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A comparative adsorption for the removal of *p*-cresol from aqueous solution onto granular activated charcoal and granular activated alumina

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Abstract

In this study, the adsorption of *p*-cresol onto granular activated alumina (AA) was investigated in batch mode and the obtained results were compared to granular activated charcoal (AC). Experiments were carried out as a function of pH, adsorbent dosage, contact time, initial concentration, temperature and ionic strength. The experimental results indicate that, the adsorption yield increases with an increase in the adsorbent dosage. Results from the effect of pH indicate that *p*-cresol is preferentially adsorbed from its neutral form. Kinetics data were properly fitted with the pseudo-first-order kinetic model. The adsorption yield decreases with an increase in solution temperature. The addition of $NaNO_3$ decreases distinctly the adsorption of *p*-cresol by the two adsorbents. The equilibrium uptake was increased with an increase in the initial concentration in solution. The equilibrium data fitted well to the Langmuir model with a maximum monolayer adsorption capacity of 55.80 and 56.61 mg/g, respectively for granular activated alumina and granular activated charcoal.

Keywords: Activated alumina; *P*-cresol; Adsorption; Isotherms; Thermodynamics.

1. Introduction

Cresols are organic compounds which are methylphenols. They are a widely occurring natural and manufactured group of aromatic organic compounds which are categorized as phenols .These pollutants are widely found in the effluent from many chemical and allied industries, namely petrochemical, oil refinery, metal refining, chemical and glass fiber manufacturing, ceramic plants, steel plants and phenolic resin manufacturing. As they are slowly oxidized by length exhibition in the air, these pollutants are known to possess high toxicity and low biodegradability, for which their occurrence in wastewater has become an important environmental issue [1, 2].

In order to decrease the potential risk of these pesticides and reduce their appearance in the water, The European Community Directive has determined a tolerance level of 0.5µg/L in water intended for human consumption. Japan's Ministry of Health, Labour, and Welfare specifies a maximum contaminant level (MCL) of 5µg/L in drinking water [3]. Therefore, to save our aqueous ecosystem, it has been essential to reduce these molecules concentration in wastewater to acceptable level before safe disposal to water bodies.

Various physical, chemical and biological processes have been used for the removal of phenols and derivates pollutants from wastewater such as membrane filtration [4], advanced oxidation [5], electrolysis [6], activated sludge and adsorption [7]. However, adsorption is most versatile due to high efficiency, simplicity in design and operation. Due to large surface area, porous structure, and favorable chemistry, activated carbon and other similar materials have been extensively tested as adsorbent for removing water pollutants such as phenols by several groups of researchers [8-11]. Nevertheless, its application is now limited due to its difficult regeneration and reuse. At present, there is a growing interest in using low-cost and non-conventional alternative materials instead of traditional sorbents. In contrast, activated alumina adsorption is known to be an effective and inexpensive technology for the removal of inorganic pollutants from drinking water [12].

The focus of the present study was to assess the potentiality of activated alumina as a low-cost adsorbent for the removal of phenolic compounds from aqueous solution. In this sense, *p*-cresol was chosen as a pollutant because it is one of most abundant phenolic compound frequently found in industrial wastewater. In recognition of its toxicity and high mobility in the environment, the Environmental Protection Agency (EPA) and the European Environmental Agency (EEA) have included this compound in the lists of priority pollutants to be monitored in industrial effluents [13-15].The adsorption performance of the activated alumina has been compared to that of activated carbons, and the effects of pH, adsorbent dosage, contact time, ionic strength, concentration and temperature on the adsorption process were investigated. The adsorption kinetic data was tested by pseudo-first-order and pseudo-second-order kinetic models. The equilibrium data were analyzed using Langmuir and Freundlich isotherm models. The thermodynamics of the adsorption was also evaluated.

2. Materials and methods

2.1. Chemicals

All chemicals were reagent grade and were used without further treatment. *P*-cresol was purchased from Fluka (>99% purity). Granular activated charcoal was supplied by sigma Aldrich (India) and granular activated alumina by Auchtel Products Ltd (Mumbai, India). Stock p-cresol solution of 1000 mg/L was prepared by dissolving 1,010 g of p-cresol commercial product in 1 L of distilled water and thereby necessary solutions were prepared by dilution.

