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Removal of Lead (II) from aqueous solutions using Fe_3O_4-MWCNTs :2/1 adsorbent

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Abstract

In the present work, a magnetic nanocomposite (Fe_3O_4/MWCNTs: 2/1) was prepared from multi-walled carbon nanotubes and magnetite using coprecipitation method. The sample was characterized by X-ray diffraction (XRD) and observed with scanning electron microscopy (SEM) analysis. The removal of lead ions was investigated using the adsorption process onto (Fe_3O_4/MWCNTs: 2/1). The effect of important parameters was studied: initial pH, initial concentration of heavy metal and temperature. As a result, the optimum adsorption conditions were estimated to be about 5, 80 $mg.L^{-1}$ and 30 ºC, respectively. Langmuir isotherm best suited the adsorption of lead (II) onto composite. Thermodynamic study suggests that the adsorption process was favorable and exothermic. This adsorbent exhibited an efficient adsorption capacity (50 $mg.g^{-1}$) and simple separation.

Keywords: Carbon nanotubes, magnetite, adsorption, lead, isotherm.

1. Introduction

Heavy metals in simple definition are metallic particles represent a significant proportion of dangerous pollutants invaded wastewater and generated by various industries. Those metals like lead, mercury, copper, cadmium, zinc, nickel, cobalt, chromium and aluminum can pose serious environmental and health hazards at certain amount due to their toxicity toward organisms[1]. In the last decades, scientists and researchers have focused on the removal of such pollutants from effluents to reduce their risks. Among wide studies, adsorption process showed an efficient removal of heavy metal and hence it will be the subject of discussion in the present work. In the aim to enhance the adsorption capacity and separation of adsorbent from solution we tried to synthesize nanocomposite from multi-walled carbon nanotubes and magnetite (Fe_3O_4/MWCNTs: 2/1) using coprecipitation method after a chemical oxidation [2]. Characterization of this sample was carried out by X-ray diffraction and scanning electron microscopy, only a few studies have interested in the removal of lead (II) from aqueous solution using the same nanocomposite at other weight ratio. Various parameters were tested to find the optimum conditions; isotherm models and thermodynamic studies were investigated as well to confirm the feasibility of results.

2. Results and Discussion

2.1. Effect of pH

Among different parameters, the effect of pH is considered as the most important condition in the adsorption mechanism of heavy metals. While it can control the surface charge of adsorbent and the adsorbate speciation and its degree of ionization in the solution as well [3]. In this regard, we have been evaluated the uptake of Pb^{2+} ions at various pH equal to 3 and 5. Figure.1 summarizes the output of this study as follow: at low pH (aggressive acidic medium) a negligible adsorption was observed due to the competition between H^+ protons and Pb^{2+} ions to achieve the available sites onto the solid surface [4]. As seen in figure.2, the surface of Fe_3O_4-MWCNTs nanocomposite is positively charged at pH lower than 6.6 (zeta potential) which can explain the absence of electrostatic interactions with Pb^{2+} cations. The results showed a significant improvement in adsorption capacity at pH close to 5 compared to lower values, just when fewer protonated active sites leaving more negatively charged active sites available for the electrostatic interaction with Pb^{2+} heavy metal[3]. At pH higher than 7, the adsorption of such metal became impossible due to the precipitation of lead hydroxide [5].

