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Removal of aniline as a health-toxic substance from polluted water by aloe vera waste-based activated carbon

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ABSTRACT

Aniline is a toxic chemical compound and one of the common pollutants found in the effluents from the pharmaceutical, pesticide, dyestuff, petrochemicals and agrochemical industries. The aim of this study was to investigate the sorption of aniline using Aloe Vera wastes-based activated carbon (AV-AC) from water. In this batch study, the effects of various factors including contact time, pH, adsorbent dosage and initial aniline concentrations were surveyed on the aniline sorption. The results illustrated that the optimum pH and contact time for the removal of aniline by AV-AC was obtained at 3 and 60 min, respectively. The decrease of pH had a significant influence on the increasing aniline adsorption. Fitting the experimental data to various kinetics and isotherms models showed that the experimental data were better described by pseudo-second order and Freundlich models, respectively. Because of low-cost, eco-friendly, non-toxicity and high sorption capacity, this sorbent can be used as a very effective option to removal of aniline from aqueous media.

Keywords: Adsorption, Aniline, Aloe Vera Wastes, Activated Carbon.

INTRODUCTION

Water pollution due to industrialization, urbanization and increasing of population is one of the important problems in the world especially in developing countries [1, 2]. Aniline is an important chemical compound, which has widely use in the production of pesticides, dyestuffs, rubbers, plastics and paints [3, 4]. It is toxic, dangerous and persistent to biological and chemical degradation and its presence in water environment even in very low concentrations can be harmful to human as well as aquatic life [5]. Aniline is an oily and colorless liquid. This chemical compound has a highly acrid poison, unpleasant odor of rotten fish and has a burning taste [6-8]. Different treatment methods such as photocatalysis, biodegradation, advanced oxidation and adsorption are commonly used to remove aniline from wastewaters. Among these technologies, adsorption process has been proven to be effective in separating a wide variety of organic pollutants from aqueous media [3, 9]. This method is one of the best treatment alternatives of pollutants such as aniline from water and wastewater, because it is possible to recover of the adsorbent and adsorbate [4, 10]. Adsorption on the surface of activated carbon because of simple operation and high sorption capacity is the most commonly used for elimination of toxic pollutants, but it is expensive and hard to recovery [2, 11, 12]. Therefore, studies on the production of activated carbon from agricultural wastes because of its cheap, non-toxicity and eco-friendly characteristics have gained notice worldwide [13]. In addition to activated carbon, use of some adsorbents such as lignin multi-walled carbon nanotubes [5], graphitic carbon nitride [14], pine sawdust [4], Cr-bentonite [15], grafted acrylic acid [8], Spherical carbon [7] have been reported for the sorption of aniline from

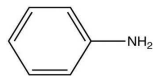
aqueous solution. The Aloe Vera is a plant that grows in the warm tropical areas such as India, United State, Mexico, Australia, Africa, South America and Iran. The Aloe Vera wastes are by-products of the agricultural industries that are used in the manufacture of a latex substance and drugs [16]. In this study, Aloe Vera wastes were used as a low-cost adsorbent to manufacture of activated carbon for the removal of aniline from water. The influence of parameters such as contact time, pH, adsorbent dosage and initial concentrations of aniline were evaluated on the sorption.

MATERIALS AND METHODS

2.1. Materials

The Aloe Vera wastes used in this study were collected from suburban farms of Ahvaz and Dezfull, Iran. Aniline (with purity greater than 99.5%), H₂SO₄, NaOH were purchased from Merck Co (Germany). The structure and general characteristics of aniline are presented in Table 1. The solution pH was adjusted by adding 0.1 N H₂SO₄ and NaOH via a pH meter (50-pp-sartorius model). All of the other chemical used in this study were of analytical pure grade. The stock solution 1 g/L (1000 mg/L) of aniline was prepared in distilled water and the working solutions were made by dilution of the stock solution. An orbital shaker (Behdad-Rotomix Model) at 200 rpm was used for mixing the solution.

