# Adsorption of Citric Acid from Aqueous Solution onto Activated P. Lentiscus Leaves

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## **Abstract**

The removal of citric acid, an organic ligand, from aqueous solution by adsorption onto activated Pistacia Lentiscus leaves' powder was investigated. Batch adsorption studies were performed to evaluate the effect of various operating parameters affecting the adsorption process such as pH, contact time, initial citric acid concentration and adsorbent dose. The optimum contact time for the equilibrium condition was 75 min. at the sorbent dose rate of 2.5g/L, while the best removal of CA was at pH 6. Isothermal and kinetic models were also carried out. The experimental kinetic adsorption data were in close agreement with second order rate kinetics expression. The obtained data were found to follow the three investigated isothermal models in the following order: Freundlich> Temkin> Langmuir, implying a heterogeneous sorption phenomenon. The infra red spactra of native and treated P. Lentiscus leaves confirmed adsorbate –adsorbent interaction responsible for sorption.

**Keywords:** Organic ligand, kinetics, isothermal model, infra red spectra, iodine number

### Introduction

Water pollution is considered one of the main problems around the world. Industrialization and agricultural development, together with population growth, has drastically reduced clean water resources <sup>1</sup>. Organic pollutants represent a major class of hazardous water contaminants especially for their persistence and poor biodegradability.

Citric acid (CA) is the most widely used organic acid in many industrial fields especially food and pharmaceuticals <sup>2</sup>. The main pathway through which citric acid enters the water bodies is from beverage, pharmaceutical, cosmetics, food, chemical as well as detergent industries<sup>3</sup>. Citric acid (CA), in excess amount, causes problems to flora and fauna and affects the aesthetic value of drinking water. Consequently, removal of CA from aqueous solution assumes great concern and is a challenge for researchers who are actively participating in the field of environmental hazardous waste management <sup>4</sup>.

Many methods have been reported for water decontamination including chemical precipitation, reverse osmosis, membrane filtration and adsorption<sup>4</sup>. In the recent years researches have been extensively directed towards adsorption process for its ease of application as well as its cost effectiveness.

A number of adsorbents have been investigated for their efficiencies towards the removal of organic contaminants from aqueous solution. Only few studies have considered the adsorption process for citric acid removal from water. The adsorbents reported in this respect included kaolinite and illite<sup>5</sup>,

activated carbon <sup>2</sup> activated charcoal <sup>6</sup>, pseudoboehmite, clays<sup>7</sup> and activated carbon prepared from *Havea braziliansis* sawdust<sup>3</sup>.

The usage of waste lignocellulosic materials as adsorbents for treating effluents has been reported by many authors. The adsorption capacity of lignocellulosic materials can be increased by chemical/physical means <sup>4</sup>

Pistacia lentiscus L. is an evergreen shrub of the Anacardiaceae family <sup>8</sup>. The tree is widely distributed in Egypt <sup>9</sup>. Thus the aim of the present work was to investigate the use of *P. lentiscus* tree leaves powder after chemical activation for the removal of citric acid from aqueous solutions and to study the effect of different operating parameters on the adsorption process.

#### **Material and Methods**

Adsorbents preparation: *P. lentiscus* leaves were collected from local gardens in Egypt. The leaves were washed with running water and air dried. Dry leaves were then ground with an electrical grinder. The leaves were then further dried at 100°C for 24 hours until constant weight. The dry leaves' powder was soaked in (8, 16 and 24 %) sodium hydroxide solution over night at room temperature. The leaves powder was collected by filtration and was washed several times with distilled water. Finally *P. lentiscus* leaves powder chemically activated by sodium hydroxide was oven dried until constant weight. The obtained adsorbents were designated PL8, PL16 and PL24 for the chemical activation using 8, 16 and 24 % sodium hydroxide; respectively.

**Adsorbent characterization:** The dried leaves powder was characterized by FTIR (Perkin-Elmer FT-IR 1650 spectrophotometer, dilution with KBr) to identify the functional groups that might be involved in the adsorption process.

