



Effect of Chemical Activation on the Surface Properties of Apricot Stones Based Activated Carbons and Its Adsorptive Properties Toward Aniline

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Abstract. The present study reports the preparation of activated carbons from apricot stones (an agricultural waste) by chemical activation with phosphoric acid (H_3PO_4) and Zinc Chloride ($ZnCl_2$) in N_2 atmosphere. The potential use of the prepared activated carbons as adsorbents and the effects of chemical activation on the surface properties and adsorptive mechanism of Aniline were investigated. The physico-chemical properties of the obtained materials were characterized by Nitrogen adsorption–desorption isotherms, Scanning Electron Microscope coupled to energy dispersive X-ray (SEM-EDX), Fourier Transform Infrared Spectroscopy (FTIR), Boehm titration and pH of point of zero charge (pH_{pzc}). The results show that the prepared samples present high apparent surface areas and pore volume with surface functional groups. Adsorption studies were carried out under varying conditions of contact time, initial concentration and temperature. Pseudo-first order and pseudo-second order kinetic models were applied, finding that the pseudo-second order model was the most suitable for the fitting of the experimental kinetic data. The equilibrium adsorption data were analyzed using Langmuir and Freundlich isotherm models. The equilibrium data were well fitted to the Freundlich isotherm. Based on the results, it is, therefore, suggested that the adsorption is mainly brought about by dispersive interactions between Aniline and activated carbon surface. The prepared activated carbons could be used as a low-cost alternative to commercial activated carbon for the removal of aniline from wastewater.

Keywords: Activated carbon · Chemical activation · Adsorption
Aniline · Surface properties

1 Introduction

Aniline is an important compound in the petrochemical industry, used primarily for the synthesis of isocyanate, an intermediate in the polyurethane manufacture. Aniline derivatives are also key precursors for the production of accelerators and antioxidants in the rubber industry, herbicides and pharmaceuticals (Pardo et al. 2016; Chen et al. 2015).

It is estimated that the world emission of aniline into the environment is 30,000 tons per year caused by accidental spills, illegal release of industrial and municipal wastewater, and excessive use of pesticides (Pardo et al. 2016; Xiao et al. 2015). Due to the high toxicity of aniline for humans and aquatic life it is necessary to remove it from wastewaters.

Previous works have studied the removal of aniline from aqueous solution using different treatments such as oxidation, extraction, biodegradation and adsorption. Among all these methods, adsorption has been widely used in industry due to its easy operation and wide adaptability (Pardo et al. 2016). Many investigations have analyzed different adsorbents for the removal of aniline such as polymers, activated carbon, inorganic layered materials, nanotubes and minerals. Activated carbon (AC) has been the most studied and used adsorbent in industrial wastewater treatments, especially for organic pollutants such as aniline.

AC is a porous carbonaceous material characterized by its well-developed porous structure and surface chemistry. It can be produced by either physical or chemical activation processes. Various categories of raw materials, rich in carbon, such as different agricultural wastes, coal, lignite, and wood can be used as precursors for the preparation of activated carbons. In recent years, agricultural residues have received an increasing interest for activated carbon production due to their natural abundance, renewability, cost effectiveness and eco-friendliness.

The aims of the present study are: (1) preparation and characterization of activated carbons from an agricultural waste (apricot stones) by chemical activation using H_3PO_4 and $ZnCl_2$ as activating agents; (2) investigation on the effect of chemical activation on the adsorption properties toward aniline.

2 Materials and Methods

2.1 Preparation of Activated Carbons

The apricot stones (AS) were used as raw materials to prepare activated carbons. First the raw AS material was carefully washed with distilled water ($d-H_2O$) and dried at 60 °C for 24 h. The dried stones were ground and sieved to obtain a particle size varying from 0.5 to 1.2 mm. The resulting product was then maintained in hermetically closed bottles.

