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Iron and manganese removal from drinking water

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Abstract

The purpose of the present study is to find a suitable method for removal of iron and manganese from ground water, considering both local economical and environmental aspects. Ground water is a highly important source of drinking water in Romania. Ground water is naturally pure from bacteria at a 25 m depth or more. However, solved metals may occur and if the levels are too high, the water is not drinkable. Different processes, such as electrochemical and combined electrochemical-adsorption methods have been applied to determine metals content in accordance to reports of National Water Agency from Romania (ANAR). Every water source contains dissolved or particulate compounds. The concentrations of these compounds can affect health, productivity, compliance requirements, or serviceability and cannot be economically removed by conventional filtration means. In this study, we made a comparison between the electrochemical and adsorption methods (using membranes). Both methods have been used to evaluate the efficiency of iron and manganese removal at various times and temperatures. We used two membrane types: composite and cellulose, respectively. Different approaches, including lowering the initial current density and increasing the initial pH were applied. Reaction kinetics was achieved using mathematical models: Jura and Temkin.

Keywords

Ground water, Solved metals, Mathematical models, Composite membranes, Different methods

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Introduction

Electrochemical treatment is an emerging technology used for the removal of organic and inorganic impurities from water and wastewater. Electrochemically processes involve redox reactions, where oxidation and reduction reactions are separated in space or time [1,2]. Usually, the electrochemically treatment of water is concerned with electron transfer at the solution/electrode interface applying an external direct current in order to drive an electrochemical process [1,3]. Electrocoagulation is an electrochemical result of destabilization agents (usually Mn or Fe ions) that neutralize the electrical charge of suspended pollutant.

Electrochemically generated metallic ions from these electrodes could undergo hydrolysis near the anode to produce a series of activated intermediates that are able to destabilize finely dispersed particles present in the water/wastewater to be treated. Electrochemical treatment methods have a future as advanced technologies for additional treatment of potable water from domestically and remote areas.

Filter media (type, size and area), hydraulic and solids loading rate and backwashing regimes are all important aspects of filter design. Autocatalytic removal of manganese can take place in a filter and could be critical for manganese removal. An investment in filter pilot testing could become significant.

The sorption of metal ions from aqueous solution plays an important role in water pollution control and in recent years there has been considerable interest in the use of low cost adsorbents. Many researchers have tried to exploit naturally, occurring materials as low-cost adsorbents, for removing of heavy metals.

Manganese and iron (especially the last) produce different problems that could be due to various causes [4]. Many types of treatment are effective for the removal of iron and manganese from water, but not all methods are equally effective under any conditions.

Oxidation of dissolved iron particles in water, change the iron to white, then yellow and finally to red-brown solid particles (precipitates) that settle out from the water. Iron that does not form particles large enough to settle out and that remains suspended (colloidal iron) leaves the water with a red tint.

Manganese is usually dissolved in water, although that some shallow wells contain colloidal manganese, leaving the water with a black tint. These sediments are responsible for the staining properties of water containing high concentrations of iron and manganese [4].

Iron and manganese are common in groundwater supplies used by many small water systems. Exceeding the suggested maximum contaminant levels (MCL) usually results in discolored water, laundry, and plumbing fixtures. This, in turn, results in consumer complaints and a general dissatisfaction with the water utility. There are secondary standards set for iron and manganese, but these are not health related and are not enforceable. ANAR establishedthe following limits (MCL): iron at 0.30 mg/L and manganese at 0.05 mg/L.

The purpose of the present study is to find a suitable method for removal of iron and manganese from drinking water.

Experimental

Materials

Iron nitrate $Fe(NO_3)_3$ was used as a source of iron in form of Fe (III) and it was supplied by Sigma Aldrich. Manganese (II) nitrate $Mn(NO_3)_2$ was used as sources of manganese in form of Mn (II) and it was supplied by Sigma Aldrich. Pure kallium chloride (KCl), purchased from Merck, was used as electrolyte. Distilled water was used throughout. Analar sulfuric acid 98 % was purchased from Chimexin.

