ADSORPTION OF Pb(II), Co(II) AND Cu(II) FROM AQUEOUS SOLUTION ONTO MANGANESE DIOXIDE (γ - MNO_2) NANOSTRUCTURE. II- Equilibrium Isotherm Studies

Đến tòa soạn 27 – 8 – 2014

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SUMMARY

HẤP PHỤ Pb(II), Co(II) VÀ Cu(II) TỪ DUNG DỊCH NƯỚC BỞI MANGANESE DIOXIDE (γ - MnO_2) CẤU TRÚC NANO II- Khảo sát đẳng nhiệt cân bằng

Đã sử dụng các mô hình đẳng nhiệt hấp phụ Freundlich, Langmuir và Redlich-Peterson để phân tích đánh giá cân bằng hấp phụ Pb(II), Co(II) và Cu(II) từ dung dịch nước bởi γ - MnO_2 có cấu trúc nano. Kết quả cho thấy các mô hình Freundlich, Langmuir và Redlich-Peterson rất thích hợp cho các ion kim loại Co(II) và Cu(II), trong khi đó mô hình đẳng nhiệt Langmuir và Redlich-Peterson thì phù hợp cho sự hấp phụ Pb(II). Dựa vào mô hình Langmuir đã tính được hấp dung tương ứng đối với Pb(II), Co(II) và Cu(II) là 200 mg/g; 90,91 mg/g và 83,33 mg/g. Khả năng hấp phụ của γ - MnO_2 cho các ion kim loại nói trên theo thứ tự Pb(II) > Co(II) > Cu(II).

Keywords: *Freundlich, Langmuir, Redlich-Peterson, Isotherm, the correlation coefficient (R^2), the separation factor (S_F), the coefficient of determination (r^2).*

1. INTRODUCTION

Nowadays the presence of heavy metals in the water sources is of major concern because of their toxicity, bio-accumulating tendency, threat to human life and the environment. Therefore the elimination of heavy metals from water and wastewater is important to protect public health [1-3].

Among the physicochemical treatment processes for elimination of heavy metals, adsorption is highly efficient, inexpensive and easy to adapt [4-5].

The adsorption process depends on parameters such as adsorbent properties, initial concentration of adsorbate, amount of adsorbent, contact time and pH [6]. The analysis and design of an adsorption process require the adsorption equilibrium which is the most important piece of information in the understanding of the adsorption process [6-10].

Equilibrium studies that give the capacity of the adsorbents for the adsorbate are described by adsorption isotherm, which is usually the ratio between the quantity adsorbed and the remaining in the solution at equilibrium and at fixed temperature. The various adsorption isotherm equations have been used to study the nature of adsorption such as Langmuir, Freundlich, Redlich-Peterson, Sips, Temkin and Radk-Prausnitz, isotherm models. The most commonly used isotherm models include Langmuir, Freundlich and Redlich-Peterson [6,11].

The aim of this work is to study equilibrium of adsorption of Pb(II), Cu(II) and Co(II) onto manganese dioxide nanostructures γ - MnO_2. Three isotherm models were used to analyze the experimental data - Langmuir, Freundlich and Redlich-Peterson.

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 initial concentration of 100-500 mg/L 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 for 3 h 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 [6-10]

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

where q is the adsorption capacity (mg/g) at equilibrium, Co and Ce 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

Adsorption isotherms are mathematical models that describe the distribution of the adsorbate specie among liquid and solid phases, based on a set of assumptions that related to the heterogeneity/homogeneity of the solid surface, the type of coverage, and the possibility of interaction between the adsorbate specie. In this study, equilibrium data were analyzed using the Freundlich, Langmuir and Redlich-Peterson isotherms expression.

3.1. Freundlich Isotherm

The Freundlich (1906) equation[6-14] is an empirical equation based on adsorption on a heterogeneous surface. The equation is commonly represented as,

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \qquad (2)$$

Where C_e (mg/L) is the equilibrium concentration and q_e (mg/g) is the amount adsorbed metal ion per unit mass of the adsorbent. The constant n is the Freundlich equation exponent that represents the parameter characterizing quasi-Gaussian energetic heterogeneity of the adsorption surface. K_F is the Freundlich constant which indicate the relative adsorption capacity of the adsorbent. The Freundlich model was chosen to estimate the adsorption intensity of the sorbate on the sorbent surface. The experimental data from the batch sorption study of the three metal ions on γ - MnO_2 nanostructures were plotted logarithmically (Fig. 1) using the linear Freundlich isotherm equation.

