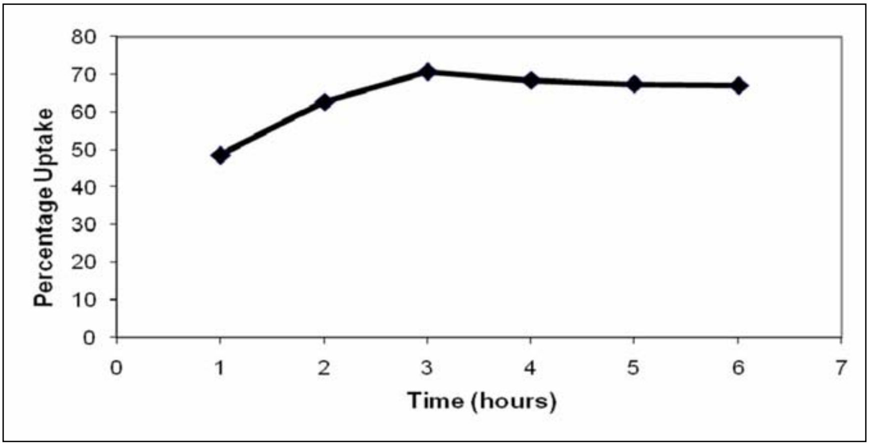

Figure 4: Cd(II) percentage uptake with contact time

Effect of Initial Concentration

It is evident from Figure 5 that the Cd(II) percentage uptake decrases significantly with increasing Cd(II) concentration, whereby percentage uptake decreased from 99.47 % at 20 mg/ℓ to 11.07 % at 150 mg/ℓ, which agrees with the work of Kay and Ho [14].

At lower metal ion initial concentrations sufficient adsorption sites are available for adsorption and it is likely that adsorption site saturation has been achieved in all cases; thus by increasing the initial Cd(II) concentration does not appear to promote further adsorption.

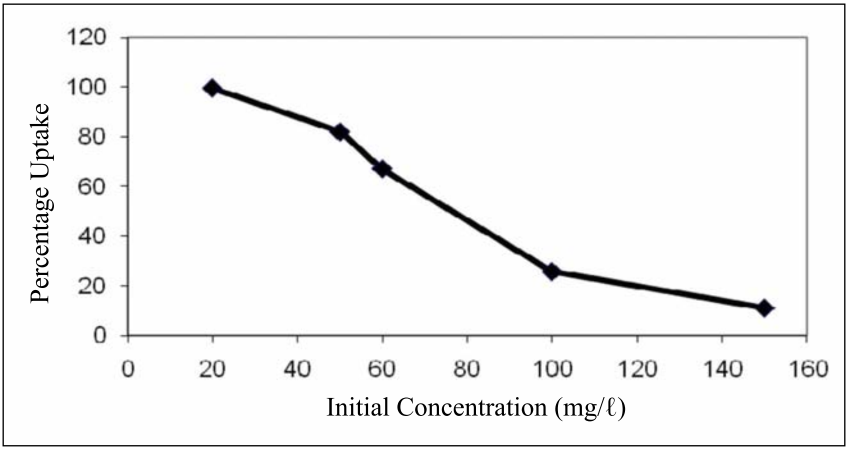

Figure 5: Cd(II) percentage uptake with intial Cd(II) concentration

Effect of pH

The effect of pH on Cd(II) adsorption was investigated at 25 ^{o}C over a period of three hours, Figure 6. The results indicate that adsorption is significantly affected by pH, since there is an evident increase in percentage uptake until pH 11 (75.90 %) after which uptake asymptotes. This pattern is a consequence of less hydrogen ions competing with the aqueous cadmium ions for the cationic adsorption sites [16-19], until saturation is attained at pH 11. It is of note that the dominant Cd(II) species at pH > 8.0 is $Cd(OH)_2$ and at pH< 8.0 is Cd^{2+} and $Cd(OH)^+$ and it is therefore plausible that above pH 9 $Cd(OH)_2$ precipitates and occupies the adsorption sites [19,20].

