Lead Adsorption from Aqueous Solution Using Manganese Oxides Recovered from Spent Alkaline and Zn/C Batteries

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Lead is a highly toxic element and can cause serious damages to the health of human beings, including cancer. For these reasons, in the recent years stringent limits have been set for this element, especially regarding drinking water. In this paper, the potential of manganese oxides (MnO_x) as adsorbents for the removal of lead from synthetically contaminated water was investigated. These oxides were recovered from alkaline batteries by a bio-hydrometallurgical process through potassium permanganate ($KMnO_4$) precipitation. The MnO_x was characterized by Scanning Electronic Microscopy (SEM), Energy Dispersive Spectroscopy (SEM-EDS) and X Ray Diffraction (XRD) analysis. The surface area of the material was determined using the N_2 isotherm by the BET method. Batch tests were performed on untreated MnOx at different temperatures, i.e. 10, 25 and 40°C, initial adsorbate concentration ranging from 5 to 100 mg L^{-1} and contact times between 1 minute and 30 minutes. The results obtained showed that the equilibrium of lead on MnOx was reached after 5 minutes. The Langmuir isotherm provided the best correlation for the adsorption process, with a maximum adsorption capacity of 9.51 mg g^{-1}. The process was exothermic and spontaneous. Kinetic studies revealed that the lead adsorption onto MnOx followed a pseudo-second order kinetic model and the activation energy value calculated was of 11.35 kJ mol^{-1}, evidencing the physical nature of the phenomenon. Hence, this study strongly supports the use of MnOx as an effective and economical adsorbent for the removal of lead from water.

1. Introduction

There is an increasing public concern regarding natural water pollution caused by heavy metals. Heavy metal is a term often used as a group name for metals and semi-metals (metalloids) having a density greater than 4–6 g cm^{-3}, an atomic weight greater than sodium, or an atomic number greater than 20 or 21 (Zhou and Haynes, 2010). Common elements considered include Cu, Zn, Co, Ni, Pb, Hg, Cd, Cr, Se, and As. They are dangerous because they produce bioaccumulation. Lead can reach the water from various anthropogenic sources as well as via natural geochemical processes. It is a toxic metal and can damage the nervous system even at low concentration (ATSDR, 2011). Lead has also been considered as a probable human carcinogen (IARC, 2018). Actually, the World Health Organization (WHO) recommends a limit dose of 10 µg L^{-1} for drinking water. From all the treatment techniques and processes studied until now to remove heavy metals from contaminated water - i.e. chemical precipitation, ion exchange, filtration, membrane separation, coagulation/flocculation-, adsorption is one of the favourite ones (Wang et al., 2014). In fact, adsorption is the most effective, efficient, facile and economic method for treating large amounts of water containing low levels of pollutants (Lee et al., 2013). During the past decades, researchers have developed various adsorbents exhibiting strong adsorption affinity for heavy metals in aqueous solutions, such as zeolite, iron oxides, activated carbon, and other carbon- based materials. However, most of them are limited in practical application because they are time-consuming and very costly. Lastly, a variety of agro-based waste materials have been studied for heavy metal ions removal from water. These biosorbants include rice husk (Abdel-

Ghani et al., 2007; Chauh et al., 2004), spent coffee grounds (Patterer et al., 2017; Lavecchia et al., 2016), olive pomace (Baccar et al., 2009; Pagnanelli et al., 2003, 2002), egg shell, tea waste, bone powder, biomass among others. However, in recent years, considerable attention has been paid to the investigation of different types of low-cost adsorbents, especially using metal-oxide adsorbents (Dong et al., 2009). Manganese oxides cover a large family of porous materials with layered and tunnel structures ranging in size from nano- to microscale (Kang et al., 2011). Because of their structure and their high surface area, there is a considerable interest in the use of these materials as adsorbents (Zhang et al., 2017). The unusual high adsorption capacities and scavenging capabilities of Mn oxides provide one of the primary controls of heavy metals and other trace elements in soils and aquatic sediments. Understanding such controls is important for mitigating health affects in humans and for treatment of water for consumption and industrial use.