For phosphoric acid activation, a granulated apricot stones were impregnated with 85% (vol) H_3PO_4 at a ratio of 1:1 (1 g of H_3PO_4 :1 g of raw material) for 24 h. Then the impregnated sample was carbonized in a horizontal furnace under a nitrogen flow with a heating rate of 5 °C/min from room temperature to the final carbonization temperature of 400 °C for two hours. After cooling under a nitrogen flow, the obtained carbon was washed with distilled water until a neutral pH was reached. This is followed by drying the activated carbon overnight at 110 °C and storing it in the hermetically sealed package. The obtained activated carbon is labeled ASPAC.

For the zinc chloride activation, the raw material was impregnated with $ZnCl_2$ at a ratio of 1:1 (1 g of $ZnCl_2$:1 g of raw material) under manual agitation for ten minutes. Then the mixture was carbonized at 600 °C for one hour under nitrogen flow with a

heating rate of 5 °C/min. The obtained carbon was treated with a hydrochloric acid solution (0.1 N) by refluxing for three hours then washed with distilled water until silver nitrate test becomes negative. Finally, the activated carbon oven dried at 110 °C for 24 h and marked as ASZAC.

2.2 Characterization

The specific surface area (BET) and the porosity of the activated carbons have been determined by N₂ adsorption at 77 K using the automatic adsorption volumetric apparatus (Micrometrics ASAP 2010). The Brunauer-Emmett-Teller (BET) is the most used method to characterize an activated carbon equation (Brunauer et al. 1938). The presence of porosity and the surface morphology of the activated carbons prepared in this study were examined using scanning electron microscopy (SEM) analysis. The surface functional groups of the activated carbons were examined by Fourier Transform Infrared Spectroscopy method. The samples were mixed with potassium bromide, pressed and analysed by using the FTIR spectroscopy (FTIR-4200, Jasco) at wavelength range of 400 and 4000 cm⁻¹. The Boehm titration method was used to measure the number of acid and basic functions in the samples produced (Boehm 1994). This method is based on the fact that the material superficial groups can react with NaHCO₃, Na₂CO₃, NaOH and HCl. The NaHCO₃ only neutralizes the carboxylic groups, Na₂CO₃ neutralizes the lactonic and carboxylic groups, while NaOH neutralizes the phenolic groups, with the acid groups mentioned before and HCl neutralizes all the basic groups. The pH_{PZC} of adsorbents was determined by the so-called pH drift method (Franz et al. 2000). Mixtures of 0.15 g of adsorbent sample and 50 ml of NaCl (0.01 mol L⁻¹) solutions of initial pH values varying from 2 to 12 were stirred for 48 h. The final pH values were plotted against the initial pH values and the pH at which the curve crosses the line pH_{final} = pH_{initial} is taken as the pH_{PZC} of the given carbon.

2.3 Batch Adsorption Experiments

The adsorption of aniline from aqueous solutions onto prepared activated carbons (ASACP and ACACZ) was performed by using batch equilibrium technique. About 25 mg of activated carbon samples were introduced into conical flasks containing 25 ml of aniline solutions with initial concentrations ranging from 20 to 300 mg L⁻¹. The mixture was shaken at fixed temperature (25, 35 or 45 °C), using a temperature controlled water bath shaker for 24 h in order to reach the adsorption equilibrium. Then, samples were filtered and the concentrations of aniline in the filtrate were analyzed by using a UV-Visible spectrophotometer (PerkinElmer UV/VIS, Lambda 20) at maximum wave length of 280 nm.

The effect of solution pH was measured by carrying out the adsorption process at different pH values ranged between 2 and 12, using aniline initial concentration of 100 mg L⁻¹ and shaking time of 24 h at 25 °C. The pH of solutions was adjusted by addition drops of 0.1 M HCl or NaOH.

The kinetic studies were carried out at 25 °C, using three initial concentrations of aniline (20, 100 and 200 mg L⁻¹) for times ranging from 5 to 480 min. For such studies, a series of 25 mg of adsorbent was added to 25 ml of adsorbate solutions.

The uptake at equilibrium, q_e (mg g^{-1}), was calculated according to the following equation:

$$q_e = \frac{(C_0 - C_e) * V}{W} \quad (1)$$

where C_0 (mg L^{-1}) is the initial concentration of solutions, C_e (mg L^{-1}) is the equilibrium concentration of solutions, V (L) is the volume of solution, and W (g) is the weight of activated carbon.

