ADSORPTION OF Pb(II), Co(II) AND Cu(II) FROM AQUEOUS SOLUTION ONTO MANGANESE DIOXIDE (γ - M_NO_2) NANOSTRUCTURE.

III- Kinetics Studies

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Le Ngoc Chung
Dalat University
Dinh Van Phuc
Dong Nai University

TÓM TẮT

HẤP PHỤ Pb(II), Co(II) VÀ Cu(II) TỪ DUNG DỊCH NƯỚC BỞI MANGANESE DIOXIDE (γ - MnO_2) CẤU TRÚC NANO

III- Khảo sát động học

Trong khảo sát này đã trình bày sự đánh giá động học hấp phụ Pb(II), Co(II) và Cu(II) từ dung dịch nước bởi vật liệu hấp phụ (γ- MnO_2 có cấu trúc nano. Phương pháp phân đoạn được lựa chọn để tiến hành thí nghiệm. Đã lựa chọn ba mô hình động học, như mô hình bậc một, mô hình bậc hai và mô hình khuếch tán nội hạt để tiến hành khảo sát động học hấp phụ cho các ion kim loại Pb(II), Co(II) và Cu(II). Kết quả cho thấy tại giá trị pH ~4, mô hình động học bậc hai rất phù hợp và hằng số tốc độ k_2 cho các ion kim loại giảm theo thứ tự Pb(II) > Cu(II) > Co(II). Sự áp dụng mô hình khuếch tán nội hạt nhằm làm rõ cơ chế của quá trình hấp phụ.

Keywords: *Models, Kinetics, Pseudo - first - order, Pseudo – second – order, Intra-particle diffusion.*

1. INTRODUCTION

In general, adsorption processes may be classified as physical or chemical depending on the nature of forces involved. Many physico-chemical factors influence the adsorption process and these include; adsorbate-adsorbent interaction, adsorbent surface area and pore structure, chemistry of the surface, nature of the adsorbate, etc. Therefore an extensive study of the adsorption kinetics is important. Various kinetic models have been reported in the literature to describe the adsorption process. Each model has its own limitations and is derived according to certain conditions [1-6].

Modeling of sorption kinetics can be carried out by employing chemical reaction-based and particle diffusion-based models. Among the most commonly encountered expressions in pollutant sorption studies are Lagregen’s pseudo-first-order and Ho’s pseudo-second--order [1-9]. However, these and other chemical reaction-based kinetic models do not consider the importance of particle diffusion processes in metal sorption by porous materials [10-14]. Therefore, it is necessary to include diffusion-based kinetic modeling in order to elucidate the role of diffusion processes, such as intra-particle diffusion.

In this research work, two kinetic models were employed to fit the experimental data, namely; the pseudo-first-order and pseudo-second-order models. Also, to use intra-particle diffusion models to ascertain the mechanism of the sorption process.

2. MATERIALS AND METHODS

2.1. Material

Manganese dioxide (γ - MnO_2) was synthesized via the reduction–oxidation reaction between $KMnO_4$ and C_2H_5OH at room temperature. The results showed that γ - MnO_2 was about 10 – 18 nm in size and the BET surface area was about 65 m^2/g. The feasibility of γ - MnO_2 used as an adsorbent for the adsorption of Pb(II), Co(II) and Cu(II) from aqueous solutions.

Pb(II), Cu(II), and Co(II) were used as adsorbate. 1000 mg/l standard stock solution of each metal ions were prepared by dissolving $Pb(NO_3)_2$, $Cu(NO_3)_2.3H_2O$ and $Co(NO_3)_2.6H_2O$ respectively in distilled water. All reagents used in the experiment were of analytical grade.

2.2. Methods

Batch adsorption studies were performed to obtain the equilibrium isotherm for adsorption of Pb(II), Cu(II) and Co(II) from water. A volume of 50 ml of metal ion solution with different time from 20 minutes to 240 minutes were taken in Erlenmeyer flasks containing a known mass of γ - MnO_2. The pH of the solution was adjusted by using 0.1N HNO_3 or 0.1N NaOH. The flasks were agitated at a constant speed of 240 rpm in a magnetic stirrer at room temperature 24^OC.

Samples were collected from the flasks at predetermined time intervals for analyzing the residual metal ions concentration in the solution. The residual amount of metal ions in each flask was investigated using atomic absorption spectrophotometer (Spectrometer Atomic Absorption AA – 7000 made in Japan by Shimadzu.). The amount of metal ions adsorbed in milligram per gram was determined by using the following mass balance equation [1-3]

$$q = \frac{\left(C_o - C_e\right).V}{m} \qquad (1)$$

where q is the adsorption capacity (mg/g) at equilibrium, C_o and C_e are the initial concentration and the equilibrium concentration (mg/L), respectively. V is the volume (mL) of solution and m is the mass (g) of adsorbent used.