The linear Freundlich isotherm constants for Pb(II), Co(II) and Cu(II) on γ-MnO_2 nanostructure are presented in table 1. The Freundlich isotherm parameter 1/n measures the adsorption intensity of metal ions on the γ - MnO_2 nanostructure. The low 1/n value of Pb(II) (0.067), Cu(II) (0.064) and Co(II) (0.164) less than 1 represent of favorable sorption and confirmed the heterogeneity of the adsorbent. Also, it indicates that the bond between heavy metal ions and γ - MnO_2 are strong. The adsorption capacity K_F of the adsorbent was calculated from the isothermal linear regression equation. The K_F value of Pb(II) (137.40 L/g) is greater than that of Cu(II) (59.98L/g) and Co(II) (40.55 L/g), suggesting and confirming that Pb(II) has greater adsorption tendency towards the γ - MnO_2 nanostructure than the other two metals.

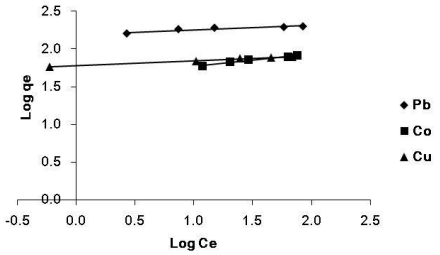

Fig 1. Freundlich equilibrium isotherm model for the sorption of the three metal ions (Pb,Cu,Co) onto γ - MnO_2.

Table 1. Freundlich isotherm parameters.

Metal ions	1/n	K_f (L/g)	R^2
Pb	0.067	137.40	0.846
Co	0.164	40.55	0.974
Cu	0.064	59.98	0.993

3.2. Langmuir Isotherm

The Langmuir (Langmuir, 1918) model[6-14] assumes that uptake of metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions. The linearized form of the Langmuir equation is given,

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

The Langmuir isotherm model was chosen for the estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the γ - MnO_2 surface. The plots of specific sorption (C_e/q_e) against the equilibrium concentration (C_e) for Pb^{2+}, Co^{2+} and Cu^{2+} are shown in Fig. 2 and the linear isotherm parameters, q_m, K_L and the coefficient of determinations are presented in table 2.

The data in table 2 indicated that, the high values of correlation coefficient (R^2 = 0.998 – 0.999) indicates a good agreement between the parameters and confirms the monolayer adsorption of Pb(II), Co(II) and Cu(II) ions on to γ-MnO_2 nanostructure surface. Furthermore, the sorption capacity, q_m, which is a measure of the maximum sorption capacity corresponding to complete monolayer coverage showed that the γ - MnO_2 nanostructure had a mass capacity for Pb^{2+} (200 mg/g) than Co^{2+} (90.91 mg/g) and Cu^{2+} (83.33 mg/g).

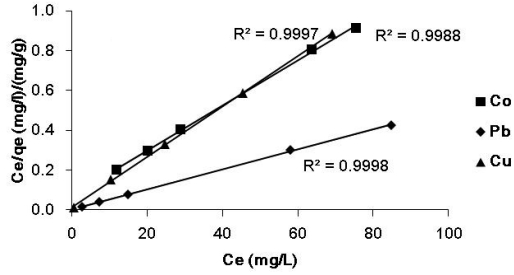

Fig. 2. Langmuir equilibrium isotherm model for the sorption of the three metal ions onto γ - MnO_2 nanostructure

Table 2. Langmuir adsorption isotherm constants for ions on γ - MnO_2

Sample	K_L	q_m (mg/g)	R^2	S_F (at lowest C_0 = 100mg/L)	S_F (at highest C_0 = 500mg/L)
Pb (II)	1.25	200	0.999	0.0079	0.0016
Co (II)	0.16	90.91	0.998	0.0588	0.0123
Cu (II)	1.09	83.33	0.999	0.0091	0.0018

An important characteristic of the

Langmuir isotherm is expressed in a dimensionless constant equilibrium parameter, S_F also known as the separation factor[7,13,14], given by

$$S_F = \frac{1}{1 + K_L.C_o} \quad (4)$$

The data in table 2 further indicated that, the dimensionless parameter S_F remained between 0.008 and 0.059 ($0 < S_F < 1$) at lowest concentration studied and between 0.0016 and 0.025 ($0 < S_F < 1$) at highest concentration studied, i.e. the separation parameters S_F for the three metals are less than unity indicating that γ-MnO_2 nanostructure is an appropriate adsorbent for the three metal ions. The smaller S_F value indicates a highly favorable adsorption. However, S_F value of Co (II) > Cu (II) > Pb (II), indicates that in a mixed metal ion system, Pb(II) will compete for binding sites faster than Zn(II) and Cu(II).