The iodine number of activated adsorbents was obtained using the standard test method, ASTM designation D4607- 86 by titration with sodium thiosulphate<sup>10</sup>. The concentration of iodine solution was thus calculated from total volume of sodium thiosulphate used and volume dilution factor.

**Batch adsorption experiment:** Adsorption of citric acid from aqueous solution by chemically activated *P. lentiscus* leaves was examined using batch experiments at various physicochemical parameters including: pH (3,4,5 and 6), contact time (15, 30, 45, 60, 75 min.), initial concentration of citric acid (1.0, 2.0, 3.0, 4.0 and 5.0 mmol/ L) and biosorbent dose (1.5, 2.5,3.5, 4.5 and 5.5 g/L) . 50 mL of the citric acid solution was mixed with the biosorbent in stoppered conical flasks and the suspensions were equilibrated by shaking (200 rpm) at a fixed temperature using a shaking water bath for the desired contact time. After equilibration, the solutions were filtered and the concentration of CA was determined using a method described earlier by Inci, 2004. The removal efficiency was calculated according to the following equation:

Removal efficiency (R) =  $(C_o-C_f) \times 100/C_o$ And the adsorbent capacity was calculated as:Q= [ $(C_o-C_f)$  V]/ m

Where, the capacity (Q) is the amount of CA adsorbed onto unit amount of adsorbent (mmol/g);  $C_o$  and  $C_f$ , initial and equilibrium solution concentration (mmol/L), respectively; V, volume of aqueous phase (mL) and m, mass of the biosorbent (g).

All chemicals/reagents used in this study were of analytical grade obtained from Merck Company.

#### Results and discussion

Effect of contact time on the adsorption of citric acid on the different adsorbents: The contact time is one of the important parameters that should be considered in batch adsorption experiments. A rapid uptake of pollutants and establishment of equilibrium in a short period signifies the efficiency of the adsorbent for its use in wastewater treatment. In addition to this, the contact time is one of the factors for the development of surface charges at the solid solution interface<sup>11</sup>.

Figure- 1 shows the effect of contact time on the removal percentage of citric acid on the three produced adsorbents (PL8, PL16 and PL24). It can be observed that the removal of citric acid increased by increasing contact time and reached equilibrium at 90 min. for PL8 and PL24, whereas in case of PL16 the equilibrium was attained at 75min. It can also be observed from Figure 1 that at the same experimental conditions

the removal percentages of CA onto the studied adsorbents was in the order PL16> PL24> PL8.

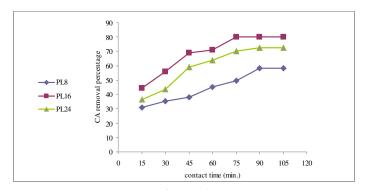


Figure -1

Effect of contact time on the removal percentage of citric acid on the three PL8, PL16 and PL24 at 1mmol/L initial CA concentration, adsorbents loading weight 2.5g/L.

Determination of the iodine number of the adsorbents: The total surface area of an adsorbent is made up of external and internal surfaces. The iodine number gives information of the internal surface of an adsorbent<sup>12</sup>. Thus the iodine numbers for PL8, PL16 and PL24 were obtained by titration with sodium thiosulphate <sup>10</sup>. Figure- 2 gives the iodine number of *P. lentiscus* leaves treated with different concentrations of NaOH. According to<sup>13</sup> the increasing amount of NaOH used for activation may contribute to the development of internal microporous cavities, resulting in an increased surface area which is considered to be the most important factor for adsorption. From figure 2 it can be concluded that the highest iodine numbers was obtained for PL16, suggesting that a concentration of 16% NaOH is more efficient than 8 and 24% in the activation of P. lentiscus leaves powder. Thus further experiments will be focused on the study of different operational conditions that affect the removal of CA onto PL16 and a reaction time of 75 min was employed for all the subsequent studies and this time was enough to ensure that adsorption equilibrium was reached.