3. RESULTS AND DISCUSSION

The kinetics of adsorption describes the rate of Pb(II), Co(II) and Cu(II) ions uptake on γ - MnO_2 and this rate controls the equilibrium time. The kinetics of adsorbate uptake is required for selecting optimum operating conditions for the full-scale batch process.

The kinetic parameter, which is helpful for the prediction of adsorption rate, gives important information for designing and modeling the processes. The kinetics of the adsorption data was analyzed using different kinetic models such as pseudo-first-order and pseudo-second-order models.

3.1. Pseudo-first-order model

The pseudo-first-order rate model equation given by Lagergren in 1898 is [1-9]:

$$\frac{dq}{dt} = k_1\left(q_e - q\right) \qquad (2)$$

Where q_e is the amount of solute adsorbed at equilibrium per unit weight of adsorbent (mg/g), q is the amount of solute adsorbed at any time (mg/g) and k_1 is the adsorption constant. Integrating equation (2) with respect to integration conditions $q = 0$ to $q = qt$ at $t = 0$ to $t = t$, the kinetic rate expression becomes:

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_1.t}{2,303} \qquad (3)$$

The first-order rate constant k_1 (min^{-1}) can be obtained from the slope of the plot of $log(q_e - q_t)$ against time t, as shown in Fig.1a and table 1. The adsorption first-order rate constants were found to be $4.606.10^{-3}$, 0.0115 and $4.606.10^{-3}$ min^{-1} for metal ions Pb(II), Co(II) and Cu(II), respectively.

If the adsorption process can be described by pseudo-first order equation, there should be good linear relationship between $log(q_e - q_t)$ and t. In the present study, the plot of $log(q_e - q_t)$ versus time t was not linear over the entire time range, the correlation coefficients in this model for all metal ions were low. Also the theoretical q_e values estimated from the first-order kinetic model were not in accordance with the experimental values. This suggests that this adsorption system is not a first-order reaction, indicating that more than one mechanism involved in adsorption.

3.2. Pseudo-second-order model

Adsorption kinetics was explained by the pseudo-second-order model given by Ho and McKay as follows [1-9]:

$$\frac{dq}{dt} = k_2\left(q_e - q\right)^2 \qquad (4)$$

Integrating equation (4) for the boundary conditions $q = 0$ to $q = q_t$ at $t = 0$ to $t = t$ is simplified as:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right).t \qquad (5)$$

Additionally, the initial adsorption rate h (mg/g.min) can be determined,

$$h = k_2.q_e^2 \quad (6)$$

Where k_2 (g mg^{-1} min^{-1}) is the second-order rate constant determined from the plot of t/q against t, as shown in Fig. 1b and table 1.

The plot of t/q against t present multi linearity for different metal ions. The adsorption second-order rate constants were found to be $1.88.10^{-3}$, $1.25.10^{-3}$ and $1.45.10^{-3}$ $g.mg^{-1}.min^{-1}$ for metal ions Pb(II), Co(II) and Cu(II), respectively. The initial sorption rate, h, is the highest for Pb(II) and the lowest for Cu(II), which reflects the affinity of the sorbent for these sorbate species.

The results showed the theoretical q_e values calculated from pseudo-second order kinetic model were found to be very close to the experimental values of equilibrium sorption, $q_{e\ (exp)}$, with correlation coefficients of determination higher than 0.999. The pseudo-second-order adsorption mechanism was predominant for adsorption of metal ions Pb(II), Co(II) and Cu(II) by γ - MnO_2. The applicability of this model showed that sorption process is complex and involves more than one mechanism.

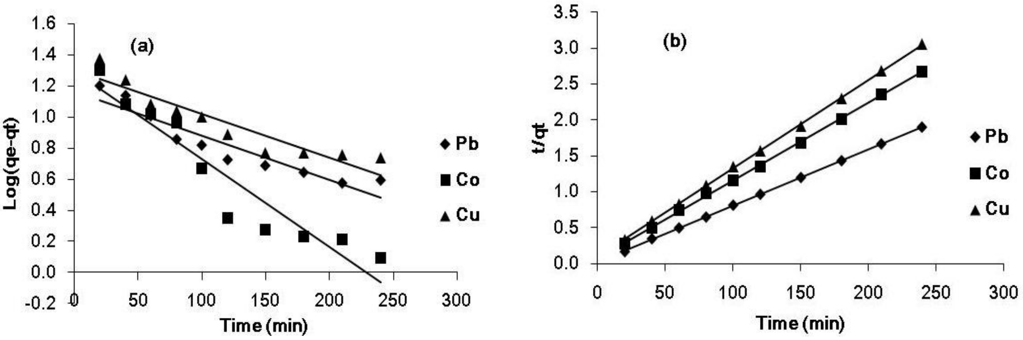

Fig. 1. (a) Pseudo-first-order kinetic plots for the adsorption of metal ions.
(b) Pseudo-second-order kinetic plots for the adsorption of metal ions