Table 1. General characteristics of the aniline

Characteristic	Aniline
Structure	
Scientific name	Aminobenzene
Chemical formula	C ₆ H ₅ NH ₂
Molecular weight (g/mol)	93.13
Color type	Colorless
Appearance	Liquid
λ _{max} (nm)	260

2.2. Characterization and analysis

Elemental analysis of samples Aloe Vera wastes-based activated carbon (AV-AC) was conducted using a Heraeus Elemental Analyzer (Jobin-Yvon Ultima ICP-AES). The surface morphology of the activated carbon before and after the aniline sorption was characterized by a scanning electron microscope (SEM, Jeol Model Jsm-T330). The concentration of aniline in the solution was measured at wavelength of maximum absorption (260 nm) by an UV-Vis spectrophotometer (PG Instrument Limited Model).

2.3. Preparation of adsorbent

Aloe Vera wastes were thoroughly washed with deionized water to remove the impurities and dried in an oven at 150 °C for 24 h. Then, the dried wastes were crushed by a Thomas-Wiley laboratory mill and sieved. Particle sizes in the range of 300-600 μm were carbonized in a furnace at 550 °C for 20 min and activated carbon was again crushed and sieved (mesh no=40) for the adsorption experiments.

2.4. Batch adsorption experiments

The batch adsorption experiments were carried out to determine the effect of parameters such as contact time (0-90 min), pH (3-11), adsorbent dosage (1-5 g/L) and initial aniline concentrations (20-100 mg/L) on the sorption of aniline by AV-AC from aqueous solutions. The experiments conditions and runs in this study are presented in Table 2. All of the adsorption experiments were conducted at room temperature (25 °C). The solutions were agitated (200 rpm) with 100 mL aniline solution in a 250 ml Erlenmeyer flask. After agitation, the suspensions were filtered and the concentrations of aniline in clear solutions were measured. The experiments were done in duplicates and the mean values were considered. The sorption capacity of AV-AC was calculated by Eq. (1):

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

Where; q_e is the adsorption capacity of adsorbent (mg/g), C_0 and C_e are the initial and equilibrium adsorbate concentration (mg/L), V is the volume of the solution (L) and m is the mass of adsorbent (g) [17].

Table 2. The experiments conditions and runs in this study

Experiment Run	Aniline Conc. (mg/L)	Adsorbent Dose (g/L)	pH	Contact Time (min)	Temp (°C)
Effect of contact time	50	2	4	0-90	25
Effect of solution pH	50	2	3-11	60	25
Effect of sorbent dose	50	1-5	3	60	25
Effect of aniline conc	20-100	1	3	60	25

RESULTS AND DISCUSSION

3.1. Characterizations of sorbent

Chemical compositions of AV-AC were determined and the results showed that C, O, Ca, K and Mg constituted 92.7% of the total weight (wt. %). Other minor compounds were included Na (5.92%) and Cl (1.35%). Fig. 1 (a) and (b) illustrates the surface morphology of sorbent before and after the sorption of aniline. As seen in Fig. 1 (a), before the sorption, the surface morphology of activated carbon has uneven cavities and fine open pores on the surface of the adsorbent that is clearly identifiable. A highly regular structure for the activated carbon can be seen after adsorption of aniline in Fig. 1 (b). Many orderly and developed pores can be seen in this figure, which shows a smoother surface due to the sorption of aniline onto the surface of activated carbon.