The main objective of this paper was to investigate the removal efficiency of Pb (II) uptaken by MnO_x recovered from spent alkaline and Zn/C batteries through a bio-hydrometallurgical process. The study consisted of batch tests carried out at different temperatures and different initial adsorbate concentrations for different contact times. Equilibrium, kinetics and thermodynamics of the process were evaluated.

2. Experimental

2.1 Materials

Lead (II) acetate 3-hydrate (CAS No. 6080-56-4) with purity >99% was purchased from Biopack (Buenos Aires, Argentina). Synthetic lead solutions were prepared by adding an appropriate amount of lead acetate to distilled water. The biohydrometallurgical process for the treatment of spent alkaline and Zn/C batteries has been described in a previous work (Gallegos et al. 2013). Briefly, batteries were first transversely cut and separated into their components, washed with distilled water, filtered and dried, leaving a powder containing 34 wt% Mn and 22 wt% Zn. Leaching tests were performed using bio-generated sulfuric acid of pH = 0.80 (produced in an air-lift bioreactor type, filled with sulfur where a strain of Acidithiobacillus thiooxidans was inoculated). The manganese oxide was obtained by adding $KMnO_4$ over the leached solution, with continuous agitation for 30 minutes. The solid synthesized was filtered, washed with distilled water, dried at 100 ºC and calcined in air at 150 ºC for 2 h. Finally, the material was sieved by an ASTM (11/70) No. 100 sieve (nominal mesh opening ≤ 149 µm) and stored in a closed container.

2.2 Methods

MnO_x was characterized by X-ray diffraction (XRD) in a Philips PW1390 Diffractometer using CuKα radiation. The Scanning Electron Microscopy (SEM) studies were carried out using a Phillips SEM 505 microscope. The quantitative and qualitative study was analyzed with an Energy Dispersive X-ray Spectroscopy (EDS), which was coupled to SEM equipment. The textural properties were carried using a Micromeritics Accussorb 2100 D sorptometer. Specific surface area was obtained by BET method.

Batch tests were undertaken by shaking Falcon flasks containing 0.15 g of MnO_x and 15 mL of lead solution at 250 rpm for a known period of time. A rotational shaker equipped with a water bath was used. After that, the samples were filtered on paper and the residual lead concentration was measured. The liquid-to-solid ratio was constant and equal to 100 mL g^{-1} for all the experiments. The initial adsorbate concentration was varied between 5 and 100 mg L^{-1}. The contact time ranged from 1 to 30 minutes. The experiments were carried out at three different temperature, i. e. 10±2 °C, 25±2°C and 40±2°C. The concentration of lead in the aqueous solution was determined by an ICP-OES spectrometer (Shimadzu, Germany). Standard lead solutions at concentrations ranging from 3 to 12 mg L^{-1} were used to construct the calibration curve (ASTM, 2015).

2.3 Adsorption isotherms

The amount of Pb(II) ions adsorbed per g of manganese oxides was calculated using the following expression:

$$q_e = \frac{V_L}{m}(c_0 - c_e) \tag{1}$$

where q_e (mg g^{-1}) is the amount of metal ions adsorbed onto the manganese oxides at equilibrium, c_0 and c_e are the concentrations of metal ions in the solution (mg L^{-1}) prior to adsorption and at the equilibrium, respectively. V_L is the volume of the aqueous phase (L) and m is the dry weight of the sorbent (g).

Adsorption isotherms describe the equilibrium between the adsorbent and the adsorbate to optimize the use of the substract. Three different models were used to analyze the equilibrium data (El-Wakeel et al., 2017; Eren et al., 2009): Langmuir (Eq. 2), Freundlich (Eq. 3) and Dubinin-Radushkevich (D-R) (Eq. 4).

$$q_e = \frac{q_{max}bc_e}{1 + bc_e} \tag{2}$$

$$q_e = K_F c_e^{1/n} \tag{3}$$

$$q_e = q_{max} \exp\left[-B\left(RT \ln\left(1 + \frac{1}{c_e}\right)\right)^2\right] \tag{4}$$

