EQUILIBRIUM AND KINETIC STUDIES ON THE TARTARIC ACID SEPARATION FROM AQUEOUS SOLUTION BY ION EXCHANGE WITH IMPREGNATED AMBERLITE IRA- 67

Natalia MARCHITAN*, Gheorghe DUCA*, Aliona Mereuta*, Ilie SIMINICEANU**

*Moldova State University, Faculty of Chemistry and Chemical Technology, Department of Ecological and Industrial Chemistry, 60 Mateevici str, Chisinau, Republic of Moldova.
** "Gh. Asachi"Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, 71 Bd. Mangeron, 700050 Iasi, Romania . isiminic@ch.tuiasi.ro

Abstract: *A new adsorbent has been prepared from Amberlite IRA- 67 impregnated with the liquid ion- exchanger Amberlite LA-2 dissolved in n- hexane to recover tartaric acid (TA) from aqueous solution.The experiments done on a batch equipment proved the effectiveness of the new material: the separation degree of TA was100% in a contact time less than 30 minutes for the following values of the 6 main factors: solid/ liquid loading > 1 g/L, T= 294 K, initial pH 2.5, initial TA concentration >1 g/L, particle diameter 0.4- 1.2 mm, stirring 200* min^{-1}. *The equilibrium* q_e- c_e *data were better correlated through the Langmuir isotherm* ($R^2 = 0.9962$) *compared to the Freundlich one* ($R^2 = 0.8535$). *The kinetic curves* q- τ *has been confronted with 4 kinetic models, and the corresponding kinetic constants have been identified. The final conclusion was that, under the investigated conditions, the slowest step of the process was the intraparticle diffusion.*

Keywords: *Freundlich, Langmuir, kinetic models, Lagergren, Ho- McKay, Weber- Morris, Dumwald-Wagner.*

Introduction

Tartaric acid (TA) was known to early Greecs and Romans as acid potassium salt, formed as a deposit from fermented grape juice. The acid was first isolated in 1769 by the Sweedish chemist *Carl Wilhelm Scheele* (1842- 1886) who boiled tartar with chalk and decomposed the product with sulphuric acid. TA, in either dextrorotary or racemic form, is used as flavouring in foods and beverages. It is also used in tanning, in photography, and as a mild laxative under the form of potassium sodium tartrate. Potassium hydrogen tartrate, also called cream of tartar is used in baking powders. Several methods can be applied to recover TA from aqueous solution [1]: chemical precipitation, solvent extraction, membrane separation, adsorption on polymeric anion exchangers.

In recent years impregnated ion exchangers have been used in order to enhance adsorption capacity, selectivity and rate [1, 2]. The impregnation was made either with transitional metal ions, like Cu(II), which is immobilized on the resin matrix [1], or with a solution of tri- n-octylamine in n- hexane [2]. This paper reports new results on the adsorption of TA from aqueous solution on weakly basic anion exchanger Amberlite IRA- 67 impregnated with a solution of liquid ion exchanger Amberlite LA-2 in n-hexane.Six main factors have been identified to influence the adsorption process in batch experiments: temperature, ion exchanger particle diameter, agitation rate, initial pH of solution, initial concentration of the tartaric acid in the aqueous solution, the ratio resin mass/ solution volume (S/L).

The solid- liquid equilibrium experimental curves (equilibrium specific adsoption q_e versus equilibrium concentration of TA in solution c_e), so called adsorption isotherms, have been confronted with two linearized models (Freundlich, and Langmuir), and the constants of these models have been identified. The primary experimental kinetic curves (specific adsorption q versus time) have been used to check several kinetic models (pseudo- first- order rate equation/ Lagergren adsorption reaction model, pseudo- second- order rate equation/ Ho- McKay adsorption reaction model, adsorption intraparticle diffusion Weber- Morris model, adsorption intraparticle diffusion Dumwald- Wagner model). The ultimate goal was to find out the rate determining step (RDT) of the process.