The adsorption capacity at time t , q_t (mg g^{-1}) was calculated using the following equation:

$$q_t = \frac{(C_0 - C_t) * V}{W} \quad (2)$$

where C_t (mg L^{-1}) is the equilibrium concentration of solutions at time t (min).

3 Results and Discussion

3.1 Characterization of Prepared Samples

The nitrogen adsorption–desorption isotherms of samples are shown in Fig. 1. The adsorption–desorption isotherms obtained are of type I according to the International Union of Pure and Applied Chemistry (IUPAC) classification (Bouras et al. 2015). This shape is characteristic of the presence of a microporous structure.

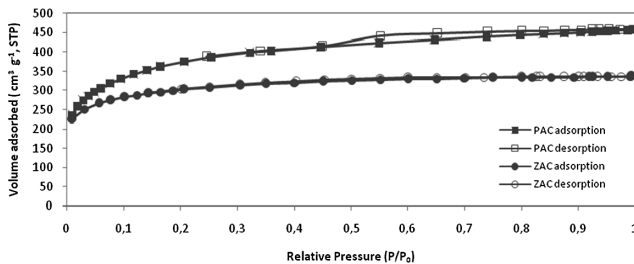


Fig. 1. Nitrogen adsorption and desorption isotherms of the ASPAC and ASZAC samples

The textural parameters of AC samples including specific surface area, pore volume and pore size are given in Table 1. It can be seen that the ASPAC is a highly-developed microporous carbon-based material in comparison with ASZAC.

The surface morphology of prepared carbons was examined using the scanning electron microscopy (SEM) and the micrographs are presented in Fig. 2. The visual appearance indicates that the external surface of the activated carbons ASZAC and ASPAC presents a series of cavities with different sizes and shapes distributed over the

Table 1. Textural characteristics of the activated carbon samples

| Samples | BET surface area (m ² g ⁻¹) | Total pore volume (cm ³ g ⁻¹) | Micro-pore volume (cm ³ g ⁻¹) | Meso-pore volume (cm ³ g ⁻¹) | External surface area (m ² g ⁻¹) | Average pore diameter (nm) |
|---------|--|--|--|---|---|----------------------------|
| PAC | 1382 | 0.7103 | 0.6714 | 0.0389 | 20.6 | 2.06 |
| ZAC | 1111 | 0.5225 | 0.5121 | 0.0104 | 4.6 | 1.88 |

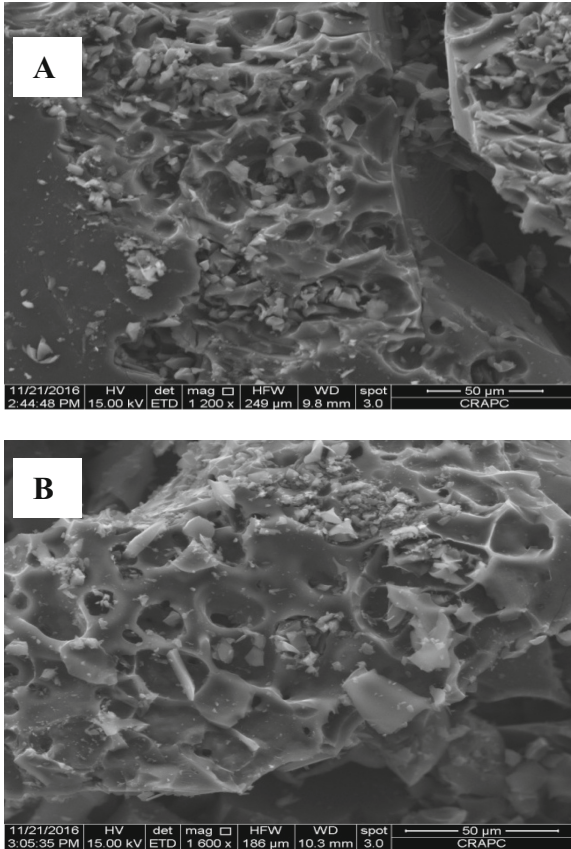


Fig. 2. SEM images of the (A) ASPAC and (B) ASZAC

surface. This texture is resulted from depolymerization and subsequent release of volatile organic substances during the carbonization process (Wang et al. 2008).