2.2. p-Cresol adsorption experiments

The physical and chemical characteristics of the adsorbents are summarized in Table 1. Adsorption experiments were conducted in 250 mL conical flasks at a constant agitation speed of 100 rpm. The experiments were carried out by varying contact time from 5 to 100 min, the adsorbent dosage from 0.1 to 2.5 g/L, the pH from 2 to 12, the initial concentration from 10 to 70 mg/L, $NaNO_3$ concentration from 0.005 to 0.1 mol/L and the temperature from 25 to 50°C. The temperature was controlled using an isothermal shaker. The pH was adjusted to a given value by addition of HCl (1N) or NaOH (1N) and was measured using a JENWAY pH-Meter 3305. After the each adsorption procedure completed, the sample were filtered on MF-Millipore membrane (0.38 µm). Each experiment was done in triplicate, with an average scattering of the results of 5%, never higher than 10%.

Table 1: Physical and chemical properties of granular activated alumina and granular activated charcoal.

Properties	Activated alumina	Activated charcoal
Surface area (m^2/g)	360	800
Particle size (mm)	1,7 ± 0.2	6–18
Pore volume (ml/g)	0.46	-
Bulk density (kg/m)	778	430
Al_2O_3	90.5	-
Na_2O	0.03	-
Fe_2O_3	0.07	-
SiO_2	0.07	-
Particle density (kg/m)	-	820
Ash content (on dry basis) (%)	-	3.8
Moisture content	-	5.9
Conductivity (µs/cm)		84.4

2.3. Adsorption measurements

Residual *p*-cresol concentrations were determined from UV-Vis absorbance characteristic with the calibration curve method at the maximum of absorbance of 278 nm using a JENWAY 6405 UV/VIS spectrophotometer.

The adsorbed amounts and the adsorption yield were calculated by measuring the concentration of *p*-cresol in solution before and after adsorption and using the following equations:

$$q = \frac{(C_0 - C)}{R} \qquad (1)$$

$$\% \text{ Removal} = \frac{(C_0 - C)}{C_0} * 100 \qquad (2)$$

Where *q* (mg/g) is the quantity of *p*-cresol adsorbed per unit mass of adsorbent, % Removal is the adsorption yield, C_0 (mg/L) is the initial concentration, *C* (mg/L) is the concentration after adsorption and *R* (g/L) is the mass of adsorbent per liter of aqueous solution.

3. Results and discussion

3.1. Effect of pH

Adsorption is highly affected by the solution pH, since it change the surface charge on the adsorbent and the adsorbate leading to influences the electrostatic interactions between them [16,17]. Theses interactions are of paramount importance in the removal of a weak electrolyte such as *p*-cresol. The effect of pH on the adsorption of *p*-cresol by AA and AC is shown in Figure 1. The adsorbed amounts were found to be constants between pH of 2 and 10 for both the adsorbents which suggest that *p*-cresol is preferentially adsorbed from its neutral form

($pK_a \approx 10.2$). This is in good agreement with previous studies [18, 19]. As the solution became more basic (pH>>10), the adsorption capacity remaining constant in the case of AA and gradually went down in the case of AC. This results perhaps due to repulsion between the negatively charged adsorbent and negatively charged p-cresol at pH higher which could be more significant in the case of AC.

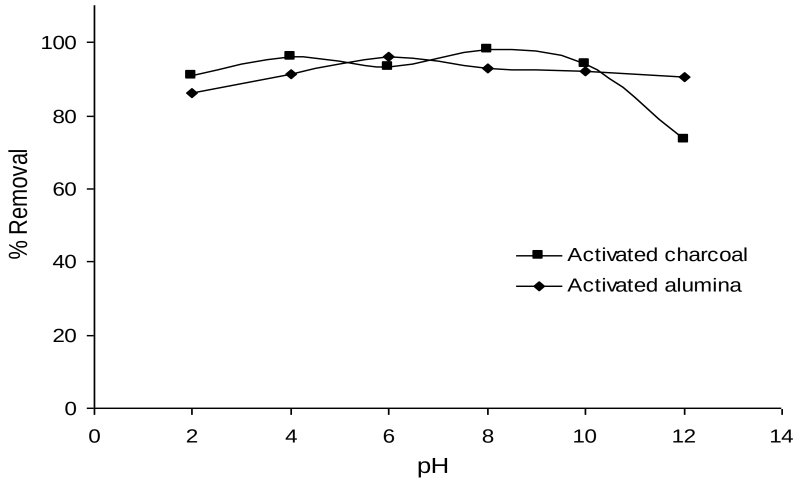

Figure 1: Effect of pH on *p*-cresol removal by AC and AA. C_0 = 50mg/L, R = 1g/L, temperature = 25°C, contact time = 2h, speed agitation = 100 rpm.

