COMPARATIVE STUDY OF TEMKIN AND FLORY-HUGGINS ISOTHERMS FOR ADSORPTION OF PHOSPHATE ANION ON MEMBRANES

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In this work there was approached a comparative study of the Flory-Huggins and Temkin isotherms that are used for adsorption of phosphate anion present in different concentrations in drinking water on membranes. The purpose of this study was to compare the experimental results obtained with the aplication of the two isotherms (Temkin and Flory-Huggins). There have been made some experiments in order to highlight phosphate anion adsorption present in drinking water on cellulose membranes. The parameters taken into consideration were the followings: the equilibrium concentrations, the maximum amount adsorbed, the temperature and type of membrane. We used two cellulose membranes with different pore sizes (10 μm and 50 μm). The 10 μm membrane has presented the best results for the adsorption of phosphate anion in drinking water.

Keywords: Flory-Huggins model, Temkin model, phosphate anion, adsorption isotherms, cellulose membrane

1. Introduction

The phosphate is considered to be one of the most important nutrients found into natural water. Although several other nutrients (eg. carbon, nitrogen, sulfur, potassium, calcium and magnesium) are required to facilitate growth of plant material, particularly algae, the phosphorus content is important in determining the level of algal growth that the water will support. The growth of the algae in the natural water will rarely occur at phosphate concentrations below 0.05 mg/L [1-3].

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Regular determinations of the phosphate content of natural waters provide information concerning the biological changes taking place into the water. In different waters from our country the concentration of phosphate is often very low (less than 1 μgP/L) so that it is essential to adopt a sensitive and precise method. Of equal importance is the method of sampling and the avoidance of errors due to changes in the phosphate concentration in the water after the sample has been collected [4-6].

Drinking water may have a maximum allowable phosphate content of 0.2 mg/dm^3, while on average, raw sewage contains about 20 mg/dm^3.

The phosphate found in natural waters mainly exists as the orthophosphate species, PO_4^{3-}, however, the polyphosphates $P_2O_7^{4-}$ and $P_3O_{10}^{5-}$ are frequently encountered. These polyphosphate species may be hydrolysed to produce the orthophosphate. However, the species which dominate will depend on the pH prevailing in the particular environment. Phosphate will already react with ammonium molybdate in the presence of suitable reducing agents to form a blue coloured complex, the intensity of which is directly proportional to the concentration of phosphate in the solution. The phosphate content of an unknown water sample can be obtained by first establishing the absorbances of a series of standard solutions against the corresponding concentrations, thus giving a calibration curve. The concentration of phosphate in the unknown sample can then be determined from the graphic [7-8].

The adsorption processes are described generally using adsorption isotherms which show that the amount of a particular solute is retained by an particular adsorbent in experimental conditions that were well-chosen (pH, temperature, and so on). For a proper understanding of the adsorption process, which allows the design of appropriate experimental strategy, it is necessary to discuss this process, both from the thermodynamic point of view (by using the adsorption isotherms), as well as the kinetic one [7-12].

The selection of the most appropriate model that can best describe the fitting of adsorption data obtained experimentally was made in this study by using linear regression for all cases studied (Temkin and Flory-Huggins isotherms).

2. Experimental Part

2.1. Materials

Ammonium molybdate, sulphuric acid, hydrazine sulfate were purchased from Sigma Aldrich. Cellulose membranes were also purchased from Sigma Aldrich. The membrane shows cylindrical shape of the pore's sizes (10 μm and 50 μm). UV-VIS spectrophotometer Jasco model V550 was used for the determination of phosphate in drinking water.

2.2. Methods

A simple spectrophotometric method has been developed for the determination of phosphate dissolved in water. The method is based on the formation of phosphomolybdate with added ammonium molybdate followed by reduction with hydrazine in acidic medium. Orthophosphate and molybdate ions condense in acidic solution to give molybdophosphoric (phosphomolybdic) acid, which upon selective reduction (with hydrazinium sulphate, for instance) produce a blue colour, due to blue molybdenum of an uncertain composition. The intensity of the blue colour is proportional to the concentration of phosphate. If the acidity during the time of reduction is due to addition of 0.5 M clorhidric acid and hydrazinium sulphate is the reductant, the resulting blue complex exhibits maximum absorption at 830 nm wavelength. The system obeys Lambert-Beer's law at 830 nm in the concentration range of 5-25 mEq/L of phosphate with a relatively standard deviation (RSD) of 0.1% and correlation coefficient of 0.99. Molar absorptivity was determined to be 2.9×10^4 L/(mol cm) at 830 nm. The concentration of phosphate anion was calculated as follows:

$$C = A \times G \tag{1}$$

where:

C - the concentration of phosphate anion,
A - the absorbance, and
G - the correction factor for the standard calibration curve of phosphate anion.