In Eq.2 q_{max} is the maximum adsorption capacity (mg g^{-1}), corresponding to a complete monolayer on the adsorbent, and b is the Langmuir constant (L mg^{-1}), which can be related to the affinity of the adsorbing species for the adsorption sites on the solid. In Eq.3 K_F is the Freundlich adsorption capacity (mg g^{-1}) and n is a dimensionless constant that represents the adsorption intensity. It is generally stated that values of n in the range 2–10, 1–2 and <1 indicate, respectively, good, moderate and poor adsorption characteristics (Lavecchia et al., 2016). In Eq.4 B (mol^2 kJ^{-2}) is a constant related to the adsorption energy, R (8.314 J mol^{-1} K^{-1}) is the gas constant, and T (K) is the absolute temperature. The constant B gives the mean free energy E (kJ mol^{-1}) of adsorption per molecule of the sorbate when it is transferred to the surface of the solid from infinity in the solution. It can be computed from the following relationship:

$$E = \frac{1}{(2B)^{0.5}} \tag{5}$$

This parameter gives information about the adsorption nature. Values of $E<$ 8 kJ mol^{-1} indicates physical adsorption meanwhile a magnitude of E between 8 and 16 kJ mol^{-1} evidences a chemisorption process (Patterer et al., 2017; Lavecchia et al., 2016).

2.4 Adsorption kinetics and activation energy
The kinetics of adsorption was studied by using two empiric models: pseudo-first order (PFO) and pseudo-second order (PSO) models (Sharma et al., 2017; Xiang et al., 2017; Wan et al., 2016). Both of them take into account the amount of solute adsorbed which is an important information for determining the batch reactor volume.
The PFO model or Lagergren model is described by the following equation:

$$\frac{dq}{dt} = k_1(q_e - q) \tag{6}$$

The PSO model or Ho model is shown in Eq.7.

$$\frac{dq}{dt} = k_2(q_e - q)^2 \tag{7}$$

k_1 e k_2 are the rate constant of the PFO and PSO models (in min^{-1} and g mg^{-1} min^{-1}, respectively).
The activation energy was calculated by using the linearized form of Arrhenius equation:

$$\ln k = \ln A_0 - \frac{E_a}{RT} \tag{8}$$

where A_o is the independent temperature factor (g mg^{-1} min^{-1}), R and T as defined previously, and the rate constant k assumes the k_2 value from the PSO kinetic model which provided the best fitting for the kinetic study. Generally, low activation energies (5-40 kJ mol^{-1}) are characteristic of the physical adsorption, while high ones (40-800 kJ mol^{-1}) suggest chemisorption (Patterer et al., 2017; Lavecchia et al., 2016).

2.5 Thermodynamic study
The thermodynamic parameters can be determined by using the equilibrium constant K_e, which depends on the temperature. The change in the standard free energy, ΔG°, the standard enthalpy, ΔH°, and the standard entropy, ΔS°, were calculated by using the following equations:

$$\Delta G^0 = -RT \ln K_e \tag{9}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{10}$$

Combining Eq. 9 and Eq. 10 van't Hoff equation is obtained:

$$\ln K_e = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{11}$$

3. Results and discussion

3.1 MnO$_x$ characterization
The obtained MnO$_x$ sample presents a BET surface (S$_{BET}$), pore volume (V$_p$) and pore diameter (d$_p$) of 66 m^2 g^{-1}, 24 cm^3 g^{-1}, 186 A, respectively. The analysis via SEM reveals the globular particles typical of the MnO$_x$ (Figure 1). The SEM-EDS analysis shows that, in addition to Mn and O, there is also Zn, K, S. A content of