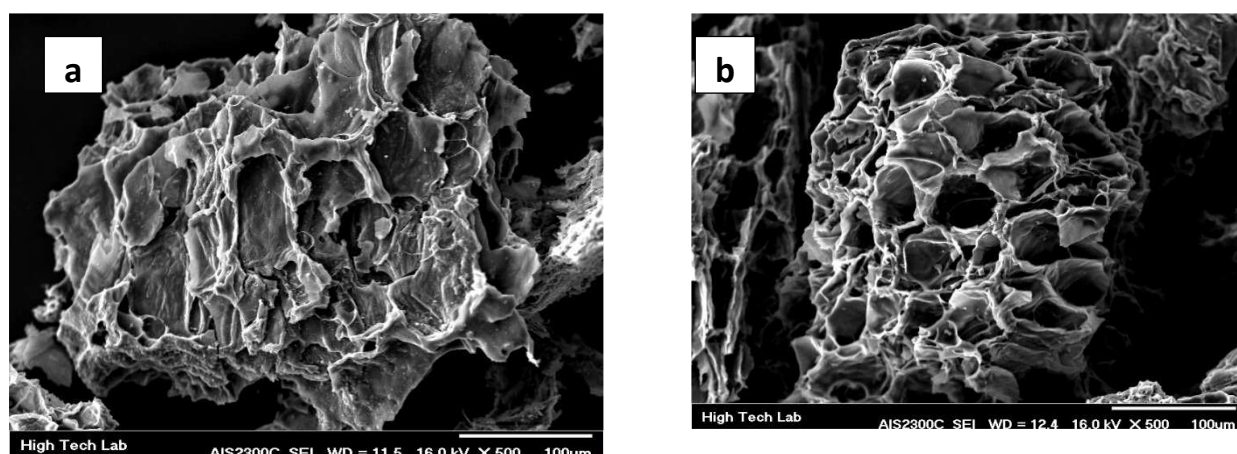


Figure 1. SEM image of sorbent (a) before and (b) after adsorption

3.2. Effect of contact time

The adsorption data versus contact time for the uptake of aniline from aqueous solution by AV-AC are indicated in Fig. 1 (a). The equilibrium reached at contact time of about 60 min ($q_e=5.93$ mg/g) and then gradually reached to a fixed state during the remaining time up to 90 min. As seen, a fast initial adsorption was occurred for aniline molecules at the beginning the process. The fast uptake of the aniline molecules at the beginning of the adsorption time can be due to the availability of large numbers of the vacant sites of the adsorbent surface to the adsorbate and with increasing contact time these vacant sites were saturated by aniline. Therefore, the contact time of 60 min was selected for the subsequent experiments. Lin *et al.* (2011) reported that the equilibrium time for the sorption of aniline by lignin grafted acrylic acid was obtained in 60 min [8]. Al-Johani *et al.* (2011) demonstrated that aniline sorption using multi-walled carbon nanotubes from aqueous solution reached to a equilibrium state at contact time of 3 h [5].

3.2.1. Kinetics study

Kinetic models are useful for describe the adsorption mechanism of aniline onto the adsorbent. In this study, experimental data of the aniline sorption were fitted by pseudo-first order and pseudo-second order kinetic models to attain the better understand of the adsorption process. The pseudo-first order kinetic model [18-20] can be expressed by Eq. (2):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

Where; q_e and q_t (mg/g) are the amounts of aniline adsorbed onto AV-AC at the equilibrium and at any time t , respectively. K_1 (1/min) is the rate constant of the pseudo-first order kinetic. K_1 and q_e are obtained from linear plot of $\ln q_e - q_t$ against time (min), which were determined from the slope and intercept of the linearized curve, respectively [20].

The experiment data were also analyzed by pseudo-second order kinetic. This adsorption kinetic model can be illustrated by the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

Where; q_e and q_t are similar to the pseudo-first order kinetic parameters. Also, K_2 (g/mg. min) is the rate constant of the pseudo-second order kinetic. K_2 and q_e can be determined from the intercept and slope of t/q_t versus t , respectively [21]. Fig. 2 (b) shows pseudo-second order kinetic model for the sorption of aniline from aqueous solutions by AV-AC. In addition, Table 3 also shows the parameters of pseudo-first order and pseudo-second order kinetic models for the sorption of aniline. The higher liner correlation coefficient ($R^2 > 0.98$) of the pseudo-second order kinetic demonstrated that this kinetic model fitted the sorption data better than other kinetic model. Lin *et al.* (2011) reported that the sorption of aniline by L-g-AA from polluted water was excellently obeyed by the pseudo-second-order model [8].

