Models of Iron Adsorption by Two Types of Membranes

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In this paper we intended to study the ability of iron adsorption from drinking water by two types of membranes: cellulose and composite. Adsorption studies were highlighted by means of adsorption isotherms: Langmuir, Freundlich, Flory-Huggins and Frumkin. The results revealed that iron adsorption was influenced by pH increase. The identification of iron in drinking water was done using two methods: spectrophotometric method and potentiometric redox titration with cerium sulphate method. The adsorption capacity of composite membrane increased when temperature was increased. Spectrophotometric method has proved to be better than potentiometric redox titration with cerium sulphate method. After 150 min was recorded the total iron removal from aqueous solution using the composite membrane. The pH value influenced significantly the adsorption capacity. As the pH increased, the adsorption capacity for both membranes decreased.

Keywords: adsorption, isotherms, iron anion, mathematical modelling

The drinking water is water that has the physical, chemical and biological qualities required to be consumed without immediate or long term risk. Drinking water is important for humanity. The World Health Organization (WHO) says: “the diseases associated with drinking water contamination represents a major concern for human health.The interventions for improving the quality of drinking water provide significant benefits to health”. During time, the treatment process and quality control has become increasingly complex due to the pollution and urban concentration increase [1-3].

Throughout history, the quality of drinking water has been a primary factor in determining human welfare. The water pollution has become a critical issue worldwide, and the quality of water resources are deteriorating day by day because of: population growth, the rapid development of industry, intensive agricultural activity, as well as other geological and environmental changes that have occurred in recent years. The metal pollution is known to be responsible for many health problems [4-7].

The supply of drinking water relies on groundwater resources. The widespread use of groundwater can be explained by the easy of access, a better protection against pollution sources, and better water quality compared to surface water and at the same time being subject to fewer seasonal and perennial changes, and the production costs are much lower in this case. These benefits resulted in groundwater use for water supplies at a large scale. When the iron anion is found in high concentrations in drinking water, the high concentration of this metal leads to a metallic taste and a water colour effect. Several techniques were applied to remove iron anion of groundwater and drinking water [5-9].

The iron anion is a fairly common pollutant in drinking water. Several processes that help to reduce the concentration of this anion in drinking water have been developed: membrane separation, ion exchange and adsorption. But the adsorption process is one of the most feasible processes because it is simple, easy to implement and is extremely effective for removing pollutants and also requires low costs. The evaluation of adsorption capacity of different anions on the surface of the membrane is carried out experimentally using a set of experimental isotherms, known for a long time in physical chemistry, among which we can mention: Langmuir [3,10-17], Freundlich, Sips [11,18]. The study of equilibrium adsorption to assess the capacity of the membrane to adsorb different anions, and in the case of this study has considered the adsorption of iron anion. The most adsorption models used to describe the adsorption at equilibrium are: Langmuir, Freundlich, Temkin , Flory-Huggins and Frumkin. Of all the “classic isotherms” because only some can be explained, and for which they have been proposed the statistical methods for the determination of these models and other isotherms cannot be justified by means of simple models.

The primary concern about the presence of iron in drinking water is its objectionable metallic taste. The taste of iron in drinking water can be easily detected even at low concentrations of about 1.8ppm. It is also causes rusty or brown stain on plumbing fixtures, fabrics, dishes and ustensils that cannot be removed by soaps or detergents [12]. Water coming from wells and springs with high iron and/or manganese may apear colorless initially but orange brown (iron) or black (manganese) stains or particles quickly appear as the water is exposed to oxygen. Iron is an absolute requirement for most forms of life, including humans. Iron can be found in wide variety of food sources and in drinking water [13]. Absence of iron gives water an insipid or flat taste. Excessive iron gives drinking water an objectionable metallic taste. It can also be potentially toxic for humans. Its ability to donate or accept electrons means that if iron is free within the cell, it can catalyze the conversion of hydrogen peroxide into free radicals [13-14].

The membranes of all types (polymeric, liquid, and composite) [19-22] are regarded as the best material of adsorbent as well as resins due to their chemical stability and their capacity to control the amount of adsorption of the pollutants at equilibrium.