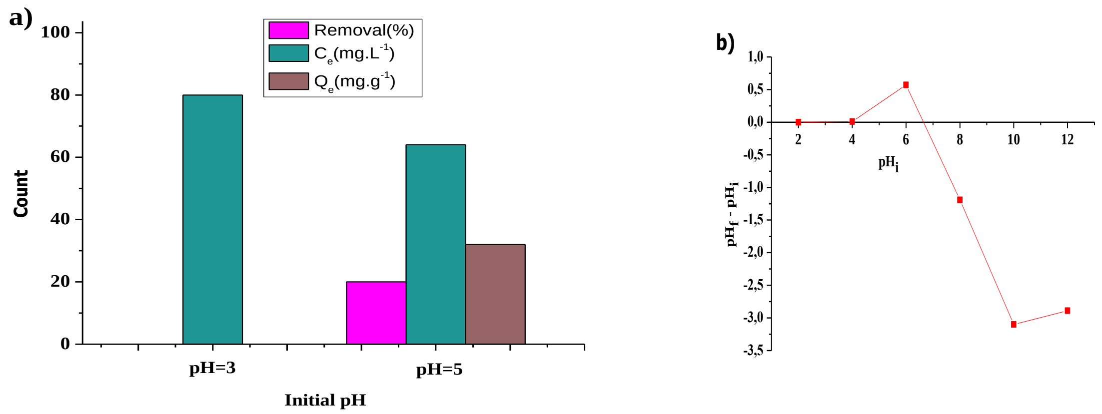

Fig.1.a. Graphical illustration: The effect of pH on percent removal, equilibrium concentration and adsorption capacity of lead ions onto Fe_3O_4-MWCNTs adsorbent. Experimental conditions: 10 mg; 20 mL; 180 rpm, 210 minutes and 20 C$^{\circ}$. **b.** Point of zero charge of Fe_3O_4-MWCNTs nanocomposite.

2.2. Effect of initial concentration of Pb^{2+} ions and temperature on the adsorption capacity

As showing in fig.2, the increase in initial concentration of lead (II) followed by a clear increase in adsorption capacity amount and 80 mg.L^{-1} was chosen to be the optimum value with 30 C° temperature.

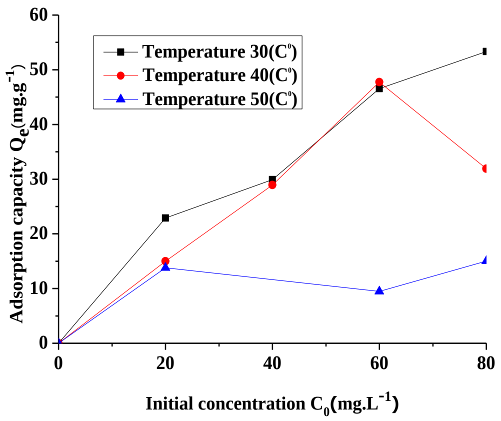

Fig.2. Effect of initial concentration of Pb^{2+} ions and temperature on the adsorption capacity. Experimental conditions: 10 mg; 20 mL; 180 rpm; 210 minutes and pH=5.

2.3. Adsorption Isotherm

2.3.1. Langmuir isotherm

The linear equation (1) of Langmuir isotherm was plotted; Q_m and k_L values were calculated using the slope and intercept of the plot, respectively: C_e/Q_e vs C_e in fig.3.

$$\frac{C_e}{Q_e} = \frac{1}{Q_m k_L} + \frac{C_e}{Q_m} \qquad (1)$$

Where Q_m represents the maximum adsorption capacity; k_L is the Langmuir constant [1, 6].

Fig.3. Langmuir isotherm of the adsorption of Pb^{2+} ions onto Fe_3O_4-MWCNTs Experimental conditions: 10 mg; 20 mL; 180 rpm; 210 minutes . 30 C° and pH=5.

2.3.2. Freundlich isotherm

This model can be expressed by the linear equation (2):

$$LnQ_e = Lnk_f + \frac{1}{n} LnC_e \qquad (2)$$

Where k_f is the Freundlich constant associated with adsorption capacity, 1/n is the heterogeneity factor, this parameters were calculated using the slope and intercept of the plot: LnQ_e vs LnC_e in fig. 4 where tab.2 shows that Langmuir isotherm is more suitable for adsorption process with a maximum adsorption capacity estimated to 50 mg.g^{-1}; Furthermore, the Freundlich parameter value $\frac{1}{n}$ included between 0 and 1 indicated that the adsorption was favorable [1, 7].