3. Results and discussion

The Temkin model of isotherm adsorption has been chosen firstly to evaluate the adsorption potential of the adsorbent and adsorbed solution. This isotherm contains a factor which explicitly takes into account the interactions of ions of the aqueous solution and the membrane (adsorbent-adsorbate).

The Temkin isotherm has been generally applied in the following equations:

$$q_e = (\frac{RT}{b}) \cdot \ln(A_T C_e) \tag{2}$$

$$q_e = \frac{RT}{b_T} \ln A_T + (\frac{RT}{b}) \ln C_e \tag{3}$$

$$B = \frac{RT}{b_T} \tag{4}$$

A linear expression of the Temkin equation is represented by:

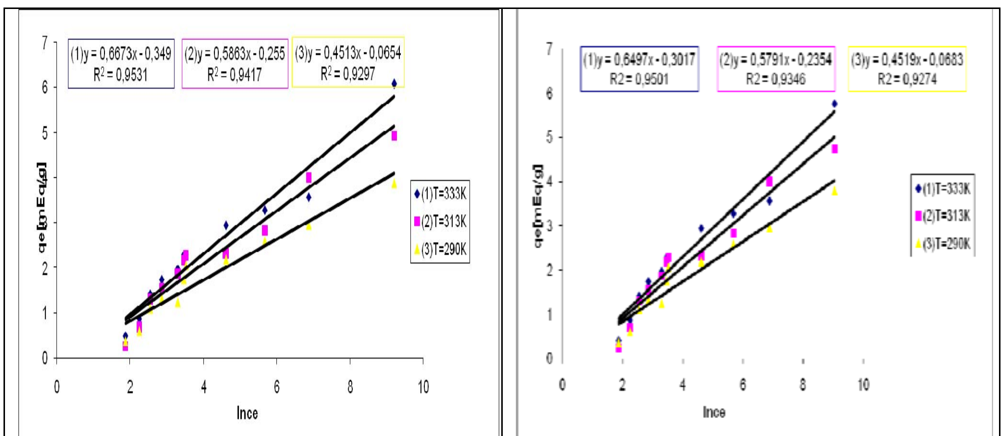
$$q_e = B \ln A_T + (\frac{RT}{b}) \ln C_e \tag{5}$$

where:

- A_T = the equilibrium binding constant [L/g],
- b_T = the adsorption constant [J/mol K]
- R = universal gas constant (8.314 J/mol K)
- T = absolute temperature value [290, 313 or 333 K],
- B = a constant related to the heat of sorption [J/mol].

In this work we studied the following parameters: temperature (290, 313, 333 K), equilibrium concentration, the maximum adsorbed amount and type of membranes and also the fitting of experimental data by using isotherms. We have used two different cellulose membranes with pores sizes of 10 µm and 50 µm. By eliminating the extremely low values of concentration, the Temkin model assumes low interactions between the adsorbent and adsorbate and the adsorption energy of all the molecules in the surface layer decrease at the cover surface.

Thus, in Fig. 1 the Temkin isotherm was represented by a linear plot of q_e to $\ln C_e$, and the constants involved (B and b) were determined using the slope and intercept of linear equation for Temkin model.



(a) (b)

Fig. 1 Graphical representations of linearized form of the model Temkin for phosphate ion on cellulose membrane of 10 µm pores (a) and 50 µm pores (b) at different temperatures

Low values of B in this study indicate a weak interaction between adsorbent and adsorbate supporting a mechanism of ion exchange. The parameters and the regression coefficients of Temkin model are presented in Table 1. Higher values of the coefficient of correlation show a good linearity regardless of the maximum capacity of adsorption used to calculate the coverage area. The value of the adsorption energy, (-ΔH), is positive for all compounds studied, which indicates that the reaction of the adsorption is exothermic.

