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Adsorptive Removal of Aniline from Aqueous Solutions Using *Prunus dulcis* (Almond): Equilibrium, Kinetics and Thermodynamics

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ABSTRACT

This study was aimed at investigating Adsorptive removal of Aniline from aqueous solutions using Prunus dulcis. The effect of different parameters such as pH, contact time, pollutant concentration and adsorbent dose was studied in absorption process. The biosorption data have been analyzed using Langmuir, Freundlich and Temkin isotherms. The process of aniline absorption on P. dulcis was depended on Freundlich (R^2=0.938) absorption isotherm more than other isotherms. Synthesis of aniline absorption on modified Almond followed on pseudo second-order model. The ΔH◦ and the ΔS° changes were determined as 5.150 kJ/mol^{-1} and 0.0178 kJ/Mol^{-1}/K^{-1} respectively. The results showed that Baneh could consider as an effective and cheap absorber in removing the aniline from aqueous solution.

Keywords: *Prunus dulcis,* Adsorption, Aniline, Thermodynamics, Kinetics

INTRODUCTION

Aromatic compounds are common pollutants in the effluents of several industries. Aniline or Amino benzene is one of the most important organic compounds, as toxic pollutants in water, consisting of a benzene ring attached to an amino group (-NH_2) [1,2]. Aniline and its derivatives were used in dyestuffs, plastics, rubbers, pesticides, paints and explosive materials industries [2]. Aniline vapor is heavier than air and may cause asphyxiation in enclosed, poorly ventilated or low-lying areas. It reacted with hemoglobin and converted to metahemoglobin, so it prevented oxygen absorption and lead to metahemoglobina [1]. More than 150 types of aniline are compounded, that can enter into the environment directly through wastewater, or indirectly through the decomposition of organic compounds [3] Aniline is used at high levels in various industries such as petrochemical and production of tires. So it can be found in the effluents of these industries [2,3]. Adsorption is an affordable method that has been approved as a method for separating organic material from the water [1,4]. The absorption method using active carbon was not cost effective because of high operating costs [4]. Many low-cost adsorbents have been studied on aniline removal, such as novel adsorbent PAM/SiO_2 [3] Baneh [1], Bentonite [5] etc. Absorber plants have been taken more attention, due to availability and cheapness in recent years [1]. Almond is a type of fruit, that its tree is native to the Middle East and South Asia [6]. In fact, almonds have a hard outer shell and an inner lining that the seed (kernel) is within it [7]. The scientific name of almond is *Prunus dulcis*, which is known by *Amygdalus communis* in some sources. Due to the easy supply of the plant, especially in the Middle East as well as an effective and low-cost adsorbent, it is used in eliminating contaminants [6-7]. Also, in recent years, chemicals such as potassium hydroxide (KOH), sulphuric acid (H_2SO_4), sodium hydroxide (NaOH), hydrochloric acid (HCl), etc. [8,9]. They are used to increase the capacity of absorption. In this study, the adsorbent reformed with NaOH and its effect was evaluated on the removal of aniline. In this research, the *P. dulcis* were applied for the adsorption of aniline from aqueous solutions as adsorbent.

MATERIALS AND METHODS

Aniline from Merck Company was prepared in determined concentration with distilled water. Stock of aniline with concentration of 1000 mg/l (purity 99%) was prepared in distilled water and the aniline standard curve was drawn. The purchased Aniline with the chemically formula of $C_6H_5NH_2$, the purity of 99 percent, has a molecular weight of 93.13, the angle between the link C-N and bisect link H-N-H and also nitrogen atom is positive end of the dipole aniline, which shown in the structure of Figure 1 [1].

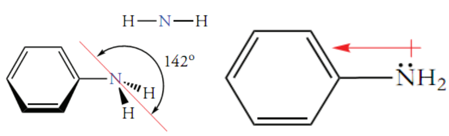

Figure 1: The structure and angle between the links C-N aniline

P. dulcis shell was collected from Zabol city, Iran. Samples were washed frequently with distilled water and after drying, it was put on furnace with temperature of 550°C for 60 min. The resulted ash was sieved after crushing by porcelain mortar using sieves with standard mesh of 20 and 100 (ASTM). The favorite diameter of ash particles was 0.15-0.85 mm. To obtain a modified adsorbent, almond shell was immersed in 30% solution of NaOH for 24 h; samples were washed with distilled water and dried in oven with temperature of 105°C for 24 h [1-10].

