

Use of Iraqi Cherry Seeds in the Removal of Paracetamol and Atenolol Medicines from Their Aqueous Solutions

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Abstract: This study describes using Iraqi cherry seeds surfaces (ICS) in the removal of paracetamol (PL) and atenolol (AL) medicines from their aqueous solutions via adsorption on the CSS. The time of adsorption equilibrium for the PL medicine was 2 hours and that for AL was one hour. The following of these medicines in their aqueous solutions were conducted using UV-Visible spectrophotometer. It was found that the optimum weight for PL was 0.1 g and it was for AL 0.05 g. Adsorption capacities for these medicines were ranged from 1.155 to 1.430 mg/g at temperature range from 313 to 333 K and pH values 2-14. Both of Freundlich and Langmuir adsorption isotherms were investigated. Thermodynamic parameters such as enthalpy ΔH , Gibbs free energy ΔG and change in the entropy ΔS for adsorption of these medicines were also performed. The negative values for ΔH indicate that, adsorption processes were exothermic, and the positive values of ΔG indicate that, it was non-spontaneous process. Also the negative value of ΔS , indicates that there was reduction in the entropy for the adsorption processes. This study showed that removal of AL on the ICS was more efficient than that for PL under the same reaction conditions.

Keyword: Cherry seeds, Adsorption of paracetamol, Adsorption of Atenolol

1. Introduction

Water is a very important solvent for all living organisms on our planet; also it is excellent solvents for a wide range spectrum of materials in our daily life. As a result of industrial revolution and consequently huge amounts of water are consumed in this manner. This leads to pollute the water; important examples of this type of pollution are the acid rains, sewage water and industrial wastewaters¹. Water is essential liquid for the life; it composes 75-95% from the total plasmatic weight in living organisms. Beside that most of biochemical processes are performed in aquatic media². Polluted water possesses changes in its physical and/or chemical properties such as appearance, color, odor, density, and electrical conductivity³. Generally, water pollution can be categorized into types; first one is the natural pollution which normally appears as change in its temperature, or increasing in the level of salts in water and increase in the amount in suspensions in the water. The second type is the chemical pollution of water; this may arises from sewage sources, oil leaks, agricultural fertilizers, and pesticides⁴. However, there are some protective arrangements that can be followed to avoid water pollution before its occurrence. These involve pretreatment of the sewage water before its follow into the water streams and pipes. Also establishment of treatment unit in each industrial activity to deal with industrial water before its effluent into the stream water⁵. Currently, there are some methods that are used in treatment of polluted water. For example, pollution with organic materials can be treated using adsorption processes over highly porous materials such as activated carbon, ash, silica and alumina⁶⁻¹⁰. In this context, cherry seeds can be used as a good candidate to adsorb pollutants from the solution^{11, 12}. It has been reported that paracetamol can be converted into toxic compounds in the sewage water as the circulation units of wastewaters is recycled this water via oxidation with javal water. Under these circumstances and in case of the presence

of hypochloride (ClO^-), paracetamol convert into n-acetyl-para-benzoquinone amine -1,4- benzoquinone. The last derivative is very toxic compound and can cause liver poisoning^{13, 14}. Generally, Industrial sewage water can be treated utilizing some methods¹⁵ such as chemical oxidation using ozone O_3 and hydrogen peroxide H_2O_2 ¹⁶ and photocatalytic oxidation¹⁷. Beside that reverse osmosis can be used to separate solvent from the solution and accordingly pure water can be obtained according to this technique¹⁸

The current study investigates the removal of some organic polluted medicines such as paracetamol and atenolol from their aqueous solutions over ICS using adsorption concept.

2. Experimental Part

2.1 Preparation of the adsorbent

Iraqi cherry seeds were collected from the local markets; the nuts of these seeds were extracted from the whole seeds. Then these nuts were washed with distilled water for some times and then immersed in distilled water for 48 hours. Then, it was filtered of and dried for 24 hour at 110°C. Then these nuts were burned at 600 for three hours under nitrogen flow. After calcination it was grinded finely and powdered with molecular sieve of porosity size of 600 micrometer. Then it was ready to be used as adsorbent to remove the medicines that were used in the current study.