Method AAS for iron and manganese

A laborator combined photo-electrochemical unit was used for the batch experiments. It consists of a cylindrical quartz photo reactor (1 L), with a coaxial and immersed medium pressure UV mercury lamp used as the UV emitter and light source (Heraeus TQ150, input energy of 150 W) emitting a polychromatic radiation in the range from 100 to 280 nm wavelength. The UV lamp was equipped with a cooling water jacket to maintain the temperature of the reaction of wastewater treatment at room temperature.

The reaction vessel was filled with solution containing both iron and manganese. The electrochemical characterization of the solution was carried out by using DC power supply GW 3030 and two electrodes: graphite cathode and platinum anode. The measurements were performed in the temperature range: 288 K to 303 K, and the mixing was accomplished by using continuous magnetic stirrer.

Photo-electrochemical method was combined with electrocoagulation in the same unit. Metal hydroxides generated during electrocoagulation were used to remove iron and manganesse from aqueous solution, and the effects of varying the current density and solution temperature of iron and manganesse adsorption characteristics were evaluated. The findings indicated that complete iron and manganese removal could be achieved within reasonable removal efficiency and with relatively low electrical energy consumption [5,6].

The experimental data have been fitted with Jura and Temkin adsorption isotherm models to describe the electrocoagulation process. The adsorption of iron preferably fitted the Jura adsorption isotherm and manganesse preferably fitted the Temkin adsorption isotherm, and these suggested monolayer coverage of adsorbed molecules.

Definite amounts of KCl were added to improve the conductivity and ionic mobility through the electrolyte. Low concentration of KCl (45 mg/L) was added to increase the conductivity and electric current beside its bactericide effect after electrolysis to chlorine. The solution was acidified to pH 3 by drops added of prepared dilute sulfuric acid 15 %. The effect of Fe^{2+} and Mn^{2+} concentrations revealed that the higher concentration of dissolved iron and manganese ions, the higher removal efficiency was obtained. The efficiency of the process was evaluated by measuring the metal removal from samples at the end of each experiment. Samples were filtered with cellulose and composite membrane, before the measurement of metals, by applying atomic adsorption (Carl Zeiss Jena AAS). For all experiments there have been used a synthetic solutions of iron and manganesse with a concentration range between 1-12 ppm (Fig. 1).

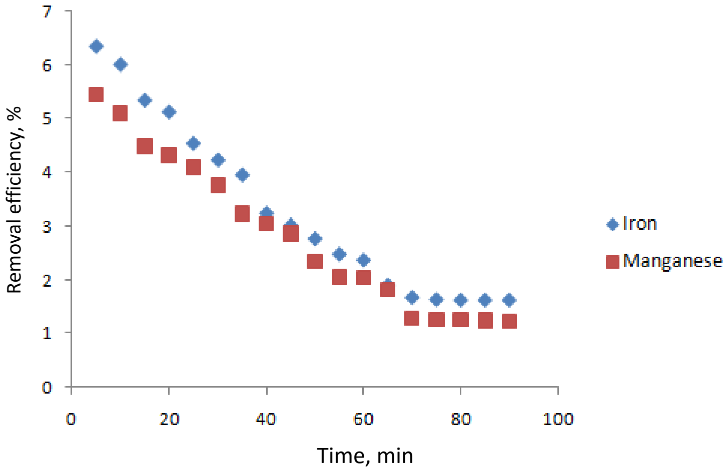

***Figure 1**. Iron and manganase concentratin evolution in time in the case photo-electrochemical combined with electrocoagulation method*

Results and discussion

The photo-electrochemical method combined with electrocoagulation method presents good results for removing iron ions from 12 ppm prepared synthetic solutions. As it could be seen from Figure 2, the removal efficiency in the case of iron was about 46 %, while in the case of manganese it was 55 %.