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The purpose of this study consisted in the adsorption of iron anion by two types of membrane (cellulose and composite). The adsorption capacity of iron anion by two types of membranes was put into evidence by four adsorption isotherms: Langmuir, Freundlich, Flory-Huggins, Frumkin.

Experimental part

Isotherms

Four adsorption isotherms were applied to the interpretation of the experimental data obtained for the adsorption capacity of the two types of membrane: cellulose and composite used as adsorbent material at different temperatures. The use purpose of these membranes has been noticed for their adsorption capacity and to obtain the optimal adsorption of iron anion, and also the parameter values specified using the equilibrium adsorption models.

Methods and materials

The reactions taking place at the surface of both membranes are the following:

$$2FeS_2 + 7O_2 + 2H_2O = 2Fe^{2+} + 4SO_4^{2-} + 4H^+ \quad (1)$$

$$5FeS_2 + 14NO^{3-} + 4CO^2 + 2H_2O =$$
$$= 5Fe_2 + 10SO_4^{2-} + 7N_2 + 4HCO^{3-} \quad (2)$$

These reactions can induce SO_4^{2-} in pumped raw water. Iron carbonate reacts with CO_2 and get Fe into the solution.

$$FeCO_3 + CO_2 + H_20 = Fe^{2+} + 2HCO_3 \quad (3)$$

If there is enough CO_2 present and H donors then it will be possible to remobilize the wide spread Fe $^{+3}$ oxyhydrates.

$$FeO(OH) + (H^+) + 2CO_2 = Fe^{2+} + 2HCO^{3-} + e- \quad (4)$$

The potentiometric redox titration with cerium sulphate method

The aim of this paper was to determine the amount of Fe (II), from a sample by redox titration with Ce(IV). The experiment will be carried out in two distinct phases. The first stage involves the standardization of titration reagent solution $Ce(SO_4)_2$, using a standard solution of Fe(II) from an unknown sample. One of the commonly methods applied in the determination of Fe(II) is redox titration, the titration reagent acting as oxidising agent, in this case cerium sulphate. The content of Fe(II) from sample is determined on the basis of the following titration reaction:

$$Fe^{2+} + Ce^{4+} \rightarrow Fe^{3+} + Ce^{3+} \quad (5)$$

Methodology

$V_{Fe(II)}$ volume of standard solution of Fe(II) shall be measured with the dropper (for example 1.5 mL) and transferred to a beaker. It is diluted with a minimal amount of distilled water.

Place the two electrodes into a glass, the magnetic stirring bar and starts shaking the solution with a moderate speed. Fill the burette with titration reagent solution. The electrodes are connected to the millivolt. Note the value of the first indication of the measuring value.Successive additions are made in the solution of $Ce(SO_4)_2$, with an increment of 0.1 mL, after each addition millivoltmeters noting the indication. The data is recorded in a table that includes column volume of titrant adage, V_a, and respectively the value of the cell, ε_{cel} mV. The titration is continued at least 8-10 additions after the jump potential sightings around equivalence [15].

Titration curve

The potentiometric method allows highlighting of titration reaction, using for this purpose an electrochemical cell in which the electrode is a metallic electrode, made of a material inert chemically (Pd).

The potential of the indicator electrode is associated to the redox couple of Fe^{2+}/Fe^{3+} during Fe(II) titration redox couple Ce^{4+}/Ce^{3+}, made by equivalence, when adding excessive titration reagent.

Thus, during the titration Fe(II), the electrode potential (expressed in mV at 25°C), is described by the Nernst equation:

$$\varepsilon_{ind} = \varepsilon^f_{Fe^{3+}/Fe^{2+}} + 59{,}2 \log \frac{[Fe^{3+}]}{[Fe^{2+}]} \quad (6)$$

It is observed that as the concentration of Fe^{3+} in the sample increases, the potential of the electrode becomes increasingly larger.