approximately 3% of Zn was estimated on the basis of the quantitative analysis. The X-ray diffraction pattern of MnO_x presents diffraction lines corresponding to α-MnO_2 phase (JCPDS 44-1386). No phases containing Zn were found. The resulting phase of manganese oxides is characterized by having a tunnel-like structure, oxygen vacancies and manganese in different oxidation state, which proves this material to be a potential absorbent of heavy metals from water.
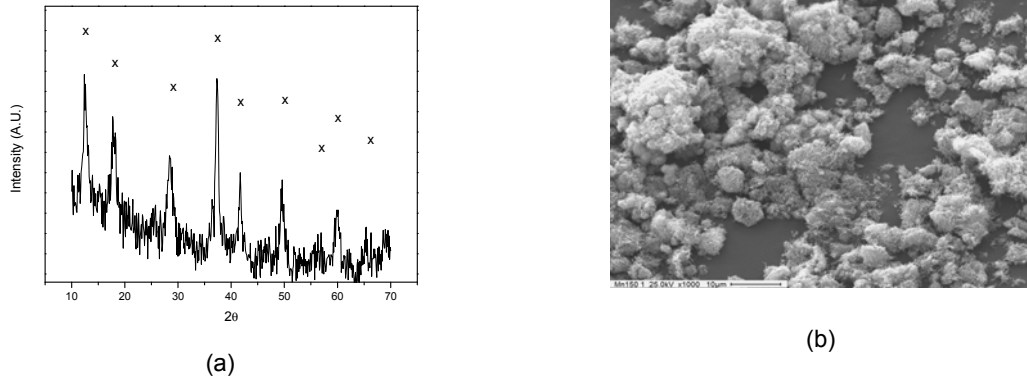

(a)

(b)

Figure 1. (a) X-ray diffraction pattern and (b) SEM image of the MnO_x solid.

3.2 Equilibrium study

The time required to reach the equilibrium was of the order of 5 minutes. Equilibrium time was independent of the initial lead concentration (Figure 2a). After that time, there is not variation in the Pb(II) concentration measured in solution, an a plateau is obtained for all the studied temperatures (Figure 2b).
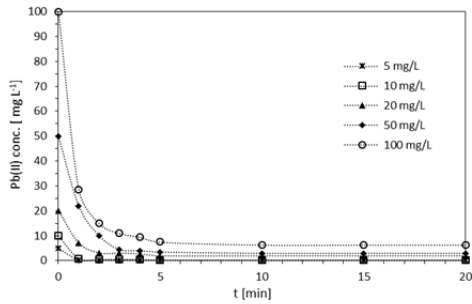

Figure 2a: Lead decay curves for different at initial concentrations at the T=25°C.

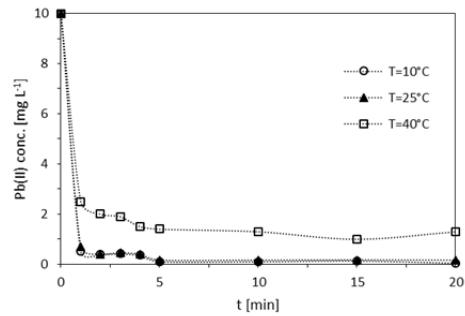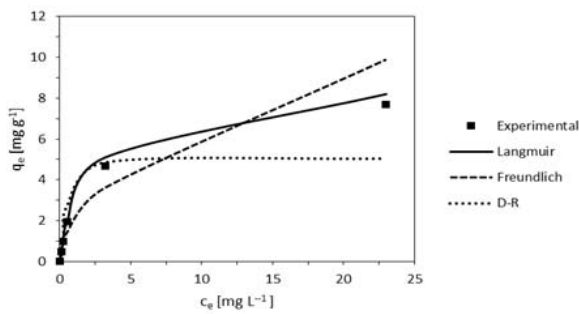*Figure 2b: Lead decay curves for c_0=10 mg L^{-1} different temperatures*

Figure 4. Comparison of adsorption model responses for lead adsorption on MnO_x at T=10°C.

Table 1. Langmuir coefficients.