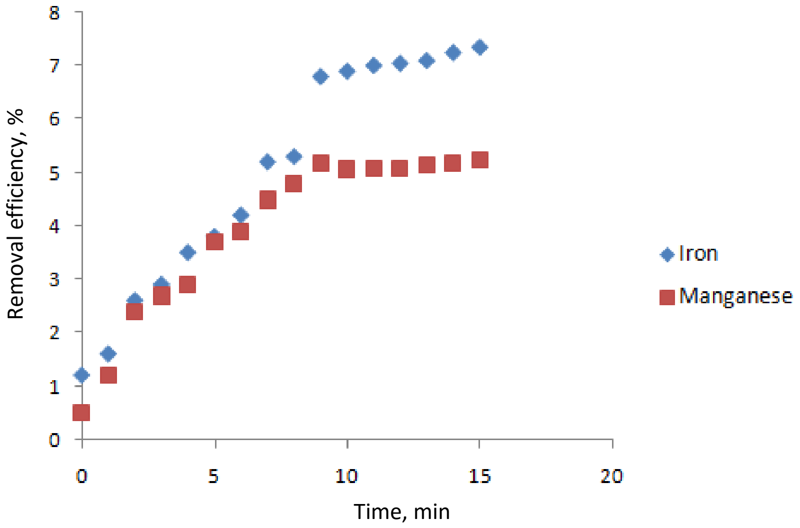

Figure 2. *Effect of different current densities on the removal efficiency of iron and manganese (*C_0 *= 12 ppm, T = 298 K,* C_{KCl} *= 45 mg/L)*

According to the applied electric current, the removal efficiency varied, while at low applied electric current, a low value of efficiency removal, % was obtained, but the removal efficiency in time was improved. The equilibrium of removal was achieved after 15 minute, from the processes' beginning.

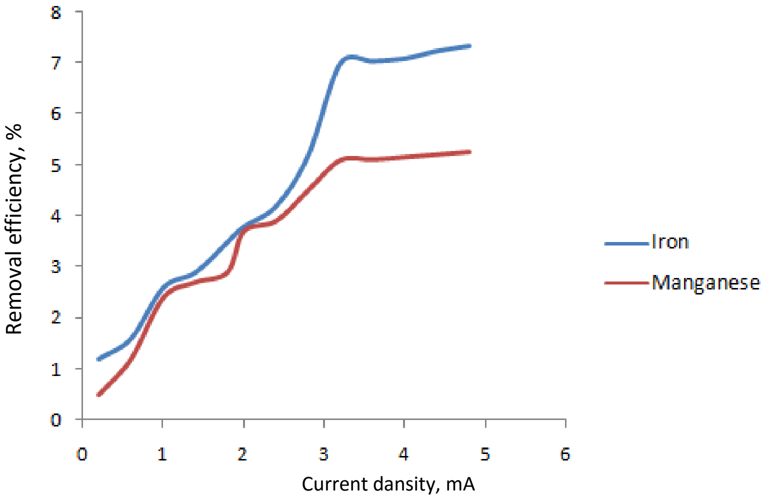

Figure 3. *Effect of current density on iron and manganese removal.*

The optimum current density and temperature have been establisheda at 3.2 mA cm^{-2} and 288 K, for iron and 3.4 mA cm^{-2} and 298 K for manganesse, respectively. Another method to remove iron and manganese from drinking water was the adsorption method using two membranes (cellulose and composite respectively).

Both methods have been used to evaluate the efficiency of removing iron and manganese from waste waters at different times and temperatures [7,8].