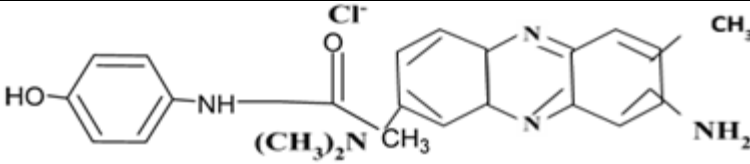
2.2 Used Materials

2.2.1 Paracetamol

Paracetamol or Acetaminophen is the used name in the United States; this is extracted from the tar, and can be used for general treatments such as high fever, headache as well as other simple infections¹⁹⁻²¹. It was provided from BDH Company and it was used in this study during its use validity

before its expiry date. Some of its chemical properties are summarized in Table 1.

Table 1: Some of chemical properties of PL medicine Paracetamol

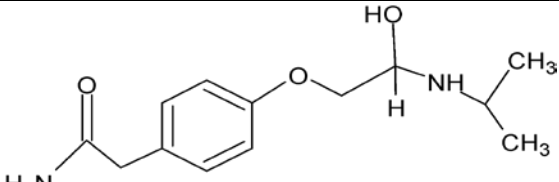
Structure of dye	Specification sheet	
		$C_8H_9NO_2$
151.17		Molar mass
169 °C		Melting point
B.D.H company		Source
Water + alcohol		Solubility
N-(4-hydroxy phenyl)acetamide		

2.2.2 Atenolol

This medicine is chemically denoted as 2-[4-(2RS)-2-hydroxy-3-[(1-methylethylethyl) amino] propoxy] phenyl] acetamide. Atenolol can be used in wide range of treatment and it works by competing for the receptor sites in case of muscle cardiac²².

This medicine was provided by BDH Company and it was used in its validity expiry date. Some of its chemical properties and structure are summarized in Table 2.

Table 2: Some of chemical properties of AL medicine

Atenolol		
Structure of dye	Specification sheet	
		$C_{14}H_{22}N_2O_3$
266.336		Molar mass
NA		Melting point
B.D.H company		Source
Water + Alcohol		Solubility
Rs-2-(4-(2-hydroxy-3-(propan-2-ylamino)propoxy)phenyl)acetamide		

2.2.3 Preparation of solutions of the used medicines

Solutions of both medicines were prepared by dissolving of 0.1 g of each one in 200 mL of distilled water volumetric flask to get a stock solution of 50 ppm. From these stock solutions a series of diluted solutions ranged from 2-20 ppm were prepared. Using these solutions in the determination of the maximum absorption for each medicine by measuring the absorbance at the range of 200-800 nm. The maximum absorption for PL was 240 nm and 220 nm for AL. Then the calibration curve was established using standard prepared solutions for each one. This calibration curve is shown in Figure 1.

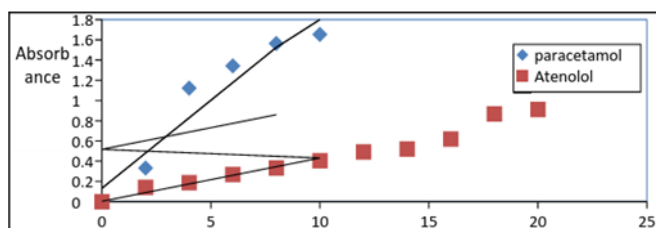


Figure 1: Calibration curve for both PL and AL recorded at 240 and 220 nm respectively

2.2.4 Determination of Optimum Time for equilibrium adsorption

In order to estimate the time that is required to reach equilibrium for the adsorption of both PL and AL from their aqueous solutions, 15 mL (20 ppm) of each medicine with 0.20 g of CSS at 313 K. The change in adsorption was followed in the range 0.5- 4.0 hour and it was found that, the equilibrium for PL was reached in 2 hr for PL and 1 hr for AL.

