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Manganese Ions Removal from Industrial Wastewater

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Abstract: *In this study the removal of Mn (II) ions from wastewater using magnetite nanomaterial was investigated. Some factors influencing the wastewater treatment process were studied such as: treatment time, pH and the concentration of Mn (II) ions from wastewater. The results showed that using magnetite nanomaterial adsorbent lead to a wastewater treatment efficiency higher than 97%. Langmuir and Freundlich models were applied to describe the adsorption process. The correlation coefficients (R^2) showed that both models are applicable to the experimental data obtained.*

Keywords*: adsorption, magnetite nanomaterial, metals manganese ions, wastewater treatment*

1. Introduction

The industrial wastewaters polluted with heavy metal ions, which are toxic, is a huge environmental issue [1]. Heavy metals ions affect seriously human health if they are entering in the human body [2-5]. The sources of heavy metal ions pollution are industrial effluents from metal plating and finishing, rubber processing, mining, agriculture and many others [6]. This category of pollutants has toxic actions for our bodies because of their bioaccumulation in the tissues [7-10]. According to the NTPA 001/2002 standard which contains the limits of loading with pollutants of the industrial and domestic wastewater discharged in the natural environment, the concentration of manganese ions should not exceed 1.00 mg/L. Moreover, the limit of Mn^{2+} accepted in drinking water is 0.05 mg/L according to the Water Law 458/2002. Nowadays, many methods are used for depollution of industrial wastewater, but some of them are not effective for removing manganese ions or they may be too expensive.

The purpose of this study was to remove low concentrations of manganese ions from wastewaters using the magnetite nanomaterial (Fe_3O_4). Also, was studied the influence of contact time, *p*H and Mn (II) ions concentration of the wastewater upon the efficiency of the depollution process.

The utilisation of nanosized magnetic oxide particles have many advantages such as: high surface area which gives high capacity of pollutants retaining from wastewater compared with other conventional adsorbents, reduced cost and easily separation from wastewater using magnetic field at the end of the process [11]. For this reason, new methods of depollution implying the use of relatively inexpensive adsorbents are researched (Table 1).

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Table 1. Manganese ions adsorption from wastewater using different materials

Adsorbent	Mn(II) conc. (mg/L)	Adsorbent dosage (g/L)	Ion solution (mL)	Temp (°C)	pH	Contact time (min)	Yield (%)	Ref.
Activated Carbon Obtained From Birbira (Militia Ferruginea) Leaves	5	4	50		4	120	95.80	[12]
	10						94.20	
	20						92.60	
	50						82.80	
RHA	20	0.60	100	25	2	-	36.00	[13]
					5	-	78.00	
					6	90	96.00	
						60	95.00	
	5						80.00	
	40						55.00	
	20	1.50					95.00	
CBC	20	0.30	100	25	5.1	60	75.00	[14]
PVA/CS	20	8	100	30	5	120	83.50	[15]
Maize stalks	-	20	25	-	1	90	16.00	[16]
				-	7		38.00	
				25	-		39.00	
				55	-		13.00	

RHA –Rice husk ash, CBC – Cow bone charcoal, PVA/CS - Polyvinyl alcohol/chitosan

2. Materials and methods

2.1. Materials

For this study, wastewater solutions having different concentrations (0.70, 1.00, 1.20, 1.40, 1.60, 1.80 and 2.00 mg/L) of Mn(II) were used. The wastewaters were studied at two different pH values. The *p*H was established by adding sodium hydroxide or hydrogen chloride. The nanomaterial used for this study was magnetite (Fe_3O_4) and its obtaining method is presented elsewhere [17].

2.2. Methods

To remove manganese ions from 100 mL wastewaters, an amount of 0.2 g of magnetite was added. These wastewaters were homogenized at room temperature. During the experiments was measured the concentration of Mn(II) ions using a photometer PhotoLab S12.

Adsorption isotherms were used for experimental data modeling.

The removal efficiency (η, %) and equilibrium adsorption amount (q_e, mg/g) of Mn (II) ions were calculated using the following formulas:

$$\eta = \frac{C_0 - C_f}{C_0} * 100 \tag{1}$$

where: C_o- represents the initial concentration of Mn(II) ions, mg/L; C_f- represents the final concentration of Mn(II) ions, mg/L.