T [°C]	q_{max} [mg g^{-1}]	b [L mg^{-1}]	R^2
10	9.51	0.46	0.998
25	6.04	0.37	0.982
40	5.88	0.36	0.977

The parameters appearing in equations (2), (3) and (4) were obtained by fitting the experimental data to the linearized form of each one. The following values were obtained: q_{max} = 9.51 mg g^{-1} and b = 0.46 L mg^{-1} for the Langmuir equation; K_F = 2.00 mg g^{-1} and n = 1.96 for the Freundlich equation and q_{max} = 5.04 mg g^{-1}, B =

0.0929 mol^2 kJ^{-2} and E = 2.32 kJ mol^{-1} for the D-R equation. These results correspond to the lowest temperature analyzed in this study, 10°C, which turned to be the most favorable temperature for lead adsorption according to the highest q_{max} value obtained (Table 1). Langmuir equation provided the best fit to the data for all cases (the highest R^2). This can be better appreciated from Figure 4, where the adsorption isotherms resulting from the three models are plotted together with the experimental data at T=10°C.

3.3 Adsorption kinetics and activation energy

The experimental data was analyzed using the linearized form of the pseudo-first order (PFO) (Eq. 6) and the pseudo-second order models (PSO) (Eq. 7). Figure 5 shows the PSO model plot for an initial concentration of 10 mg L^{-1} and for the different temperatures considered. From the R^2 values obtained, it can be concluded that the Ho model gives the best fit to the data and the k_2 values were estimated (Table 2).
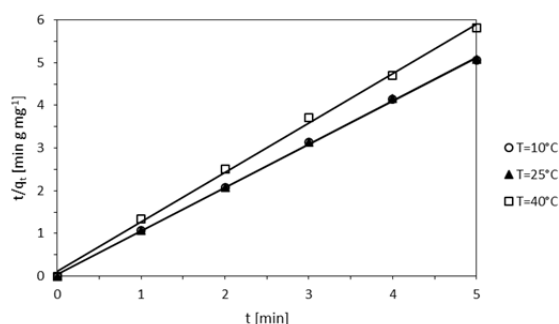
Table 2: Pseudo-second order model coefficients.

T [°C]	q_e [mg g^{-1}]	k_2 [g mg^{-1} min^{-1}]	R^2
10	0.98	24.0	0.999
25	0.98	24.1	0.999
40	0.87	38.4	0.998

Figure 5: PSO plot for lead adsorption on MnO_x at different temperatures (c_o=10 mg L^{-1}).

These results agree with those of Wan et al. (2018) and of Zhang et al. (2017). Otherwise, the q_e values calculated with this model were similar to the experimental data. Hence, it can be concluded that the lead adsorption by MnO_x follows a pseudo-second order kinetics. Zhang et al. (2017) and Lee et al. (2013) have obtained the same conclusion. Moreover, the low values obtained for E_a and the parameter E from D-R isotherm (11.35 kJ mol^{-1} and 2.32 kJ mol^{-1}, respectively) confirm the physical nature of the process.

3.4 Thermodynamic parameters

In this study, where the Langmuir isotherm is the model that best described the data, K_e assumes the value of the parameter b of Langmuir, according to the model's mathematical deduction. From the thermodynamic analysis, the following values were estimted: ΔG°=- 10.63 kJ mol^{-1} (at 283,15 K), ΔH°=- 5.95 kJ mol^{-1}, ΔS°= 0.02 kJ mol^{-1} K^{-1}. The negative results for ΔG° and ΔH° confirmed the spontaneity and the exothermicity of the process, while the positive value of ΔS° indicated a much more chaotic distribution of Pb^{2+} in the solid phase compared with the bulk phase. Similar results were obtained by Eren et al. (2011).

4. Conclusions

Lead adsorption from aqueous solution by manganese oxides was studied at different initial pollutant concentration and for three different temperatures. MnO_x showed promising properties as low-cost and effective adsorbents, especially taking into account that they come from a battery recycling process. Experimental data showed that adsorption equilibrium of lead on MnO_x was well described by the Langmuir equation evidencing a monolayer-type adsorption. The phenomenon followed a pseudo-second order kinetics. Evaluation of activation energy indicated the physical nature of the process, which was also confirmed by the parameter E from the D-R model. Thermodynamic study showed that the process was exothermic and spontaneous. Further research aimed to determine the suitability of MnO_x for the removal of other heavy metals in mono- and bicomponent solutions is on progress.

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