Adsorptive removal of aniline from aqueous solutions by *Pistacia atlantica* (Baneh) shells: isotherm and kinetic studies

Shahin Ahmadi¹ and Ferdos Kord Mostafapour²

¹Department of Environmental Health, School of Public Health, Zabol University of Medical Sciences, Zabol, Iran  
²Department of Environmental Health, School of Public Health, Zahedan University of Medical Sciences, Zahedan, Iran.

**ABSTRACT**

Aniline is widely used as raw material in many chemical industries. This study was aimed at investigating Adsorptive removal of Aniline from aqueous solutions using *Pistacia atlantica* (Baneh) shells. The effect of different parameters such as pH (2-8), contact time (10-105 min), pollutant concentration (50-150 mg/L) and adsorbent dose (0.4-1.5 gr/L) was studied in absorption process. Qm of the baneh was 9.23 mg/L when 96% of the aniline was removed. The process of aniline absorption on *P. atlantica* (Baneh) shells ash was depended on Freundlich absorption isotherm more than other isotherms. Synthesis of aniline absorption on modified Baneh followed on pseudo second-order model. The results showed that Baneh could consider as an effective and cheap absorber in removing the aniline from aqueous solution.

I. Introduction

Aromatic compounds are common pollutants in the effluents of several industries. Among these aromatic pollutants, aniline (slightly yellow-to-brown, clear oily liquid, Specific gravity: 1.02) is very hazardous compound to humans as well as the environment. Aniline and its derivatives were used in dyestuffs, plastics, rubbers, pesticides, paints and explosive materials industries. (Gu et al., 2008; Kord Mostafapour et al., 2016). Aniline vapor is heavier than air and may cause asphyxiation in enclosed,
poorly ventilated or low-lying areas. When aniline was released, it disturbed the aqueous life cycle and cause cancerous tumors in animal and increases the risk of bladder cancer in human. It reacted with hemoglobin and converted to Met hemoglobin, so it prevented oxygen absorption and lead to metahemoglobin (Matsushita et al., 2005; Han et al., 2006). Studies indicated that absorption process is an effective physical method to remove the organic compounds from polluted waters with more than 98% efficiency (Sena et al., 2009). The absorption method using active carbon was not cost effective because of high operating costs. Many low-cost adsorbents have been studied on aniline removal, such as novel adsorbent PAM/SiO2 (An et al., 2009) Bentonite (Taherkhani et al., 2015), Ostrich Feathers Ash (Crisafully et al., 2008; Daraei et al., 2010), etc. *Pistacia atlantica* is a species of pistachio tree known as Baneh in Iran, is the most economically important species for rural people in areas of natural forest (Pourreza et al., 2008; Bozorgi et al., 2013). Three *Pistacia* species naturally occur in Iran: *P. Vera* L, *P. khinjuk* Stocks and *P. atlantica* Desf. *P. atlantica* has three subspecies or varieties which have been described as cabulica, kurdica and mutica (Itzhak Martinez et al., 2008). Baneh was studied as it is a fast growing plant in East of Iran (Pourreza et al., 2008). Baneh because of its high absorption properties has many applications in several countries to remove the organic material such as colors. It used in food and medical industries as its high absorption efficiency and cost effective (Iranjo et al., 2016). In this research, the *Pistacia atlantica* shells were applied for the adsorption of aniline from aqueous solutions as adsorbent.

II. Materials and Methods

**Characteristics of aniline:** 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. General characteristics of aniline are provided in Table 01 and Figure 01, respectively.

<table>
<thead>
<tr>
<th>Name</th>
<th>Molecular weight</th>
<th>λ_max(nm)</th>
<th>Molecular formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aniline</td>
<td>93.13 mg/mol</td>
<td>198</td>
<td>C₆H₅NH₂</td>
</tr>
</tbody>
</table>

![Figure 01. Chemical structure of aniline (Kord Mostafapour et al., 2016).](image)

**Preparation procedure of adsorbent:** *Pistacia atlantica* (Baneh) was collected from Zahedan 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. Resulted ash was sieved after crushing by porcelain mortar using sieves with standard mesh of 20 and 100 (ASTM). Favorite diameter of ash particles was 0.15 to 0.85 mm. Each 10 gr of *P. atlantica* was activated by using of 20 ml sulphuric. In next step, samples were washed with distilled water and dried in oven with temperature of 105°C for 24 hours (Zazouli et al., 2013).