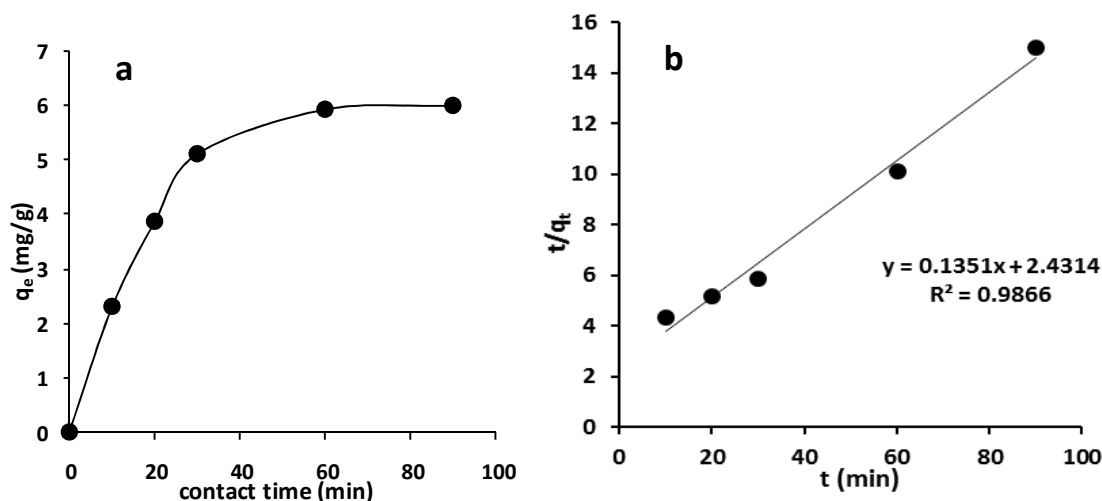


Figure 2. (a) The effect of contact time on the sorption capacity of aniline (sorbent dosage=2 g/L, aniline concentration=50 mg/L at pH=4) and (b) pseudo-second order kinetic model.

Table 3. Parameters of pseudo-first order and pseudo-second order models.

Adsorbate	Pseudo-first order			Pseudo-second order			
	q_e , experimental (mg/g)	K_1 (1/min)	R^2	q_e , experimental (mg/g)	K_2 (g/mg.h)	q_e , calculated (mg/g)	R^2
Aniline	2.12	0.016	0.72	5.93	0.021	7.40	0.98

3.3. Effects of solution pH and adsorbent dosage

The pH has a determine influence on the ionization, dissociation and surface properties of adsorbent [12]. The effect of different ranges of pH on the sorption of aniline is illustrated in Fig. 3 (a). As it can be observed, an increasing solution pH had a significant decreasing effect on aniline adsorption by AV-AC. This result may be due to change in surface charge of aniline molecules and functional groups of the sorbent. At the acidic pH, the functional groups of sorbent became protonated. These groups are mainly carboxylic groups ($-\text{CO}-\text{OH}_2^+$), phenolic ($-\text{OH}_2^+$) and chromenic group, which the surface charge of AV-AC becomes more positive charge at pH 3 and they enhances more electrostatic attraction between sorbent and aniline. The isoelectric point of the activated carbon from natural sorbent was found to pH of 11.3. At the lower pH of this point, there were positive charges onto the adsorbent, which it will promote reaction with aniline. The effects of different dosage of AV-AC were investigated in an initial concentration of 50 mg/L at the room temperature and the results are presented in Fig. 2 (b). As observed, with increasing the adsorbent dosage from 1 g/L up to 5 g/L, the adsorption capacity was reduced. Decrease in the uptake capacity of aniline in higher dosage of activated carbon may be due to the unavailability of pollutant molecules that cannot cover all the active sites on the adsorbent surface. In other words, a large number of the surface active sites of the adsorbent cannot reach to saturation state at high dosages of AV-AC. Therefore, dose of 1 g/L of the adsorbent was selected as the optimum dosage for the next stages.