Batch adsorption experiments

The effect of different parameters such as pH, contact time, pollutant concentration and adsorbent dose was studied in absorption process and shaker with 150 rpm was used to improve the condition. All the methods in this study was describes in standard of sewage experiment methods [1,10] the adsorbent was added to each 1 L of sample water containing various concentrations of aniline, the pH of the water sample was adjusted by adding 0.1 N HCl (hydrochloric acid) or 0.1 N NaOH solutions in each bottle. The initial and final aniline concentrations remaining in solutions were analyzed by a UV–Visible Recording Spectrophotometer, (Shimadzu Model: LUV-100A) Construction Japan was determined at a wavelength of maximum absorbance λ_{max}=198 nm. The pH was measured using a MIT65 pH meter respectively [1,5]. The sorption capacity of the studied parameters from aniline was calculated based on the following formula [11]:

$$Qe=\frac{(C_0-C_e)V}{M} \qquad (1)$$

Where C_0 and C_e are equilibrium concentration (mg/l) of aniline, M weight of adsorbent (g) and V (L) is the volume of the solution.

RESULTS AND DISCUSSION

Effect of pH

pH has been introduced as the important effective parameter on aniline adsorption process [1]. The effect of different pH (3-11) in absorption of aniline on almond in contact time of 60 min was shown in Figure 2. The results showed that increase of pH 7 lead to increase of removing aniline. Aniline is a weak base the nature of the anionic that changes to positively charged anilinium ion sunder acidic conditions. Thus, under acidic conditions and lower than this amount has a positive charge due to the increased concentration of H^+; In this situation, efficiency is reduced due to electrostatic disposal. In addition, at alkaline pH, the adsorption of aniline decreases in competition with ambient OH^- [1,10,12].

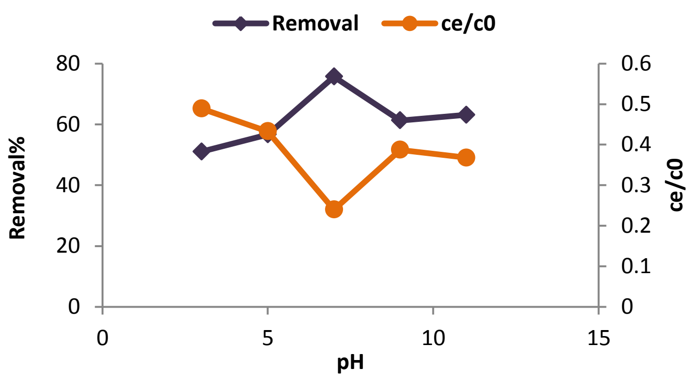

Figure 2: Effect of pH on percentage removal of aniline (Time: 60 min, dosage: 0.8 g/l, aniline concentration: 60 mg/l)

Effect of initial aniline concentration

The effect of different initial aniline concentrations (20-150 mg/l) in absorption of aniline on almond in dosage 0.8 g/l and contact time of 60 min was shown in Figure 3, with increasing initial concentrations of aniline from 90-150 mg/l, percentage removal of aniline decreased with increasing of aniline concentration, so maximum percentage removal of aniline was achieved at initial aniline concentration 90 mg/l (64.5%). The adsorption rate decreased by increasing of initial concentration. This may be owing to the finite number of active sites on the adsorbent that becomes saturated at high concentration of aniline. In other words, at low concentrations, the availability of aniline molecules to adsorption sites is more than high concentrations [1,13].