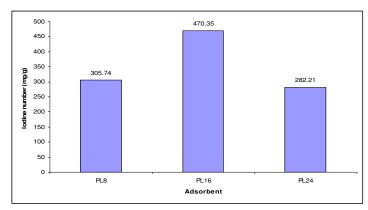


Figure -2

Effect of different NaOH percentages on the produced activated adsorbents' in terms of their iodine adsorption values.

Effect of pH on citric acid removal: The influence of pH on the removal of citric acid onto PL16 was investigated at different pH values ranging from 3.0 to 6.0 at the predetermined equilibrium time (75 min.) and at fixed citric acid concentration (1mmol//L) with and adsorbent loading weight of 2.5g/L figure- 3. The amount of CA adsorption on activated *P. lentiscus* leaves increased with increasing pH from 3 to 6 at 1mmol CA after 75 min. Our findings are in good agreement with those of <sup>3</sup> who found that at low pH values (pH<5) there is a steady decrease in the adsorption of citric acid on sawdust activated carbon (SDAC) used as adsorbent. These findings were attributed to the possibility that increasing concentration of CA which is unable to adsorb on the carbon surface.

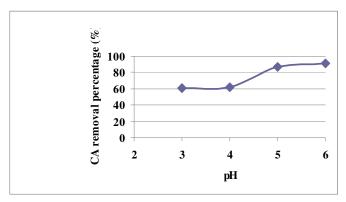


Figure- 3
Effect of solution pH on the removal percentage of citric acid on PL16 at 75min. contact time, 1mmol/L initial CA concentration, and adsorbents loading weight 2.5g/L.

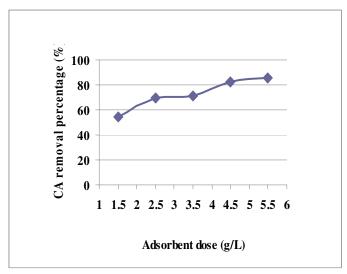


Figure- 4
Effect of adsorbent loading weight on the removal percentage of citric acid on PL16 at 75min. contact time, 1mmol/L initial CA concentration.

**Effect of adsorbent dose:** The effect of PL16 loading weight (1.5, 2.5, 3.5, 4.5 and 5.5 g/L) on the removal of CA from aqueous solutions of initial concentration 1 mmol was investigated figure- 4. It is expected that an increase in the dosage of adsorbent should yield a corresponding increase in the amount of metal ion adsorbed onto the surface of the adsorbent since there will be more sites for the adsorbate to be adsorbed. Therefore, competition for bonding sites between molecules of the adsorbate should decrease with increase in dosage of the adsorbent 14.

From the figure it is clear that as the adsorbent dose increase the amount of adsorption also increase. This is attributed to the fact that increasing the adsorbent's dose leads to the increase of its surface area and thus to the availability of more adsorption sites that are produced 15, 16,17,3.

Effect of initial citric acid concentration: The effect of initial citric acid concentration (1, 2, 3, 4 and 5 mmol/L) on its removal by adsorption onto PL16 is illustrated in figure 5. It is clear from the figure that there is maximum CA removal with lower initial concentrations. These observations can be explained by the fact that at low CA concentration, the ratio of adsorption sites of the adsorbent surface to the total CA molecules available is high and thus, there is a greater chance for its removal.

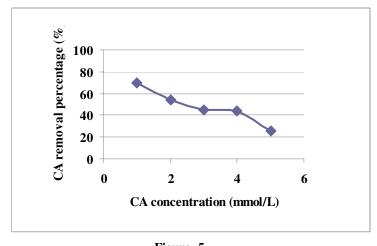


Figure -5
Effect of initial CA concentration on its removal percentage on PL16 at 75min. contact time, adsorbent loading weight 2.5g/L.

