ADSORPTION AND DESORPTION OF LEAD (II) IONS FROM AQUEOUS SOLUTION BY GAMMA – MnO_2 NANOSTRUCTURE

Đến tòa soạn 17 – 6 - 2015

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TÓM TẮT

HẤP PHỤ VÀ GIẢI HẤP ION CHÌ (II) TỪ DUNG DỊCH NƯỚC BỞI GAMMA – MnO_2 CẤU TRÚC NANO

Trong công trình này, chúng tôi đã nghiên cứu sự hấp phụ và giải hấp phụ Pb (II) từ dung dịch nước bởi vật liệu gamma – MnO_2 cấu trúc nano. Các yếu tố ảnh hưởng đến quá trình hấp phụ như pH, thời gian khuấy và nồng độ đầu đã được nghiên cứu. Động học và cân bằng hấp phụ đạt được từ các thí nghiệm. Kết quả cho thấy động học tuân theo phương trình động học bậc 2. Cân bằng hấp phụ được mô tả bởi 5 mô hình đẳng nhiệt: Langmuir, Freundlich, Redlich – Peterson, Tempkin và Dubinin – Redushkevich. Dung lượng hấp phụ được tính toán từ mô hình đẳng nhiệt Langmuir là 200 mg/g tại 297 độ K và pH = 4. Nhiệt hấp phụ và năng lượng tự do được dự đoán từ mô hình Tempkin và Dubinin – Redushkevich nhỏ hơn 8 KJ/mol – điều này có thể khẳng định rằng quá trình hấp phụ tuân theo quá trình hấp phụ vật lý. Các nghiên cứu giải hấp cho thấy rằng, dung dịch hỗn hợp HNO_3 2M và HN_4NO_3 4M là dung dịch tối ưu cho quá trình giải hấp Pb (II) với thời gian rửa giải là 15 phút.
Từ khóa: Chì, hấp phụ, giải hấp phụ, gamma – MnO_2, cân bằng đẳng nhiệt.

1. INTRODUCTION

Lead is one of the three most toxic heavy metals which is widely used in many important industrial applications, such as storage battery, manufacturing, printing pigments, fuels, photographic materials, and explosive manufacturing. Lead may cause a range of health effects, from behavioral problems and learning disabilities to seizures and death. There are a variety of treatment techniques which have been applied to remove Lead (II) ions

from contaminated waters, such as chemical precipitation, adsorption and ionic exchange, membrane technology and solvent extraction [1-11]. Adsorption technology is considered as one of the most efficient and promising methods for the treatment of trace amount of heavy metal ions from large volumes of water because of its high enrichment efficiency, and the ease of phase separation [1-11].

Manganese oxides with many types of crystalline structures, such as α-, β-, γ- and so on, have been extensively studied due to their structural varieties and excellent chemical characteristic. Therefore, they were applied for different areas, such as batteries, molecular sieves, catalysts, and adsorbents [2-11]. However, the use of MnO_2 nanoparticles to remove Lead (II) from aqueous solution has not been widely studied.

In this study, we used gamma-MnO_2 nanostructure (γ-MnO_2 nanostructure) as a low cost adsorbent for the adsorption – desorption of Pb(II) ions from aqueous solutions. The sorption capacity of MnO_2 and the heat of sorption process were evaluated using Freundlich, Langmuir, Redlich - Peterson, Tempkin and Dubinin - Redushkevich isotherm models and the desorption was also examined by using various concentration of HNO_3 and the mixture (HNO_3 + NH_4NO_3) solution.

2. EXPERIMENTAL

2.1. Chemicals and Instruments

- Chemicals:

Potassium permanganate ($KMnO_4$), ethyl alcohol (C_2H_5OH), $Pb(NO_3)_2$, HNO_3 and NaOH. All reagents used in the experiment were of analytical grade and pure of Merck. Lead (II) ion were used as adsorbate. 1000 mg/l standard stock solution of Pb^{2+} ions was prepared by dissolving $Pb(NO_3)_2$ (Merck) respectively in distilled water. The concentration of metal ions in the aqueous solutions was analyzed by using AA-7000 atomic absorption spectrometer (Shimadzu Corporation).