A characteristic point on the titration curve in this area is measured electrode potential when the two forms of the redox couple have equal concentrations. This point corresponds to the formal potential of the couple Fe^{3+}/Fe^{2+}:

$$(\varepsilon_{ind})_{[Fe^{3+}]=[Fe^{2+}]} = \varepsilon^f_{Fe^{3+}/Fe^{2+}} \quad (7)$$

The equivalence of electrode potential characterized by a specific value, which is characteristic to the two redox couples involved in the titration reaction will be:

$$\varepsilon_{ind,echiv} = \frac{\varepsilon^f_{Fe^{3+}/Fe^{2+}} + \varepsilon^f_{Ce^{4+}/Ce^{3+}}}{2} \quad (8)$$

The addition of excess reagent titration will cause further change to the potential of the electrode according to the Nernst equation for redox couple custom Ce^{4+}/Ce^{3+}:

$$\varepsilon_{ind} = \varepsilon^f_{Ce^{4+}/Ce^{3+}} + 59{,}2 \log \frac{[Ce^{4+}]}{[Ce^{3+}]} \quad (9)$$

in which the independent variable is the concentration of Ce^{4+}. The amount of Ce^{3+} remains constant at the corresponding value achieved at the equivalence point.

The relation (9), when the two forms of the redox couple Ce^{4+}/Ce^{3+} concentrations have equal logarithmic term shall be cancelled. The particular indicator electrode potential measured under these conditions, it is even formal potential of the couple Ce^{4+}/Ce^{3+}:

$$\varepsilon_{ind,([Ce^{4+}]=[Ce^{3+}])} = \varepsilon^f_{Ce^{4+}/Ce^{3+}} \quad (10)$$

In conclusion, by recording the titration curve (ε_{gel} - V_a, where V_a is the volume of solution added titration reagent) we will be able to obtain the following important dates:

- equivalence volume, by means of which is calculate the amount of Fe(II) in the unknown sample;
- the formal potential of the redox couple Fe^{3+}/Fe^2;
- formal potential of the redox couple Ce^{4+}/Ce^{3+}.

Spectrophotometric method – Reducing Fe^{3+} to Fe^{2+}

The aim of the study was to determine the iron content in drinking water using spectrophotometric method. It was carried out reduction of Fe^{3+} to Fe^{2+} with hydroxylamine , that is considered a reducing agent [16].

At the beginning of the analysis a series of 10 standards were prepared in order to obtain the calibration curve. The initial iron concentration was 10 mg/L. Based on the calibration curve the calibration equation will be determined. Using equation will be calculated the unknown concentration of iron in drinking water. Based on data obtained will be validated the spectrophotometric method for analysis of iron. Prepare 10 samples that contain: 0.3 mL of hydroquinone; 2.5 mL sodium acetate; 2.5 mL a-fenantrolina and sol iron, one at a time: 0.5; 1; 1.5; 2; 2.5; 3; 3.5; 4; 4.5; 5.

Results and discussions

The procedure for this study type was well known from previous works [21-25]. So, the drinking water sample was filtered through two membranes: cellulose and composite. The sample was degassed. In the 50 mL Berzelius beakers, were introduced the exact volumes for the 10 concentrations of iron and is inserted: 2 mL 10% hidroxilamina and 2.5 mL of 1M sodium acetate solution. The reaction mixture will heat up to 70-80^{0}C, 5-10 min. After baking, cool and fill upto 25 mL volumetric flask, add each 2.5 mL 0.1% o-phenanthroline and make up to volume with distilled water. The *p*H domain will be between 3-9 (*p*H = 5, for drinking water). Iron absorption spectrum (absorption in red) is at a *p*H = 5.

The maximum of the absorption band is located at 511 nm.

