

Synthesis and characterization of MnO₂ nanoparticles loaded Chitosan and its application in Pb²⁺ adsorption

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Abstract– A Manganese dioxide/Chitosan (MnO₂/CS) composite was prepared by a simple solution mixing-reduction-oxidation method. The structure and morphology features of the composite were characterized by X-ray diffraction, scanning electron microscopy (SEM) and Energy Dispersive X – Ray (EDX), Brunauer–Emmett–Teller (BET) surface area and Fourier Transform Infrared (FTIR). The results obtained from these analyses revealed that Chitosan was loaded by manganese dioxide nanoparticles which were smaller than 18 nm in size. The surface area of the solid material was found to be 15.7 m².g⁻¹, respectively. The resulting EDX spectra showed that there was about 0.1 gram MnO₂ loaded on 1.0 gram material. This MnO₂/CS was utilized as adsorbent to remove Pb²⁺ ions from aqueous solutions. Adsorption features of MnO₂/CS composite were investigated as a function of initial pH, contact time and initial Pb (II) concentrations. For adsorption isotherms, the Sips isotherm model was provided to be the best correlation (R²= 0.9990) compared to the Freundlich and Langmuir isotherms. The maximum adsorption capacity from Langmuir isotherm was 129.8 mg/g at 297K and pH 4.0.

Key words: Chitosan, Manganese, MnO₂/CS, adsorption, Lead

1. Introduction

Chitosan, which mainly consists of 2- amino-2-deoxy-D-glucose units through a β (1→4) linkage, is a nontoxic produced by the partial deacetylation of chitin, isolated from naturally occurring crustacean shells. Chitosan has been widely studied for biosensors, tissue engineering, separation film, water treatment and so on, due to its good biocompatibility, biodegradability and multiple functional groups. However, the relative poor mechanical properties and thermal stability of Chitosan restrict its wide application.[1- 2]

Manganese oxides with many types of crystalline structures such as α-, β-, γ- and δ-, have been extensively studied due to their structural varieties and excellent chemical characteristics^[2]. Therefore, they were applied for different areas,

such as batteries, molecular sieves, catalysts, and adsorbents [3-4]. However, the use of biological materials loaded MnO₂ nanoparticles to remove heavy metal ions has not been widely studied.

Lead has been introduced into natural waters from a variety of sources such as storage batteries, lead smelting, tetraethyl lead manufacturing, mining, plating, ammunition, and the ceramic glass industries. The permissible limit of lead in drinking water by Environmental Quality Act is 0.10mg/L. The presence of excess lead in drinking water causes diseases such as anemia, encephalopathy and hepatitis. Lead ions have an affinity for ligands containing thiol and phosphatic groups and they inhibit the biosynthesis of heme, causing damage to both the kidney and liver. However, lead can remain immobilized for years, and hence it is difficult to detect the metabolic disorders it causes [5]

Various treatment techniques have been applied to remove Lead (II) ions from contaminated waters such as chemical precipitation, adsorption and ionic exchange, membrane technology and solvent extraction [6-8]. 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 [4-10].

In this work, we applied the method of mixing-reduction-oxidation to synthesize Chitosan loaded MnO₂ nanoparticles, used as a low cost adsorbent for the adsorption of Pb(II) from aqueous solutions. The influence of various experimental parameters on Pb²⁺ adsorption and the optimum adsorption conditions were studied. The sorption capacity of MnO₂/CS was evaluated using Freundlich, Langmuir and Sips isotherm models.

2. Experimental

2.1. Materials

- Chemicals include:

Potassium permanganate (KMnO₄), ethyl alcohol (C₂H₅OH), Pb(NO₃)₂, HNO₃ and NaOH. All reagents used in the experiment were of analytical grade and pure of Merck. Chitosan was purchased from Japan.

Pb(II) ions were used as adsorbate. 1000 mg/l standard stock solution of each metal ions were prepared by dissolving Pb(NO₃)₂ respectively in distilled water. The concentration of metal ions in the aqueous solutions was analyzed by using AA-7000 atomic absorption spectrometer (Shimadzu Corporation).