- Instruments include:

Atomic Absorption Spectrophotometer (Spectrometer Atomic Absorption AA – 7000 made in Japan by Shimadzu.)

The pH measurements were done with a pH-meter (MARTINI Instruments Mi-150 Romania); the pH-meter was standardized using HANNA instruments buffer solutions with pH values of 4.01±0.01, 7.01±0.01, and 10.01±0.01.

Temperature-controlled shaker (Model IKA R5) was used for equilibrium studies.

Centrifuge machine (made in Germany)

2.2. Adsorption – Desorption study

Adsorption experiment was prepared by adding 0.1g γ-MnO_2 nanostructure to 50 mL heavy metal ion solution in a 100 mL conical flask. Effect of pH of the initial solution was analyzed over a pH ranges from 2 to 6 using HNO_3 0.1M or NaOH 0.1M solutions. The adsorption studies were also conducted in batch experiments as function of contact time (20, 40, 60, 80, 100, 120, 150, 180, 210, 240 minute) and initial metal ions concentration (Co) (from 100 mg/L to 500 mg/L) for maximum adsorption. The obtained mixture was centrifugal at 5500 rpm within 10 minutes,

then was purified by PTFE Syring Filters with 0.22 μm of pore size to get the filtrate. Atomic Absorption Spectrophotometer (Spectrome
ter Atomic Absorption AA – 7000) was used to analyze the concentrations of the different metal ion in the filtrate before and after adsorbent process.

Desorption of adsorbed Lead from exhausted γ - MnO_2 nanostructure were studied with 4 types of solvent including HNO_3, HCl, NH_4NO_3 and the mixtures HNO_3 – NH_4NO_3. The eluent concentration, volume and time were also examined. Pre-adsorbed γ - MnO_2 nanostructure (0.5 g) was taken in 100 ml of above mentioned medium and shaken at 240 rpm for optimal time.

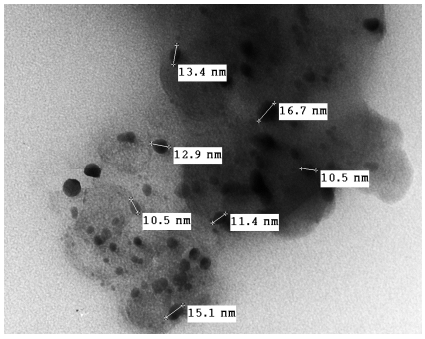
Adsorption and desorption capacities (q_e) at specified time (t) were calculated as:[7-16]

$$q_e = \frac{(C_o - C_e).V}{m} \quad (1)$$

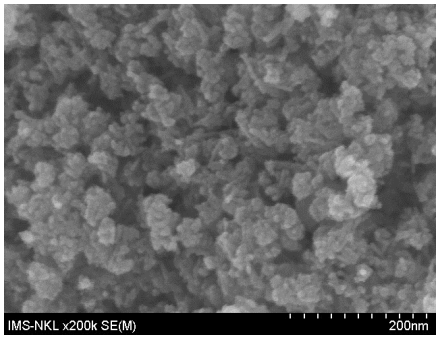
where, q_e, is the equilibrium adsorption/desorption capacity (mg/g); C_o and C_e, the initial and equilibrium Lead concentrations in the water (mg/l), respectively; V, volume of used solution (l); and m, the mass of used adsorbent (g).

3. RESULTS AND DISCUSSION

3.1. Charaterization of γ - MnO_2



(a)



(b)

Figure 1. SEM image (a) and TEM image (b) of γ - MnO_2

Gamma-MnO_2 nanostructure (γ-MnO_2 nanostructure) was synthesized via the reduction–oxidation reaction between $KMnO_4$ and C_2H_5OH at room temperature at Institute for Enviromental Studies, Dalat University, Vietnam [10-11]. The SEM and TEM image results showed that γ - MnO_2 consisted of a large amount of uniform nanospheres, with size of about 10 nm – 18 nm. Results also showed that the surface is porous which may offer more adsorption sites for adsorbate.