**Batch adsorption experiments:** Effect of different parameters such as pH (2, 4, 6, 8), contact time (10, 20, 30, 45, 60 and 105 min.), pollutant concentration (50, 100, 102 and 150 mg/L) and adsorbent dose (0.4, 0.8, 0.6, 1 and 1.5 g/L) 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 (Eugene et al., 2012) 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 (Sodium hydroxide) 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 $\lambda_{\text{max}} = 198$ nm. The pH was measured using a MIT65 pH meter respectively (Kord Mostafapoor et al., 2016; Zazouli et al., 2013). Removal and sorption capacity of the studied parameters from aniline was calculated based on the following formula: (Deng et al., 2010).

\[
R = \left(\frac{C_0 - C_f}{C_0}\right) \times 100 \quad (1)
\]

\[
Qe = \frac{(C_0 - C_e)V}{M} \quad (2)
\]

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

III. Results and Discussion

SEM has been a primary instrumentation for characterizing the surface morphology and essential physical virtues of the adsorbent surface. SEM of $P. \text{atlantica}$ (Baneh) after and before aniline adsorbed is shown in Figure 02.

![Figure 02. SEM image of modified $P. \text{atlantica}$ before (a) and after (b) used as adsorbent.](image)

Effect of pH on adsorption

Effect of different pH (2.0 to 8.0) in absorption of aniline on ash of $Pistacia \text{Atlantic}$ shell in contact time of 60 minutes was shown in figure 03. Results showed that increase of pH to 6.0 lead to increase of removing aniline. As shown in figure 03, the removal percent increased from pH 2.0 to pH 6.0 up to 60.7% and 70% at biosorbent dosage from 0.6 g/L, respectively.

![Figure 03. Effect of pH on percentage removal of aniline (Time: 60 min, dosage: 0.6g/L, aniline concentration: 100 mg/L).](image)
Effect of initial aniline concentration

Effect of different initial aniline concentrations (50 to 150 mg/L) in absorption of aniline on ash of *Pistacia Atlantica* shell in dosage 0.6 g/L and contact time of 60 minutes was shown in figure 04, with increasing initial concentrations of aniline from 50 to 150 mg/L, percentage removal of aniline decreased within ceasing of aniline concentration, so maximum percentage removal of aniline was achieved at initial aniline concentration 50 mg/L (%95).

![Figure 04. Effect of aniline concentration on percentage removal of aniline (Time: 60 min, dosage: 0.6 g/L, pH 6.0).](image)

Effect of absorbent concentration

Figure 05 indicated that increase of absorbent concentration decreased the efficiency. When the absorbent concentration increased from 0.4 to 1.5 g/L for improved concentration 50 mg/L aniline, the efficiency decreased from 99.9% to 72% because of reduction of surface or availability of aniline molecules to active sites, while the biosorption capacity (qe) of aniline on the biomass increased from 2.5 to 12.5 mg/g when biosorbent dosage increased from 0.4 to 1.5 g/L.

![Figure 05. Effect of adsorbent dose on percentage removal of aniline (Time: 60 min, pH 6.0, aniline concentration: 50 mg/L).](image)
Effect of time on adsorption

Figure 06 showed the effective contact time in absorption of aniline on *P. atlantica* (Baneh) surface in improved concentration and pH for 105 minutes. As it is seen, the increase of contact time from 10 to 30, the absorption rate increased too and the efficiency was 95.7% and then slowed from 45 min to 60min, reaching equilibrium after 60 min.