**Adsorption kinetics:** Adsorption kinetic studies are important for the evaluation of the basic traits to determine of a good adsorbent. The present work considered the application of three kinetic models namely, pseudo-first and second order kinetics, and intra-particle diffusion to fit the obtained experimental data. Pseudo-first-order and pseudo-second-order equations developed by<sup>18,19</sup>

The Lagergren pseudo-first-order developed by  $^{18}$  is represented by the equation:  $\log (Q_e-Q_t) = \log Q_e-K_1t/2.303$ 

Where,  $k_1$  is the rate constant of pseudo-first-order adsorption and  $Q_{\rm e}$  and  $Q_{\rm t}$  denote the amount of adsorption at equilibrium and at time t respectively.

The pseudo-second order equation is expressed in the equation given by  $^{19}$  as:  $t/Q_t = 1/k_2 Q_e^2 + t/Q_e$ 

Where,  $q_e$  and  $q_t$  are the amount of metal ion adsorbed (mmol/g) at equilibrium and at time t respectively.

The intraparticle diffusion mechanism  $^{20}$  can be described as:  $Q_t = K_b t^{1/2}$ 

Where,  $K_b$  is intraparticle diffusion rate constant (mg/g min<sup>1/2</sup>). The  $K_b$  is the slope of the straight line portion of the plot of  $Q_t$  vs.  $t^{1/2}$ 

Plots of the Lagergren, pseudo-second order and intraparticle diffusion kinetic models are presented in figures- 6, 7 and 8; respectively.

The first-order, the second-order and intraparticle diffusion sorption rate constants as well as their correlation coefficients obtained for each model are presented in table -1. It can be concluded that the obtained correlation coefficients for the second-order kinetic model is greater than those obtained for the first-order and intraparticle models. The theoretical Qeq value calculated from the pseudo second-order kinetics was found to be very close to the experimentally obtained Qeq value. This suggests that the sorption system is the second-order model, based on the assumption that the rate determining step may be the adsortion which provides the best correlation of the data<sup>21</sup>.

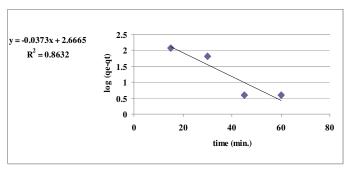


Figure-6

The Lagergren first order kinetic model for the adsorption of CA onto chemically activated *P. lentiscus* leaves (PL16).

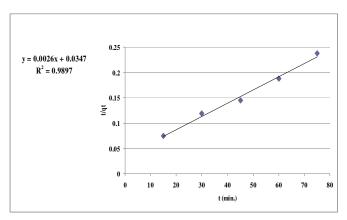


Figure -7

The pseudo-second order kinetic model for the adsorption of CA onto chemically activated *P. lentiscus* leaves (PL16).

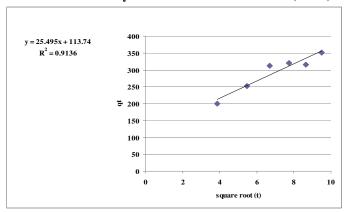


Figure -8

The intraparticle diffusion kinetic model for the adsorption of CA onto chemically activated *P. lentiscus* leaves (PL16).

**Adsorption isothermal modeling:** The adsorption isotherm indicates how the molecules subjected to adsorption distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The analysis of the isotherm step to find the suitable model that can be used for design purposes <sup>22</sup>. The present adsorption isotherm study was carried out on three isothermal models such as Langmuir, Freundlich and Temkin.