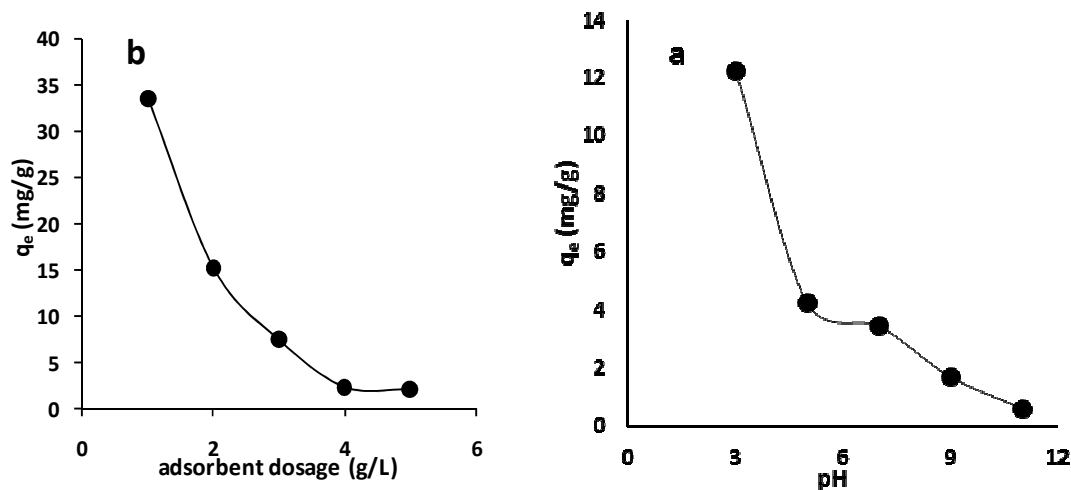


Figure 3. (a) The effect of pH on the sorption capacity of aniline (contact time=60 min, adsorbent dosage=2 g/L and aniline concentration=50 mg/L) and (b) effect of the adsorbent dosage on the sorption capacity of aniline (contact time=60 min, aniline concentration=50 mg/L and pH=3).

3.4. Effect of aniline concentration

The influence of initial concentrations of aniline was investigated on the adsorption capacity of AV-AC and the results are illustrated in Fig. 4 (a). It can be seen that the adsorption capacity of the adsorbent was rapidly increased from 7.5 mg/g to 64.3 mg/g with increasing aniline concentration from 20 mg/L to 100 mg/L in the solution. This can be resulted from the increase in driving force of aniline molecules (including van der Waals's force) to the active sites of the adsorbent, which this state provided at higher concentrations of the adsorbate [21].

3.4.1. Isotherm study

Isotherm models can provide information about the heterogeneity and homogeneity of the adsorbent surface and also present whether interaction between adsorbate and adsorbent occurred or not [22]. Two Isotherms including Langmuir and Freundlich models are usually applied for these purposes. In this study, the experimental data were analyzed by Langmuir and Freundlich isotherms in initial concentration of 20-100 mg/L. The Langmuir isotherm assumes that monolayer sorption occurs at binding sites with homogenous energy levels [10, 23]. The Langmuir isotherm is linearized using Eq. (4):

$$\frac{C_e}{q_e} = \frac{C_e}{Q_m} + \frac{1}{bQ_m} \quad (4)$$

Where; C_e is the equilibrium concentration of aniline (mg/L), q_e is the adsorption capacity of AV-AC in the equilibrium time (mg/g). Q_m (maximum adsorption capacity, mg/g) and b (the Langmuir constant, L/mg) are taken from the slope and intercept of linear plots of C_e/q_e against C_e , respectively [23]. A dimensionless constant separation factor, R_L is used in relation to Langmuir isotherm model. This factor called also the equilibrium parameter [24, 25] and is defined by Eq. (5):

$$R_L = \frac{1}{1 + bC_0} \quad (5)$$

Where; b and C_0 were defined in the above for Langmuir isotherm. The value of R_L demonstrates that adsorption system is unfavorable ($R_L > 1$), irreversible ($R_L = 0$), liner ($R_L = 1$), and favorable ($0 < R_L < 1$). In this study, based on the value of $R_L = 0.83$, the adsorption system of aniline onto AV-AC was favorable.

The Freundlich isotherm model applies for non-ideal sorption on heterogeneous surface of the sorbent [26, 27]. The Freundlich isotherm model is described by Eq. (6):

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \quad (6)$$

Where; q_e and C_0 were presented above. K_f (L/g) and n are constants of the isotherm and illustrates the capacity and intensity of the adsorption, respectively. The parameter of K_f is obtained from the intercept and n is achieved from the slope of plotting $\ln q_e$ versus $\ln C_e$ [26, 27]. Fig. 4 (b) shows the Freundlich isotherm plot for the adsorption of aniline on the activated carbon. Table 4 also shows the parameters of Langmuir and Freundlich isotherm models in

this study. As shown, the adsorption data were well described by the Freundlich isotherm. Zhang and Li (2012) showed that the experimental data the sorption of aniline via Hypercross-Linked Fiber were obeyed from Freundlich isotherm model [28].