![Figure 06. Effect of time on percentage removal of aniline of aniline (pH 6.0, dosage: 0.4g/L, aniline concentration: 50mg/L).](image)

Adsorption Isotherms

Several models were suggested for analysis of experiment results in different studies that the most important one is absorption isotherms. The interpretation of absorption isotherms in order to developing an equation, presenting the results and designing the system in these four models showed the relation between absorbed aniline. These models were Langmuir, Freundlich, Tekmin and Harkins Jura isotherms. The Langmuir isotherm was based on single layer and homogenous absorbed material with same energy in surface. Freundlich isotherm was calculated using heterogeneous surface with non-uniform distribution of surface absorption heat (SL et al., 2009). Linear equations relating to isotherms is showed as follow. The Langmuir isotherm modal is presented the Eq. 3 (Kakavandi et al., 2013).

\[
\frac{c_e}{q_e} = \frac{1}{q_m} \times \frac{1}{K_L} + \frac{c_e}{q_m}
\]

Where, \(q_m\) (Maximum adsorption capacity) is monolayer adsorption capacity (mg/g), \(q_e\) 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 equation4 (Hall et al., 1996):

\[
R_L = \frac{1}{1 + K_L C_o}
\]

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

The Freundlich isotherm was showed by Eq. 5 (Kakavandi et al., 2013).

\[
\log q_e = \frac{1}{n} \log c_e + \log k_f
\]

where \(q_e\) is the amount of aniline adsorbed (mg/g), \(C_e\) is the equilibrium concentration of aniline in solution (mg/L), and \(K_f\) and \(n\) are constants incorporating the factors affecting the adsorption capacity and intensity of adsorption, respectively.
The Harkins Jura (Ibrahim and Sani, 2014) is given by the following: Eq. 6

$$\frac{1}{q_e} = \frac{B_{HJ}}{A_{HJ}} - \frac{1}{A_{HJ}} \log C_e$$

(6)

The values of constants B and A were obtained from linear plot of 1/qe² and log Ce at 30 °C. The values of constants A and B along with regression coefficient are listed in Table 02. A_HJ parameter which accounts for multilayer adsorption and explains the existence of heterogeneous pore repartition while B_HJ is the isotherm constants (Mustafa et al., 2014).

The Tempkin isotherm has been expressed by the following Eq. 7 (Ibrahim and Sani, 2014)

$$Q_e = B_1 \ln (A_T) + B_1 \ln (C_e)$$

(7)

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

**Adsorption Kinetics**

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

The pseudo-first-order rate equation is defined as Eq. 8 (Sui et al., 2011; Ali, 2014):

$$\log (q_e - q_t) = \log(q_e) - \frac{k_1}{2303} t$$

(8)

Where, qt and qe are the amount adsorbed at time t and at equilibrium (mg/g) and k1 is the pseudo first-order rate constant for the adsorption process (min⁻¹).

The pseudo second-order model can be represented in the following form equation 9 (Mahvi and Heibati, 2010)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

(9)

And Where K₂, the second-order rate constant (g mg⁻¹ min⁻¹), q and qe are the amount of theadsorbed on the adsorbent (mg/g) at equilibrium and at time t.

The Intraparticle diffusion model is given by the Matching equation: Eq. 10 (El-Latif et al., 2010)

$$q_t = K_{pi} t^{0.5} + c$$

(10)

Where, c is constant and kid is the intraparticle diffusion rate constant (mg/g min¹/2), qt is the amount adsorbed (mg/g) at time t (min.).

As it is showed in Table 02 and 03, the correlation coefficient in this model for P. Atlantic shell was high. The study showed that aniline on dried baneh better according to Freundlich Model isotherm model (R²=0.9713). Furthermore, it agreed with Tempkin isotherm (R²=0.963) that better than Harkins Jura (R²=0.95) and Langmuir model (R²=0.92).