Table 1. Pseudo-first-order and pseudo-second-order for the adsorption of metal ions on γ - MnO_2

Models	Parameters	Metal ions		
		Pb (II)	Co (II)	Cu (II)
	$q_{e\ (exp)}$	126.10	89.76	78.58
Pseudo – first – order kinetic	$K_1(min^{-1})$	$4.606.10^{-3}$	0.0115	$4.606.10^{-3}$
	r^2	0.886	0.898	0.870
	$q_{e\ (cal)}$	14.62	19.23	19.91
Pseudo – second – order kinetic	K_2 $(g.mg^{-1}.min^{-1})$	$1.88.10^{-3}$	$1.25.10^{-3}$	$1.45.10^{-3}$
	h (mg/g.min)	38.46	12.5	10.10
	r^2	1	0.999	0.999
	$q_{e\ (cal)}$	142.86	100	83.33

3.3. Intra-particle diffusion model

Because the pseudo-first-order and pseudo-second-order kinetic models cannot identify the diffusion mechanisms. The most commonly used technique for identifying the diffusion mechanism involved in the adsorption process is by using intra-particle diffusion model.

The intra-particle diffusion model used here refers to the theory proposed by Weber and Morris, based on the following equation for the rate constant [10-14]:

$$q_t = k_d t^{1/2} + C \qquad (7)$$

where q_t *is* the quantity of metal ions adsorbed at time *t* ($mg.g^{-1}$), k_d the initial rate of intra-particular diffusion ($mg.L^{-1}.min^{-1/2}$), and *C* is the y-intercept which is proportional to the boundary layer thickness.

According to this model, when the metal ion solution is mixed with the adsorbent, transport of the metal ions from the solution through the interface between the solution and the adsorbent occurs into pores in the particles, if adsorption of a solute is controlled by the intra-particle diffusion process, a plot of q_t versus $t^{1/2}$ gives a straight line [10-12]. Fig. 2 illustrates the diffusion of Pb(II), Co(II) and Cu(II) ions within γ - MnO_2 as a function of time and shows that intra-particle diffusion occurred in two stages, first linear portion (stage I) and second curved path followed by a plateau (stage II). In stage I, the metal ions were up taken by γ - MnO_2.This is attributed to the utilization of the most readily available adsorbing sites on the adsorbent surfaces. In stage II, very slow diffusion of adsorbate from surface site into the inner-pores is observed. Thus initial portion of adsorption of Pb(II), Co(II) and Cu(II) ions by γ - MnO_2 adsorbents may be governed by the initial intra-particle transport of Pb(II), Co(II) and Cu(II) ions controlled by surface diffusion process and later part is controlled by pore diffusion. The intra-particle diffusion constants for all two stages (k_{d1}, k_{d2}) are given in Table 2.

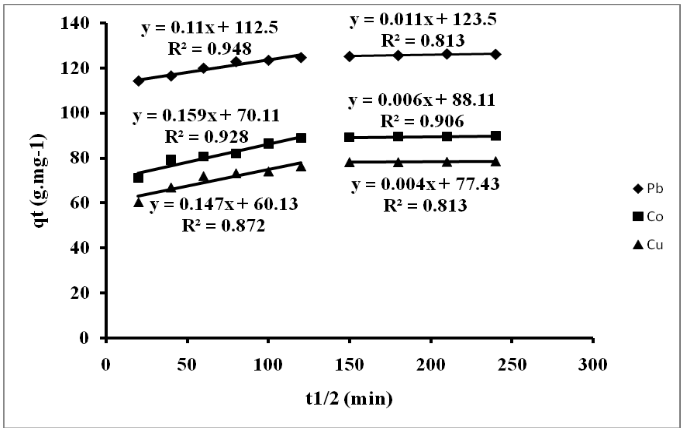

Fig 2. Plot of the intra-particle diffusions kinetics for the three heavy metal ions Pb(II), Co(II) and Cu(II).

Table 2. The values of the intra-particular diffusion coefficients

Metal ion	**K_{d1} (mg.L^{-1}.min$^{-1/2}$)**	**K_{d2}(mg.L^{-1}.min$^{-1/2}$)**
Pb(II)	0.11	0.011
Cu(II)	0.147	0.004
Co(II)	0.159	0.006

4. CONCLUSION

Batch kinetic experiments were carried out for the sorption of Pb(II), Co(II) and Cu(II) from aqueous solution onto manganese dioxide (γ - MnO_2) nanostructure. Kinetic studies showed that a pseudo – second – order model was more suitable than the pseudo – first – order model. Also, to use intra-particle diffusion models to ascertain the mechanism of the sorption process.

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