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- Instruments include:

X-ray Diffractometer D5000 made in Germany by Siemens with X-ray radiation: $\text{CuK}\alpha$, $\lambda = 1,54056 \text{ \AA}$.

Ultra High Resolution Scanning Electron Microscopy S – 4800.

Bruker Tensor 27 spectrometer (Germany) using KBr pellets in the $4000 - 500 \text{ cm}^{-1}$ region.

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.

2.2. Synthesis of MnO_2/CS composite

MnO_2/CS composite was synthesized via the mixing - reduction - oxidation between KMnO_4 and $\text{C}_2\text{H}_5\text{OH}$ at room temperature for 5h by adding gradually KMnO_4 saturated solution to the mixture of Chitosan, $\text{C}_2\text{H}_5\text{OH}$ and H_2O . After the reaction was completed, the solid precipitate was washed with distilled water, and then dried at 60°C for 12h to get the product.

Characterization of the products: Phase identification was carried out by X-ray diffraction. The surface morphology of the samples was monitored with SEM. The specific surface area was evaluated by nitrogen adsorption-desorption isotherm measurements at 77K.

2.3. Adsorption study

Adsorption experiment was prepared by adding 0.1 g MnO_2/CS 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 5 using HNO_3 0.1M or NaOH 0.1M solutions (Merck). 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 metal ion concentration (from 100 mg/L to 500 mg/L) for maximum adsorption. Atomic Absorption Spectrophotometer (Spectrometer Atomic Absorption AA – 7000) was used to analyze the concentrations of the metal ion in the filtrate before and after adsorbent process.

Adsorption capacity was calculated by using the mass balance equation for the adsorbent [11-15]:

$$q = \frac{(C_o - C_e) \cdot V}{m} \quad (1)$$

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 discussions

3.1. Characterization of the $\text{MnO}_2/\text{Chitosan (CS)}$

Figure 1 shows XRD patterns of CS (a) and MnO_2/CS composite (b). In Figure 1a, the XRD pattern of CS reveals peaks at $2\theta = 10.8^\circ$ and $\sim 20.1^\circ$. Comparing with Figure 1a, some new diffraction peaks can be observed in Figure 1(b). In Figure 1b, the diffraction peaks were positioned at $2\theta = 22.2^\circ, 37.8^\circ, 42.5^\circ, 56.3^\circ,$ and 65.7° , respectively. All characteristic peaks can be indexed to the (110), (201), (211), (221), and (520) planes of orthorhombic $\gamma\text{-MnO}_2$ (JCPDS card no. 82-2169). Therefore, it can actually be considered that the composite is consisted of CS encapsulated by $\gamma\text{-MnO}_2$ nanoparticles.

SEM pictures of the surfaces of CS and MnO_2/CS composite are depicted in Fig. 2. As shown in Fig. 2a, the CS shows a smooth and tight fracture surface. A uniform distribution of MnO_2 on CS observed in Fig 2b, presents the morphology of the MnO_2 nanoparticles which are roughly spherical shape and smaller than 18 nm in size and create a porous surface, which may offer more adsorption sites for adsorbate. This result also indicated that chitosan has been chemically modified.

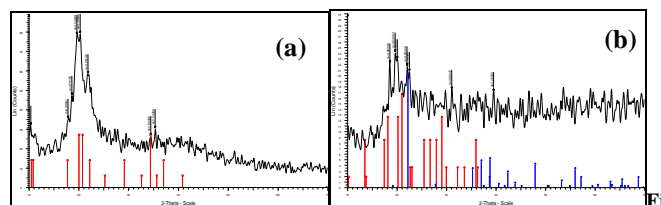


Figure 1. XRD image of CS (a) and MnO_2/CS (b)

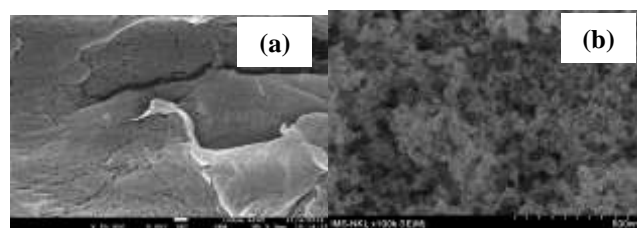


Figure 2. SEM images of CS (a) and MnO_2/CS (b)

The chemical composition of CS and MnO_2/CS was analysed using EDX. According to the results of EDX analysis (Fig. 3a and 3b), there was approximately 10% MnO_2 which was loaded onto 1 gram material.