The surface functional groups are very important characteristics of the activated carbons because they determine the surface properties of the carbons and hence their feature as ion exchangers, adsorbents, catalysts, and catalyst supports (Budinova et al. 2006). Carboxyls, carbonyls, phenols, lactones, aldehydes, ketones, anhydrides,

quinines and hydro quinones are some of the various forms of functional groups in the structure of which oxygen takes part. Delocalized electron of the graphitic structure and such functional groups determine the acidic or basic character of activated carbon structure (Boehm 1994).

Figure 3 shows the FTIR spectra of the produced activated carbons ASPAC and ASZAC. It was obvious that the samples exhibited similar FTIR spectra characteristic of carbonaceous materials and show that the same functional groups are present in the four oxidized activated carbons.

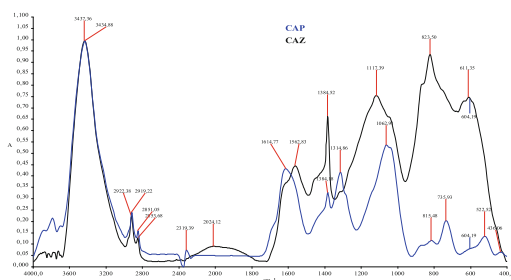


Fig. 3. FTIR spectra of PAC and ZAC

The Boehm's titration method was investigated to determine the amounts of surface functional existing in prepared activated carbons. The results obtained through the Boehm titration; show that ASPAC and ASZAC samples have approximately similar amount of basic groups, and exhibit relatively larger amount of acid groups than basic groups.

3.2 Adsorption Investigation

3.2.1 Effect of Contact Time and Initial Concentration

The adsorption of aniline onto ASPAC and ASZAC was studied in various contact times at initial concentrations of 20, 100 and 200 mg/l. The evolution of the concentration of aniline as a function of time, plotted as qt along time, is shown in Fig. 4. It can be observed that the adsorption was found to be extremely rapid at the initial stage and then gradually increases with rising the time until equilibrium was reached. This result was attributed to the large amount of adsorption sites available on adsorbent at the beginning of adsorption. Adsorption became less efficient, resulting in the second slower phase, with the gradual saturation of adsorption sites on adsorbent surface (Kayranli 2011; Chu et al. 2014; Daoud et al. 2017).

3.2.2 Kinetic Adsorption of Aniline

In order to assess the adsorption kinetics of aniline by ACs, the two mostly applied kinetic models, namely, pseudo-first order and pseudo-second order kinetic models were tested.

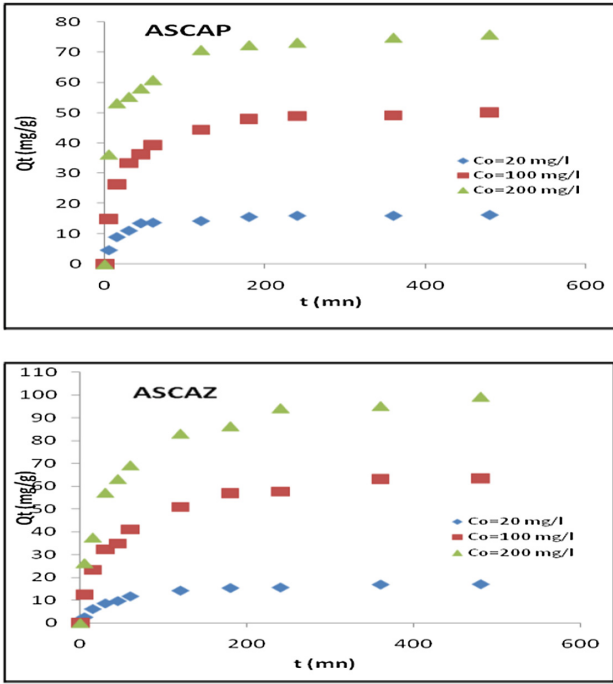


Fig. 4. Kinetic experimental data for the adsorption of aniline onto ASPAC and ASZAC (conditions: adsorbent dose = 1 g L⁻¹, temperature = 25 °C, agitation speed = 150 rpm and natural pH)