Experimental

The experimental protocol included three steps: the preparation of the impregnated ion exchanger, equilibrium experiments, and kinetic experiments.The impregnation procedure was adapted to a method described in the literature [2]. The solvent used to dissolve the liquid ion exchanger Amberlite LA-2 was n- hexane (1 mL Amberlite LA-2 in 2 mL n- hexane). This solvent gave the highest swelling rate of the resin. The swelling improved the penetration of the impregnation solution leading to a more homogeneous loading of the matrix ion exchanger.After a contact time of 3 hours the resin was died with air. After drying, the resin was screened into 3 granulometric classes with average size of 0.38 mm, 0.75 mm, and 1.25 mm respectively.

To perform equilibrium experiments, an amount of 0.5 g resin and 25 mL of TA aqueous solution were placed in flask and stirred for 3 hours at constant temperature. The concentration of residual TA was determined spectrophotocolorimetrically according to the protocol described in a previous paper [3]. The kinetic curves have been generated using the same batch equipment. The influence of 7 factors has been studied: (1) nature of the basic ion exchange resin ; from the five tested (IRA-67, AV-17, IRA- 410, Purolite A-400, AN-31) Amberlite IRA- 67 has been finally choosen; (2) reaction temperature (294 K, 306 K, 325 L); (3) mixing speed (100, 200, 300 min-1); ion exchanger partcile diameter (0.25- 0.5 mm, 0.5- 1.0 mm, 1.0-1.5 mm); (4) initial solution pH (2.5 at time zero, rising to 11.5 due to the exchange with hydroxyd ions); (5) solid/ liquid loading (1 g/ 100 mL, 2 g/100 mL, 4 g/ 100 mL); (6) initial concentration of the tartaric acid solution (1.0 g/L, 3.0 g/L, 5.0 g/L); (7) the dose of impregnation liquid(mL/ g). From the results obtained, only those necessary to verify the adequacy of the equilibrium adsorption isothems and of the kinetic models are discussed in the next section.

Results and discussion

Adsorbtion isotherms. The equilibrium adsorption curves obtained for three temperatures (290 K, 306 K, 325 K) have been correlated to two isotherm equations: Van Bemmelen- Freundlich equation[4,5], and Langmuir equation [6]. Other isotherms proposed in the literature (Brunauer- Emmett- Teller/BET, Temkin-Frumkin, Elovic, Redlich- Petersen, Dubinin- Radushkevich, Kisliuk, Henderson) are not suitable for this liquid-solid system [7,8,9,10]. In 1888, van Bemmelen [4] published the first adsorption isotherm in the form now used.Our isotherm at 290 K is in figure 1. In 1906, *Freundlich* published the first equation for the adsorption isotherm [5]. The data in figure 1, correlated with the linear form of the equation (1) are presented in figure 2.

$$q_e = K_F \cdot c_e^{1/n}$$
$$\ln q_e = \ln K_F + \frac{1}{n} \ln c_e \qquad (1)$$