The specific surface area (m^2/g) and pore volume distribution were determined by BET and BJH-analysis of N_2 adsorption–desorption isotherms measured on the CS and MnO_2/CS samples (Table 1). According to the International Union of Pure and Applied Chemistry (IUPAC) classifications, the pores can be divided into macropores ($d > 500\ A^0$), mesopores ($20 < d < 500\ A^0$) and micropores ($d < 20\ A^0$). In this study, γ - MnO_2 correspond to mesopores with average pore diameter higher than $20\ A^0$ and less than $500\ A^0$.

Moreover, the γ - MnO_2 has high BET surface area (average 65 m^2/g) that facilitates the adsorption of Pb^{2+}. The feasibility of γ - MnO_2 nanostructure used as an adsorbent for the adsorption of Pb(II) from aqueous solutions.

Table 1. B.E.T and B.J.H analysis results

	Pore size		Surface Area	
γ - MnO_2	BJH Adsorption	BJH Desorption	BET Surface	BJH Adsorption cumulative surface area
	417.8 Å	340.2 Å	5.00 m^2/g	71.04 m^2/g

3.2. Affecting factors

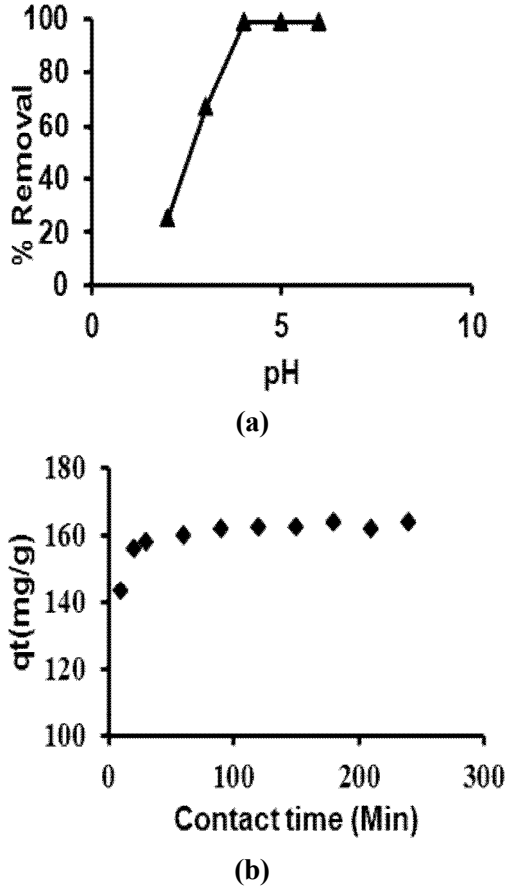


Figure 2. Effects of experimental conditions on Lead removal from water by γ - MnO_2 nanostructure

The effect of pH was studied from a range of 2 to 6 under the precise conditions (at optimum contact time of 120 min, 240 rpm of shaking speed, with 0,1g of the adsorbents used, and at a room temperature of 24^0C). From Fig.2a, with γ - MnO_2 nanostructure used as adsorbent, it was observed that with increase in the pH (2 - 6) of the aqueous solution, the adsorption percentage of Lead (II) ion increased up to the pH = 4. At pH > 6.0, the Pb(II) gets precipitated due to hydroxide anions forming a lead hydroxide precipitate. For this reason, the maximum pH value was selected to be 4.0. The increase in adsorption percentage of the Pb^{2+} ions may be explained by the fact that at higher pH the adsorbent surface is deprotonated and negatively charge; hence attraction between the positively metal cations occurred [11]

The effect of contact time was studied at a room temperature of 24^0C, at intervals of 240 min (Fig. 2b). From the obtained result, it is evident that the adsorption of Pb^{2+} ions increased as contact time increases. The adsorption percentage of Pb^{2+} ions approached equilibrium within 80 min with Pb^{2+} recording 92.47% adsorption.

3.3. Adsorption isotherm study

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, Redlich - Peterson, Tempkin and Dubinin – Redushkevich isotherms expression (Table 1)[14]

3.3.1. Langmuir Isotherm [12-18]

The Langmuir isotherm model was chosen for the estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the γ - MnO_2 nanostructure surface. The plot of specific sorption (C_e/q_e) against the equilibrium concentration (C_e) for Pb(II) is shown in Fig. 3b and the linear isotherm parameters, q_m, K_L and the coefficient of determinations are presented in Table 3.