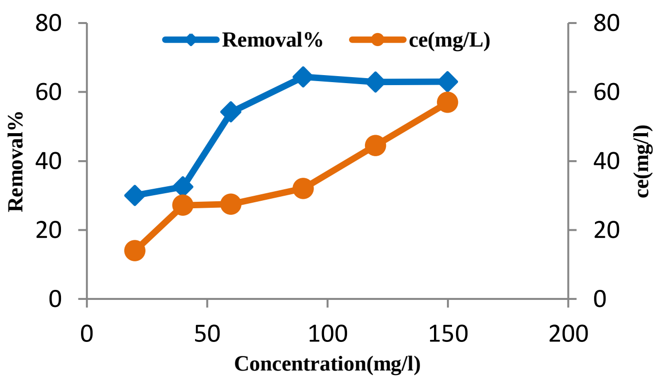

Figure 3: Effect of aniline concentration on percentage removal of aniline (Time: 60 min, dosage: 0.8 g/L, PH: 7)

Effect of absorbent concentration

The Figure 4 indicated that increase of absorbent concentration decreased the efficiency. The absorbent concentration increased from 0.8-1.5 g/l. The efficiency decreased from 85%-80% because of reduction of surface or availability of aniline molecules to active sites. It is indicated that increase of absorbent dose lead to decrease the efficiency and it was because of decreasing the active surface of absorbent [1,14].

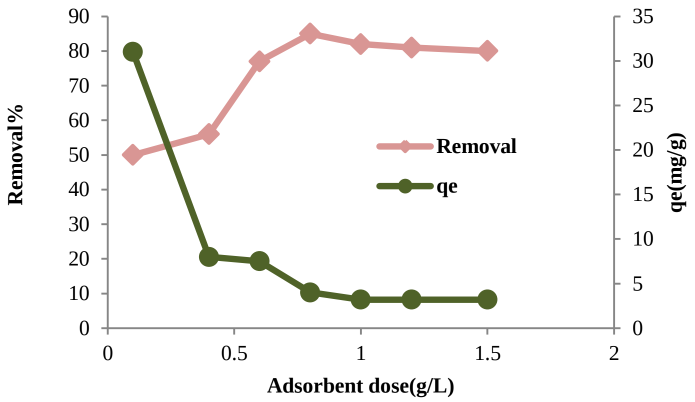

Figure 4: Effect of adsorbent dose on percentage removal of aniline (Time: 60 min, PH: 7, aniline concentration: 90 mg/l)

Effect of time on adsorption

Figure 5 showed the effective contact time in absorption of aniline on Almond surface in improved concentration and pH for 120 min. As it is seen, the increase of contact time from 10-120 min, the absorption rate increased too and the efficiency was 97% and then slowed from 150 min. The increase of contact time from 10-120 min resulted increase of aniline absorption and efficiency of 97% because of more frequency of collisions between pollutants and absorbents. The more retention time resulted in more collision and increasing the pollutant absorption by absorbent. Then, the absorption process was slow [15].

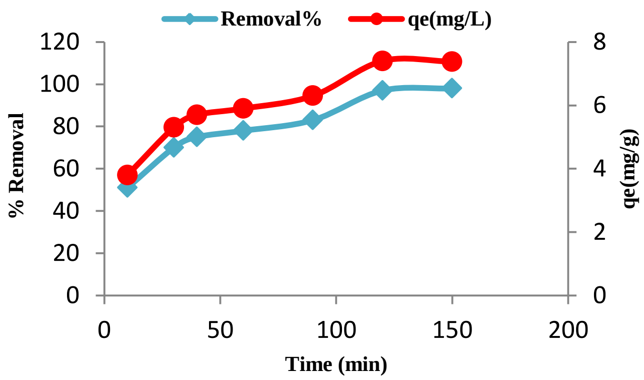

Figure 5: Effect of time on percentage removal of aniline of aniline (PH: 7, dosage: 0.8 g/l, aniline concentration: 90 mg/l)

Adsorption isotherms

The interpretation of absorption isotherms in order to developing an equation, presenting the results and designing the system in these three models showed the relation between absorbed aniline. These models were Langmuir, Freundlich and Tekmin isotherms [16]. The Langmuir isotherm modal is presented the Eqn. 2 [16,17].

$$\frac{c_e}{q_e} = \frac{1}{q_m} \times \frac{1}{k_1} + \frac{c_e}{q_m} \qquad (2)$$

Where, maximum adsorption capacity (qm) is monolayer adsorption capacity (mg/g), qe amount adsorbed on adsorbent (mg/g), K_L is Langmuir isotherm constant related to the affinity of the binding sites and energy of adsorption (l/mg). The essential specifications of a Langmuir isotherm can be expressed in idiom of a dimensionless constant separation factor or equilibrium parameter, RL, which is defined by Eqn. 3 [17]:

$$R_L = \frac{1}{1+K_L C_0} \qquad (3)$$

The RL values indicate the kind of the isotherm to be either unfavorable (RL > 1), linear (RL=1), favorable (0 < RL < 1).