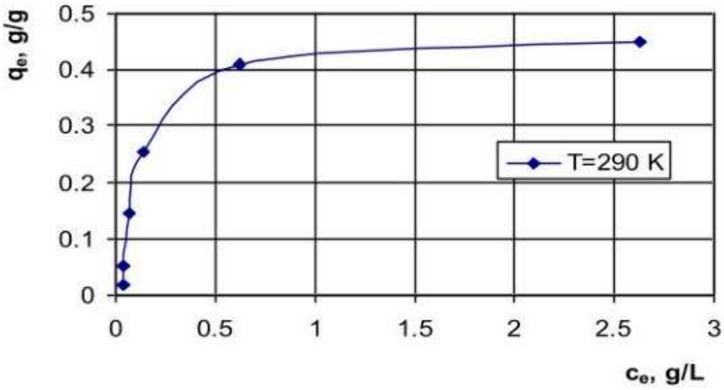

Figure 1. Experimental adsorption isotherm at 290 K

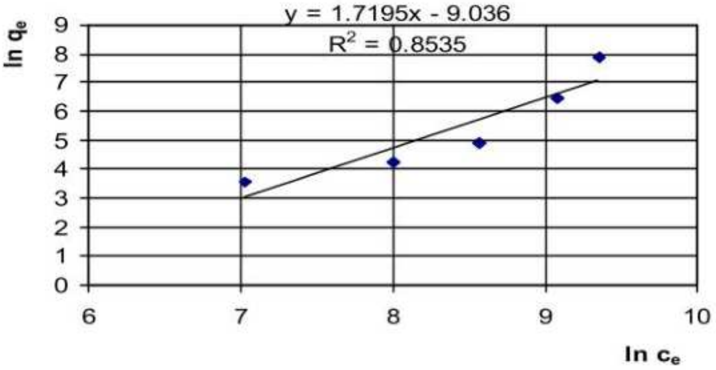

Figure 2. Equilibrium data at 290 K correlated with Freundlich equation

In 1918, Langmuir established the equation (2), considering the surface energetically uniform and maximum one layer of molecules adsorbed [6]:

$$q_e = \frac{q_m \cdot K_L \cdot c_e}{1 + K_L \cdot c_e} \qquad (2)$$

This becomes (3) by linearisation:

$$\frac{c_e}{q_e} = \frac{c_e}{q_m} + \frac{1}{q_m \cdot K_L} \qquad (3)$$

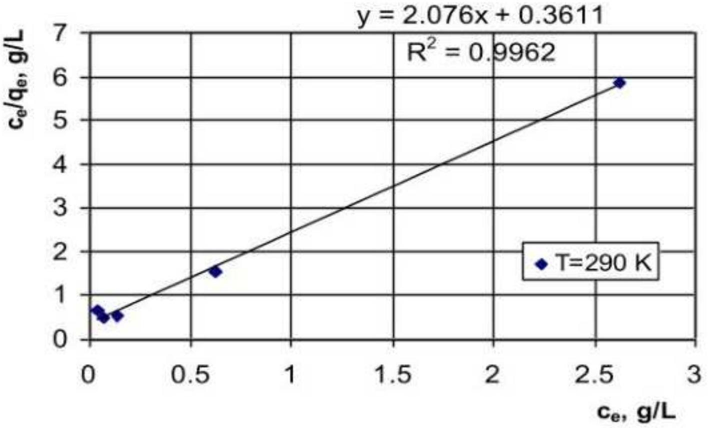

Figure 3. Equilibrium data correlated with Langmuir equation (3).

The constants and the correlation coefficient (R^2) for the two isothems are presented in the table 1. The data are better correlated by Langmuir equation (R^2 is 0.9962, compared to 0.8635).

Table 1. The constants of the isotherms derived from experimental data at 290 K.

T, K	Freundlich			Langmuir		
	n	K_F	R^2	b (K_L)	q_m	R^2
290	0.581	1.19×10^{-4}	0.8635	5.749	0.481	0.9962

Kinetic models. The kinetic approach of ion exchange is rather poor both in older [11] and newer [12] "classical" monographs on the subject. Therefore, confusion still persists and many empirical "kinetic models" are being used. Attempts to review and clarify have been recently done [13, 14]. According to Qiu et al. [14], the adsorption kinetic models are grouped into two classes: *adsorption reaction models* (pseudo- first- order rate equation/ Lagergren model, pseudo- second- order rate equation/ Ho- McKay model, Elovich's equation, second- order rate equation) , and *adsorption diffusion models* (liquid film linear driving force rate equation, liquid film diffusion mass transfer rate equation, homogeneous solid diffusion model, Weber- Morris model, Dumwald- Wagner Model, double exponential model). Four of these ten kinetic models are taken into consideration in this paper.