The pseudo-first order model proposed by Lagergren and Svanska (1898) is expressed as follows:

$$\ln(q_e - q_t) = \ln q_e + K_1 t \tag{3}$$

where q_e and q_t are the amount of solute adsorbed at equilibrium and at time t , respectively; and k_1 (min⁻¹) is the pseudo-first order rate constant which could be obtained from lineal regression analysis of the $\log(q_e - q_t) = F(t)$ function.

The linear form of the pseudo-second order kinetic model (Tütem et al. 1998; Vinod and Anirudhan 2003) is expressed as follows:

$$\frac{t}{qt} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

where k_2 is the rate constant of pseudo-second order model. Note that K_2 and q_e could be obtained from lineal regression analysis of the $t/q_t = F(t)$ function.

The R_2 and constants values for those adsorption kinetic models were calculated and summarized in Table 2, where $q_{e,cal}$ and $q_{e,exp}$ are the calculated and measured adsorption values. It was found that the experimental data were well fitted by the

Table 2. Pseudo-first order and pseudo-second order kinetic model parameters for the adsorption of aniline on ASCAP and ASCAZ

| | | PFO model | | | |
|-------|-----------|-----------|-------|-------|-------|
| Acs | Co (mg/l) | Qe exp | Qe th | K1 | R2 |
| ASCAP | 20 | 16.3 | 32.7 | 0.010 | 0.91 |
| | 100 | 50.3 | 26.6 | 0.010 | 0.906 |
| | 200 | 75.8 | 7.9 | 0.010 | 0.88 |
| ASCAZ | 20 | 20.0 | 62.6 | 0.008 | 0.926 |
| | 100 | 63.6 | 54.7 | 0.012 | 0.954 |
| | 200 | 99.2 | 13.6 | 0.011 | 0.969 |
| | | PSO model | | | |
| | | Qe exp | Qe th | K2 | R2 |
| ASCAP | 20 | 16.3 | 16.8 | 0.072 | 0.999 |
| | 100 | 50.3 | 51.8 | 0.061 | 0.999 |
| | 200 | 75.8 | 76.9 | 0.090 | 0.999 |
| ASCAZ | 20 | 20.0 | 20.9 | 0.048 | 0.999 |
| | 100 | 63.6 | 71.9 | 0.025 | 0.996 |
| | 200 | 99.2 | 102.0 | 0.050 | 0.998 |

pseudo-second order model with high correlation coefficient values ($R_2 > 0.999$), and the $q_{e,cal}$ value was also very close to that of experimental value. This result indicates that the adsorption of aniline onto the prepared activated carbons follows the pseudo-second order kinetic model. It is also seen that the pseudo-first order model cannot fit the experimental data accurately. In many cases, the first-order model of Lagergren does not fit well with the whole range of contact time and is generally applicable over the initial stage of the adsorption processes (Ma et al. 2015). Consequently, it can be concluded that the adsorption of aniline onto ASPAC and ASZAC obeys the pseudo second order kinetic model.

3.2.3 Intraparticle Diffusion Analysis

The intra-particle diffusion model proposed by Weber and Morris (1963), was used to identify the diffusion mechanism of aniline into the prepared activated carbons during the adsorption process. The rate of the adsorption process may be assumed by four steps. These include (1) molecular diffusion of aniline from the bulk solution to a film layer surrounding the adsorbent particle; (2) diffusion of aniline through the boundary layer to the surface of the solid phase (film diffusion); (3) migration of aniline inside the adsorbent particle by surface diffusion or diffusion within liquid filled pores (pore diffusion); (4) adsorption of aniline at an active site on the solid phase surface (adsorption reaction). The slowest step affects the rate of the adsorption process and furthermore, it is necessary to determine the rate-limiting step (Daoud et al. 2017).