Table -1
Kinetic parameters for the adsorption of CA onto treated *P. lentiscus* leaves

First-order kinetic model			Second-order kinetic model			Intra-particle diffusion model		q <sub>e</sub> (exp)
$\mathbf{K}_{1}$	Qe	$R^2$	$K_2$	Qe	$\mathbb{R}^2$	K <sub>p</sub>	$R^2$	216
0.085	463	0.863	1.176×10 <sup>-4</sup>	384	0.989	25.49	0.913	316

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In the Langmuir theory, the basic assumption is that the sorption takes place at specific homogeneous sites within the adsorbent, this equation can be written as follows  $^{23,24}$   $C_e/Q_e = 1/bQ_0 + C_e/Q_e$ 

Where Qe is the amount of CA adsorbed on activated treated P. *lentiscus* leaves (mg/g), Ce is the equilibrium concentration (mg/l), b is the adsorption equilibrium constant (l/mg) and Qo is the maximum adsorption capacity. A plot of Ce/Qe versus Ce figer- 5 gives the adsorption coefficients. A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter ( $R_L$ ), which is indicative of the isotherm shape that predict whether an adsorption system is favourable or unfavourble.  $R_L$  is defined as  $^{25}$ :

$$R_L = 1/(1+bC_0)$$

where, b is the Langmuir constant. Values of  $R_L$  for citric acid concentration are given in table- 2. The adsorption process as a function of  $R_L$  may be described as  $^{26}$ : unfavourble when  $R_L > 1$ ; linear when  $R_L = 1$ ; favorable when  $0 < R_L < 1$ ; irreversible when  $R_L = 0$ . In all cases, the  $R_L$  values for the present experimental data fall between zero and one, which is an indication of the favourable adsorption of the treated P. lentiscus leaves.

 $Table - 2 \\ Different \ values \ of \ R_L \ for \ the \ different \ concentration \ of \ citric \\ acid$ 

Concentration of Citric acid mmol/ L	$\mathbf{R}_{\mathrm{L}}$
1	0.347826
2	0.210526
3	0.150943
4	0.117647
5	0.096386

The Freundlich isotherm is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface, Freundlich equation is expressed by the flowing equation <sup>27</sup>:

 $\log Q_e = \log K_f + 1/n \log C_e$ 

Where  $k_f$  and n are the Freundlich constants which represent adsorption capacity and adsorption intensity, respectively. The Freundlich constants were determined from the slope and intercept of a plot of log  $Q_e$  versus log  $C_e$  figer- 6. The correlation coefficient of the Freundlich plots is relatively higher according to Langmuir plots.

The Temkin equation suggests a linear decrease of sorption energy as the degree of completion of the sorption centers of an adsorbent is increased. The heat of adsorption of all molecules in the layer would decrease linearly with coverage due to adsorbent-adsorbate interactions. The adsorption is characterized by a uniform distribution of binding energies, up to maximum binding energy. The Temkin isotherm can be expressed in the flowing linear form<sup>28,27</sup>

 $Q_e = B \ln A + B \ln C_e$ 

Where B = RT/b, A is the equilibrium binding constant (l/mg), B is related to the heat of adsorption. A plot of Q<sub>e</sub> versus ln C<sub>e</sub> figer- 7 enables the determination of the isotherm constants. The Temkin isotherm constants were given in table 3. The three models adsorption constant evaluated from isotherms with their corresponding correlation coefficient are presented in table 3. As seen from table -3, very high regression correlation coefficients ( $R^2 > 0.9$ ) were found the Freundlish model. According to these results, the freundlish model is more suitable for describing the biosorption equilibrium of CA by treated P. lentiscus leaves with 4M NaOH an adsorption isotherm is characterized by certain constants; the values of which express the surface properties and affinity of the sorbent and can also be used to find the biosorpitive capacity of biomass. The values of R<sup>2</sup> are regarded as a measure of the goodness of fit of experimental data on the isotherm models <sup>29</sup>. The applicability of the three isotherm model for the present data follows approximately the order: Freundlich> Temkin> Langmuir.