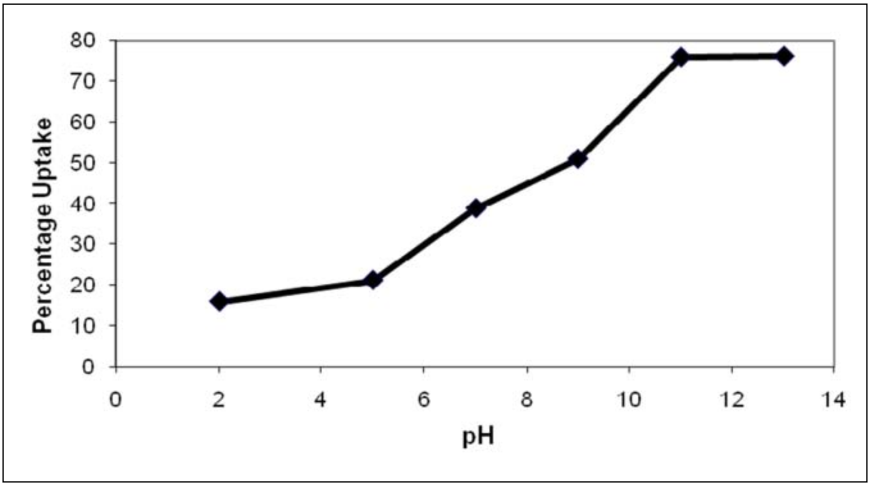

Figure 6: Cd(II) percentage uptake with pH

Effect of Adsorbent Dosage

Solutions of initial Cd(II) concentration, 150 mg/ℓ, at the solution's natural pH and 25 °C were prepared and dosed with adsorbent quantities varying from 0.05 – 2.00 g for a period of three hours, Figure 7. The results indicate that Cd(II) percentage uptake increases with increasing adsorbent loading, 0.05 g (7.38 %) to 2.0 g (61.05 %), which is anticipated since more adsorbent sites are available and hence there is a far greater chance of adsorption [21].

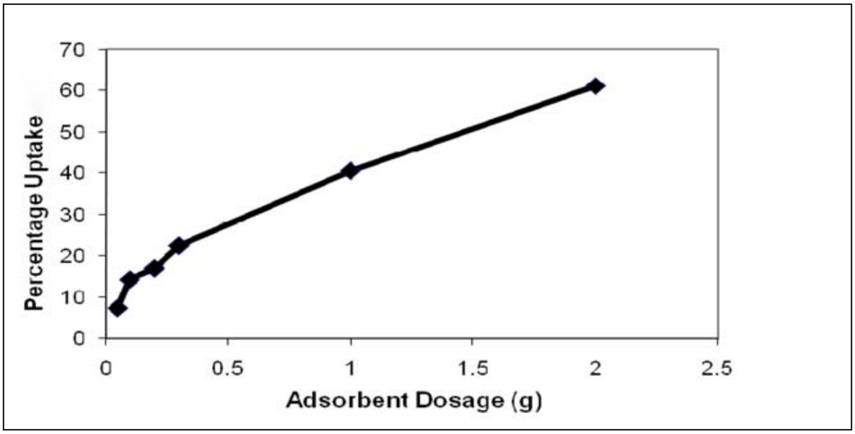

Figure 7: Cd(II) percentage uptake with adsorbent dosage

Effect of Temperature

The effect of temperature on Cd(II) uptake percentage was investigated using a 50 mℓ solution of concentration 150 g/ℓ with an adsorbent content of 0.1 g at the solution's natural pH over a period of three hours, Figure 8. From the results presented it is obvious that the percentage uptake decreases reciprocally with increasing temperature, achieving a maximum at 25 °C (71.56 %) and minimum at 65 °C (18.94 %). The decrease in uptake is a consequence the thinning boundary layer about the surface of the adsorbent due to increased metal ion solubility [22]. This suggests that there is weak adsorption between the adsorbate surface and cadmium ions, which indicates that adsorption proceeds by physisorption.