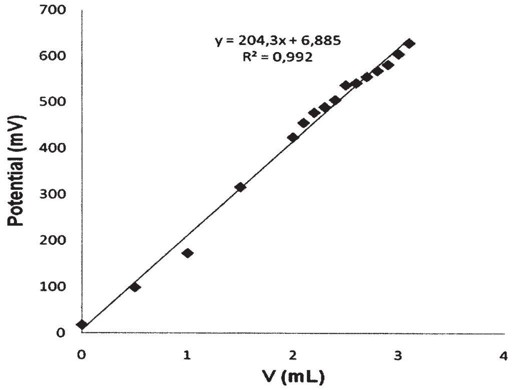


Fig. 1.Standardization curve for iron anion

Table 1
LINEARITY OF THE RESPONSE FUNCTION

Parameters	**Analytical domain (mg/L, Fe^{3+}/Fe^{2+})**
The regression line equation	Y=168.2*X+103.38
Regression coefficient, R^2	0.9989
Gradient	0.158
Intercept	0.0259

The equations of the regression straight lines were calculated by the method of least squares for each area of concentration.

The linearity of results was evaluated, through the graphical representation of concentration variation based on the regression line equation as a function of the concentration of iron anion. The calculated values indicate a linear relationship , presented in table 2.

We calculated the detection limit LD = 0.004mg/L and the limit of quantification LQ = 0.012mg/L, for the Fe^{3+}/Fe^{2+} anion. The estimation of these boundaries was based on the standard deviation of the slope of the regression line.

Table 2
LINEARITY RESULTS

Parameters	**Analytical domain (mg/L, Fe^{3+}/Fe^{2+})**
Gradient	0.9990
Intercept	0.005
Regression coefficient , R^2	0.9989

For the estimation of accuracy were used:

- determination of repeatability (precision system) for a total of 10 determinations, the relative standard deviation (RSD) was 0.93% for Fe^{3+}/Fe^{2+} anion;
- analysis repeatability (precision of the method) for three independent solutions to three different concentrations and levels of precision for intermediate three independent solutions to three different concentration levels.

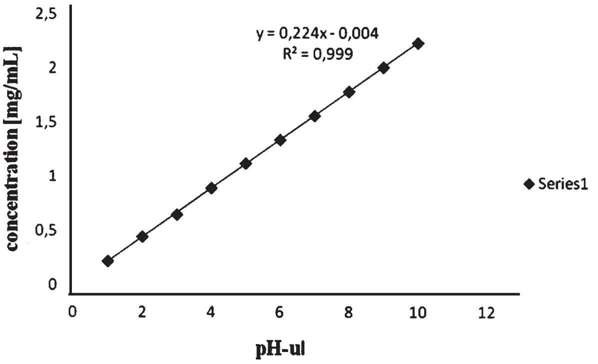


Fig.2. Influence of *p*H on Fe^{3+}/Fe^{2+} concentration variation cellulose membrane

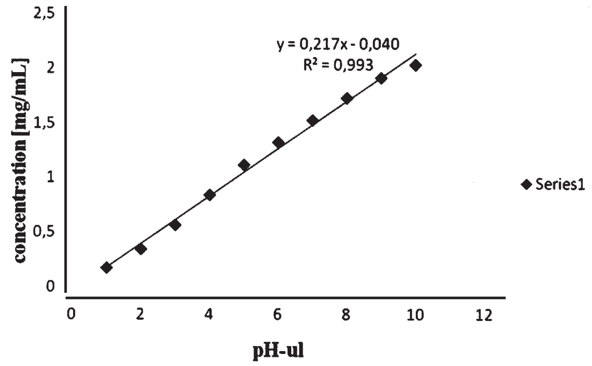


Fig.3. Influence of *p*H on Fe^{3+}/Fe^{2+} concentration variation composite membrane

Table 3
ACCURACY AND PRECISION OF INTERMEDIATE METHOD

Parameters	**Analytical domain (mg/L, Fe^{3+}/Fe^{2+})**	
	Precision of the method	**Intermediate precision**
Relative standard deviation RSD	3.02%	2.56%
Confidence interval of the mean value	94.85% 103.42%	94.24% 102.68%