The Freundlich isotherm was showed by Eqn. 4 [18]:

$$\text{Log } q_e = \frac{1}{n} \log c_e + \log k_f \qquad (4)$$

Where, qe is the amount of aniline adsorbed (mg/g), Ce is the equilibrium concentration of aniline in solution (mg/l), and Kf and n are constants incorporating the factors affecting the adsorption capacity and intensity of adsorption, respectively.

The Tempkin isotherm has been expressed by the following Eqn. 5 [1,19]

$$Q_e=B_1\ln (A_T)+B_1\ln (Ce) \quad (5)$$

A plot of qe versus ln Ce enables the determination of the constants A_T and B_1.

The study showed that aniline on Almond better according to Freundlich Model isotherm model (R^2=0.938). Tempkin isotherm (R^2=0.902) that better than Langmuir model (R^2=0.807) (Table 1).

Table 1: The adsorption isotherms constants for the removal aniline

Temperature 298 (°K)	Tempkin			Freundlich			Langmuir		
	B_T	K_T	R^2	k_f	1/n	R^2	q_m	b	R^2
	10.2	27.5	0.902	0.001	2.3	0.938	3.3	0.02	0.807

Adsorption kinetics

The pseudo-first-order model

The synthetic of absorption depended on chemical and physical absorbent that was influenced on absorption mechanism. Linear equations relating to synthetics are showed as follow (pseudo second-order, pseudo first order and intraparticle diffusion model).

The pseudo-first-order rate equation is defined as Eqn. 6 [20]:

$$\mathrm{Log}\,(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \quad (6)$$

Where, q_t and q_e are the amount adsorbed at time t and at equilibrium (mg/g) and k_1 is the pseudo first-order rate constant for the adsorption process (min^{-1}).

The pseudo second-order model

The pseudo second-order model can be represented in the following form Eqn. 7 [20,21]:

$$\frac{t}{q_t} = \frac{1}{k_2 q^2} + \frac{t}{q_e} \quad (7)$$

And where K_2 the second -order rate constant ($g/mg^{-1}/min^{-1}$), q and qe are the amount of the adsorbed on the adsorbent (mg/g) at equilibrium and at time t.

The intraparticle diffusion model

The Intraparticle diffusion model is given by the matching Eqn. 8 [22]:

$$q_t = K_{pi}t^{0.5}+c \quad (8)$$

Where, c is constant and kid is the intraparticle diffusion rate constant ($mg/g.min^{1/2}$), q_t is the amount adsorbed (mg/g) at time t (min).

The correlation coefficient ($R^2 > 0.989$) in pseudo second- order model was better than other models. In this model, pseudo first-order model, it agreed with intraparticle diffusion mod. Therefore, pseudo second-order synthetic model showed suitable correlation for aniline absorption on almond. As it is showed in Table 2, the correlation coefficient in this model for *P. dulcis* shell was high (Figures 6 and 7).

