Adsorption of organic compound by calcined hydrotalcite materials: modeling and experimental validation

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Abstract

The chemical contamination of water from a wide range of toxic derivatives, in particular organic molecules, is a serious environmental problem owing to their potential human toxicity. Among all the treatments proposed, adsorption is one of the most current methods for the removal of pollutants from the water. In this paper, we addressed the issue of using calcined double layered hydroxides (ZnAl-CO_3DLH) at molar ration r=4 as adsorbent for Diclofenac sodium (DS) under the batch reactor operations in order to remove DS from aqueous solution. This work focused on the equilibrium isotherms and kinetics of the adsorption. The adsorption data fitted well to Langmuir isotherm. The maximum adsorption capacity of diclofenac was estimated to be 451.66 mg/g.

In conclusion, the expanding of calcined ZnAl-CO_3LDH adsorption represents a plausible and powerful circumstance, leading to a great improvement of environmental protection.

Keywords: *Adsorption; isotherm; kinetics; Diclofenac sodium; Calcined layered double hydroxide.*

I. Introduction

Adsorption is one of the several process used to remove diclofenac from water using different adsorbent solids such as clays and Layered double hydroxides (LDH). Layered double hydroxides or hydrotalcite are a family of natural or synthetic materials with a formulation of $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2][A^{n-}_{x/n}zH_2O]$ where M^{2+} and M^{3+} are divalent and trivalent metals, respectively. A^{n-} is the intercalated hydrated counter anion. Layered double hydroxides (LHD) display unique physical and chemical properties, and they can be easily and inexpensively synthesized.
Diclofenac sodium, which is a non-steroidal anti-inflammatory drug (NSAID), is widely used with very important consumption quantities. It has been detected in 83% of water samples [1] and even in drinking water in many countries [2]. Continued intake of Diclofenac has shown several adverse biochemical effects [3-7]. Therefore its presence in waters presents a huge problem toward environment and health.
The aim of this work was to prepare and characterize a calcined ZnAl-CO_3 layered double hydroxides. Once synthesized, the most novel aspect of this work lied in the investigation of Diclofenac sodium adsorption results using the synthesized materials. The objectives of the present study were:

(i) The preparation and characterization of calcined ZnAl-CO_3 layered double hydroxides at molar ratio r=4 by a coprecipitation method.
(ii) Its application in the removal of Diclofenac sodium from water under batch experimental conditions.

II. Materials and methods

$ZnCl_2 6H_2O$ (99%) is procured from Biochem, $AlCl_3 6H_2O$ (95%) is supplied by PRS Panreac, and Na_2CO_3 (99%) is obtained from Flucka. NaOH

(99%) is obtained from Recta pur Diclofenac sodium was supplied by Sigma Aldrich. (Table 1 provides the structural and chemical properties of Diclofenac [8]). All chemicals were used without further purification.

ZnAl (molar ratio r=4) layered double hydroxides containing carbonate as the interlayer anion were obtained using a conventional coprecipitation method. A base solution was prepared by dissolving an amount of Na_2CO_3 in 800mL of deionized water. This solution was then added dropwise to 800mL of a mixed salt solution prepared by dissolving $Zn(CO_3)_2 6H_2O$ and $Al(CO_3)_3 9H_2O$ under vigorous stirring. The solution pH was adjusted to 10 by dropwise addition of 1 M NaOH solution into the mixed solution for 5 hours at 298 K. A suspension was formed and stirred at 353 K for 18 hours. The products were filtered, washed with deionized water to remove any precursor impurities and then dried at 338 K. The obtained ZnAl LDH were calcined at 773 K with the same rate of heating (1°C/min) for 4 hours in the absence of air and oxygen. The calcined and not calcined adsorbents were characterized by X-ray diffraction using Bruker Advanced X-ray machine (Cu Kα wavelength =1.5418 Å).

Batch adsorption isotherm experiments were performed with predetermined initial concentration DS solutions (5-500 mgL^{-1}). A dose of $1g.L^{-1}$ of adsorbent was added to each solution, and the solution was stirred at 295 K for 2 hours. After that, the DS solutions were centrifuged, filtrated and the filtrates were subjected to the bulk concentration of diclofenac at λ_{max}= 267-264 nm using PharmaSpec-1700 UV-Visible spectrophotometer Shimadzu UV type.