3.2. Influence of adsorbent dosage

In order to investigate the effect of adsorbent dosage on the adsorption of *p*-cresol and to optimize the dose, series of adsorption experiments were carried out by varying the amounts of adsorbents from 0.1 g/L to 2.5 g/L. Data obtained are presented in Figure 2. From this figure it is clear that AC has more adsorption capacity than AA. The figure also showed that increasing adsorbent dosage resulted in a sharply increase in the adsorption yield. The adsorption yield increased from 29 to 97 % and from 20 to 96 %, when the adsorbent dosage was increased from 0.1 to 0.7 g/L and from 0.1 to 1 g/L, respectively for AC and AA. This enhancement in adsorption removal with increasing adsorbent dosage could be due to fact that higher adsorbent dosage provides more possible active sites for the adsorption process which results in the overall increase in the removal efficiency [20]. A further increase in adsorbent dose over 0.7 g/L for AC and 1 g/L for AA did not lead to a significant improvement in adsorption yield. Therefore, amount of *p*-cresol adsorption per unit mass of adsorbent decreases with increase in adsorbent dosage. This fact leads to the estimation of the optimum adsorbent dose required for the removal of *p*-cresol by using the two adsorbents at prevailing operating conditions as 0.7 g/L of AC against 1 g/L of AA. Although the dose of AA required is more than the dose of AC.

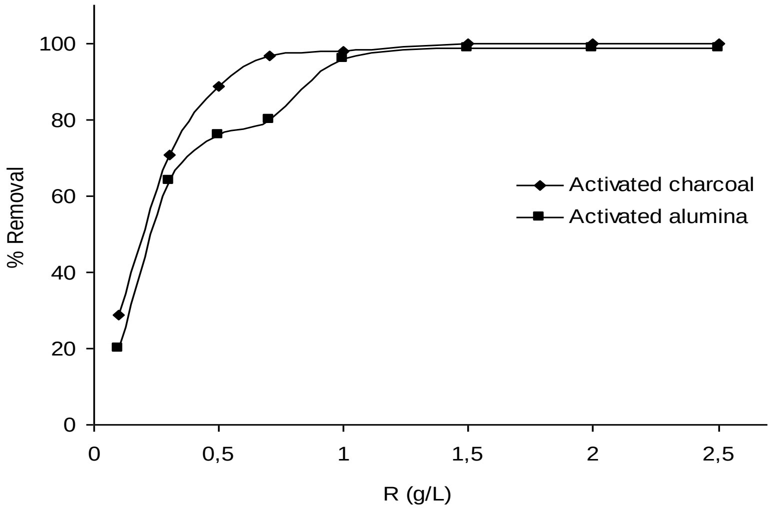

Figure 2: Effect of adsorbents dosage on *p*-cresol removal by AC and AA. C_0 = 50mg/L, pH = 7, temperature = 25 °C, contact time = 2h, speed agitation = 100 rpm.

3.3. Influence of contact time

Kinetics gives important information for designing batch adsorption systems. Information on the kinetics of solute uptake is required for selecting optimum operating conditions for full-scale batch process [21]. Figure 3 shows the adsorbed amounts of *p*-cresol per unit mass of AC and AA, as a function of time. For the two adsorbents, the kinetics was found to be rapid at the first stage of the process and then the rate of adsorption be slower and stagnates with the increase in contact time. The kinetics of *p*-cresol adsorption is much faster onto AC than onto AA. In fact, equilibrium times were 30 and 60 min, respectively for AC and AA.

Adsorption kinetics data were analyzed using two kinetic models; pseudo-first-order model and pseudo-second-order model. The pseudo-first-order rate expression of Lagergren based on solid capacity is generally expressed as follows [22]:

$$\frac{dq}{dt} = k_1 (q_e - q) \quad (3)$$

After integrating and applying the boundary conditions, for q = 0 at t = 0 and q = q at t = t, the integrated form of equation 3 becomes:

$$q = q_e (1 - e^{-k_1 t}) \quad (4)$$

Where q_e and q (both in mg/g) are respectively the amounts of *p*-cresol adsorbed at equilibrium and at any time '*t*', and k_1 (1/min) is the rate constant of adsorption

The pseudo-second-order model proposed by Ho and McKay [23] was used to explain the sorption kinetics. This model is based on the assumption that the adsorption follows second order chemisorption. The pseudo-second-order model can be expressed as:

$$\frac{dq}{dt} = k_2 (q_e - q)^2 \quad (5)$$

After integrating for the similar boundary conditions, the following equation can be obtained:

$$q = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (6)$$

Where k_2 (g/mg.min) is the rate constant of pseudo-second order adsorption.