The data in Table 3 indicated that, the high values of correlation coefficient (R^2 = 0.999) indicates a good agreement between the parameters and confirms the monolayer adsorption of Pb(II) ion onto 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 is 200 mg/g.

Table 2. Lists of adsorption isotherms models.

Isotherm	Nonlinear form	Linear form	Plot
Langmuir	$q_e = \frac{q_m.K_L.C_e}{1+K_L.C_e}$	$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m.K_L}$	$\frac{C_e}{q_e}$ vs C_e
Freundlich	$q_e = K_F.C_e^{1/n}$	$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e$	$\log q_e$ vs $\log C_e$
Redlich - Peterson	$q_e = \frac{K_{RP}.C_e}{1+\alpha_{RP}.C_e^{\beta}}$	$Ln\left(K_{RP}\frac{C_e}{q_e}-1\right) = \beta Ln C_e + Ln\alpha_{RP}$	$Ln\left(K_{RP}\frac{C_e}{q_e}-1\right)$ vs $Ln C_e$
Tempkin	$q_e = \frac{RT}{b_T} Ln(K_T C_e)$	$q_e = \frac{RT}{b_T} \ln K_T + \frac{RT}{b_T} \ln C_e$	q_e vs $\ln C_e$
Dubinin - Radushkevich	$q_e = q_m.e^{(-\beta.\varepsilon^2)}$	$\ln q_e = \ln q_m - \beta.\varepsilon^2$	

Table 3. Langmuir, Freundlich and Redlich - Peterson isotherm parameters.

Langmuir			Freundlich			Redlich - Peterson			
K_L	q_m	R^2	1/n	K_F	R^2	K_{RP}	α_{RP}	β	R^2
1.25	200	0.999	0.067	137.4	0.846	307.3	1.562	0.998	0.999

3.3.2. Freundlich Isotherm [12-18]

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. 3c) using the linear Freundlich isotherm equation.

The linear Freundlich isotherm constants for Pb(II) on γ-MnO_2 nanostructure are presented in Table 3. 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) less than 1 represent of favorable sorption and confirmed the heterogeneity of the adsorbent. Also, it indicates that the bond between Pb^{2+} ions and γ - MnO_2 nanostructure are strong.

3.3.3. Redlich-Peterson Isotherm [12-18]

The Redlich–Peterson isotherm constants can be predicted from the plot between $\mathrm{Ln}\left(K_{RP}\frac{C_e}{q_e}\text{-}1\right)$ 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 Pb(II) ion is presented in Fig. 3d 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.

3.3.4. Temkin Isotherm [12-18]

The Temkin adsorption isotherm model was chosen to evaluate the adsorption potentials of the adsorbent for adsorbates. The Temkin isotherm plot for the five metal ions are presented in Figure 4a and the isotherm parameters is given in Table 4.

The Temkin constant, b_T, related to heat of sorption for Pb(II) ion was 0.23 kJ/mol. The low values in this study maybe indicates a weak interaction between sorbate and sorbent, supporting an physical adsorption process for the present study [11].