3.3. Redlich-Peterson Isotherm

Redlich–Peterson isotherm [6-14] is a hybrid isotherm featuring both Langmuir and Freundlich isotherms, which incorporate three parameters into an empirical equation. Then, Redlich and Peterson equation designated the "three parameter equation," which may be used to represent adsorption equilibria over a wide concentration range. The linearized form of the Redlich–Peterson equation is given,

$$\mathrm{Ln}\left(K_{RP}\frac{C_e}{q_e}-1\right)=\beta \mathrm{Ln}C_e + \mathrm{Ln}\alpha_{RP} \quad (5)$$

Where K_{RP} (L/g), α_{RP} (L/mg) and β are the Redlich-Peterson isotherm constants. The value of β is the exponent which lies between 0 and 1. In the limit, the Redlich–Peterson isotherm approaches Freundlich isotherm model at high concentration (as the β values tends to zero) and is in accordance with the low concentration limit of the ideal Langmuir condition (as the β values are all close to one).

The Redlich–Peterson isotherm constants can be predicted from the plot between $\mathrm{Ln}\left(K_{RP}\frac{C_e}{q_e}-1\right)$ versus $\mathrm{Ln}C_e$. However, this is not possible as the linearized form of Redlich–Peterson isotherm equation contains three unknown parameters α_{RP}, K_{RP} and β. Therefore, a minimization procedure is adopted to maximize the coefficient of determination r^2, between the theoretical data for q_e predicted from the linearized form of Redlich–Peterson isotherm equation and the experimental data. The Redlich–Peterson isotherm plot for the three metal ions (Pb^{2+}, Co^{2+} and Cu^{2+}) are presented in Fig. 3 and the isotherm parameters is given in table 3.

The data in table 3 indicated that, the higher R^2 values for Redlich–Peterson shows the experimental equilibrium data

was found to follow Redlich–Peterson isotherm equation. This was expected, because a degree of heterogeneity (β) is included and this equation can be used successfully at high solute concentrations. Langmuir is a special case of Redlich–Peterson isotherm when constant β is unity.

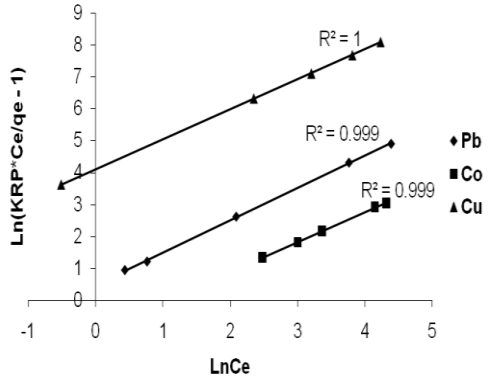

Fig. 3. Redlich–Peterson equilibrium isotherm model for the sorption of the three metal ions onto γ - MnO_2

Table 3. Redlich–Peterson isotherm parameters.

Metal ions	K_{RP}	a_{RP}	β	R^2
Pb	307.346	1.562	0.998	1.000
Co	24.134	0.378	0.932	0.999
Cu	3693.189	60.167	0.941	0.999

3.4. Coefficients of Determination.

It has been suggested that linearization plots may not be a significant basis to reject or accept a model. To further analyze the suitability of the three models (Freundlich, Langmuir and Redlich-Peterson), their fitness to the experimental data was assessed. The fitness of the data was established using a single statistical parameter (r^2) which is called the coefficient of determination[13,14]. The coefficient of determination values for the three models as shown in Table 4. The r^2 values suggest that the Freundlich, Langmuir and Redlich-Peterson isotherms provide a good model for the sorption of Co (II) and Cu(II) - $r^2 > 0.97$. While the Langmuir and Redlich-Peterson isotherms produce a reasonable fit to the experimental data for Pb(II).

Table 4. Adsorption isotherm coefficients of determination (r^2).

Adsorption Isotherm	Heavy metals		
	Pb (II)	Co (II)	Cu (II)
Freundlich	0.846	0.974	0.992
Langmuir	0.999	0.998	0.999
Redlich – Peterson	1	0.999	0.999

4. CONCLUSION

This study investigated the feasibility of γ - MnO_2 nanostructure used as an adsorbent for the removal of Pb(II), Co(II) and Cu(II) from aqueous solution. The experimental results were analyzed using three adsorption isotherm models, the Freundlich, Langmuir and Redlich-Peterson, isotherm models. By using the Langmuir isotherm, the adsorption capacities for Pb(II), Co(II) and Cu(II) are found as 200 mg/g, 90.91 mg/g and 83.33 mg/g respectively. The

effectiveness of γ - MnO_2 nanostructure in the sorption of the three metals from aqueous system was Pb(II) > Co(II) > Cu(II).The separation parameters, S_F, for the three metals are less than unity indicating that γ - MnO_2 nanostructure is an appropriate adsorbent for the three metal ions. However, S_F value of Pb(II) > Cu(II) > Co(II), indicate that in a mixed metal ion system, Pb(II) will compete for binding sites faster than Co(II) and Cu(II).

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