2.2.5 Adsorption of isotherms

The adsorption isotherm for each medicine was conducted by preparing ten concentrations for each medicine in 100 mL. Then 15 mL was taken from each solution and added to the weighted quantity of CSC at an optimum time in 50 mL conical flask. These flasks then shaken in water bath controlled temperature shaker at 313 K. Then these solutions were filtered off, and then the absorbance was recorded for the supernatant liquids.

2.3 The effect of dosage of the adsorbent

To investigate the effect of the amount of the adsorbent on the adsorption of the medicines, 15 mL (20 ppm) of each medicine with different masses of CSS (0.05, 0.10, 0.20, 0.30, 0.40, and 0.50 g) at 313 K with the optimum time for each medicine. (The best weight was 0.2 g for PL and 0.05 g for AL) 2.7 The effect of pH

To study the effect of pH, 15 mL (20 ppm) of each medicine was taken at pH ranged from 2 to 14 at 313K

2.4 The effects of temperature

In order to study the effect of temperature on the adsorption of these two medicines, 15 mL (20 ppm) of the aqueous solution of each medicine was taken with the best weight for each case in the range of temperature (313, 323, and 333 K). After recording the absorption of the supernatant liquid, from the obtained results it can be indicated that if the reaction was exothermic or endothermic. This can be concluded from the relation between the amount of the adsorption and the temperature of the adsorption process. If the amount of adsorbate was increased by increasing temperature then it will be endothermic reaction and the vice versa.

3. Results and Discussion

3.1 Adsorption ability on the cherry seeds surfaces

The adsorption ability of CSS was investigated by following the removal of both PL and AL from their aqueous solutions. The time that is required to reach equilibrium for the adsorption of both PL and AL. These results are shown in Figure 2. From these results it was found that, the equilibrium for PL was reached in 2 hr and 1 hr for AL. The reason for that is probably due to the presence of negatively charged species that are facilitated their adsorption on the surface of cherry seeds. These results are summarized in Figure 2.

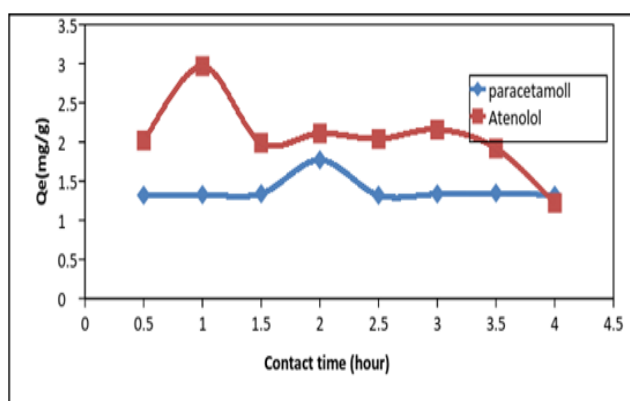


Figure 2: The effect of contact time on the adsorption of PL and AL on the ICS

3.2 Effect of the weight of the adsorbent

The effect of the amount of the used adsorbent on the adsorption was investigated by following the adsorption of PL and AL from their aqueous solutions at 313 K. The best optimum weight for PL was 0.2 g for PL and 0.05 g for AL.

This arises from the adsorption of the adsorbate species on the surface of the adsorbent²³. These results are shown in Figure 3.

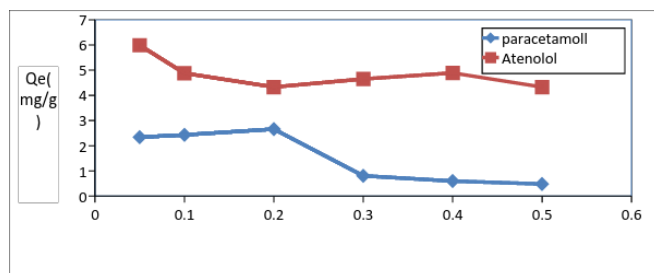


Figure 3: The effect of the weight of the adsorbent on the adsorption of the medicines from their aqueous solutions