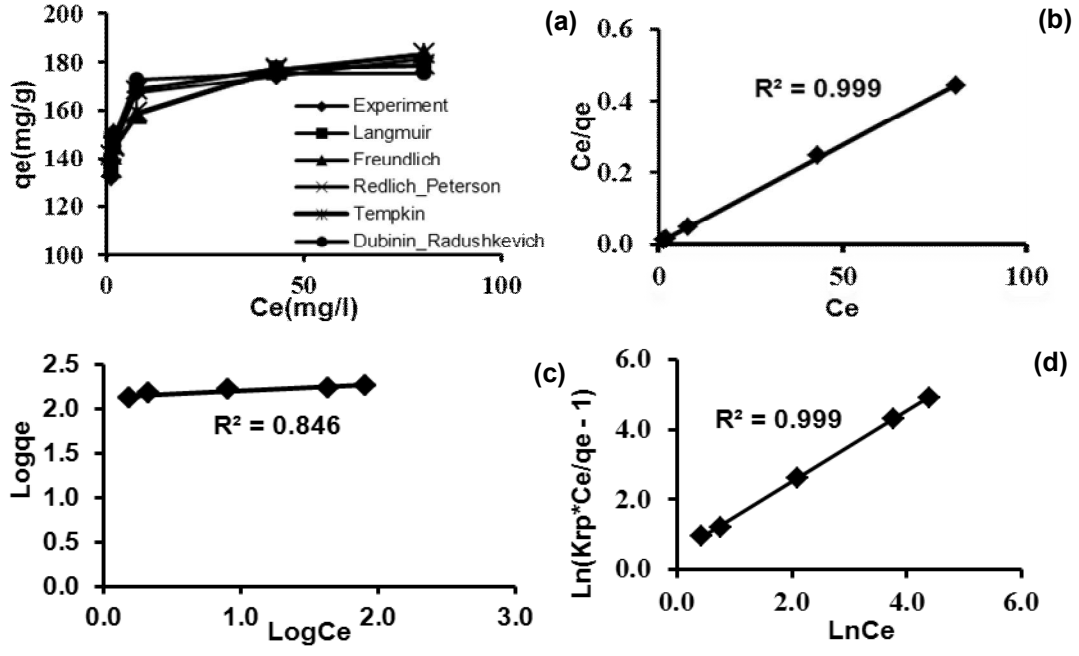


Figure 3. Linear and Nonlinear forms of isotherm modelling of adsorption of Lead (II) ion onto γ - MnO_2 nanostructure: (a) nonlinear forms, (b) Langmuir model, (c) Freundlich model, (d) Redlich – Peterson model

3.3.5. Dubinin – Radushkevich (D–R) Isotherm Equation [12-18]

The Dubinin – Radushkevich adsorption isotherm model was chosen to evaluate the value of mean sorption energy which gives information about chemical and physical sorption. The E value ranges from 1 to 8 kJ/mol for physical sorption and from 8 to 16 kJ/mol for chemical sorption [8,12]. The E values (Table 4) were less than 8 kJ/mol, indicating that the type of sorption of Pb(II) on γ - MnO_2 nanostructure is essentially physical.

Values of q_m and β are calculated from the intercept and slope of the plot by plotting lnq_e versus ε^2 (Figure 4b) and are listed in Table 4.

Table 4. Tempkin and Dubinin - Radushkevich isotherm parameters.

Tempkin			Dubinin - Redushkevich			
K_T (L/mg)	b_T (KJ/mol)	R^2	q_m (mol/g)	β	E (kJ/mol)	R^2
$0.41.10^6$	0.23	0.874	175.7	-0.184	1.65	0.964

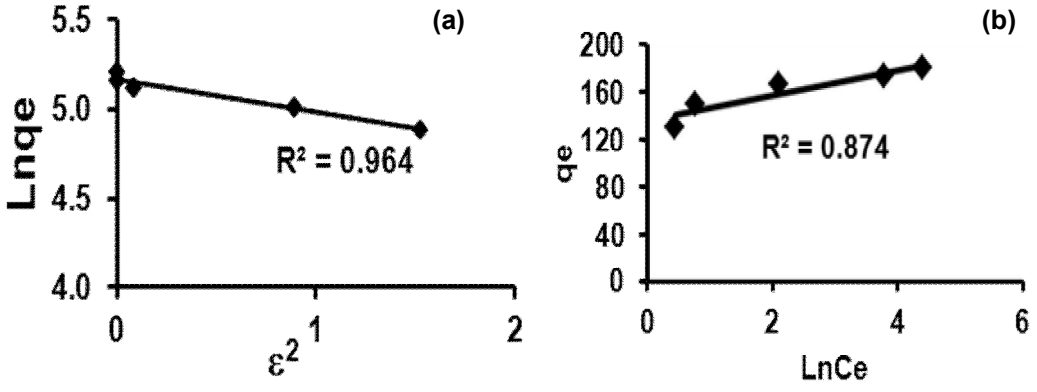


Figure 4. Tempkin (a) and D–R Models of adsorption of Lead (II) ion onto γ - MnO_2 nanostructure

3.4. Comparision with other studies

The applicability of adsorbent depends on the higher metal adsorption capacity, specific surface area, user friendly, availability, low cost and environment friendly uses. In this context, the adsorption capacities (calculated from the Langmuir isotherm model) of Lead with other parameters obtained from γ-MnO_2 and other adsorbents are compared in Table 5. It could be concluded that the γ-MnO_2 adsorbs Lead from water more than other adsorbent.

