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KINETIC AND THERMODYNAMIC STUDY OF THE ADSORPTION OF MANGANESE (II) ON ACTIVATED CARBON

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Abstract: Recent studies revealed the Bay of Algiers was being polluted by manganese. Similar pollution was also reported in Azemmour, Morocco alongside the estuary of Oum Er Rbia, but also in the waters of developed countries (i.e. Canada, especially following the replacement of tetraethylplumbane in gasoline by methylcyclopentadienyl manganese). Treatment of polluted waters by manganese is therefore essential prior to their release, which is within the purpose of the present study. Commercial activated carbon (AC) was used for treating synthetic aqueous solution containing different concentrations of Mn. Adsorption kinetics was studied under agitation at different temperatures between 295 and 318 K. Results show that there are two areas where adsorption occurs according to a first-class model. In the first one, rate constant is $k_1 = 0.001610 \text{ min}^{-1}$, meanwhile in the second, it is $k_2 = 0.000488 \text{ min}^{-1}$. Equilibrium is reached in 7 hours. The obtained adsorption isotherm is a V type and follows Freundlich model for low concentrations and Langmuir model for high concentrations. The isotherm part described by Freundlich model lessens with the rise of temperature, increasing adsorption maximum capacity from 3.49 mg Mn/g AC (at 295 K) to 4.78 mg Mn/g AC (at 318 K). Adsorption is endothermic. Standard enthalpy ($14.4869 \text{ kJ}\cdot\text{mol}^{-1}$) and standard entropy ($36.25 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) have been calculated. The free energy was positive in all the studied temperatures range. The values of adsorption heat indicate a physical adsorption.

Keywords: *activated carbon, adsorption, enthalpy, entropy, manganese*

INTRODUCTION

Methylcyclopentadienyl manganese is being currently added to gasoline in order to substitute to tetraethylplumbane as an anti-detonating additive combustible. Manganese concentrations in the soil and plants alongside the roads are increasing. Manganese is issued mainly by industries like the production of iron alloys, and iron and steel foundries. The major sources issuing combustion are the electric plant and coal ovens. A part of this manganese passes in water resources.

The European standard for the limit value of manganese waste in industrial liquid effluents is 1 mg/L if the exhaust exceeds 10 g/day. The presence of this element in water supplies is unwanted. At higher concentrations with 0.15 mg/L, manganese stains the piping parts and the fabrics. Besides, in high concentrations, it gives bad taste to beverages. Like iron, it may cause problems in the water distribution systems enhancing the growth of microorganisms. Even at lower concentrations of 0.05 mg/L, manganese can form deposits in the piping and can appear as black precipitates.

Manganese of natural origin is commonly found in drinkable water at low concentrations and is essential to human health [1]. The maximal value that is admissible by WHO is 0.5 mg/L. Most European countries have a much lower standard than the previous one. It is 0.05 mg/L in Scotland for example. In this country, manganese concentration in underground waters used for drinkable water supply in certain layers reached 1.9 mg/L [2]. In a recent study in Ghana, 11 % of water springs studied had a manganese concentration that is higher than the recommendation of the WHO with a maximum 2.051 mg/L [3].

A study on two mollusks (*Scrobicularia plana* and *Cardium edule*) collected alongside Oum Er Rbia estuary (Azemmour, Morocco) revealed that they contained manganese with a concentration varying from 3.4 to 28.3 mg/kg of dry weight [4].

Several studies in different contexts revealed a connection between the consumption of water from a manganese-rich layer and the negative effects on human health. In Bangladesh, it was reported [5] a negative relation between the intellectual function of 142 children of 10 years and the consumption of a well water rich in manganese (concentration ranging from 0.004 to 3.91 mg/L). A study in Quebec on 46 children showed a relationship between their hyperactivity and the consumption of water rich in manganese [6].

A study in Bulgaria [7] showed elements like manganese present in the soil do not contaminate ethereal oils of certain plants such as coriander, sage, dill, basil, hyssop, balm and chamomile.

The aim of this paper is to reveal the possibility of eliminating manganese (II) from aqueous solutions through adsorption on commercial activated carbon.