The experiments showed the feasibility of removing iron and manganese by adsorption and co-precipitation with aluminum hydroxides. Photo-electrochemical method was combined with electrocoagulation in the same unit and were used for oxidation of soluble forms Fe^{2+} and Mn^{2+} to the insoluble forms Fe^{3+} and Mn^{4+}. The combined method revealed better efficiency compared with a single electrochemical method. The presence of both dissolved iron and manganese has the advantage of less resistivity of the waste water solution. Low concentration of KCl (45 mg/L) was added to increase the conductivity and electric current. Higher removal efficiency was obtained when Fe^{2+} and Mn^{2+} are presented in higher concentration (12 ppm). The study showed a more rapid oxidation of Fe^{2+} than of Mn^{2+} due to the lower oxidation potential of iron ion than of the manganese ion [9,10].

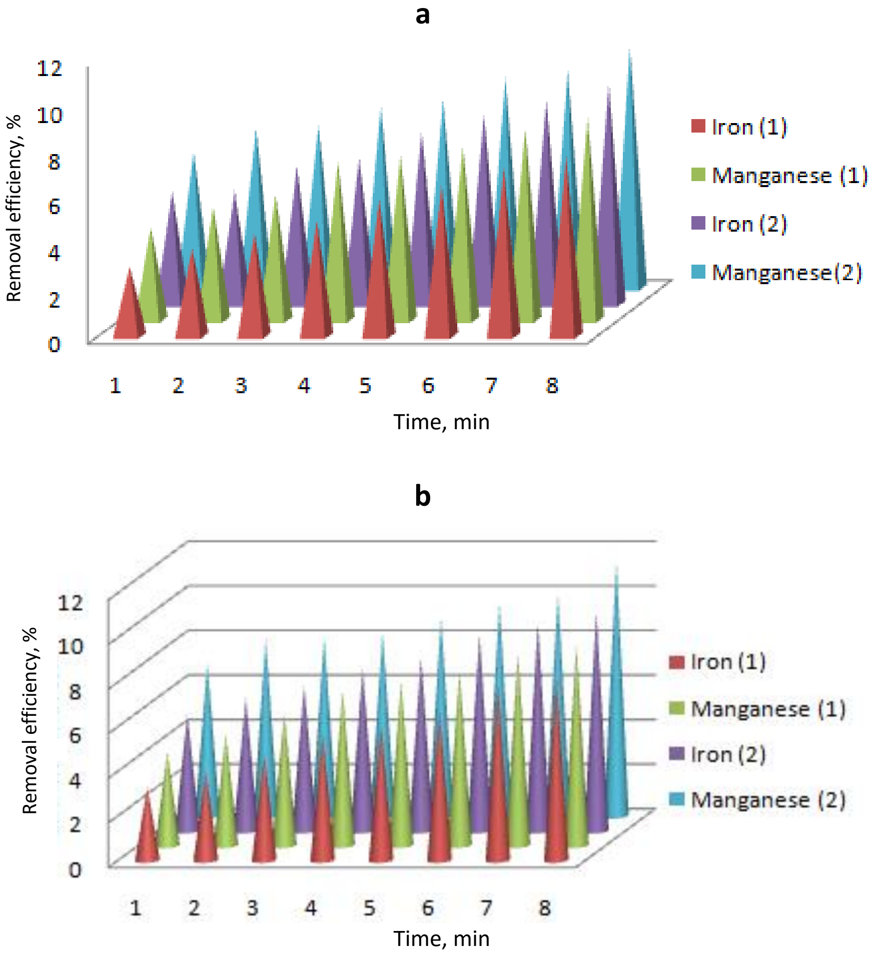

***Figure 4**. Iron and manganese removal efficiency evolution in time when using cellulose membrane (a) and composite membrane (b)*

Composite membranes presented a better adsorption behavior for manganese ion (10.75 ppm) compared with the cellulose membranes (8.78 ppm).

For iron ion the composite membranes' adsorption behavior (9.57 ppm) was better compared with the cellulose membranes (7.89 ppm) as they are presented in Figure 4.