Time dependence adsorption of Diclofenac by these materials was obtained at different time intervals and at different Diclofenac initial concentrations (20, 50 and 100 mgL^{-1}). The adsorption experiments were conducted at constant Diclofenac solution pH and at temperature 295 K. The results are presented as adsorption capacity $q_t(mgg^{-1})$ as a function of time (min) and initial DS concentration.

III. Results and discussion

A. Characterization of adsorbent

The XRD diagrams for the host solids are shown in *Fig. 2*. The XRD patterns exhibited the characteristic reflections of LDH with a series of sharp symmetric peaks at low 2θ angle, and broad asymmetric peaks at higher 2θ angle [9]. The XRD patterns of the not calcined $ZnAl\text{-}CO_3$ LDH showed three peaks at 2θ values of 11.63°, 23° and 34.51° consistent with hydrotalcites with an hexagonal crystal structure [10]. The X-ray pattern of calcined $ZnAl\text{-}CO_3$ showed that LDH structure was destroyed and converted to an amorphous material with formation of metal oxides corresponding to d_{200} and d_{220} reflections.

B. Effect of contact time and initial concentration on DS adsorption

The effect of initial DS concentration and the effect of contact time were shown in Figure 2. An increase in the DS concentration led to an increase in adsorbed quantity of DS, which revealed the important capacity of this material to adsorb DS presenting a high affinity toward DS. To estimate the rate constants and the removal capacity of this adsorbent, a kinetic modeling was required.

C. Kinetics modelling

Using a linear regression method, pseudo-first-order (PFO) expressed by (Eq. 1) [11] and pseudo-second-order (PSO) expressed by (Eq. 2) [12] kinetic models were used:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (1)$$

$$\frac{t}{q_t} = \frac{1}{q_e^2 k_2} + \frac{1}{q_e} t \qquad (2)$$

The calculated values of q_e, $k_1$and k_2 are shown in Table 2. According to the correlation coefficient, results are best fitted to the PSO model. According to k_2 values adsorption took place in two stages: the first one was fast (from 20 to 50min), whereas the second was slow (from 50 to 100 min) [13].

D. Adsorption Equilibrium Study

Langmuir, and Freundlich adsorption isotherms were applied to describe the adsorption process of the experimental results of DS onto calcined $ZnAl\text{-}CO_3$ hydrotalcite. Non linear form of Langmuir (Eq. 3) [14] and Freundlich (Eq.4) [15] equations were used.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

$$q_e = K_F C_e^{1/n} \quad (4)$$

The results are listed in Table 3. The value of the constant 1/n is0.75. Since 1/n is less than 1, the adsorption of DS was favorable onto calcined $ZnAl\text{-}CO_3$ hydrotalcite[16, 17].

According to error functions R^2, Langmuir model fit the experimental data well with a monolayer adsorption capacity of 451.66mgg^{-1}, which is very promising compared to other adsorbents for DS adsorption in Table 4.

The calcined LDH used in this research showed a favorable adsorption capacity for diclofenac sodium. The high performances of diclofenac uptake could be explained by the electrostatic attractions between negative charged DS and positive charged surface of calcined ZnAl-CO_3 LDH.

IV. Conclusion

The uptake of Diclofenac by calcined ZnAl-CO_3 LDH at r=4 was found to be efficient. The equilibrium was achieved in only20 min of contact. The pseudo-second-order model fitted the experimental data very well. The batch data implies that the uptake of Diclofenac by calcined ZnAl-CO_3 adsorbent was dependent on the DS initial concentration. Langmuir adsorption isotherm model showed the best fit with the experimental adsorption data with a monolayer adsorption capacity of 451.66mgg-1. Calcined ZnAl-CO_3 hydrotalcite at molar ratio r=4 was considered as a useful adsorbent for an efficient removal of diclofenac sodium from aqueous solutions.