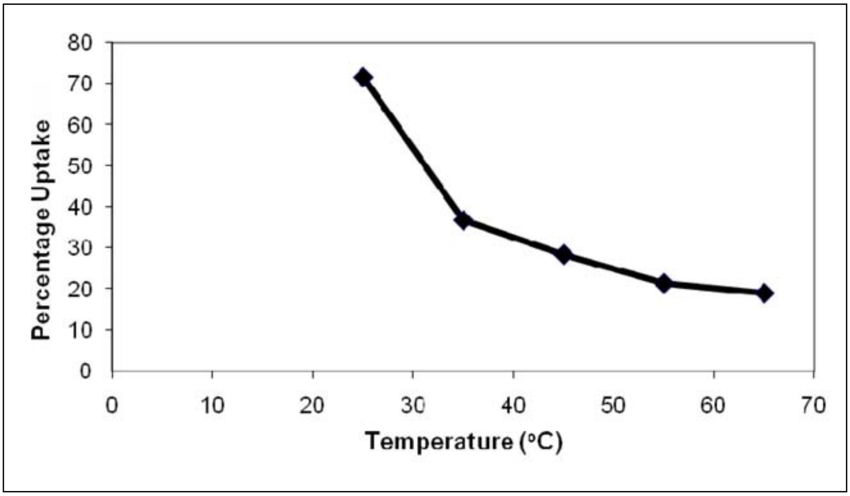

Figure 8: Cd(II) percentage uptake with temperature

Isotherm Studies

The Langmuir isotherm is based on the assumption the adsorption occurs as a monolayer and there are no interactions between the adsorbed molecules. Hence once a cadmium ion occupies a site, no further adsorption can take place at that site. The linear form of the Langmuir isotherm may be expressed as [23]:

$$\frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{bQ_oC_e} \tag{3}$$

where Q_o is the maximum sorption capacity (mg/g) and b is constant related to the energy of adsorption (ℓ/mg). A plot of $1/q_e$ versus $1/C_e$ yields a straight line of gradient $1/bQ_o$ and intercept $1/Q_o$. The Freundlich isotherm is an empirical equation used to describe heterogeneous systems and may be express logarithmically as [24]:

$$\log q_e = \log K_F + \frac{1}{n \log C_e} \tag{4}$$

where K_F and n are the Freundlich constants. n indicates the favourability of adsorption; if $n > 1$ then adsorption is favourable, and K_F (mg/g) $^{1/n}$ is the adsorption capacity of the sorbent. Values of K_F and n are determined from the intercept and gradient of a plot of log q_e versus log C_e.

From the Langmuir isotherm presented in Figure 9 it has been determined that the maximum sorption capacity, Q_o for cadmium is 25.00 mg/g and the Langmuir constant, b, is 6.855×10^{-3} ℓ/mg, which indicates that $MgAlCO_3$-LDH has a high affinity for cadmium adsorption [25].

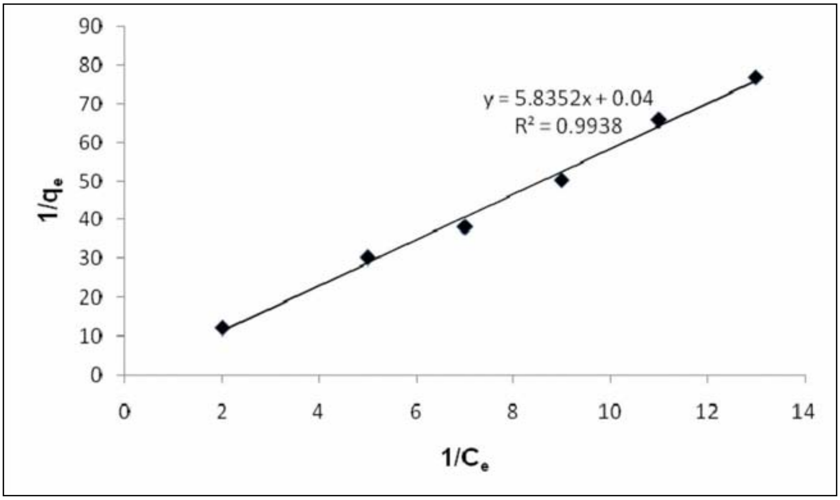

Figure 9: Langmuir isotherm plot for the adsorption of Cd(II) by $MgAlCO_3$ LDH

The Freundlich isotherm presented in Figure 10 according to equation (4) indicates that the adsorption capacity is 0.1616 mg/g and n is 1.0295, which indicates that adsorption is favourable [26].