Table 5. Comparision of sorption capacity of lead (II) by some manganese oxide materials

Materials	q_m	References
MnO_2-loaded resin	80.64 mg/g	[2]
Diatomite	24.00 mg/g	[3]
Manganese oxides –modified Diatomite (Mn-diatomite)	99.00 mg/g	[3]
MnO_2/CNTs	78.74 mg/g	[4]
Manganese oxide-modified biochars (MPB)	4.91 mg/g	[5]
Manganese oxide -modified biochars (BPB)	47.05 mg/g	[5]
β - MnO_2	29.40 mg/g	[6]
Hydrous manganese dioxide (HMO)	352.55 mg/g	[7]
Low grade manganese ore	142.85 mg/g	[8]
γ - MnO_2	200.00 mg/g	This study

3.5. Desorption study [16-18]

Desorption ratio was calculated from the amount of metal ions adsorbed on the biomass and the final metal ion concentration in desorption medium, as the following equation:[15]

$$\text{Desorption ratio} = \frac{\text{Amount of metal ions desorbed}}{\text{Amount of metal ions adsorbed}} \times 100$$

3.5.1. Effect of eluent type and concentration

Various concentration of 20 ml of HNO_3, the mixtures (HNO_3 2M and NH_4NO_3 xM) and the mixtures (HNO_3 xM and NH_4NO_3 4M) were used for elution of Lead (II) ion adsorbed on the γ-MnO_2 nanostructure. The results are shown in Table 6 and Figure 5. When used the mixtures (HNO_3 xM and NH_4NO_3 4M) with concentration of NH_4NO_3 higher than 2 $mol.l^{-1}$, the recovery values for Pb(II) ion were quantitative (> 90%), so the mixture (HNO_3 2M and NH_4NO_3 4M) was selected as eluent.

3.5. 2. Effect of eluent volume and time

In the volume scanning of 5, 10, 15, 20, 30, 50 ml of the mixtue (HNO_3 2M and NH_4NO_3 4M) from 15 minute to 120 minute, the recovery values for Pb(II) ion were quantitative (> 90%) when the eluent volume higher than 15 ml after 15 minute (Figure 5). Therefore, in the subsequent experiments, 15 ml of the mixture (HNO_3 2M and NH_4NO_3 4M) was used for elution.

Table 6. Effect of concentration of eluents on the recovery of Pb(II) adsorbed on the γ-MnO_2

HNO_3 x ($mol.l^{-1}$)		HNO_3 2$mol.l^{-1}$ + NH_4NO_3 x ($mol.l^{-1}$)		HNO_3 x($mol.l^{-1}$) + NH_4NO_3 4 ($mol.l^{-1}$)	
Conc. of HNO_3 ($mol.l^{-1}$)	R (%)	Conc. of NH_4NO_3 ($mol.l^{-1}$)	R (%)	Conc. of HNO_3 ($mol.l^{-1}$)	R (%)
1.0	12.43%	0.1	50.32%	*0.0*	0.80%
1.5	20.73%	0.2	54.37%	0.5	70.83%
2.0	23.18%	0.5	55.67%	1.0	74.29%
3.0	27.92%	1.0	59.72%	2.0	90.95%
4.0	30.46%	2.0	75.28%	3.0	90.96%
5.0	61.01%	3.0	77.20%	4.0	90.44%
6.0	73.01%	4.0	90.95%		
8.0	72.92%	5.0	86.13%		
10.0	73.09%	6.0	84.13%		