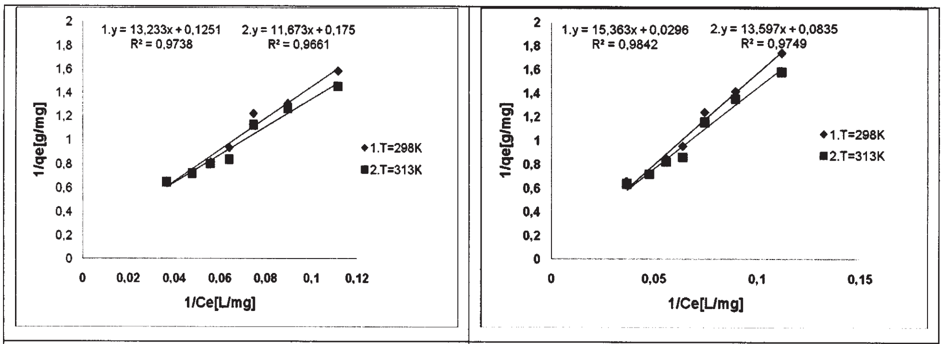
Table 4
ACCURACY OF THE METHOD

Parameters	**Analytical domain (mg/L, Fe^{3+}/Fe^{2+})**
Retrieving average (%)	99.2%
The confidence interval	95.2% - 102%

The accuracy of retrieval was determined for a number of three samples at three levels of different concentrations on the two concentration ranges studied, for Fe^{3+}/Fe^{2+} anion, presented in table 4.

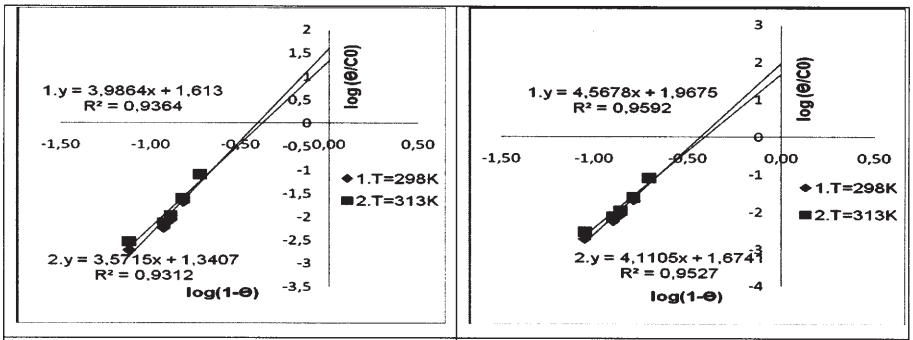
Considering the results obtained for Fe^{3+}/Fe^{2+} anion, the method can be successfully applied to the determination of these ions from drinking water at various concentrations.

We used a range of *p*H values in order to highlight the adsorption capacity of each membrane:celullose and composite (fig. 2 and 3).



a) cellulose membrane b) composite membrane

Fig.4.. Graphical representation of the linearized form of the Langmuir model for iron anion on two types of membranes at different temperatures



a) cellulose membrane b) composite membrane

Fig.5. Graphical representation of the linearized form of the model Flory - Huggins for iron anion on two types of membranes at different temperatures

The procedure was in the range of *p*H: 4.2 to 8.5.

At a *p*H higher than 8.5 the cellulosic membrane does not adsorb good.

Adsorption isotherms

The purpose of adsorption isotherms studied in this paper refers to the maximum adsorption capacity of the membrane for iron anion and also the amount of adsorbed on the surface of the membrane. The results were analyzed using Langmuir, Freundlich, Flory-Huggins, Frumkin isotherms. Both the membranes: composite and cellulose showed a different behaviour for iron anion adsorption by using four adsorption isotherms. This process of selective adsorption has been successfully demonstrated by applying adsorption models mentioned above.

Langmuir isoterm

Langmuir model has been chosen in order to determine the maximum capacity of adsorption of iron anion in drinking water corresponding to complete monolayer coverage on the surface of iron anion membrane without having a lateral interaction between the molecules of this anion adsorbent material.

Langmuir model presents the following equation:

$$q = \frac{K_L q_m Ce}{1 + K_L Ce} \tag{11}$$

where:

q the amount adsorbed in solution at equilibrium [mg g^{-1}];

Ce the concentration in solution at equilibrium [mg L^{-1}].;

K_l is the balance of the exchange reaction of Langmuir model;

q_m maximum amount adsorbed on the membrane of iron anion [mg g^{-1}].