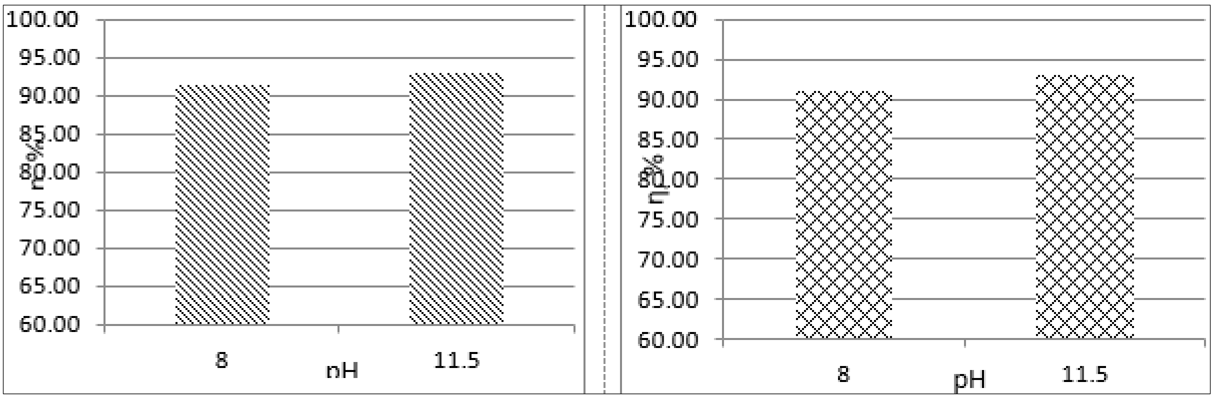
$$q_e = \frac{(C_0 - C_f) * V}{W} \tag{2}$$

where: C_o- represents the initial concentration of Mn(II) ions, mg/L; C_e- represents the equilibrium concentration of Mn(II) ions, mg/L; V - represents the volume of the wastewater, L; W - represents the amount of the magnetite nanomaterial, g.

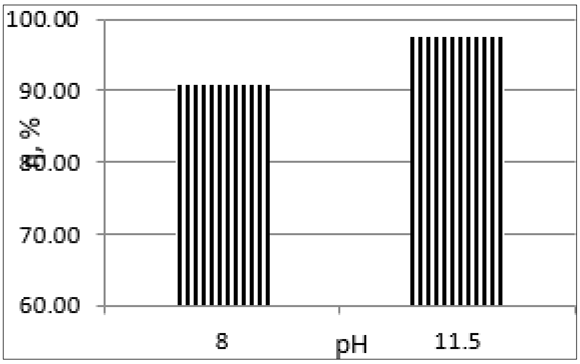
3. Results and discussions

3.1.Effect of *p*H

The removal of Mn(II) ions was studied at two *p*H values (8 and 11.5), and the results are shown in Figure 1. It can be observed that in the case of the concentration of 0.70 mg/L the removal efficiency increases with the increase of the *p*H from 91.4% to 92.8% (Figure 1a). In the case of the concentration of 1.00 mg/L the removal efficiency increases with the increase *p*H from 91.0% to 93.0% (Figure 1b). For the wastewater having 1.20 mg/L concentration Mn (II) the removal efficiency increases with increasing *p*H from 90.0% to 97.5% (Figure 1c). These observations lead to the conclusion that a basic wastewater is a more favorable medium for the removal of manganese ions from industrial wastewater.



a b



c

Figure 1. Effect of *p*H of the wastewater upon the treatment process for three different concentrations of Mn^{2+}: 0.70 mg/L (a); 1.00 mg/L (b); 1.20 (c) mg/L

3.2. Effect of contact time

The effect of contact time was studied for the removal of Mn (II) ions from wastewater and the results are shown in Figure 2. It can be seen that the removal efficiency of pollutant removal from wastewater increases with increasing time up to 500 min after which it remains constant, resulting in a removal efficiency of 90.0% for *p*H 8 and 97.5% for *p*H 11.5.

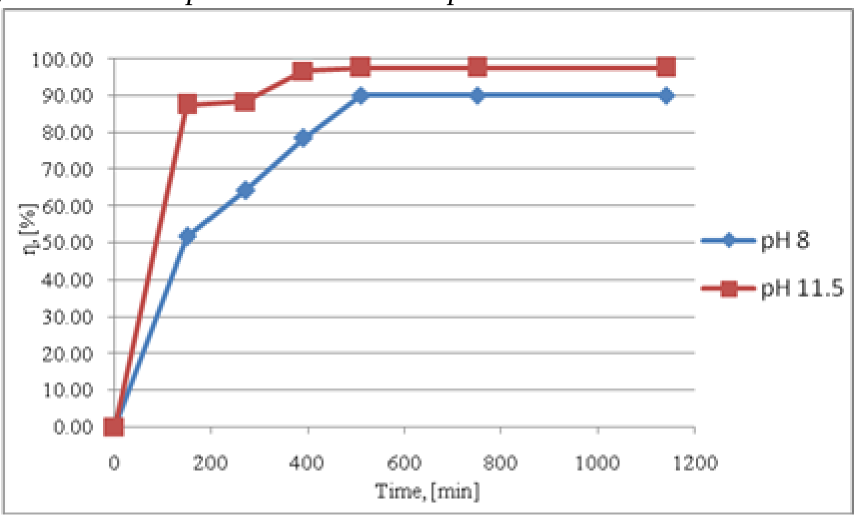


Figure 2. Effect of wastewater treatment time on the removal process of Mn (II) ions (conditions: metal concentration 1.20 mg/L; nanomaterial dosage 0.20g/100mL)

3.3.Adsorption isotherms

Two models were applied in the study of removal of Mn(II) ions from wastewater, Langmuir and Freundlich.