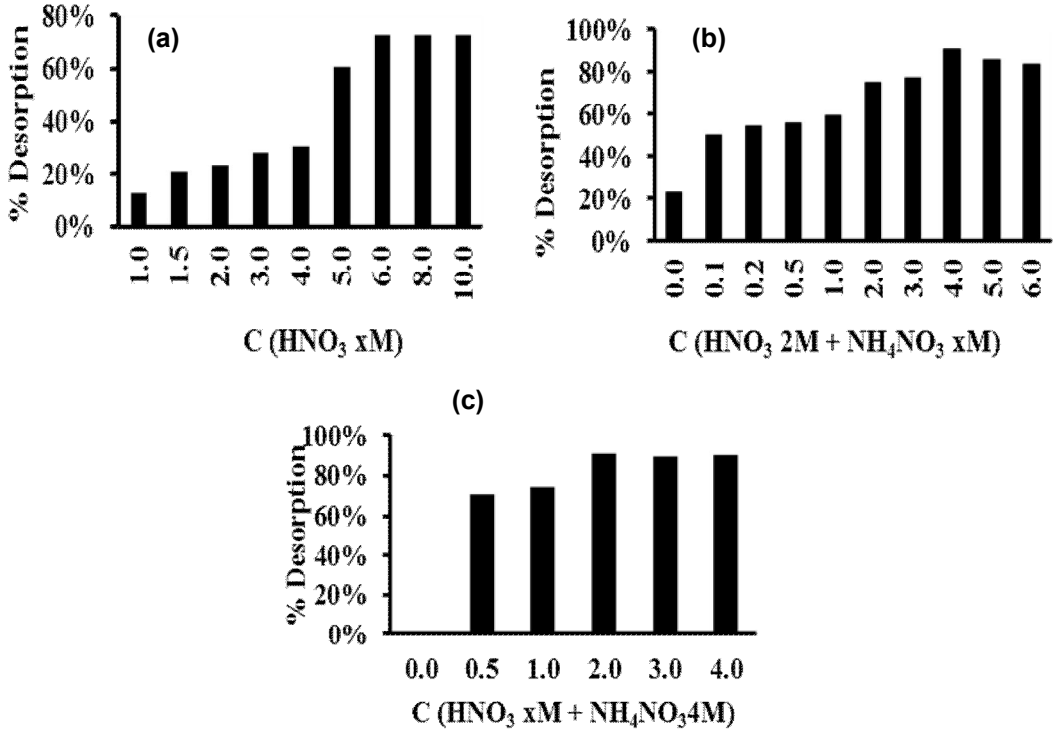


Figure 5. Effect of eluent type and concentration for elution Lead (II) ion adsorbed on the γ-MnO_2 nanostructure

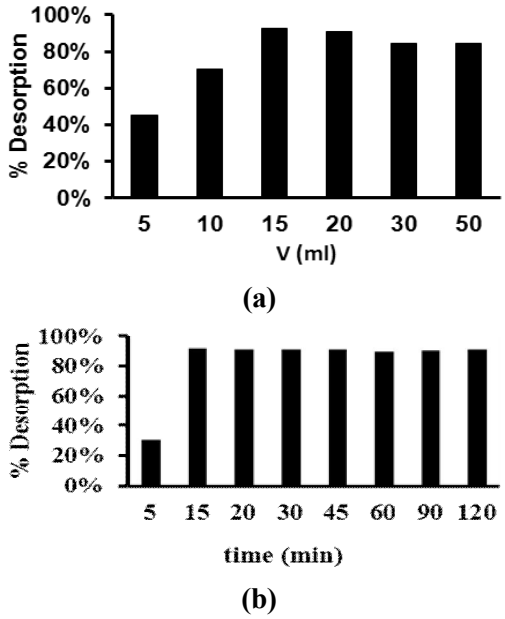


Figure 6. Effect of eluent volume (a) and time (b) for elution Lead (II) ion adsorbed on the γ-MnO_2 nanostructure

4. CONCLUSION

This study indicated that γ-MnO_2 nanostructure, which is widely available at low cost, can be used to remove Pb(II) from wastewater. The adsorption isotherms at room temperature could be well described by the Langmuir, Redlich – Peterson and Dubinin – Redushkevich isotherm models. The maximum adsorption capacity was 200 mg/g at 297K, pH 4.0 and contact time 250 minutes. The heat of sorption process and the mean free energy for these heavy metal ions caculated from Temkin and Dubinin – Redushkevich isotherm models can be estimated the adsorption experiment followed a physical process. Desorption experiments proved that 15 ml of the mixture (HNO_3 2M and NH_4NO_3 4M) was an efficient desorbent for the recovery of Pb(II) from aqueous solution after 15 minutes of eluent time.

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