Langmuir equation can be written in the form linearized, as follows:

$$\frac{1}{q} = \frac{1}{q_m} + \frac{1}{K_L q_m Ce} \tag{12}$$

An important parameter which has influenced the process of adsorption of iron anion, has been its concentration at equilibrium.

Langmuir isotherm was successfully used to explain iron anion adsorption from aqueous solutions. In figure 4 is the function f(1/Ce) the concentration at equilibrium versus the maximum amount adsorbed (1/qe) for iron anion. Langmuir model for composite membrane presented higher values for the regression factor (R^2 = 0.9842), compared to the values obtained on cellulose membrane (R^2 = 0.9661).

Florry – Huggins isoterm

Equation underlying this model is written as:

$$\log\frac{\Theta}{C_0} = \log K_{FH} + a \cdot \log(1 - \Theta) \tag{13}$$

where:

a is the scale parameter and measures the number of molecules adsorbed of iron an ion in drinking water on the adsorbent material;

K_{FH} is constant of this model;

$\Theta = (1 - C_e / C_o)$ is coverage the surface of the membrane;

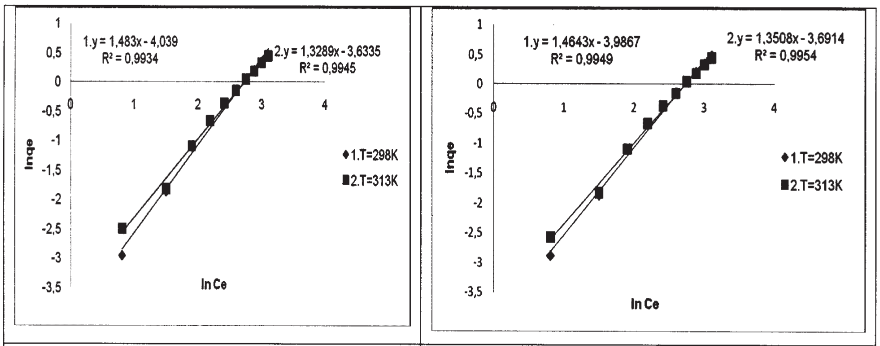
C_e - equilibrium concentration of iron anion [mg L^{-1}];

C_0 - the initial concentration of iron anion [mg L^{-1}].

The graphical representation of the Flory-Huggins isotherm (fig. 5), provides information on the degree of coverage of the membrane, since it presents the smaller pores 0.20 μm (composite membrane) that would adsorb much more molecules of iron anions on its surface, than the cellulose membrane with pores with average size of 0.45 μm.

Freundlich isoterm

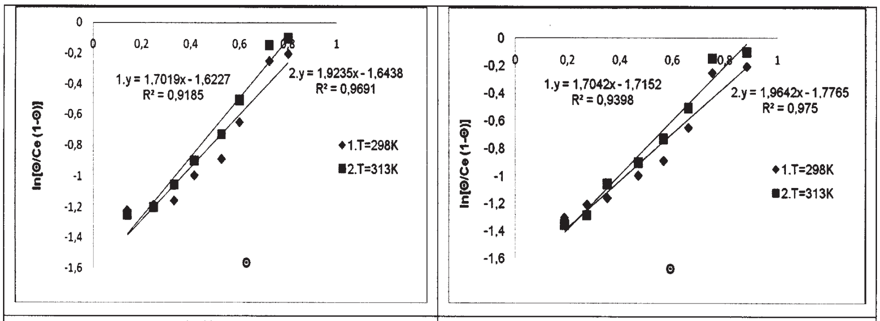
Mathematical model of Freundlich isotherm, was used in this study because as you can see from the experimental data obtained for iron anion, this model fits very well for adsorption of this anion in drinking water.



a) cellulose membrane

b) composite membrane

Fig.6. Graphical representation of the linearized form of the model Freundlich for iron anion on two types of membranes at different temperatures



a) celullose membrane

b) composite membrane

Fig.7.Graphical representation of the linearized form of the model Frumkin for iron anion on two types of membranes at different temperatures

Freundlich isotherm shows an empirical formula of this model for adsorption on the two membranes, the iron anion and it is given by the equation:

$$q = K_F \cdot C_e^{1/n} \qquad (14)$$

where:

qe (mg g^{-1}) is the amount the balance of iron anion adsorbed on the adsorbent material;

C_e (mg L^{-1}) the equilibrium concentration of iron anion in the aqueous solution;

n and K_E represents specific constants for Freundlich isoterm (are empirical), which depends on temperature. Report 1/n is a constant feature of this model, which measures the intensity of adsorption.