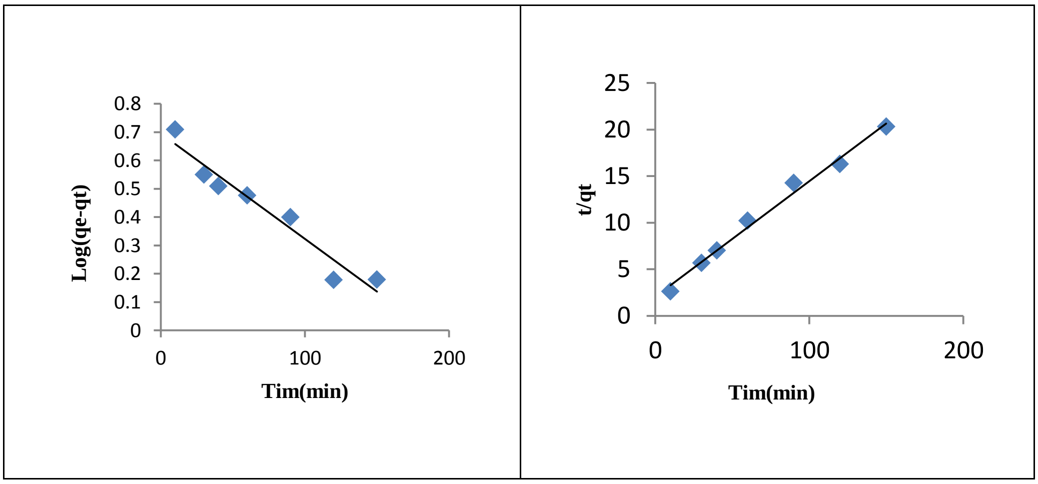

Figure 6: Adsorption kinetics; pseudo-first-order; pseudo second-order

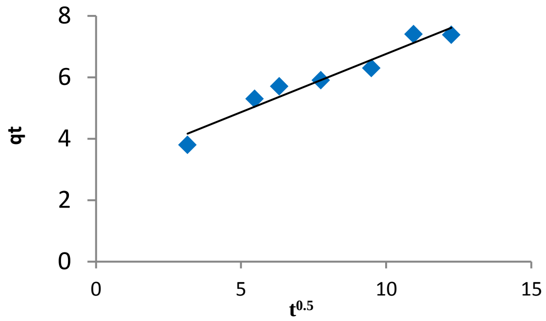

Figure 7: Intraparticle diffusion plot of IP adsorption on almond

Table 2: The adsorption kinetic model constants for the removal aniline

Temperature 298 (°K)	Pseudo-first order			Pseudo-second order			Intraparticle diffusion		
	K_1	qe	R^2	K_2	qe	R^2	k_p	c	R^2
	0.008	4.95	0.94	0.007	8.06	0.989	0.38	2.96	0.945

Thermodynamic studies

The 3 basic parameters for thermodynamic study contain Standard enthalpy (ΔH°), Gibbs free energy (ΔG°) and Standard Entropy (ΔS). The ΔH° and ΔS° values are derived from linear plot against 1/T, which are the slope and width of the graph linear equations, respectively. The sorption behaviors of different concentrations aniline onto *P. dulcis* were critically investigated at 293, 308 and 318 K, respectively. Thermodynamic parameters were calculated from following equations [23,24]:

$$lnk_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (9)$$

$$K_c = \frac{q_e}{C_e} \quad (10)$$

Where, Ce is the equilibrium concentration of aniline and qe is the amount of aniline adsorbed per unit weight of *P. dulcis* at equilibrium concentration (mg/g).

$$\Delta G° = -RT \ln K \quad (11)$$

Where, R is the universal gas constant (8.314 $J.mol^{-1}.K^{-1}$), T is the temperature (K) and K is the distribution coefficient.

The three thermodynamic parameters of Aniline adsorption on almond tree are shown in the Table 3. It can be seen that positive ΔH° values equal to 5.15 kJ/mol and also ΔG° values for each three positive temperatures equals to 1.98, 3.84 and 4.8 kJ/mol, respectively. The positivity of enthalpy ΔH° and ΔG° state that the process of aniline absorption is endothermic and not spontaneous. Furthermore, the positivity of standard entropy Δs° caused by increasing efficiency of the reaction to higher temperature.

Table 3: Thermodynamic parameters for the adsorption of aniline on almond

C° (mg/l)	ΔH° (kJ/mol)	ΔS° (kj/mol.K)	ΔG° (kj/mol)		
			298 K	308 K	318 K
90	5.150	0.0178	1.98	3.84	4.8

CONCLUSION

This study reports kinetic, thermodynamic and equilibrium studies on biosorption of aniline dye by *P. dulcis* (almond**)**. The maximum biosorption capacities of biomass and removal was 3.3 mg/g and 73%, at optimum conditions of pH=7 and temperature (25°C) according to Freundlich isotherm model and pseudo-second-order kinetic model. The thermodynamic optimal was reached in 298 K.

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