Table 1

Characteristic values of the constants in Temkin model calculated from the regression equations presented in Figs. 1, for the adsorption of phosphate anions on cellulose membranes of 10 µm and 50 µm pore diameter

Temperature T [K]	**Temkin model for membrane of 10 µm**			**Temkin model for membrane of 50 µm**		
	R^2	**b_T [J/mol K]**	**A_T [L/g]**	**R^2**	**b_T[J/mol K]**	**A_T [L/g]**
Phosphate						
290	0.9297	5305.633	0.8651	0.9274	5298.588	0.8597
313	0.9417	4367.58	0.6473	0.9346	4421.882	0.6660
333	0.9531	4086.606	0.5927	0.9501	4197.31	0.6285

The membrane with 10 µm size of pore showed a different behavior adsorption of anions on the membrane surface because it presented a cylindrical shape and small pore size and therefore this type of membrane has adsorbed a greater amount of phosphate ions. This process of selective adsorption has been successfully demonstrated by application of Flory-Huggins and Temkin models.

Flory-Huggins model was chosen to account for the characteristic surface coverage of the adsorbed on the adsorbent. The graphical representation of the model for the two membranes for phosphate anion is given in Figs. 2(a) and 2(b), and the obtained characteristic constants values of this model are presented in Table 2.

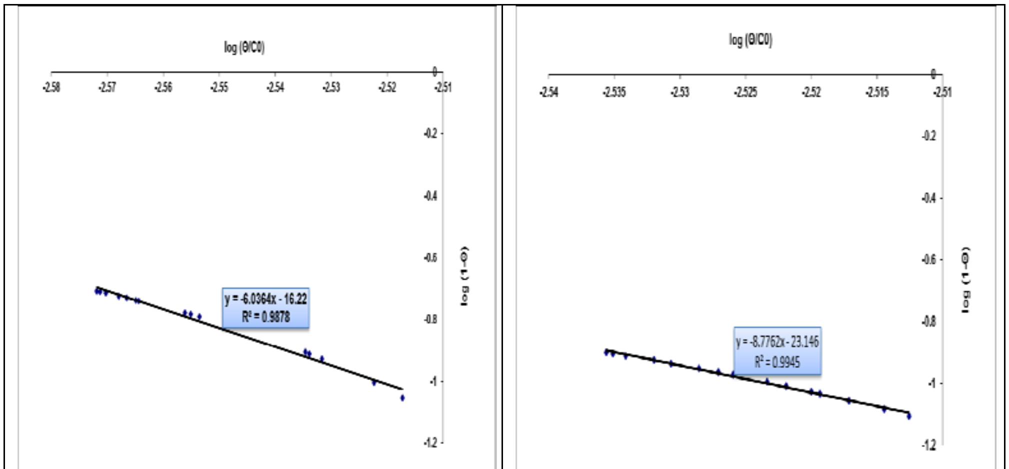
The linearized form of this isotherm is given by equation:

$$\log \frac{\Theta}{C_0} = \log K_{FH} + n \cdot \log(1 - \Theta) \tag{6}$$

where:

- n is the ions number occupying adsorption sites on two membranes and K_{FH} is the equilibrium constant in this model calculated and presented in table below;
- $\Theta = (1 - C_e/C_0)$ is the degree of surface coverage membrane;
- C_e - is the equilibrium concentration of phosphate anions [mEq/L];

- C_0 – is the initial concentration of phosphate anions [mEq/L].



(a) (b)

Fig. 2 Graphical representation of linearized form of the Flory-Huggins model for phosphate anions on cellulose membrane of 10 µm (a) and 50 µm (b) at different temperatures

The kinetic coefficient K_{FH} of the cellulose membrane for Flory-Huggins isotherm was determined from the linear representation of the function $\log(\Theta/C_0)$, against $\log(1-\Theta)$, (Figs. 2a and 2b).

Tabel 2

The obtained parameters of the Flory-Huggins model calculated from regression equations for the adsorption of phosphate anions on cellulose membranes of 10 µm and 50 µm pore size

Anion	Flory-Huggins model for membrane of 10 µm				Flory-Huggins model for membrane of 50 µm			
	R^2	n	K_{FH}	ΔG° [kJ/mol]	R^2	n	K_{FH}	ΔG° [kJ/mol]
phosphate	0.9878	-6.0364	$9*10^{-8}$	-39.10	0.9945	-8.7762	1.12	-55.80

In addition, by using the values of the equilibrium constants K_{FH} obtained from Flory-Huggins isotherm model, we can determine the ΔG°.

