Kinetics of the Sorption of Cobalt Onto Mg/Al Layered Double Hydroxide†

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The sorption behaviour of cobalt by Mg₂Al layered double hydroxide (Mg₂Al LDH) was investigated as a function of contact time under ambient conditions. The sorption of cobalt onto Mg₂Al layered double hydroxide increases sharply within the first 1 h, then it rises slowly and reaches equilibrium in 5 h. The kinetic sorption is fitted by the pseudo-second-order model very well. The results manifest that Mg₂Al layered double hydroxide is a promising material for the preconcentration and separation of pollutants from large volumes of aqueous solutions.

Key Words: Cobalt, Sorption, Mg₂Al layered double hydroxide.

INTRODUCTION

It is well known that cobalt is one of the most important elements for human beings and that the contamination caused by cobalt is a serious environmental problem. Therefore, the removal of cobalt is a subject of great concern as it is a potentially dangerous pollutant to the environment. The removal of heavy metal ions from industrial wastewaters using different adsorbents is currently of great interest[1-3]. In the past years, a series of approaches can be applied to metal ion removal from waters, based on precipitation, exchange resins, membrane filtration and adsorbing methods. As a low cost and high efficiency method, sorption of cobalt on different kinds of adsorbents from aqueous solution has been studied previously[4].

Layered double hydroxides are inorganic layered materials consisting of positively charged brucite-like layers and charge-balancing interlayer anions related to hydrotalcite. Layered double hydroxides have the structural formula $[M_{1-x}^{II}M_x^{III}(OH)_2]^{x+}A_{x/n}^{n-}\cdot yH_2O$, where M^{II} and M^{III} denote divalent (*e.g.*, Zn, Ni and Mg) and trivalent metals (*e.g.*, Fe, Al and Cr), respectively; A^{n-} represents interlayer anions, such as CO_3^{2-}, NO_3^- and SO_4^{2-} and x typically ranges from 0.17 to 0.33 [5]. Such substitution gives rise to a positive residual charge in the layers that should be balanced by intercalation of anionic species together with water molecules[6,7]. Since the interlayer anions are easily exchangeable, the anions in the interlayer can be exchanged by other anions so that high anion exchange capability is the most remarkable characteristic of layered double hydroxides. Meanwhile, the ease of preparation and widely variable ways in which their components can be combined make layered double hydroxides useful for many applications[8]. Many researches on sorption of pollutants onto this Mg₂Al layered double hydroxide have been done and the results show that it has a particularly high affinity for many cations and anions[9-11].

The objectives of this work are to: (1) Study the effect of different parameters on cobalt sorption, such as contact time, HA and temperature by using batch techniques; (2) Determine the thermodynamic parameters of cobalt sorption on Mg₂Al layered double hydroxide; and (3) Presume the sorption mechanism of cobalt on Mg₂Al layered double hydroxide and to estimate the possible application of Mg₂Al layered double hydroxide in wastewater treatment.

EXPERIMENTAL

Mg₂Al layered double hydroxide was prepared according to a method described in previous study[12,13].

All other chemicals were purchased in analytical purity and used without further purification and all solutions were prepared with Milli-Q water under ambient conditions.

All the experiments were carried out by using batch techniques in polyethylene centrifuge tubes under ambient conditions. The stock solutions of Mg₂Al layered double hydroxide, NaClO₄ and cobalt were added to achieve the desired concentrations of different components. The pH of each test solution was adjusted to desired values by adding negligible volumes
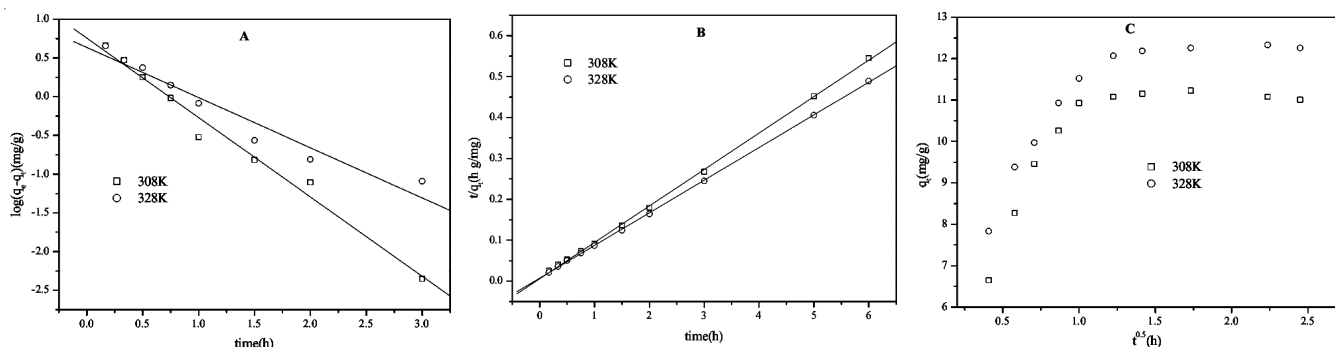
Fig. 1. Effect of contact time on Co(II) sorption on Mg$_2$Al layered double hydroxide and the pseudo-first-order (A), pseudo-second-order (B) and intraparticle diffusion model (C), pH = 6.7 ± 0.1, I = 0.01 mol/L NaClO$_4$, m/V = 0.4 g/L, C$_{Co(II)\ initial}$ = 10 mg/L

of 0.01 or 0.1 M NaOH or HClO$_4$. After the suspensions were shaken for 2 days, the solid and liquid phases were separated by centrifugation at 9000 rpm for 0.5 h. The sorption of cobalt on the tube wall was negligible according to the test of cobalt adsorption in the absence of Mg$_2$Al layered double hydroxide.