The solution pH is an important parameter which controls the adsorption process. It influences the ionization of the adsorptive molecule and hence the adsorbent's surface charge. Therefore, investigating the pH effect on the adsorption is essential in adsorption experiments. In this particular case, the solution pH can change the surface charge of the adsorbent as well as different iron and manganese ionic formsions.

Model Temkin

Energy adsorption and ion interactions between aqueous solutions and membrane (adsorbent-adsorbed) were studied by Temkin-Pzyhev model [10-13].

The Temkin assumed that due to such interactions, the adsorption energy of all layer molecules decreases with surface coating.

This pattern was obtained in view of adsorption phenomena and the interaction between adsorbed substance and was achieved by designing the chart functions: q_e versus ln C_e.

The Temkin isotherm considers the interaction between the aqueous solution and solid (composite or cellulose membrane) that contained the free energy adsorption as a function of coating the surface of the adsorbent material. The equation underlying the Temkin model adsorption heat is:

$$q_e = B \ln K_T + B \ln C_e \tag{1}$$

The linearized form of the Temkin'equation is:

$$q_e = \frac{RT}{b_T \ln K_T} + \frac{RT}{b_T \ln C_e} \tag{2}$$

where b_T - is the Temkin constant sorption heat, J/mg and the corresponding maximum energy constant connection between adsorbent and adsorbed is K_T / (L/g).

The isotherms of this model are shown in Figure 5.

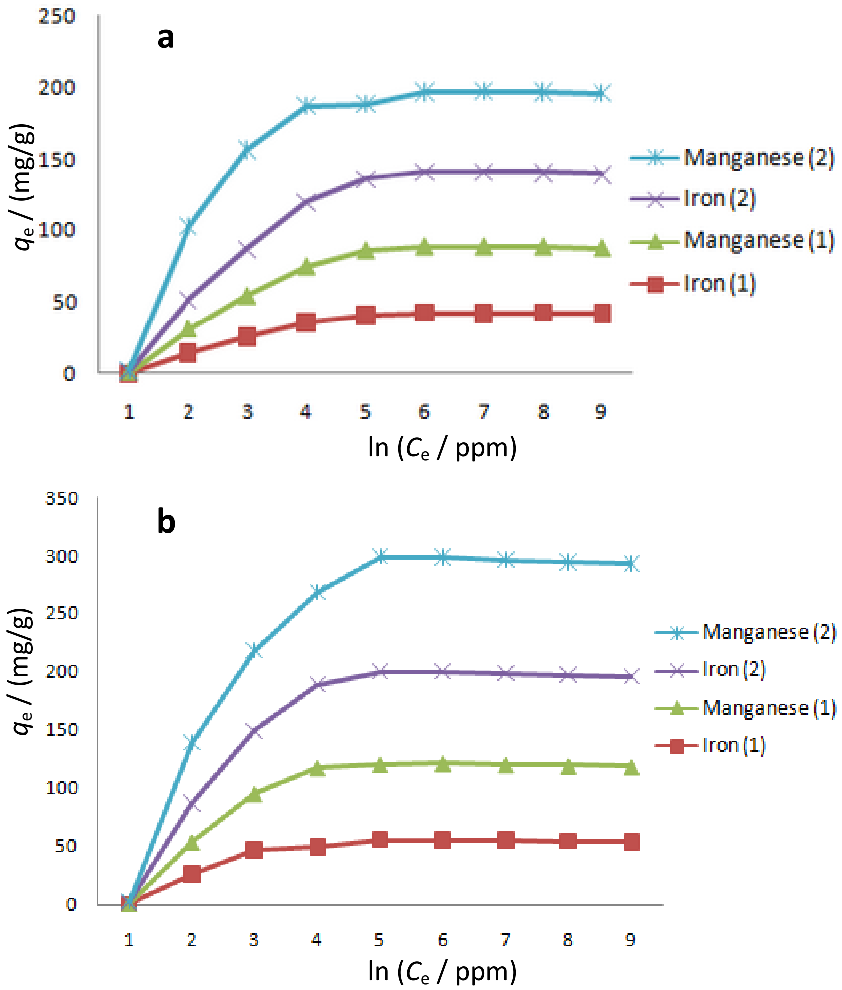

Figure 5.*Temkin adsorption isotherms of maganese and iron ions: cellulose membrane (a) and composite membrane (b)*