Lagergren's model. Lagergren [15] published a first- order rate equation to describe the liquid solid phase adsorption of oxalic acid and of malonic acid onto charcoal. It is based on the adsorption capacity (q), not on the liquid phase concentration (C). Therefore, it was named "pseudo- first- order model" [16]. The integrated Lagergren equation (5) is confronted with our experimental data in the figure 4.

$$\frac{dq}{d\tau} = k_1\left(q_e - q\right) \tag{4}$$

$$\ln\left(q_e - q\right) = \ln q_e - k_1\tau \tag{5}$$

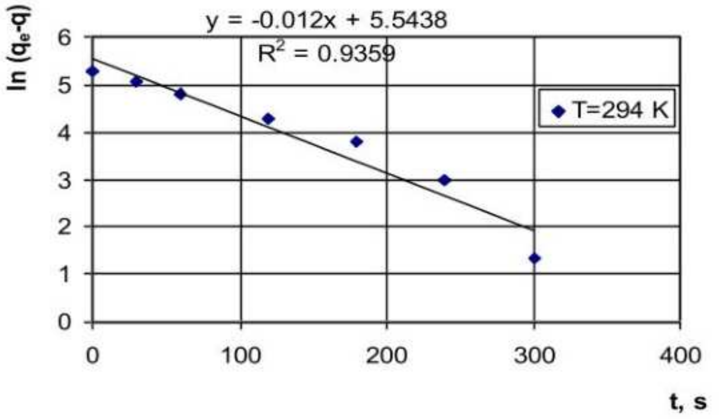

Figure 4. Experimental validation of the Lagergren equation (5).

Ho- McKay's model. The pseudo- second order kinetic model, described by the equation (6) was proposed by Ho and McKay [17] for the adsorption of divalent metal ions onto cation- exchangers. Here, the driving force (q_e- q) is proportional to the available fraction of active sites. The integration of (6) with the boundary conditions yields the linear form (7), suitable for graphical correlation (figure 5).

$$\frac{dq}{d\tau} = k_2 \left(q_e - q \right)^2 \tag{6}$$

$$\frac{\tau}{q} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e} \right) \cdot \tau \tag{7}$$

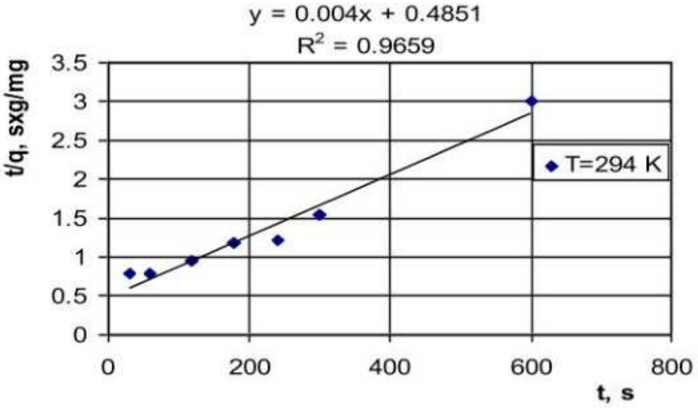

Figure 5. Experimental validation of the equation Ho- McKay at T= 294 K

The value of k_2 derived from figure 5 is: $k_2 = 3.2982 \text{x } 10^{-5}$ g/mg s. The values of k_1 and k_2 obtained from our data at three temperatures a presented in the table 2. They show a better correlation, measured through R^2, with the pseudo- second order model. In addition, these results allowed the identification of the **activation energy (E_2)**, using the Arrhenius equation (8) in the logarithmic form (9).