The equation of the Intra-particle-diffusion model is shown below:

$$q_t = k_{id}\sqrt{t} + C \quad (5)$$

where q_t (mg g^{-1}) is the amount of solute adsorb at time t , K_{id} ($\text{mg/g min}^{1/2}$) is the initial rate of intra-particle diffusion and C (mg/g) is the intercept which is related to the thickness of the boundary layer. Plotting q_t versus $t^{1/2}$, provides an indication of the dependency of adsorption on intraparticle diffusion. If the plot produces a straight line, thus the adsorption process is controlled only by intraparticle diffusion. In contrast, if it exhibits multi-linear plots, then there are two or more steps affecting the adsorption process (Sun et al. 2012).

The plot of the Morris-Weber relationship for the sorption of aniline by ASPAC and ASZAC, at initial concentrations of 20, 100 and 200 mg g^{-1} (figure not shown). Based on this figure, it may be concluded that the intraparticle diffusion of aniline within the ASPAC and ASZAC occurred in three stages for all the range of aniline concentrations. The first linear portion is due to the instantaneous adsorption or external mass transfer or film diffusion (boundary layer). The second linear portion is due to the intraparticle diffusion and binding of aniline molecules into the internal active sites of the CAs. Finally, the third linear portion indicated a saturation of the adsorption process (the equilibrium stage).

3.2.4 Adsorption Isotherms

The adsorption isotherm is the equilibrium relationship between the amount of solute adsorbed onto the solid q_e and the equilibrium concentration of the solute in solution C_e at a given temperature. The experimental equilibrium isotherms for the adsorption of aniline on prepared activated carbons are given in Fig. 5.

The experimental equilibriums data were described by optimum isotherm model. The linear forms of isotherm model of Langmuir and Freundlich equations were used to correlation coefficients R^2 to compare the equations applicability.

The linear expression of the Langmuir isotherm equation is given as:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{\max}} + \frac{C_e}{q_{\max}} \quad (6)$$

The linear expression of the Freundlich isotherm equation is given as:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (7)$$

where q_e (mg g^{-1}) is the adsorption capacity at equilibrium; C_e (mg L^{-1}) is the concentration of aniline solution at equilibrium; q_{\max} (mg g^{-1}) is the maximum amount of aniline that activated carbon can adsorb; K_L (L mg^{-1}) is the Langmuir isotherm constant that reflects the adsorption energy; K_F ($\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$) is the Freundlich isotherm constant and $1/n$ is the value that is used to indicate the heterogeneity of the adsorbent's surface. As $1/n$ is closer to zero, the surface becomes more heterogeneous.

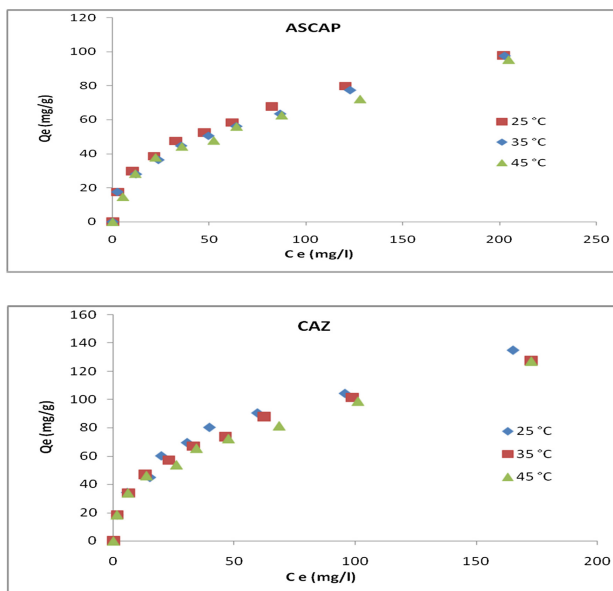


Fig. 5. Experimental adsorption isotherms of aniline onto prepared activated carbons (conditions: adsorbent dose = 1 g L^{-1} , contact time = 24 h, agitation speed = 150 rpm and natural pH)

The parameters of these models were calculated and summarized in Table 3. According to the results, the Freundlich model was best fitted equilibrium data since the correlation coefficient, R^2 values obtained Freundlich isotherm yielded the best fit (>0.99) at all temperatures in comparison to Langmuir isotherm. This means that the adsorbents (ASPAC and ASZAC) provide a heterogeneous surface. Similar trend was observed for adsorption of nitrobenzene onto commercial activated carbon (Jadhav and Srivastava 2013).