The results of the experimental model are best described by Flory-Huggins model where the values of the regression coefficients (R^2) are higher than the ones obtained in the case of Temkin model. Therefore, even after activation, the retention of phosphate anions on the cellulose membranes is as a monolayer and in entire process have only concerned functional groups on the surface of the adsorbent.

The adsorption of phosphate anion has been accomplished as follows: we have prepared several synthetic solutions concentration: 5, 10, 15, 20 and 25 mEq/L, which were adjusted to a pH 4.5 with 1 M H_2SO_4 . Synthetic solutions of phosphate anions were analyzed before and after filtering through a membrane, in order to record the maximum amount of adsorbate on each membrane, at three different temperatures (290, 313, 333 K). At a pH 4.5 and at temperature of 333 K, there has been recorded the highest adsorption capacity.

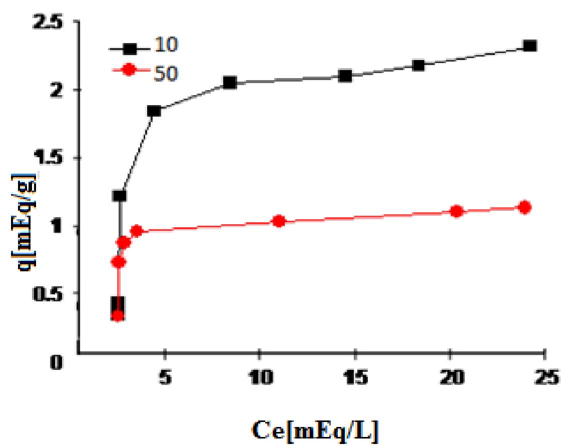


Fig 3. The equilibrium adsorption capacity versus concentration for two types of cellulose membrane (10µm and 50µm)

Another important parameter which affects the process of the adsorption was the concentration at equilibrium. Phosphate anion corresponds to a certain equilibrium concentration and any other level over this concentration no longer retains ions. The process of adsorption remains at a constant value, meaning no longer adsorption and desorption activity.

Using the synthetic 25 mEq/L solutions of phosphate anions, there have been carried out many experiments to record the behavior of two membranes in the case of phosphate adsorption. The membrane of the pore size of 10 µm presented a better adsorption behavior comparing with the other membrane, of 50µm. This result corresponds to the small size of the pores and the good distribution of the cylindrical pores.

These features are in good agreement with the manufacturer's data sheet (the size and shape of the pores). The maximum adsorption capacity of the membrane of 10 µm was 2.397 mEq/g, while for the membrane of 50 µm was 0.980 mEq/g (Fig. 3). The maximum capacity of the adsorber increases with decreasing pH and temperature rise.

As concerning the nature of the sorbent used for retention of phosphate anions from aqueous solutions, there resulted spontaneously the adsorption process which is characterized by a negative value of the Gibbs free energy

($\Delta G°<0$) and it is also less influenced by the treatment used to activate the adsorbent.

4.Conclusions

A detailed analysis of the experimental data was performed to determine the best models of isothermal equilibrium data sets for phosphate anion.

This study indicates a low-cost adsorbent-cellulose membrane for the removal of phosphate anion from drinking water. In the present case there have been used synthetic solutions of 25 mEq/L concentration of phosphate ions. The adsorption process is described using Temkin and Flory-Huggins models.

The experimental results were analyzed using the following parameters: temperature, concentration at equilibrium, the ability of adsorption, pH and different pore sizes of cellulose membranes for adsorption of phosphate ion.

The evaluation equation of the regression coefficients from two isotherms obtained at pH 4.5 for analytical data processing indicated that the data of the Flory-Huggins model isotherm are much higher than those obtained using Temkin model.

The maximum capacity of the adsorbent increases with decreasing pH and also with an increasing temperature. The cellulose membrane with pore size of 10μm reached a value of 2.397 mEq/g for the adsorption of phosphate anion in drinking water, and the cellulose membrane with pore size of 50μm has a value of 0.980 mEq/g.These results have been highlighted based on the regression coefficients obtained using Temkin and Flory Huggins isotherm models.

This study was performed to demonstrate the ability of cellulose membrane for removal of phosphate anion in drinking water and by using Temkin and Flory Huggins isotherms to fitting the experimental data.

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