B and K_T are Temkin equation parameters and respectively adequate with adsorption condescended and boundary constant adequate with maximum of boundary energy. Amount of *B* is RT/b_T and b_T is based on Temkin isotherm constant. By observing that we can see in Figure 5, the maximum amount adsorption of K_T for two ions: manganese and iron, these with be much better uptake by the composite membranes.

Taking into consideration the correlation coefficient for the surves presented in Figures (5,6), we observe that there is an accessible competition between this model and Harkins-Jura model.

Harkins-Jura adsorption isotherm

The Harkins-Jura adsorption isotherm could be expressed as [14, 15]:

$$\frac{1}{q_e^2}=\frac{B}{A}-\frac{1}{A}\log C_e \tag{3}$$

where: q_e is the adsorbed ions amount at equilibrium (mg/g) and C_e is the concentration at equilibrium for two ions (ppm).

Harkins-Jura model is presented in Figure 6, and from the diagram log C_e against $1/q_e^2$, considering *A* as parameter slope and from intercept , we could compute *B* parameter.

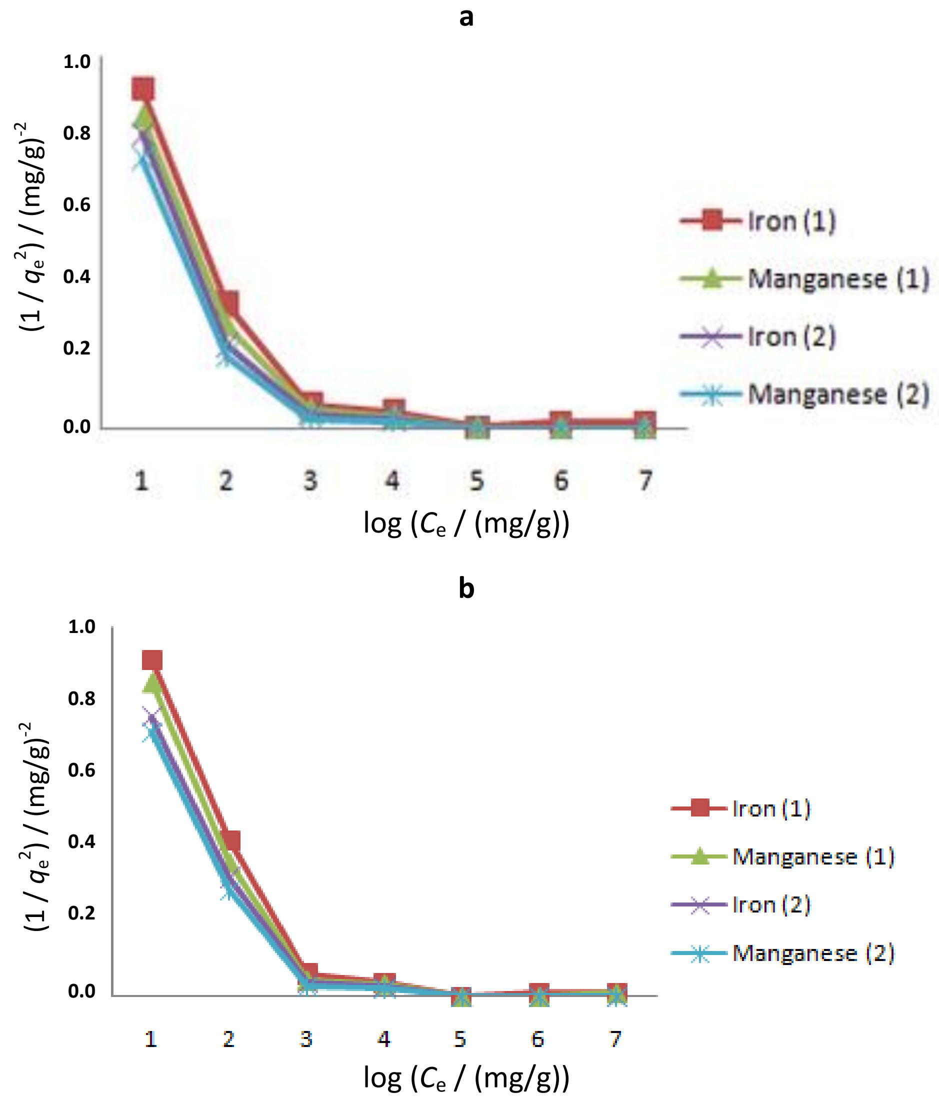

Figure 6. *Harkins-Jura adsorption isotherms of maganese and iron ions: cellulose membrane (a) and composite membrane (b)*

In this paper, the experimental adsorption data were tested applying the Temkin and Harkins-Jura equations.

It was observed that the correlation coefficient has a good correlation with experimental data.

In Figure 6 the specific amount capacity adsorption is in mg/g and equilibrium concentration in ppm.

The validity of the Harkins-Jura solute adsorption isotherm to systems, it could be used for the determination of the specific surface area of solids (composite and cellulose membrane).

All the plots contain two intersecting straight lines (for these two metals: iron and maganese) and according to the Harkins-Jura solute adsorption equation. The Harkins-Jura equation applies to these systems for the entire concentration range studied. The existence of two or more intersecting straight lines in the Harkins-Jura plot indicates that there are two, or many isotherms corresponding to each of these lines with different values for the constants A and B. As it could be seen from Figure 6, in the case of Jura isotherm representation there are two linear parts derivated from model equation. The difference between the surface tensions caused by the adsorbent material and aqueous solutions is a linear function of the molecule and therefore the area is indicated using the isotherm Harkins-Jura.