From these results it was found that the adsorption of AL over ICSS was more efficient than that for PL under the same adsorption conditions. This probably arises from a higher molecular weight of AL which results in reduction in its polarity and its ionization in the solution. Besides that, molecules of AL may adsorb vertically on the surface and hence occupy small adsorption sites on the surface and accordingly adsorb extra amounts of this medicine in comparison with that for PL²⁴. Lower adsorption of PL probably arises from electrostatic repulsion between the medicine molecules and the surface of the adsorbent. Also the presence of hydroxyl group in the structure of PL molecule makes this dye adsorb horizontally with the surface and hence occupy large adsorption sites on the surface which leads to reduce the amount of the adsorbed medicine in this case²⁴

3.3 Adsorption isotherms

The adsorption isotherm for each medicine was conducted by preparing ten concentrations for each medicine in 100 mL. Then 15 mL was taken from each solution and added to the weighted quantity of CSC at an optimum time in 50 mL conical flask. These flasks then shaken in water bath controlled temperature shaker at 313 K. Then these solutions were filtered off, and then the absorbance was recorded for the supernatant liquids. The amount of the adsorbate for each case was estimated according to the following equations²⁵⁻²⁷:

$$Q_e = \frac{V_{sol}(C_o - C_e)}{m}$$

Where, (Q_e) is the amount of the adsorbate in mg/g, (C_e) is the concentration of each adsorbate at equilibrium mg/L, (C_o) is the initial concentration of the adsorbate in mg/L and (V_{sol}) is the total volume of the used solution of the adsorbate in L, and (m) is the weight of the adsorbent in g. Figure 4 below shows adsorption isotherms for the adsorption of the medicines PL and AL from their aqueous solutions on the Iraqi cherry seeds surfaces at 313 K under optimum weight of adsorbent and optimum pH for each case. However, the general features of these isotherms indicate that there is strong interaction between adsorbate and the surface of the adsorbent. These results are summarized in Figure 4.

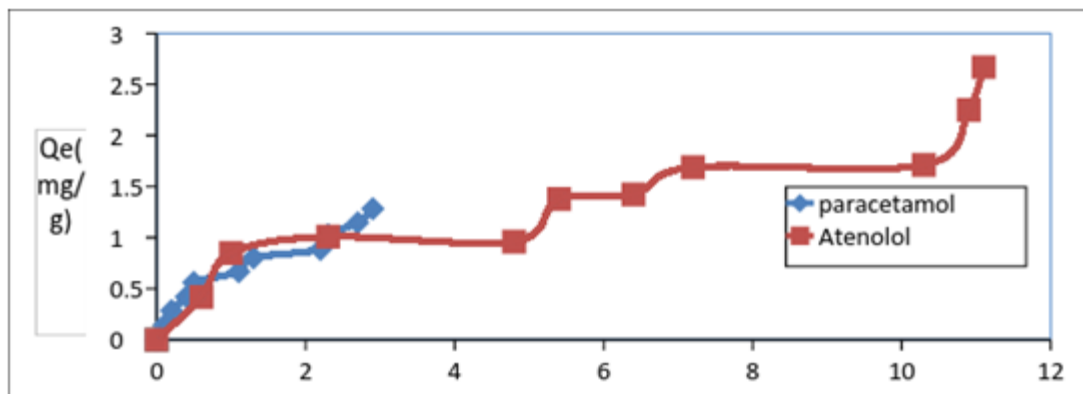


Figure 4: Adsorption isotherm for the adsorption of both the PL and AL from their aqueous solutions on the ICS at 313 K

These results were re-plotted according to Freundlich isotherm (Figure 5) and Langmuir isotherm Figure 6.