MATERIALS AND METHODS

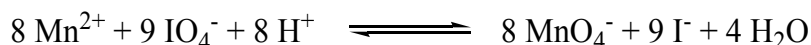
Materials

The manganese ion parent solution was a standard commercial solution 1000 mg/L (Merck). The solutions used in the tests were obtained by successive dilutions.

For the experiments, activated vegetal carbon in commercial granulate (Prolabo) has been used. The optic density was measured by a UV-visible spectrophotometer Techomp 8500.

Dosing of manganese

Manganese is oxidized into permanganate with acid-medium potassium periodate according to the following reaction:



Permanganate once formed is dosed at 525 nm after setting a standard curve.

Experimental

Adsorption tests were performed in 100 mL beakers containing 125 mg activated carbon added to 25 mL solution with a set concentration in manganese ions. Beakers are tightly closed during the test with Parafilm and placed at constant temperature in double-boiler for 16 h, fairly enough time to achieve equilibrium because the kinetic study showed that it is achieved within approximately 7 h. Residual concentration is dosed after filtering with paper filter.

Concentration of manganese ions was varied during the study between 2.5 and 100 mg/L. The temperature was set between 295 and 318 K. The performed tests were reproducible with very accurate measuring.

Kinetic study was performed at 298 K. Several beakers containing a 100 mg/L manganese concentration solution were put in contact with 0.125 g of activated carbon at time $t = 0$. Stirring speed was set at 300 rpm. Each beaker served for determining an instant concentration of manganese.

RESULTS AND DISCUSSIONS

Adsorption kinetics

Figure 1 shows a decrease of manganese concentration and an increase of the quantity adsorbed on a gram of activated carbon in relation to time at 298 K and for an initial manganese concentration of 100 mg/L. The fast kinetics in the beginning of the adsorption reaction is interpreted by the important number of active sites available at the surface of adsorbent material. After the occupation of these sites by manganese ions, the reaction rate decreases.

For the first order, the reaction rate is described by the equation:

$$-\frac{dC_{\text{Mn}^{2+}}}{dt} = k \cdot C_{\text{Mn}^{2+}} \quad (1)$$

After integration between limits:

$t = 0$, $C_{\text{Mn}^{2+}} = [\text{Mn}^{2+}]_0$ and $t = t$, $C_{\text{Mn}^{2+}} = [\text{Mn}^{2+}]$, equation (1) comes:

$$\ln \frac{[\text{Mn}^{2+}]}{[\text{Mn}^{2+}]_0} = -kt \quad (2)$$

The constant k of the reaction rate is obtained from the function slope:

$$\ln \frac{[\text{Mn}^{2+}]}{[\text{Mn}^{2+}]_0} = f(t) \quad (3)$$

The kinetic results show that there are two fields where adsorption is described by the expression of the first order model. In the first field, the reaction rate constant is $k_1 = 0.001610 \text{ min}^{-1}$, in the second, it is $k_2 = 0.000488 \text{ min}^{-1}$.

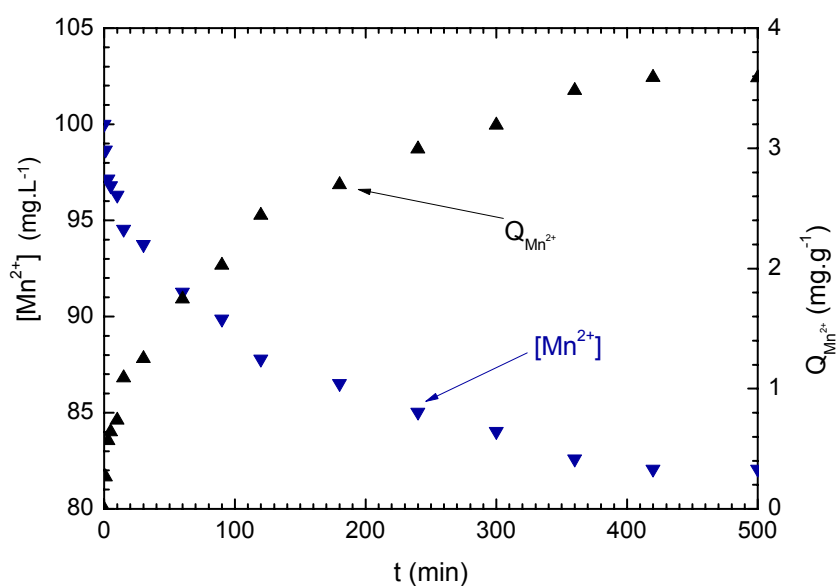


Figure 1. Decrease of manganese concentration ($[\text{Mn}^{2+}]$) and increase of quantity adsorbed in a gram of activated carbon ($Q_{\text{Mn}^{2+}}$) in relation to time;

$$T = 298 \text{ K and } [\text{Mn}^{2+}]_0 = 100 \text{ mg/L}$$

Langmuir and Freundlich isotherms

Adsorption of manganese (Figure 2) was correlated using the Langmuir model and Freundlich model.