Table -3
Isothermal parameters for citric acid removal onto chemically activated P. *Lentiscus* leaves' powder

enemically activated 1. Lettiscus leaves powder									
Isotherm	Constants								
	$\mathbf{Q_0}$	b	$\mathbf{R}_{\mathrm{L}}$	$\mathbb{R}^2$					
Langmuir	666.66	1.875	0.347826	0.9093					
		K	n	$R^2$					
Freundlich		384.5	1.388	0.9986					
		В	A	$R^2$					
Temkin		584.2	1.7688	0.934					

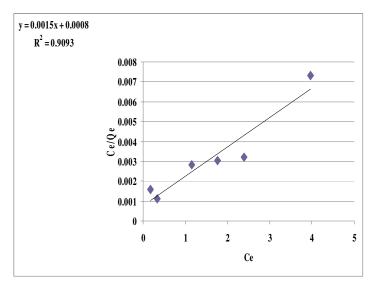


Figure-9
Langmuir isotherms linear adsorption for citric acid.

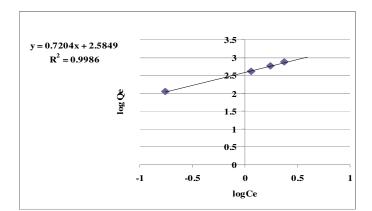


Figure-10 Freundlich isotherms liner adsorption for citric acid.

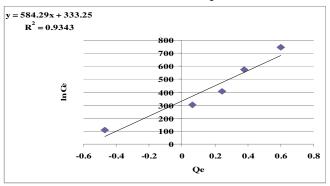


Figure-11
Temkin isotherms liner adsorption for citric acid

FTIR characterization of P. Lentiscus leaves' powder: Activated P. Lentiscus leaves' powder was characterized by Fourier transformation infra red spectroscopy (FTIR) to identify the functional groups that might be involved in the adsorption process. Figures -12 and 13 show the FTIR spectra of treated P. lentiscus leaves before and after adsorption experiment. Several peaks were observed from the spectra indicating that P. lentiscus leaves are composed of various functional groups and the differences observed between the spectra before and after adsorption indicate the involvement of the adsorbent surface functional groups in the adsorption process. The spectra revealed the presence of a broad peak at wave number 3426.89/cm indicating surface bonded hydroxyl groups (OH) this band was shifted to 3423.99/ cm after adsorption. A peak at 2932.23/cm that was attributed to the presence of C-H stretching, this peak was shifted to 2924.52/ cm after adsorption. The band observed at 1610.27/cm representing carboxylic group was shifted to 1621.84/cm which was more intense after adsorption. The bands indicating the symmetric bending of CH<sub>3</sub> observed at 1449.24, 1409.71/ cm were merged after adsorption in one band at 1423.21/cm. A sharp peak at 1067.4/cm that might be attributed to the presence of O-H alcohols (primary and secondary) and aliphatic ethers was transformed to broad peak at 1054.87/cm. The bands at 1220.72/cm and 740.531/cm assigned to the C-O stretching of COOH and C-H bending respectively disappeared after adsorption.

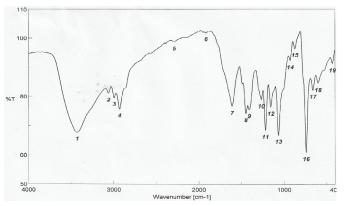


Figure-12
FTIR spectra of activated *P. lentiscus*leaves before adsorption

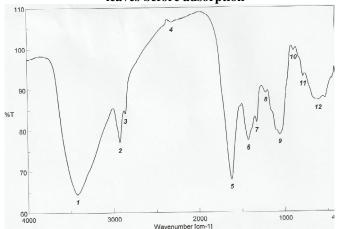


Figure-13 spectra of activated *P. lentiscus* leaves after adsorption

#### Conclusion

The results obtained from the present study suggest the possible use of a widely available and environmental friendly material as an adsorbent for water treatment. *P. lentiscus* leaves powder chemically activated by sodium hydroxide showed good capability for the removal of citric acid present in aqueous solutions. Further studies could be directed towards the investigation of the use of P. *lentiscus* leaves powder for the removal of other organic pollutants.

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