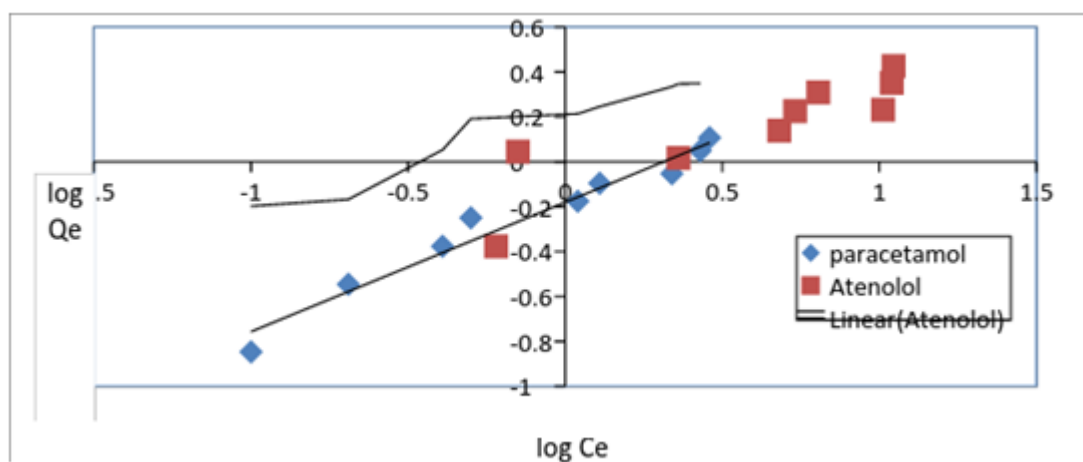


Figure 5: Freundlich adsorption isotherm for the adsorption of PL and AL at 313 K on ICS

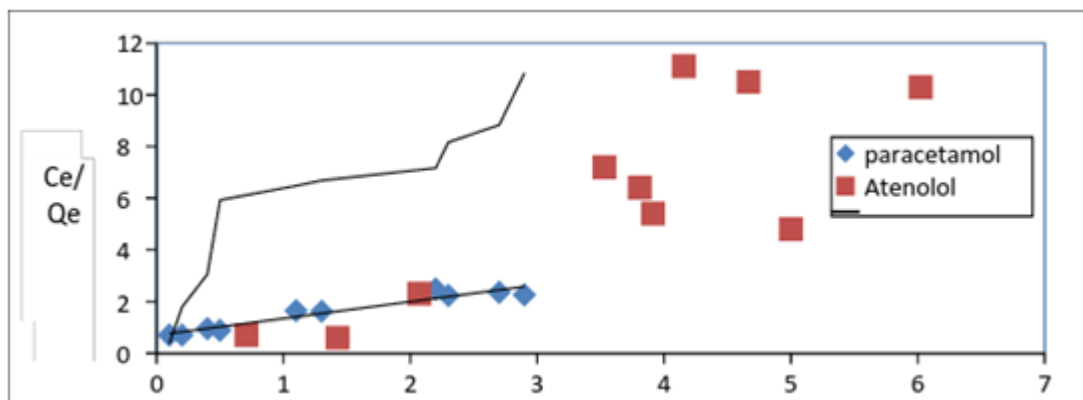


Figure 6: Langmuir adsorption isotherm for the adsorption of PL and AL at 313 K on ICS

3.4 Effects of pH on the adsorption

The effect of pH of solution on the adsorption of each of PL and AL from their aqueous solutions on ICS was studied at different pH values (pH=2-14). It was found that the effect of pH was varied according to the type of the used medicine. The best absorption was obtained at pH =4, this probably arises from the effect of the activity of the basic groups on these medicines. This relatively lower pH value can minimize the repulsion forces between adsorbate molecules

and the surface. This can promote molecules to adsorb on the surface with high efficiency under this conditions²⁸⁻³⁰. These results are summarized in Figure 7.