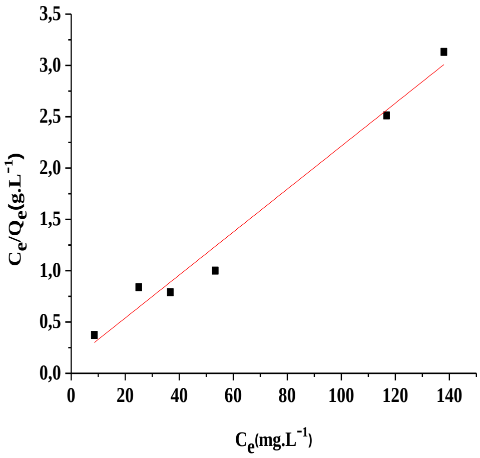

Fig.3. Langmuir isotherm

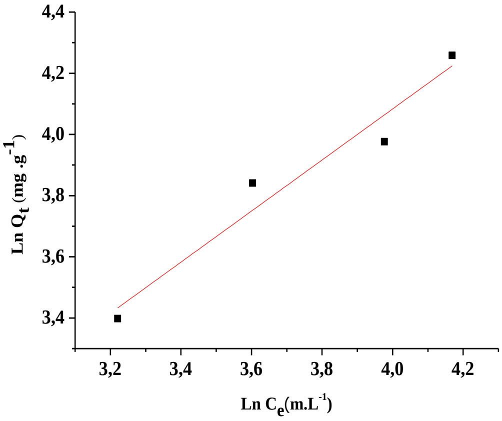

Fig.4. Freundlich isotherm

Table1. Parameter models of Langmuir and Freundlich isotherms.

Langmuir parameters			**Freundlich parameters**		
Q_m (mg.g^{-1})	**k_L (L.mg^{-1})**	**R^2**	**k_F (mg. g^{-1})**	**(mg.L^{-1})$\frac{1}{n}$**	**R^2**
50	**0.166**	**0.974**	**2.104**	**0.830**	**0.930**

3.1. Thermodynamic study

Tthermodynamic study was investigated to estimate standard Gibbs free energy change (ΔG^0), standard enthalpy change (ΔH^0), and standard entropy change (ΔS^0) [1]. The different energies can be related with each other by equation (4):

$$\Delta G^0 = -RTLnK_e \quad (3)$$
$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (4)$$
$$K_e = \frac{Q_e}{C_e} \quad (5)$$
$$LnK_e = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (6)$$

R: is the universal gas constant; Q_e: is the adsorption capacity at the equilibrium thermodynamic (mg.g^{-1}),C_e: is the concentration at the equilibrium of the solute in solution, T: is the temperature (K); K_e is the equilibrium thermodynamic constant [16]. **Tab.3** indicated that adsorption process is exothermic due to negative value of ΔH^0. ΔG^0 less than zero suggests the favorability of adsorption [8,9].

Table2. Thermodynamic parameters of $Pb2^+$ adsorption onto Fe_3O_4-MWCNTs

ΔG^0 (kJ.mol^{-1})			**ΔH^0(kJ.mol^{-1})**	**ΔS^0(J.mol^{-1}.K^{-1})**	**R^2**
303 K	**313 K**	**323 K**	**-4.032**	**-0.012**	**0.985**
-0.169	**-0.529**	**-0.611**			

3. Conclusion

In this work, the adsorption of lead (II) ions was studied onto (Fe_3O_4-MWCNTs: 2/1) nanocomposite in order to determine the maximum adsorption capacity which was estimated by the Langmuir isotherm to be about 50 $mg.g^{-1}$. The optimum values of most important parameters that can affect the adsorption of the heavy metal are pH= 5, initial concentration around 80 $mg.L^{-1}$ and 30 C° for temperature. Thermodynamic study reveals that the adsorption is exothermic and favourable. As a result, the Fe_3O_4-MWCNTs composite showed a good performance toward heavy metal removal. In addition, a simple separation offered by magnetite to make annoying filtration or centrifugation easier and faster.

References

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