Table 2. Rate constants

T, K	k_1			k_2		
	s^{-1}	min^{-1}	R^2	g/mg s x 10^5	g/mg min x 10^3	R^2
294	0.0120	0.720	0.9359	3.2982	1.9790	0.9659
306	0.0100	0.600	0.9930	3.7919	2.2752	0.9946
325	0.0158	0.948	0.9748	6.7142	4.0285	0.9964

$$k_2 = k_{02} \cdot e^{-E/RT} \tag{8}$$

$$\ln k_2 = \ln k_{02} - \frac{E}{RT} \tag{9}$$

From table 2 and figure 6 results: E_a = 1000x 8.314x 2. 2486 = 18 694. 86 J/ mol = 4.47245 kcal/ mol.The activation energy is less than 5 kcal/ mol. This value indicates that the rate determining step is transport phenomen: either intraparticle diffusion or film diffusion. Therefore, this is "apparent activation energy". In order to distinguish between the two transport models, the Weber- Morris equation is further tested.

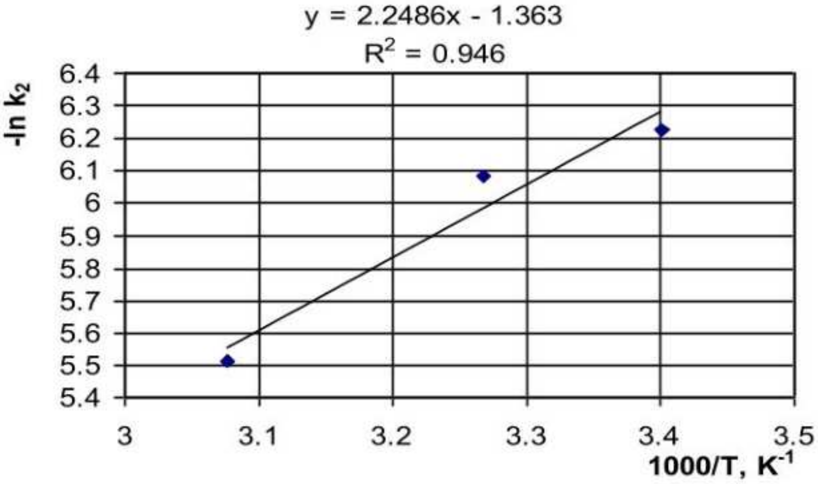

Figure 6. Activation energy determining from the values of k_2 at three temperatures.

Weber- Morris model [18]. According to the equation (10), a plot q versus $\tau^{1/2}$ should be a straight line with a slope K when the intraparticle diffusion is the rate determining step (RDS) of the process. When the line does not go through origin the intraparticle diffusion could be accompanied by slow film diffusion.

$$q = K \cdot \tau^{1/2} \tag{10}$$

The plots of our data are presented in figure 7 and the results are summarised in the table 3.

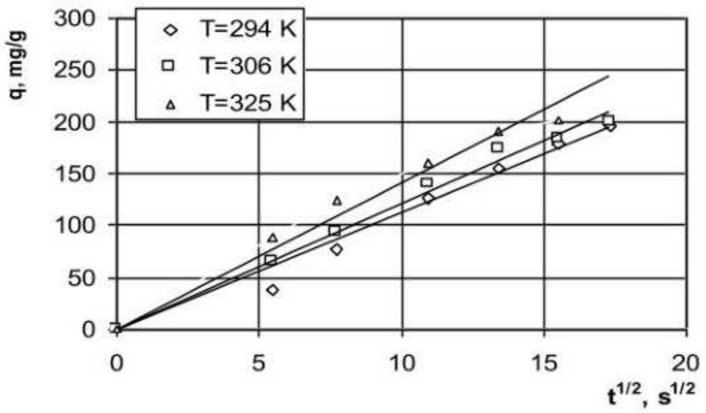

Figure 7. Verificarea modelului Weber- Morris

Table 3. Weber- Morris model checking

Temperature, K	Equation	K, $s^{-1/2}$	R^2
294	y= 11.224 x	11.224	0.9702
306	y= 12.086 x	12.086	0.9901
325	y= 14.070 x	14.070	0.9758

An additional confirmation of these results is supplied by the Dumwald- Wagner model.

