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Removal of Citric Acid by Activated Carbon Adsorption

ISMAIL INCI
Department of Chemical Engineering, University of Istanbul,
Engineering Faculty, 34850 Istanbul, Turkey

The possibilities of removal of citric acid using activated carbon have been investigated. During the analysis initial citric acid concentration and amount of activated carbon have been taken into account. The experimentrs were conducted with aqueous solutions containing citric acid in four different concentrations (4, 4.5, 7, 13%, w/w). As adsorbent activated carbon was used in five different amount (0.005, 0.010, 0.015, 0.020, 0.025 g). Considerable amount of citric acid was removed by activated carbon. The amount of acid removed by activated carbon depends upon activated carbon amount. Experimental data were fitted into the Freundlich isotherm to obtain the values of adsorption parameters.

Key Words: Removal, Citric acid, Activated carbon, Adsorption.

INTRODUCTION

Schelle first isolated citric acid in the crystalline form in the year 1784 from the juice of lemons. Although an alchemist, Vincentius Bellovacensis in the year 1200 recognised that lemon juice and lime juice contained a special acid substance and referred in his Speculum Naturale, to the use of lemon juice as an acid solvent, citric acid (2-hydroxy-1,2,3-propanetricarboxylic acid) from the Latin word citrus, meaning originally the fruit of the lemon.

Citric acid is the most widely used organic acid in the field of foods and pharmaceuticals. Its palatabilty and the readiness with which it is assimilated have led to its utilization as an acid ingredient for maintaining pH or for adjusting to a favourable pH and to enhance flavour in a wide variety of products in these industries. Recently it has become an important raw material for general industrial use with many varied and expanding applications, as in the cleaning and polishing of iron and steel, as a component in certain nonferrous plating solutions, and in the treatment and conditioning of industrial water supplies. Citric acid is used in the preparation of alkyl resins, paints and lacquers and in printing and textile industries. Many salts, especially the neutral sodium salt, are extensively used in food and pharmaceutical products.

Production by the mold fermentation of sugar solutions, extraction from lemon and lime juice and extraction from pinneapple-canning residues constitute the three important methods of commercial manufacture of citric acid.

The traditional method of preparing citric acid was by extraction from the juice of acidulous fruits of certain citrus species. Besides the juice of genuine lemon, *Citrus medica*, there also was used, to a lesser extent, the juice of bergamot fruit, *Citrus bergamia.* The citric acid content of these juices is from 5 to 8%[1].

Adsorption is governed by the physcio-chemical properties of the adsorbent and adsorbate. In liquid phase adsorption, it is established that the adsorption capacity of an adsorbent depends on many factors, Firstly, it is in the form of adsorbent, such as its pore structure, ash content and functional groups. Secondly, the nature of adsorbate (*e.g.*, its functional groups, polarity, molecular weight, and size). Lastly, the solution conditions, referring to its ionic strength and adsorbate concentrations[2–9].

For removal of citric acid from aqueous solutions a lot of methods have been investigated . Inci[10–12] has used organic solutions of tertiary amines for recovering of citric acid and he obtained high distribution coefficients for citric acid. However, in this study the possibilities of citric acid from aqueous solutions have been investigated using activated carbon. Keeping in view the low cost investment, easiness of operation, physico-chemical treatment, an adsorption process has been selected. In this work, experimental results for adsorption of citric acid by activated carbon at 298 K are presented. All experimental data were then fitted into the Freundlich isotherm equation to obtain the corresponding factors.

Langmuir and Freundlich isotherm equations were found most suited for the present equilibria. The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. This model assumes uniform energies of adsorption into the surface and no transmigration of adsorbate in the plane of the surface. Langmuir equation is represented in the following equation:

$$(C_e/Q_e) = (K_1/Q^0) + (C_e/Q^0) \qquad (1)$$

where C_e is the equilibrium concentration (mg/L), Q_e is the adsorbed at equilibrium (mg/g) and K, Q^0 can be related to the equilibrium constant and sorption maxima respectively. The plot of C_e/Q_e *vs.* C_e gives a straight line showing the applicability of Langmiur isotherm. The values of K and Q^0 at different concentrations have been determined from the slope and intercept of the plot. The Freundlich equation is used for heterogeneous surface energies in which the energy term in the Langmuir equation varies as a function of the surface coverage strictly due to variation in the heat of adsorption. The Freundlich equation has the general form,

$$Q_e = K_f C_e^{1/n} \qquad (2)$$

A logarithmic plot linearizes the equation enabling the exponent n and the constant K_f to be determined [5–8],

$$\log Q_e = \log K_f + (1/n) \log C_e \qquad (3)$$

The constants are listed in Table-2 for the batch system. The values of K_f and 1/n at different concentrations were determined from the slope and intercept of the linear plots of Q_e *vs.* log C_e.

EXPERIMENTAL

The granular activated carbon and citric acid (99%) used in this work were supplied by Merck Co.

The adsorption experiments were carried out by placing different amounts of activated carbon with 5 mL of solutions containing different concentrations of citric acid. To observe the effect of initial citric acid concentrations on the adsorption, citric acid solutions were prepared at three different concentrations 4, 4.5, 7 and 13% (w/w). Aqueous solutions of citric acid and activated carbon at 5 different amounts (0.005, 0.010, 0.015, 0.020 and 0.025 g) were agitated in shaking bath for 4 h. All solutions were left in a temperature controlled shaking bath at 298 K. After adsorption experiments, the residue concentrations of the citric acid after filtration were determined by titration with 0.1 N aqueous sodium hydroxide[13]. Acid analysis was checked against a material balance.