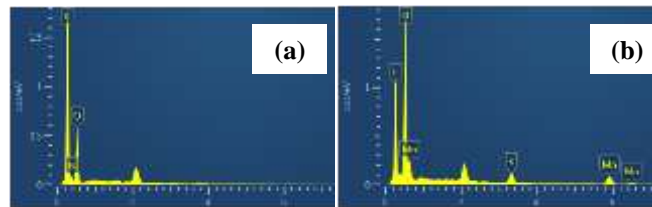


Figure 3. EDX images of CS (a) and MnO_2/CS (b)

The synergistic effect on the properties of CS by adding MnO₂ nanoparticles was observed by FTIR and the result is shown in Fig. 4. For the MnO₂ nanoparticles, the peaks at 525.33 cm⁻¹ ascribe to Mn-O group (Fig. 4a). In the spectrum of CS (Fig. 4b), the characteristic absorption band appeared at 1656.75 cm⁻¹ ascribes to the amide I (C=O stretching), at 1598.94 cm⁻¹ ascribes to amide II (N-H bending modes) and the peak at 1423.08 and 1382.31 cm⁻¹ ascribe to -C-O stretching of primary alcoholic group in CS. In the spectrum of MnO₂/CS composite (Fig. 4c), compared with that of CS and MnO₂, the 1656.75 cm⁻¹ peak of amide I, the 1598.94 cm⁻¹ peak of amide II, the 1423.08 and 1382.31 cm⁻¹ peak of -C-O stretching vibration of primary alcoholic group and the 525.33 cm⁻¹ peak of Mn - O were shifted to 1633.12, 1554.27, 1411.37, 1343.25, 518.32 cm⁻¹, respectively. The shifting of these peaks indicates that MnO₂ nanoparticles was loaded onto the CS successfully.

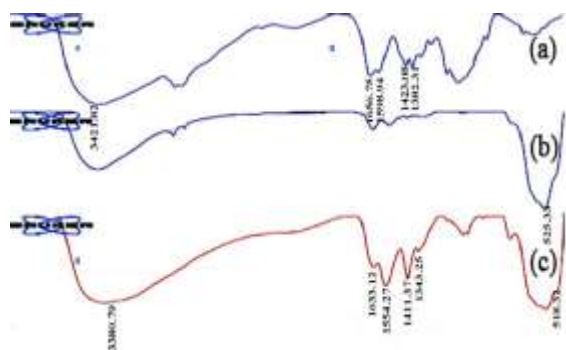


Figure 4. IR spectroscopy of CS (a), MnO₂ (b), MnO₂/CS (c)

The specific surface area (m²/g) and pore volume distribution were determined by BET and BJH-analysis of N₂ adsorption-desorption isotherms measured on the CS and MnO₂/CS samples (Fig.). According to the International Union of Pure and Applied Chemistry (IUPAC) classifications, the pores can be divided into macropores (d > 50 nm), mesopores (2 < d < 50 nm) and micropores (d < 2 nm). In this study, chitosan and chitosan loaded MnO₂ correspond to macropores with average pore diameter higher than 50 nm. Moreover, the MnO₂/CS have higher BET surface area (average 15.75 m²/g) that facilitates the adsorption of Pb²⁺ with its loose pore structure as compared to chitosan (0.23 m²/g).

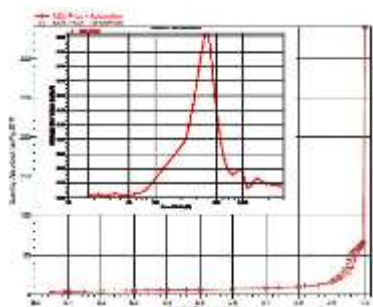


Figure 5. B.E.T and B.J.H of MnO₂/CS

3.2. Study of Adsorption of Pb²⁺

3.2.1. Affecting factors

The pH is one of the imperative factors governing the adsorption of the heavy metal ions. The effect of pH was studied from a range of 2 to 5 under the precise conditions (at optimum contact time of 120 min, 240 rpm shaking speed, with 0.1g of the adsorbents used, and at a room temperature of 24°C). From Fig.6a, with MnO₂/CS composite used as adsorbent, it was observed that with increase in the pH (2 - 5) of the aqueous solution, the adsorption percentage of Lead (II) ions increased up to the pH = 4, after that the adsorption percentage of Lead (II) ions decreased. At pH = 4, the maximum adsorption was obtained.