Dumwald- Wagner model. The equation (11) proposed by Dumwald and Wagner for intraparticle model, cand be simplified as (12). A lot of ln (1- F^2) versus time should be linear [19] and the rate constant K can be obtained from the slope (Figure 8). The values obtained with our data are presented in the table 4.

$$F = \frac{q}{q_e} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-n^2 k\tau\right) \tag{11}$$

$$\ln\left(1 - F^2\right) = -K\tau \tag{12}$$

Table 4. The Dumwald - Wagner rate constant and the correlation coefficient

Temperature, K	Equation	K, s^{-1}	R^2
294	y= 0.0058 x	0.0058	0.9181
306	y= 0.0075 x	0.0075	0.9582
325	y= 0.0113 x	0.0113	0.9212

The application of this model is much simpler than the Boyd- Reichenberg procedure [20, 21] or other sophisticated models [22].But it does not allow to identify the effective diffusion coefficient inside the particle.

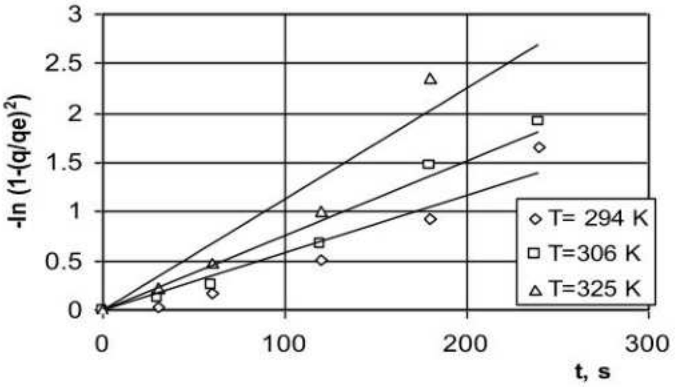

Figure 8. The validation of the Dumwald- Wagner model

Conclusion

The adsorption of tartaric acid (TA) from aqueous solution on weakly basic anion exchanger Amberlite IRA- 67 impregnated with a solution of liquid ion exchanger Amberlite LA-2 in n- hexane has been studied in batch equipment. The separation degree of TA was100% in a contact time less than 30 minutes for the following values of the 6 main factors: solid/ liquid loading > 1 g/L, T= 294 K, initial pH 2.5, initial TA concentration >1 g/L, particle diameter 0.4-1.2 mm, stirring 200 min^{-1}. These results proved the high effectiveness of the new sorbent.

The equilibrium q_e- c_e data were better correlated through the Langmuir isotherm (R^2= 0.9962) compared to the Freundlich one (R^2= 0.8535).This means the process was dominated by a chemosorption on energetically homogeneous surface.

The experimental curves q- τ has been confronted with 4 kinetic models, and the corresponding kinetic constants have been identified. The apparent activation energy has been obtained from the pseudo- second order rate constant. Its value (18.692 kJ/mol) indicated a mass transport phenomenon as rate determining step.Finally, the reasonable kinetic data correlation with the Weber- Morris model as well as with the Dumwald- Wagner model has shown that, under the investigated conditions, the slowest step of the process was the intraparticle diffusion.

Notation

c, adsorbate concentration in aqueous phase at the time τ, mg/L;

c_e, adsorbate concentration in aqueous phase at equilibrium, mg/L ;

d_p, resin particle diameter, mm;

E_a, activation energy, J/mol;

k_1, first- order rate constant, s^{-1};

k_2, second- order- rate constant, g mg $^{-1}$s^{-1};

k_{02}, frequency factor in Arrhenius equation;

K, rate constant of adsorption;

K_F, Freundlich adsorption constant;

K_L, Langmuir adsorption constant;

q_e, adsorption capacity at equilibrium, mg/g;

q_m, maximum adsorption capacity (monolayer) in Langmuir equation;

q, adsorption capacity at time τ, mg/g;

n, mixing rate, rpm (min^{-1}); empirical exponent in the Freundlich equation;

R_o, initial / total particle radius, mm;

R, gas constant (8.314 J/mol K);

τ, contact time, s.

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