The velocity constant of Pseudo second-order, Pseudo First-order and Intraparticle diffusion was presented in Table 03. In this model, correlation coefficient (R²) of Pseudo First-order and Intra particle diffuse of aniline was low that was deducted to low correlation. Therefore, Pseudo second-order synthetic model showed suitable correlation for aniline absorption on P. atlantica.
Table 02. Adsorption isotherms constants for the absorption aniline

<table>
<thead>
<tr>
<th>Tem. (°C)</th>
<th>Langmuir Model</th>
<th>Freundlich model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>q_0 (mg/g)</td>
<td>k_L (L/mg)</td>
</tr>
<tr>
<td>30</td>
<td>9.23</td>
<td>0.04</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Tempkin Model</th>
<th>Harkins Jura Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>B_T (mg/L)</td>
<td>A_T (L/mg)</td>
</tr>
<tr>
<td>18.67</td>
<td>5.1</td>
</tr>
</tbody>
</table>

Table 03. The adsorption kinetic model constants for the absorption aniline

<table>
<thead>
<tr>
<th>C_0 (mg/L)</th>
<th>K_2 (g/mg min)</th>
<th>R²</th>
<th>q_e (mg/g)</th>
<th>K_1 (1/min)</th>
<th>R²</th>
<th>Q_e (mg/g)</th>
<th>k_p</th>
<th>c</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.6</td>
<td>0.999</td>
<td>10.8</td>
<td>0.08</td>
<td>0.58</td>
<td>1.96</td>
<td>0.087</td>
<td>10.17</td>
<td>0.52</td>
</tr>
</tbody>
</table>

Discussion

pH has been introduced as the most effective parameter on aniline adsorption process (Kord Mostafapour et al., 2016). In the present study, maximum aniline removal was obtained in pH=6 and it was observed that the aniline removal decreased by increasing pH to 8. Aniline is a weak base the nature of the anionic that changes to positively charged anilinium ion under acidic conditions. PKa value for aniline is 4.6; so at pH less than 4.6 have a positive charge and above this amount is negatively charged and in this value and closest to this value is neutral. Thus under acidic conditions and lower than this amount has a positive charge due to the increased concentration of H⁺; consequently, with regard to positive levels the absorbent willing to absorb anilinium ions cationic nature will not be. 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⁻ (Kord Mostafapour et al., 2016; Taherkhani et al., 2015). Another effective parameter on aniline removal adsorption is the initial Aniline concentration which has been studied in this work. As observed in Figure 4, 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. On the other hand, modify absorbent with acid and change its surface charge, puts the more external exchange position of at the disposal of NH⁻ anion of the aniline and has an increasing trend up to reach the saturation point and then due to lack of connection between absorbent molecules and aniline declining trend and absorption is reduced (Taherkhani et al., 2015). It is indicated that increase of absorbent dose lead to decrease the efficiency and it was because of decreasing the active surface of absorbent (Balanay et al., 2014). The contact time has a significant effect in aniline adsorption studies. The increase of contact time from 10 to 30 minutes resulted increase of aniline absorption and efficiency of 95.7% 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. As was mentioned above the aniline removal efficiency is enhanced by increasing the time up to 30 min and significant change can’t be seen after this time. This result can be supported by results of various studies (Santhy and Selvapathy, 2006; Sun et al., 2010) the comparison of the R² values can help to determine the effective isotherm model in aniline removal. The correlation coefficient of Freundlich was more than other models in such a way that the aniline value in Freundlich Isotherm was R²> 0.9713. The value(R_L) of 0 to 1 in Langmuir model indicated that aniline adsorption on P. Atlantic shell was good. The Freundlich Constant value (1/n) was less than 1; therefore, aniline absorption on Baneh was optimal. It is indicated that Freundlich isotherm was optimal based on adsorption rate and mathematically. Freundlich isotherm, compared to Langmuir, was
based on multi layers and heterogeneous absorption of absorbed material on absorbent. The correlation coefficient ($R^2 > 0.999$) in pseudo second-order model was better than other models. In this model, correlation coefficient ($R^2$) of Pseudo First-order model and intraparticle diffusion of aniline was low that was deducted to low correlation. Therefore, pseudo second-order synthetic model showed suitable correlation for aniline absorption on *P. atlantica*. The modified *P. atlantica* (Baneh) ash with acid showed suitable capacity to remove aniline.

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**V. References**