Langmuir theory means that adsorption occurs in monomolecular layer on identical sites that have uniform energy and that are not capable of retaining more than one molecule per site. The molecules adsorbed do not interact with one another. Langmuir equation can be formulated as follows:

$$\frac{x}{m} = \frac{k_1 \cdot k_2 \cdot C}{1 + k_1 \cdot C} \quad (4)$$

As x/m represents the quantity of manganese ions adsorbed per gram of activated carbon, C being their concentration and k_1 and k_2 are constants of the system.

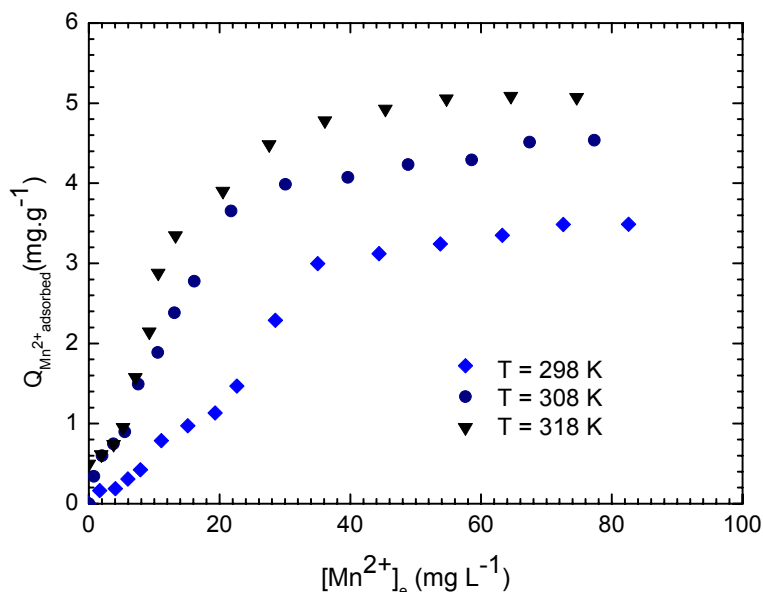


Figure 2. Adsorptions isotherms of manganese ions on activated carbon at 298, 308 and 318 K

For determining k_1 and k_2 , it is suitable to do a graphic mapping of Langmuir equation (4), that can be transcribed as follows:

$$\frac{C}{x/m} = \frac{1}{k_1 \cdot k_2} + \frac{C}{k_2} \quad (5)$$

Freundlich isotherm is purely empirical; it can be represented by the equation:

$$\frac{x}{m} = k \cdot C^n \quad (6)$$

wherein k and n are constants.

Linearization of equation (6) allows graphic determination of k and n ; it then takes the following form:

$$\log \frac{x}{m} = \log k + n \log C \quad (7)$$

Theoretically for the adsorption of gases on solids, Langmuir or Freundlich model can fit. IUPAC established six different forms of adsorption isotherms. In an aqueous solution, isotherms obtained through testing hardly ever correspond rigorously to one of the previous types, and our results make no exception. We are likely to choose a type V isotherm for our experiments.

There are observed two distinct parts on isotherms (Figure 3). Freundlich model seems adequate for low manganese concentrations. When concentrations rise, there is a divergence between this model and the experimental results. These therefore comply with Langmuir model.

The first part of the isotherm better represented by Freundlich model seems to blur with temperature decrease.

Langmuir model implies that adsorption energy is continual whereas Freundlich model makes it dependent on the covering rate. It can be inferred that the energy-friendly sites are occupied in the first place. The rest of the sites with similar energy are occupied after the occupation of the first one is completed. With the rise of temperature, the number of sites requiring less energy to be occupied is reduced. Hence, the isotherm range mentioned by Langmuir model is broader. Additionally, the quantity of adsorbed manganese increases along with the rise of temperature, which leads to suggest there is a phenomenon of endothermic adsorption, ultimately confirmed by the thermodynamic calculations.