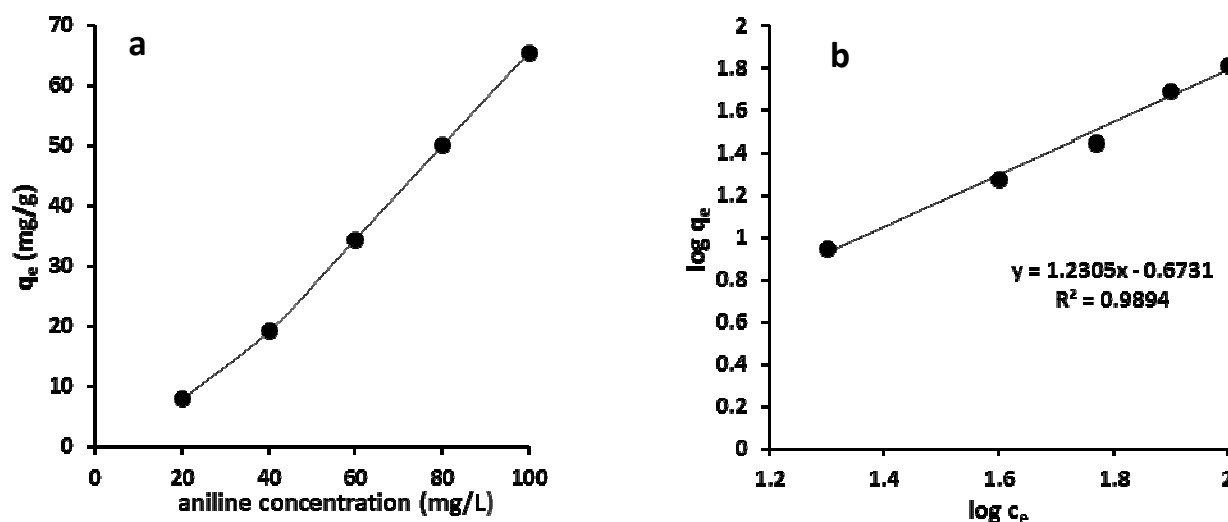


Figure 4. (a) The effect of initial aniline concentrations on the sorption capacity of aniline (contact time=60 min, adsorbent dosage=1 g/L and pH=3) and (b) Freundlich isotherm model.

Table 4. Parameters of Langmuir and Freundlich isotherm models in this study.

Adsorbate	Langmuir				Freundlich		
	Q_m (mg/g)	b (L/mg)	R^2	R_L	K_f (L/g)	n	R^2
Aniline	106.38	0.004	0.96	0.83	0.09	0.81	0.98

3.5. Comparison with other studies

In this study, the value of maximum adsorption capacity of aniline by AV-AC was obtained 106.38 mg/g. This value was compared with the maximum sorption capacities obtained from other studies (Table 5). As seen, the Q_m of the sorbent in the present study was higher than other sorbents. The sorption was also happened at very low time toward other sorbent (except to spherical carbon). It can be concluded that the activated carbon prepared from Aloe Vera wastes (AV-AC) can be considered as a very effective adsorbent for the uptake of aniline from aqueous media.

Table 5. Comparison the maximum monolayer adsorption capacity of aniline by various sorbents.

Adsorbent	Equilibrium time (min)	Max. sorption capacity (mg/g)	Ref.
Pine sawdust	80	1.50	[4]
Activated carbon/chitosan composite	120	22.90	[29]
PAM/SiO ₂	300	52.00	[30]
Fe ₃ O ₄ -AC magnetic nanoparticles	300	90.91	[9]
Graphitic carbon nitride	1200	93.40	[14]
Spherical carbon	10	93.59	[7]
Bamboo based activated carbon	450	104.17	[31]
Cr-bentonite	30	21.60	[15]
C-MCM	60	16.64	[32]
AV-AC	60	106.38	This study

CONCLUSION

In this batch sorption research, activated carbon prepared from Aloe Vera wastes (AV-AC) was used as a new low-cost sorbent for uptake of aniline from aqueous solutions. The optimum contact time in the sorption process was

obtained during 60 min. Moreover, the optimum pH was also achieved at pH 3. The pseudo-second order kinetic and Freundlich isotherm models described the data better than other isotherm and kinetic models, respectively. The present study concludes that AV-AC due to low-cost, non-toxicity and high sorption uptake toward other sorbents can be employed as a very effective material for the removal of aniline from aqueous media.

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