Table 3. Parameters obtained for the isotherm models used in the studies

| Adsorbent | Langmuir parameters | | |
|-----------|-----------------------|------------|--------|
| | Q_m | K_L | R^2 |
| ASCAP | 115 | 0.02087833 | 0.9541 |
| ASCAZ | 147 | 0.03549061 | 0.9635 |
| | Freundlich parameters | | |
| | n | K_f | R^2 |
| ASCAP | 2.54000508 | 11.8484849 | 0.998 |
| ASCAZ | 2.32666356 | 15.483888 | 0.996 |

3.3 Adsorption Thermodynamics

The thermodynamic study was realized by using the experimental data obtained from the effect of solution temperature studies carried out earlier. The thermodynamic parameters, that is, standard free energy (ΔG^0), standard enthalpy (ΔH^0), and standard entropy (ΔS^0), can be calculated by the following equations:

$$k_d = \frac{q_e}{C_e} \quad (8)$$

$$\Delta G^0 = -RT \ln k_d \quad (9)$$

where R (8.314 J/mol K) is the universal gas constant, T is absolute temperature (K) and K_d is the distribution coefficient which can be calculated as:

$$\ln(K_d) = \frac{\Delta H^0}{R} + \frac{\Delta S^0}{RT} \quad (10)$$

where C_0 and C_e (mg/L) are the initial and the equilibrium aniline concentrations, respectively.

The values of ΔH^0 and ΔS^0 were calculated from the slope and intercept of the linear regression of $\ln K_d$ versus $1/T$.

The thermodynamic parameters are listed in Table 4. The negative values of ΔG^0 at different temperatures indicate the spontaneous nature of the adsorption process. These values became more negative as the temperature increased, indicating the exothermic nature of the adsorption of aniline by ASPAC and ASZAC. The values of ΔH^0 of adsorption were found to be negative, indicating exothermic process. In addition, the negative values of ΔS^0 showed the decreased randomness at the solid/liquid interface during the adsorption of aniline on the examined activated carbons.

Table 4. Thermodynamic parameters of adsorption of aniline onto ASPAC and ASZAC at different initial concentrations

| | ΔH^0 (kJ/mol) | ΔS^0 (J/mol) | ΔG^0 (kJ/mol) | | |
|-----|-----------------------|----------------------|-----------------------|---------|---------|
| | | | 25 °C | 35 °C | 45 °C |
| CAP | -3.4528 | -10.7334 | -0.2471 | -0.1517 | -0.0317 |
| CAZ | -6.9613 | -16.5532 | -2.0462 | -1.8155 | -1.7180 |

4 Conclusions

The present work shows that local apricot stone based granular activated carbons with highly developed porosity can be prepared using chemical activation with H_3PO_4 or $ZnCl_2$. It was found that the chemical activation influences the textural characteristics and surface chemistry of prepared carbons. Aniline was selected as simple aromatic compound model to study the effect of surface properties on the adsorptive properties.

Isotherm studies favor Freundlich model suggesting multilayer adsorption of aniline over the heterogeneous surface of ASPAC and ASZAC. The maximum monolayer adsorption capacities Q_m (mg/g) are 115 and 147 mg/g for ASCAP and ASZAC respectively. The kinetics modeling studies revealed the applicability of pseudo-second order model. Multi-linearity and deviation of intercept from the origin in Weber and Morris plots suggested that intra-particle diffusion was not the only rate-controlling step. The thermodynamic parameters suggested that $\Delta G^0 < 0$, $\Delta H^0 < 0$, and $\Delta S^0 < 0$, which indicated that the adsorption of aniline onto tested activated carbons were a spontaneous and exothermic adsorption process.

Therefore, the apricot stones based activated carbons was considered a high-efficiency adsorbent for aniline, which presents great potential in applications aiming the removal of aromatic pollutants from aqueous solutions.

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