Langmuir model

The Langmuir model is presented in the form of the following equation:

$$C_e = {}^{1}/_{K_L} - Q_{max}({}^{C_e}/_{q_e}) \quad (3)$$

where: K_L - is the Langmuir isotherm constant, L/mg; Q_{max} - is the maximum quantity, mg/g as the amount corresponding to complete monolayer coverage; C_e - is the concentration at equilibrium, mg/L; q_e - is the amount of metal adsorbed per gram of the adsorbent at equilibrium, mg/g.

Using the following equation was calculated the equilibrium parameter R_L:

$$R_L = \frac{1}{1+K_L * C_0} \quad (4)$$

where: R_L - value indicates that the process is unfavourable if R_L>1, linear if R_L=1, favourable if 0< R_L<1 and irreversible if R_L=0; K_L is the Langmuir constant; C_0 - is the initial concentration, measured in mg/L.

Freundlich model

Freundlich model is presented as the equation:

$$q_e = K_F * C_e^{1/n} \quad (5)$$

where: q_e - is the quantity of metal adsorbed by adsorbent at equilibrium, mg/g; K_F - is the Freundlich isotherm constant, mg/g; C_e - is the equilibrium concentration of adsorbate, mg/L; n - is the adsorption intensity;

The Langmuir and Freundlich models based on experimental data were graphically represented (Figure 3,4). The constants of both models are presented in Table 2. It is observed that the experimental values fit the isotherms adequately. In the case of the Langmuir model, its applicability indicates the monolayer coating of the magnetite surface by the manganese ions. The Langmuir constant R_L is in the range 0-1, indicating that the retention process of Mn (II) ions is favorable. The linear graph between log (C_e) and log (Q_e) confirm the applicability of the Freundlich model.

Table 2. The constants of Langmuir and Freundlich models

	Langmuir isotherm			Freundlich isotherm		
Adsorbent	K_L (L/mg)	R_L	R^2	n	K_F (mg/g)	R^2
Fe_3O_4	6.58	0.71	0.88	0.93	3.15	0.98

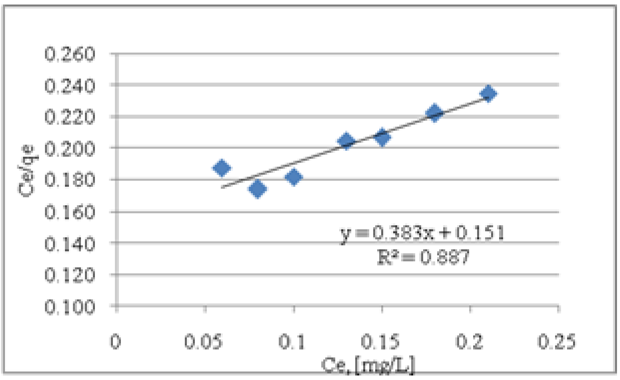


Figure 3. The plot of the Langmuir model

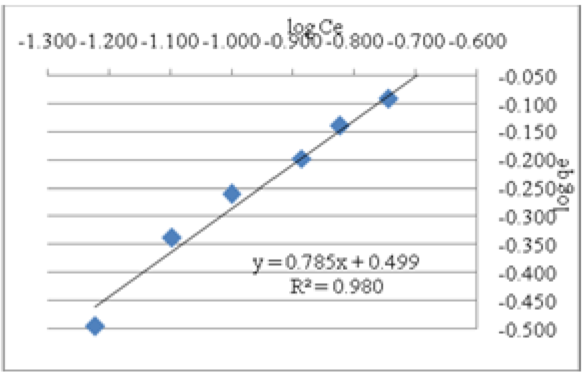


Figure 4. The plot of the Freundlich model

The results suggest that this type of magnetic nanomaterial could be successfully used for manganese ions removal from industrial wastewaters. The possibility of fast separation by magnetic field of magnetite from the wastewater at the end of the treatment and the high removal efficiency recommend it as a useful adsorbent. Also, future regeneration studies will be undertaken in order to establish the life duration use of the magnetite adsorbent. It is a very high probability that the magnetite nanomaterial can be adapted to the removal of other types of heavy metals from wastewater.

4. Conclusions

The study focused on the removal of manganese ions from wastewater. The removal of Mn(II) ions from wastewater using Fe_3O_4 nanomaterial reveal that the process was *p*H dependent and the maximum efficiency was observed at *p*H 11.5 resulting in a yield of 97.50%. At a lower *p*H (8) the maximum depollution efficiency was 91.00%. The treatment time required to reach the maximum capacity of the magnetite nanomaterial in order to remove the Mn(II) ions was 500 min, then the Mn(II) ions concentrations remained constant in the wastewaters. The R^2 values indicate that adsorption process take place onto heterogeneous material, according to Freundlich model. Values of n lower than 1 indicates possible binding between magnetite and manganese ions.

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