RESULTS AND DISCUSSION

Results of adsorption of citric acid by activated carbon are given in Table-1. Effects of activated carbon amounts on adsorption are shown in Fig. 1. It will be seen from Table-1 that considerable amounts of citric acid are removed by activated carbon from aqueous solutions. The amount of acid removed strongly depends upon the activated carbon amount and initial citric acid concentration. The maximum removal of citric acid is 72.20% with 7% initial concentration of citric acid by 0.025 g activated carbon.

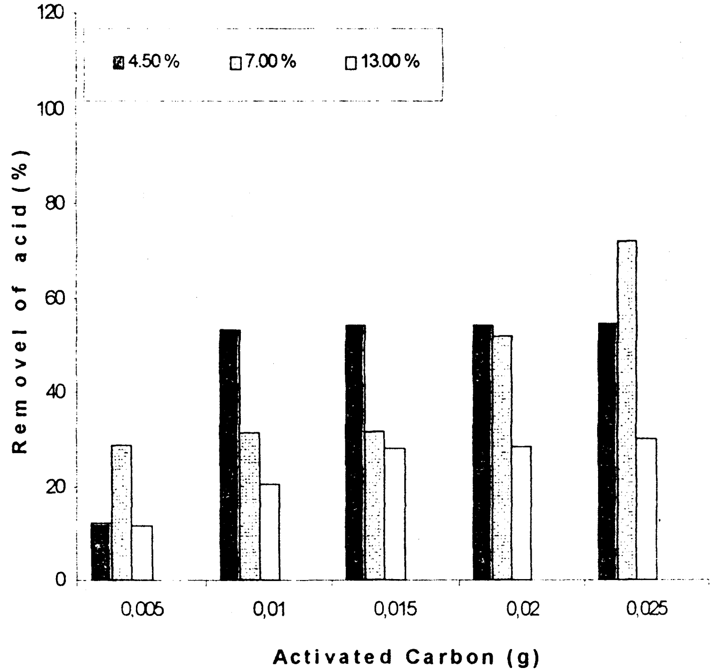

Fig. 1 Adsorption of citric acid

TABLE-1
EXPERIMENTAL RESULTS OF THE ADSORPTION OF CITRIC ACID INTO ACTIVATED CARBON

Initial concentration (g/L)	Initial concentration (% w/w)	Amount of activated carbon (mg)	Equilibrium concentration C_e (g/L)	Removal of acid (%)
47.12	4.50	0.005	41.36	12.22
47.12	4.50	0.010	24.97	47.00
47.12	4.50	0.015	21.55	54.26
47.12	4.50	0.020	21.50	54.37
47.12	4.50	0.025	21.48	54.41
75.26	7.00	0.005	53.63	28.74
75.26	7.00	0.010	51.74	31.25
75.26	7.00	0.015	51.41	31.69
75.26	7.00	0.020	36.27	51.80
75.26	7.00	0.025	20.92	72.20
149.42	13.00	0.005	132.06	11.61
149.42	13.00	0.010	119.00	20.35
149.42	13.00	0.015	107.45	28.08
149.42	13.00	0.020	107.12	28.30
149.42	13.00	0.025	104.23	30.24
41.66	4.00	0.010	24.38	41.47

It can be seen that the adsorption of citric acid increases with increasing amounts of activated carbon. The liquid concentration at equilibrium (C_e) decreases from 41.36 to 21.48 g/L with increase in the amount of activated carbon from 0.005 to 0.025 mg for 4.50 % (47.12 g/L) of initial concentration of citric acid. C_e decreases from 53.63 to 20.92 g/L with increase in the amount of activated carbon from 0.005 to 0.025 mg for 7.00% (75.26 g/L) of initial concentration of citric acid. The liquid concentration at equilibrium decreases from 132.06 g/L to 104.23 g/L with increase in the amount of activated carbon for 13.00% of initial concentration of citric acid. Isotherms of citric acid carbon are given in Fig. 2. The isotherms are plotted using a mass based acid concentration, Q_e (in mg of the solute adsorbed per gram of the carbon) *vs.* the liquid concentration (C_e) at equilibrium conditions. Adsorption isotherm was fitted into the Freundlich isotherm equations to calculate the isotherm parameters. The values of Freundlich parameters are $K_f = 3.78$ and $1/n = -1.04$.

The removal of citric acid from aqueous solutions by activated carbon could be due to physical mechanism. It should be remembered that carbons physically adsorb on their tremendous internal surfaces molecular compounds such as acids, complex ions, high molecular weight polymers or other nonpolar species.

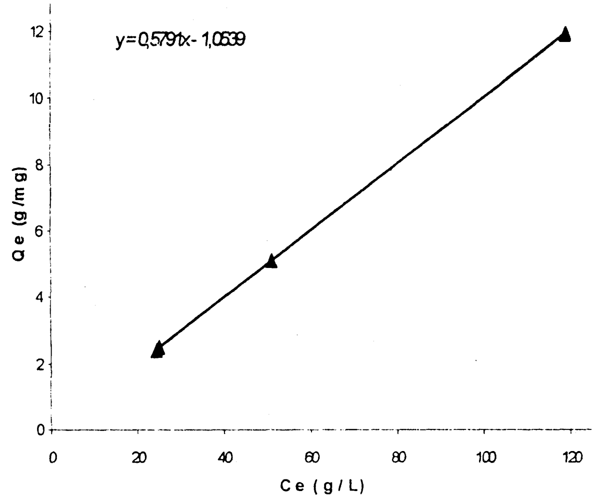

Fig. 2 Effect of activated carbon amount on citric acid adsorption

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