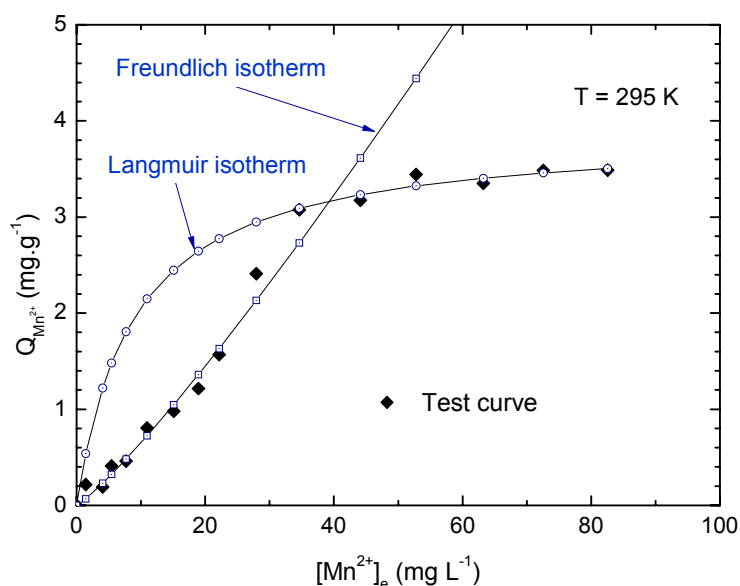


Figure 3. Freundlich and Langmuir models for the adsorption of manganese on activated carbon at $T = 295\text{ K}$

Adsorption energy

Adsorption equilibrium constant K_a is linked to free energy ΔG by the equation:

$$\Delta G = -RT \ln K_a \quad (8)$$

where R is the ideal gas constant and T the temperature.

As free energy ΔG is linked to enthalpy ΔH and entropy ΔS by the equation:

$$\Delta G = \Delta H - T\Delta S \quad (9)$$

Thus it results into:

$$\ln K_a = -\frac{\Delta H}{RT} + \frac{\Delta S}{T} \quad (10)$$

ΔH and ΔS are obtained by linearizing equation (10) and representing it as the function:

$$\ln K_a = f\left(\frac{1}{T}\right) \quad (11)$$

Value K_a is calculated from the equation:

$$K_a = \frac{C_a}{C_e} \quad (12)$$

where C_a is the quantity adsorbed per liter of solution and C_e is the concentration at equilibrium.

The calculations of free energy, enthalpy and entropy deliver the results presented in Table 1.

Table 1. Adsorption energies of manganese on activated carbon

Temperature (K)	Free energy, ΔG ($\text{kJ}\cdot\text{mol}^{-1}$)	Standard entropy, ΔS^0 at 298 K ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)	Standard enthalpy, ΔH^0 at 298 K ($\text{kJ}\cdot\text{mol}^{-1}$)
295	3.81325	36.25	14.4869
298	3.85168		
303	3.34448		
308	3.13854		
313	3.19708		
318	3.06255		

Adsorption standard enthalpy being positive indicates that the adsorption is endothermic; its relatively low value shows that the adsorption is physical. Positive entropy suggests an increased disorder and randomness at the solid solution interface of the adsorbent. This phenomenon, that has been previously noticed, was attributed in the case of the treatment of water having metal ions to kaolinite through a variation in the adsorbent and adsorbate during the adsorption process [8].

CONCLUSION

Currently, manganese is present as a pollutant in the aquatic layers in many countries. These negative effects on health are obvious. Its elimination by the use of activated vegetal carbon seems possible. Kinetic results show that there are two fields where adsorption is mentioned by the formulation of the first class model. In the first field the reaction rate is higher. The most active sites on the adsorbent material are occupied during this period. The isotherms obtained belong to the V type and follow Freundlich model for the low concentrations and that of Langmuir for the high concentrations. The part mentioned by Freundlich model decreases along with the increase of temperature. The adsorption of manganese on the studied activated carbon is physical and endothermic. Temperature increases adsorption maximum capacity.

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