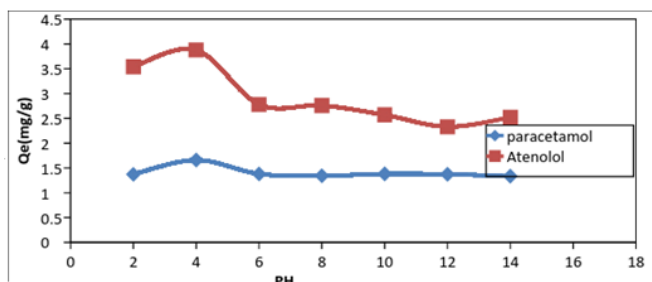


Figure 7: The effect of pH on the adsorption of PL and AL on the surface of ICS

3.5 Effects of temperature on the adsorption of medicines

In this study, it was found that the amount of the adsorbed medicine was reduced with increasing reaction temperature. The negative values of ΔH indicate that, this process is an exothermic reaction. This also means that there is absorption processes beside adsorption processes³¹. Increase in temperature of reaction leads to increase amount of molecules that are adsorbed on the surface and then these molecules are diffused into the internal pores in the surface of the adsorbent³²⁻³⁵. The results of effect of temperature on the adsorption are shown in Figure 8.

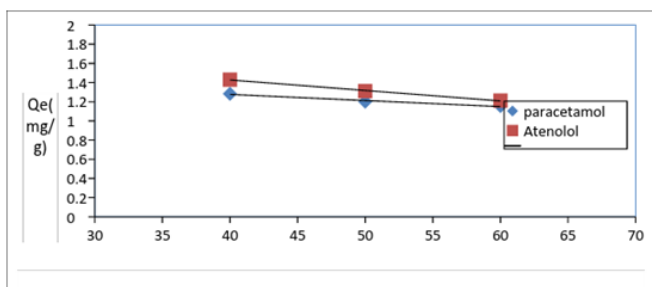


Figure 8: The effect of temperature on the adsorption of the used medicines on the surface of ICS

Table 1: Freundlich adsorption constants calculated at 313 K

Dyes	K_f	n	R^2	a	k	R^2
Paracetamol	0.661	1.736	0.966	0.649	1.436	0.927
Atenolol	0.791	2.3148	0.799	1.970	0.975	0.692

Table 2: Thermodynamics values for adsorption of AL and PL medicines on ICS at 313 K

Dyes	$\Delta H(Kj.mol^{-1}.k^{-1})-$	$\Delta G(Kj.mol^{-1}.k^{-1})+$	$\Delta S(j.mol^{-1}.k^{-1})-$
Paracetamol	1.5319	2.124	11.68
Atenolol	0.962	3.708	14.92

The values of ΔH were obtained using Van-Hoff equation as follows^{31, 36}:

Plotting $\log X_m$ against $1/T$ gives linear relationship as shown in Figure 9.

$$\log X_m = \frac{-\Delta H}{2.303RT} + con$$

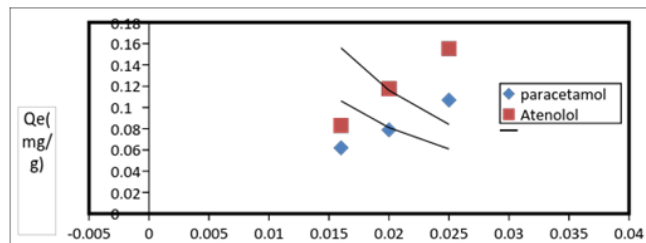


Figure 9: Plotting $\log X_m$ versus $1/T$ for adsorption of PL and AL on ICS at 313 K and pH=4.

Gibbs free energy ΔG was calculated from the following equation⁴²:

$$\Delta G = -RT.Ln\left(\frac{Q_e}{C_e}\right)$$

Entropy change ΔS for adsorption process can be calculated using the following equation⁴³:

$$\Delta G = \Delta H - T\Delta S$$

Generally, positive values of ΔS indicate that the adsorption of these medicines on the surface leads to reduce the entropy due to adsorb these molecules on the surface and form bonding with the surface as well as electrostatic attraction between molecules and the surface of the adsorbent molecules. The values of Freundlich constants at 313 K are shown in Table 1.

4. Conclusions

This study showed that both paracetamol and atenolol can be removed from their aqueous solutions by adsorption over Iraqi cherry seeds. Also it was found that removal of atenolol over ICS was more efficient than that for paracetamol under the same conditions. Also the adsorption of these medicines over ICs was exothermic process and it possessing reduction in the entropy upon adsorption.

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