The relationship between contact time and the adsorption percentage of Pb²⁺ ion from aqueous solution with MnO₂/CS adsorbent is shown in Fig. 6b. The effect of contact time was studied at a room temperature of 24°C. From the obtained result, it is evident that the adsorption of metal ions increased as contact time increases. The adsorption percentage of Pb (II) approached equilibrium within 120 min with Pb (II) recording 83.87% adsorption.

3.2.2. 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 was analyzed using the Freundlich, Langmuir and Sips isotherms expression.

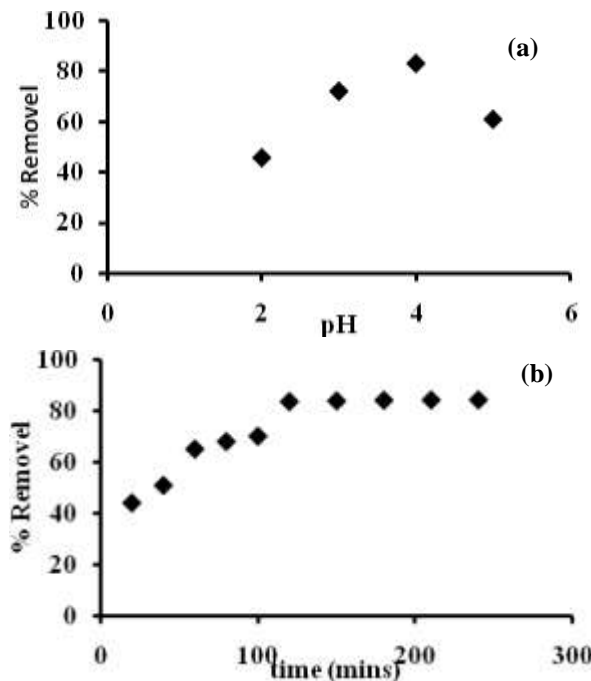


Figure 6. Effect of pH (a) and contact time (b)

3.2.2.1. Langmuir Isotherm

The Langmuir (Langmuir, 1918) model[11-15] 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,

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m \cdot K_L} \quad (2)$$

The Langmuir isotherm model was chosen for the estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the MnO₂/CS composite surface. The plot of specific sorption (C_e/q_e) against the equilibrium concentration (C_e) for Pb(II) is shown in Fig. 7a and the linear isotherm parameters, q_m, K_L and the coefficient of determinations are presented in Table 1.

The data in Table 1 indicated that, the high values of correlation coefficient (R² = 0.9965) indicates a good agreement between the parameters and confirms the monolayer adsorption of Pb(II) ion onto MnO₂/CS composite surface. Furthermore, the sorption capacity, q_m, which is a measure of the maximum sorption capacity corresponding to complete monolayer coverage is 129.8 mg/g.

3.2.2.2. Freundlich Isotherm

The Freundlich (1906) equation[11-15] is an empirical equation based on adsorption on a heterogeneous surface. The equation is commonly represented as,

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \quad (3)$$

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 indicates 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 Pb(II) ion on MnO₂/CS composite were plotted logarithmically (Fig. 7b) using the linear Freundlich isotherm equation.

The linear Freundlich isotherm constants for Pb(II) on MnO₂/CS composite are presented in Table 1. The Freundlich isotherm parameter 1/n measures the adsorption intensity of metal ions on the MnO₂/CS composite. The low 1/n value of Pb(II) (0.1666) less than 1 represents of favorable sorption and confirms the heterogeneity of the adsorbent.