As the temperature rises (fig. 6), we note that the amount of iron anion adsorbed on composite membrane grows much more slowly than in the case of cellulose membrane, and at the same time as is increased the concentrations at equilibrium, it is observed that the surface of the cellulose membrane is saturated, which means you get the maximum amount of adsorption of iron anion on adsorbent material.

Frumkin isoterm

The linear form Frumkin adsorption isotherm equation is written as:

$$\log\frac{\Theta}{C_0} = \log K_{FR} + a\cdot\log(1-\Theta) \qquad (15)$$

where:

K_{FR} is the constant adsorption-desorption and α is a term lateral interaction that =(1-C_e/describes the interaction of membrane pores layer that has the capacity to adsorb the iron anion in the drinking water;

C_e (mg / L) the equilibrium concentration of iron anion in the aqueous solution;

$\Theta = (1-C_e / C_o)$ is coverage of the surface membrane.

Graphical representation of the isotherm is a straight line determined by linear representation of the function log (concentration) versus Θ. Considering the values of the regression factors for the two temperatures, the two membranes, as well as the positive values of the constant, we suggest that the behaviour of the composite membrane attractive to adsorb iron anion, takes place almost entirely in drinkingwater.

These models have been used to determine the adsorption capacity of the iron anion in different concentrations at equilibrium, at two different temperatures in aqueous environments using two types of membranes: composite and cellulose.

The figures 4-7((a) - (b)) have different profiles of the various concentrations at equilibrium of iron anion adsorption capacity versus the iron anion, which may be deducted from the linear representations. Linear representation of the isotherm in figure 7b shows that the optimal removal of the maximum amount of iron anion adsorbed to a regression factor of 0.975 which leads to the reduction of its time of adsorption at 150 min.

In this study we can see that between 1-150 min is obtained total removal of iron from aqueous solution on the composite membrane. This means that the adsorption process is terminated when all of the adsorption centers or pores on the surface of the membrane are charged for example when forming one molecule thick layer at the interface of phase one.

Conclusions

In this paper has been traced the mathematical modelling of data obtained from experiments for adsorption of iron in drinking water using two membranes (cellulose and composite).

Experiments were performed with two methods for the determination of iron in water: the spectrophotometric method and potentiometric redox titration with cerium sulphate method.

The experimental data were processed using four adsorption isotherms: Langmuir, Freundlich, Flory-Huggins, Frumkin.

Spectrophotometric method is an easier and faster method in terms of determining iron in drinking water than the method of potentiometric titration with cerium sulphate.

According to Freundlich isotherm concerning equilibrium concentration values, it is observed that the saturation of the surface membrane, i.e. it is obtaind the maximum amount of of adsorption of iron anion on the adsorbent material.

According to the isoterm Flory-Huggins, composite membrane (0.20 μm) has pores smaller than cellulose membrane (0.45) μm and therefore adsorbe better iron ions from drinking water.

As in the case of Freundlich model, the model Langmuir presented higher values for the composite membrane ($R^2 = 0.9842$), compared with cellulose membrane ($R^2 = 0.9661$), explained on the basis of regression factor obtained in both cases.

According to four isotherms used can be seen that between 1-150 min is obtained the total removal of iron from aqueous solution on the composite membrane. The absorption process is terminated when the pores are saturated with the membrane on the surface of iron anion.

*p*H significantly affected the adsorption capacity. As the pH increased the adsorption capacity of the two membranes has decreased. It has been noted that the optimal *p*H for the adsorption of iron in drinking water was five.

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