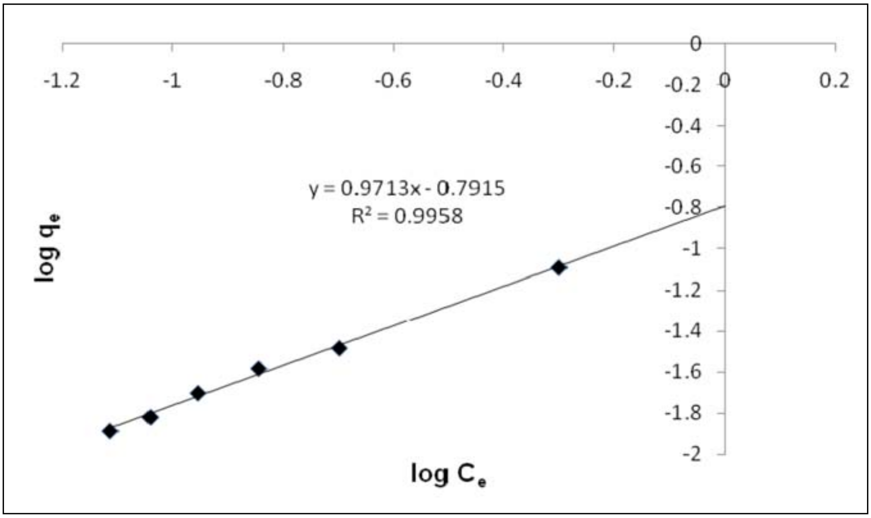

Figure 10: Freundlich isotherm plot for the adsorption of Cd(II) by $MgAlCO_3$ LDH

The highest initial adsorbate concentration, C_o, and Langmuir constant, *b*, determined from the Langmuir isotherm can be expressed in terms of a dimensionless parameter known as the separation factor, R_L, according to:

$$R_L = \frac{1}{1 + bC_o} \qquad (5)$$

The isotherm R_L values indicate whether adsorption is unfavourable (R_L>1), linear (R_L=1), favourable or irreversible (R_L=0).

$$(0<R_L>1)$$

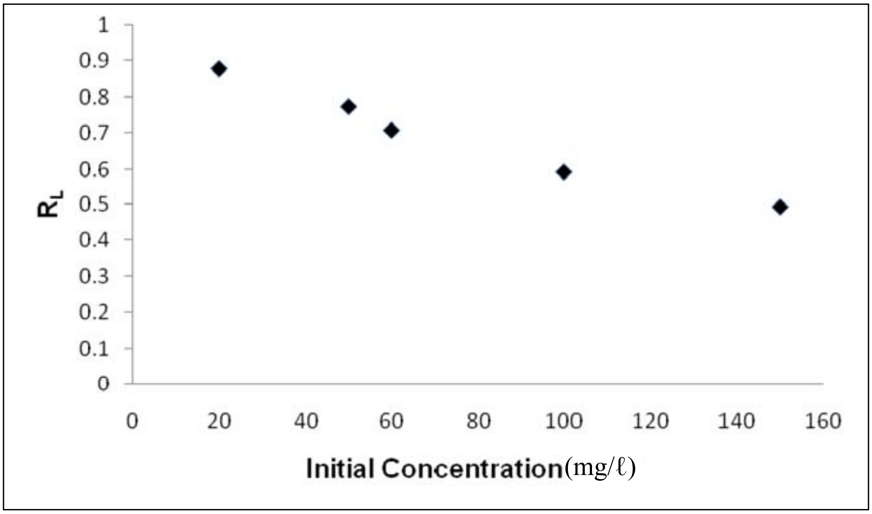

Figure 11: R_L plot with initial adsorbate concentration

The presented R_L-values lie between zero and one indicating that the adsorption of cadmium ions on the $MgAlCO_3$ LDH is favourable at the concentrations studied, as shown in Figure 11. Isotherm parameters for the Freundlich and Langmuir models are summarized in Table 2. The results indicate that cadmium ion adsorption can be described adequately by both Langmuir and Freundlich type isotherms.

Table 2: Langmuir and Freundlich constants for the adsorption of Cd(II) ions on $MgAlCO_3$ LDH

	Langmuir			Freundlich		
	Q_o (mg/g)	**b (L/mg)**	**R^2**	**n**	K_F (mg/g)	**R^2**
Cadmium aqueous solution	25.00	6.855×10^{-3}	0.9938	1.0295	0.1616	0.9958

Conclusion

The results of the performed study indicate that $MgAlCO_3$ LDH has the potential to be an adsorbent in the removal of cadmium in aqueous solutions. The synthesized hydrotalcite exhibits good crystallinity in the absence of other undesirable phases with respect to PXRD and FTIR. Investigation of the effects of contact time, initial cadmium concentration, pH, adsorbent dosage and temperature on Cd(II) uptake indicates that contact times longer than three hours do not promote further adsorption, maximum adsorption occurs even at relatively low concentrations, at pH 11 adsorption is maximised, increased dosage increases adsorption and higher temperatures inhibit adsorption hence adsorption is believed to be exothermic, respectively. Both Langmuir and Freundlich isotherms describe cadmium adsorption adequately; further to which the separation factor, R_L, values indicate that the $MgAlCO_3$ LDH is capable of adsorption over the range of concentrations considered.

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