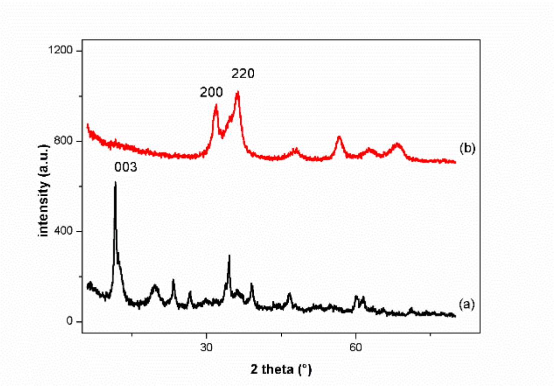


Figure 1.*XRD pattern of (a) not calcined LDH (b) calcined LDH.*

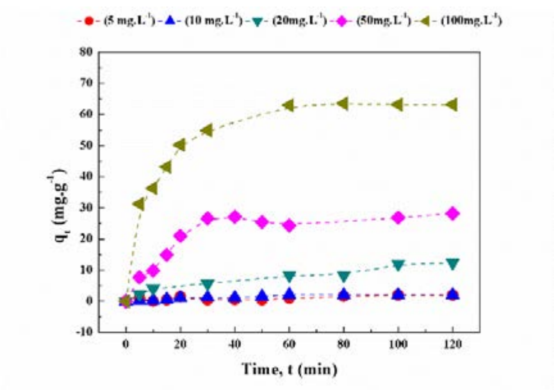
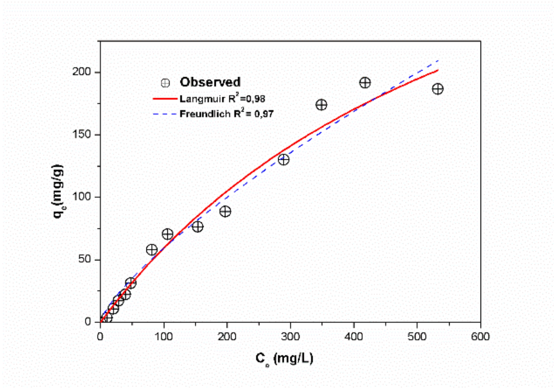


Figure 2. *Effect of contact time and initial DS concentration on the removal of DS*



*.**Figure 3.** Adsorption isotherm of DS onto calcined LDH.*

Table 1: *The structural and chemical properties of Diclofenac.*

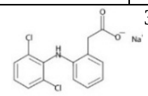
Molecular formula	Structural formula	Molecular wt (g mol^{-1})	log K_{ow}	Dipole moment (Debye)
$C_{14}H_{10}Cl_2NNaO_2$		318.13	4.5	0.966

Table 2: *Kinetic parameters estimated using PFO and PSO model for the removal diclofenac calcined by ZnAl-CO_3LDH.*

C	Pseudo-first-order			Pseudo-second-order		
mg.L^{-1}	q_e	k_1	R^2	q_e	k_2	R^2
20	13	0.0251	0.74	14.87	0.0018	0.88
50	15.24	0.0309	0.55	31.35	0.0023	0.98
100	52.46	0.0650	0.95	67.79	0.0021	0.99

Table 3: *Langmuir and Freundlich isotherm model constants and correlation coefficients for adsorption of DS on prepared samples.*

Model	Parameters	MK10-C16
Langmuir	q_m(mg/g)	451.66
	R^2	0.98
	K_L (dm^3/mg)	0.18
Freundlich	1/*n*	0.75
	R^2	0.97
	K_F(mg/g (dm^3/mg)$^{1/n}$)	1.84

Table 4: *Maximum adsorption capacities for Diclofenac removal by various organo-adsorbents.*

Adsorbents	q_{max} (mg g^{-1})	References
CalcinedZnAl-CO_3, r=4	451.66	This work
CalcinedZnAl-CO_3, r=2	737.02	[18]
Organo-k10montmorillonite	63.33	[19]
BH pillered with Aluminium (BAH)	13.99	[20]
HDTMA modified clay	0.88	[21]
HDTMA-Mt	52.51	[22]

List of symbols:

q_t: the amount of DS removed at time t.
q_e: the amount of DS removed at equilibrium.
k_1: the pseudo-first order rate constant.
k_2:pseudo-second-order rate constant.
K_L: the Langmuir constant.
K_F: the Freundlich constant.
1/n: the adsorption intensity.
q_m:the monolayer capacity of the adsorbent.

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