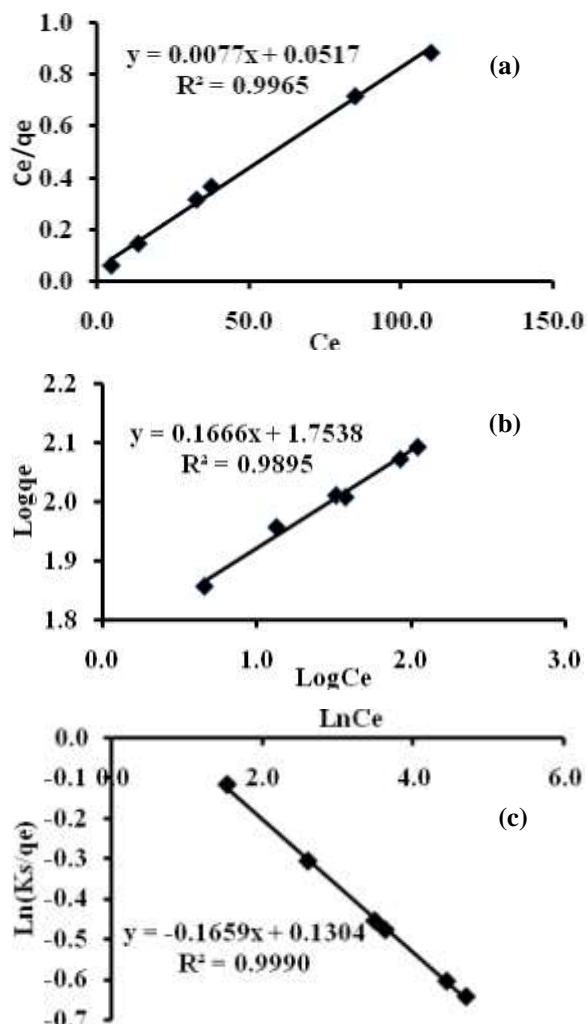


Figure 7. Plot of Langmuir (a), Freundlich (b) and Sips (c) isotherm models

3.2.2.3. Sips Isotherm

Sips isotherm [13] is a combined form of Langmuir and Freundlich expressions deduced for predicting the heterogeneous adsorption systems and circumventing the limitation of the rising adsorbate concentration associated with Freundlich isotherm model. At low adsorbate concentrations, it reduces to Freundlich isotherm; while at high concentrations, it predicts a monolayer adsorption capacity characteristic of the Langmuir isotherm. The linearized form of the Langmuir equation is given,

$$\beta_s \ln(C_e) = -\ln\left(\frac{K_s}{q_e}\right) + \ln a_s \quad (4)$$

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. β_s is Sips isotherm model exponent; a_s (L/mg) and K_s (L/g) are Sips isotherm model constants.

The plot of Ln(K_s/q_e) against the Ln(C_e) for Pb(II) is shown in Fig. 7c and the linear isotherm parameters and the coefficient of determinations are presented in Table 1. The data in Table 1 indicated that the high value of correlation

coefficient ($R^2 = 0.9990$) is more than correlation coefficient of Langmuir and Freundlich isotherms. This indicates the adsorption Pb^{2+} onto MnO_2/CS surface followed the both Langmuir and Freundlich isotherms.

Table 1. Langmuir, Freundlich and Sips isotherm parameters.

Isotherm Models	Parameters	
Langmuir	K_L	0.1489
	q_m	129.8
	R^2	0.9965
Freundlich	$1/n$	0.1666
	K_F	56.73
	R^2	0.9895
Sips	K_s	64.80
	α_s	0.1873
	β_s	0.2305
	RMSE	1.722
	R^2	0.9990

4. Conclusion

In this study, we synthesized successfully chitosan loaded Manganese dioxide nanoparticles by the simple solution mixing-reduction-oxidation method. The results showed that MnO_2 nanoparticles with less than 18 nm in size were loaded on Chitosan surface. This material was used as adsorbent to remove Pb^{2+} from aqueous solutions in the optimal conditions (pH = 4, time = 120 minutes and shaking speed = 240 rpm). The experimental results were analyzed using three adsorption isotherm models, the Langmuir, Freundlich and Sips isotherm models. By using the Langmuir isotherm, the adsorption capacity for Pb^{2+} ions was found as 129.8 mg/g respectively.

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