The amount of cobalt adsorbed on Mg$_2$Al layered double hydroxide was calculated from the difference between the initial concentration and the equilibrium one. The sorption percentage (sorption % = (C$_0$-C$_e$)/C$_0$ × 100 %) was derived from the difference of the initial concentration (C$_0$) and the final one (C$_e$) in supernatant after centrifugation. All experimental data were the average of triplicate determinations and the relative errors were about 5 %.

The sorption of cobalt was expressed in terms of distribution coefficient (K$_d$) and sorption percentage (%), which were derived from the following equations:

$$K_d = \frac{(C_0 - C_e)}{C_e} \frac{V}{m} \tag{1}$$

$$Sorption\ (\%) = \frac{(C_0 - C_e)}{C_0} \times 100\ \% \tag{2}$$

where C$_0$ is the initial concentration, C$_e$ is the equilibrium concentration in supernatant after centrifugation, *m* is the mass of Mg$_2$Al layered double hydroxide and V is the volume of the suspension.

RESULTS AND DISCUSSION

Kinetic sorption of cobalt on Mg$_2$Al layered double hydroxide: Fig. 1 indicates the sorption of cobalt on Mg$_2$Al layered double hydroxide as a function of contact time. The sorption of cobalt onto Mg$_2$Al layered double hydroxide increases sharply within the first 1 h, then it rises slowly and reaches equilibrium in 5 h. The fast cobalt removal rate in the beginning is attributed to the rapid diffusion of cobalt from the solution to the external surfaces of Mg$_2$Al layered double hydroxide. The subsequent slow sorption process is attributed to the longer diffusion range of cobalt into the inner-sphere of Mg$_2$Al layered double hydroxide or the ion-exchange in the inner surface of Mg$_2$Al layered double hydroxide. Such slow diffusion will lead to a slow increase in the sorption curve at later stages. Moreover, the initial rapid sorption may be due to an increased number of available sites at the initial stage. The increase in concentration gradient tends to increase in cobalt

sorption rate at the initial stages. As time proceeds, the concentration gradients become reduced owing to the accumulation of cobalt adsorbed on the surface sites, leading to the decrease in sorption rate at the later stages. Here, the three kinetic models have been employed to fit the experimental data. The pseudo-first-order kinetic model[14] describes the sorption of liquid/solid system based on solid capacity. The model can be written as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{3}$$

where q$_e$ and q$_t$ is the capacity of metal ions adsorbed (mg g^{-1}) at equilibrium and time t (h), respectively and K$_1$ is the pseudo-first-order rate constant (h^{-1}). After integration between boundary conditions (t = 0 to t and q$_e$ = 0 to q$_e$), eqn. (3) can be rewritten as:

$$\log\ (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{4}$$

Thus the values of q$_e$ and k$_1$ can be determined experimentally by plotting log (q$_e$-q$_t$) *versus* t and extracting information from the least squares analysis of slope and intercept and substituting into eqn. (4).

The pseudo-second-order adsorption kinetic model is expressed as following formulation[15]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{5}$$

where k$_2$ (g.mg^{-1}.h^{-1}) is the pseudo-second-order rate constant for the sorption and is a complex function of the initial concentration of solute. eqn. (5) can be rearranged to give the linear expression:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{6}$$

Thus the values of k$_2$ and q$_e$ can be calculated from the intercept and the slope of the linear relationship, eqn. (6), between t/q$_t$ and t.

The intraparticle diffusion model can be used to determine whether diffusion-controlled phenomena are a rate-limiting step during adsorption[16]. The parabolic diffusion model can be written as:

$$\frac{q_t}{q_e t} = k_3 t^{0.5} + a \tag{7}$$

where q_e and q_t are the adsorbed cobalt $(mg.g^{-1})$ at equilibrium and at time t (h), a is a constant and k_3 is the overall diffusion constant for sorption.

The kinetic model parameters are obtained from fitting results and presented in Table-1. From the fit curve shown in Fig. 1(A, B, C) and the relative coefficient, it can be seen that the pseudo-second-order kinetic model fit the sorption of cobalt on Mg_2Al layered double hydroxide better than the pseudo-first-order and intraparticle diffusion model. According to the above results, the shaking time is fixed at 2 days in the following experiments to ensure that the sorption reaction can achieve complete equilibrium.

TABLE-1
KINETICS PARAMETERS FOR THE SORPTION OF Co(II)
ON Mg_2Al LAYERED DOUBLE HYDROXIDE

	308 K	328 K
Pseudo first-order		
k_1 (h^{-1})	15.12	16.33
$q_{e\ mod}$(mg/g)	14.56	16.38
R^2	0.954	0.963
Pseudo second-order		
k_2 (g.mg^{-1}.h^{-1})	3.67	2.43
$q_{e\ mod}$(mg/g)	14.33	15.12
R^2	0.998	0.996
Intraparticle diffusion		
K_3 (mg g^{-1} h$^{-0.5}$)	3.2	4.1
$q_{e\ mod}$(mg/g)	15.22	16.43
R^2	0.933	0.920

Conclusion

From the results of cobalt sorption on Mg_2Al layered double hydroxide under our experimental conditions, the following conclusions can be obtained: (1) The kinetic sorption is fitted by the pseudo-second-order model very well. (2) Mg_2Al layered double hydroxide has good potentialities for cost-effective removal of cobalt from cobalt -contaminated wastewaters.

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