It argues that the two straight lines correspond for two different orientations of the adsorbent (composite or cellulose membrane) in the process of adsorption and high slope corresponding to a plane in surface and the slope shows lower values corresponding to a vertical orientation, for the two metals adsorption.

This point of view was supported by the research of Soriaga *et al.* [13] work, where, using thin layer electrochemical techniques, it has been shown that admolecules assume a parallel orientation to the solid surface when adsorbed from solutions.

Therefore, we can see that a straight line with a higher slope in the Harkins-Jura model corresponds to a flat orientation adsorption process that changes from a vertical orientation as this initial concentrations becames greater.

As consequence, by making this orienting change of the adsorption process, a new phase it would be obtained, which presents a new point of intersection between the lines of the model representation of the two ions by their adsorption through the two membranes. Thus are obtained very good values for the adsorption capacity of the two membranes.

The Temkin and Harkin-Jura models are often used to describe the equilibrium sorption isotherms.

Conclusion

pH is an important parameter influencing heavy metal adsorption from aqueous solutions. It has no influence on the adsorbent surface charge, the degree of ionization of material present in the solution, and also the dissociation of functional groups on the active sites of the adsorbent.

The method applying the composite and cellulose membranes adsorption presented the best results compared to photo-electrochemical method for removing iron and manganese ions from drinking water. The adsorption membrane method has the advantage of simplicity in terms of installation compared to photo-electrochemical method. The disadvantage is the high cost of composite and cellulose membranes.

Considering the high consumption of electricity which is used for photo-electrochemical method, the adsorption membrane method has the advantage of low power consumption.

In addition, the adsorption kinetic studies showed that the electrocoagulation process was best described using the pseudo second-order kinetic model [16] at the various current densities and temperatures.

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