Parameters of the pseudo-first-order and pseudo-second-order models were estimated with the aid of the non-linear regression. The obtained data and the correlation coefficients, r^2, are given in Table 2.

The table shows that the correlation coefficients for the two models are nearly equal to 1. However, estimated adsorbed amounts at equilibrium q_e are reasonably close to experimental q_e values in the case of pseudo-first-order model.

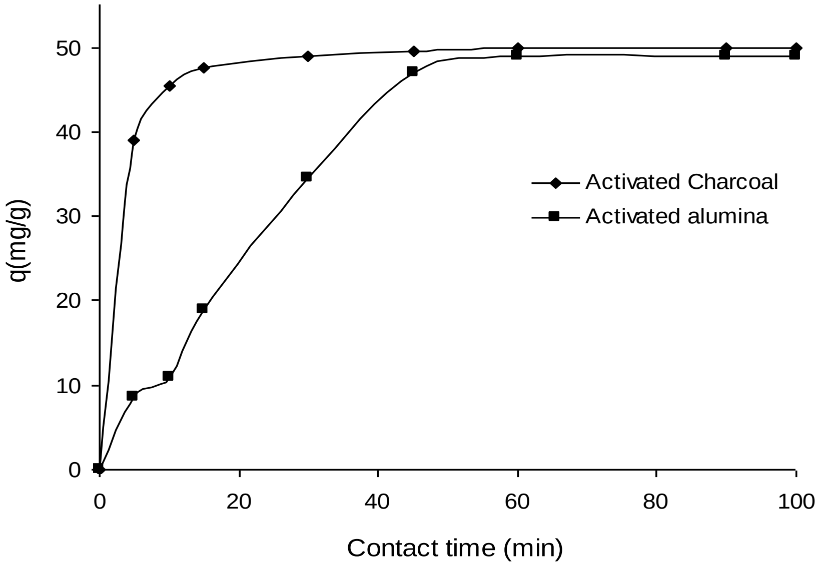

Figure 3: Effect of contact time on *p*-cresol removal by AC and AA. C_0 = 50mg/L, R = 1g/L for AA and 0.7 g/L for AC, pH = 7, temperature = 25°C, speed agitation = 100 rpm.

Table 2: Kinetic constants for *p*-cresol adsorption onto AC and AA.

		Pseudo-first-order			Pseudo-second-order		
Adsorbent	q_{exp} (mg/g)	q_e(mg/g)	k_1(min^{-1})	r^2	q_e (mg/g)	k_2 (g/mg.min)	r^2
AC	50	49.32	0.298	0.997	51.18	0.0136	0.999
AA	50	54.22	0.0336	0.981	58.45	0.0010	0.988

3.4. Effect of temperature

Figure 4 show the interactive effects of temperature on the adsorption of *p*-cresol. It was observed that adsorbed amounts decreased with the increase in temperature, indicating an exothermic process. This decrease in adsorption with the increase in temperature can be due to the deformation in the active sites at higher temperatures [24]. Generally, the temperature has two major effects on the biosorption process. Increasing the temperature is known to increase the rate of diffusion of the biosorbed molecules across the external boundary layer and the internal pores of the biosorbent particles, owing to the decrease in the viscosity of the solution [20]. In addition, changing temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate.

3.5. Calculation of thermodynamic parameters

Thermodynamic parameters such as the change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were calculated by considering the following reversible process [25]:

$$\text{p}-\text{cresol in solution} \Leftrightarrow \text{adsorbed p}-\text{cresol}$$

For such equilibrium reactions, K_D, the distribution constant, can be expressed as:

$$K_D = \frac{q_e}{C_e} \qquad (7)$$

The Gibbs free energy is:

$$\Delta G° = -RT \ln (K_D) \qquad (8)$$

where R is the universal gas constant (8.314 J mol/K) and T is solution temperature in K.

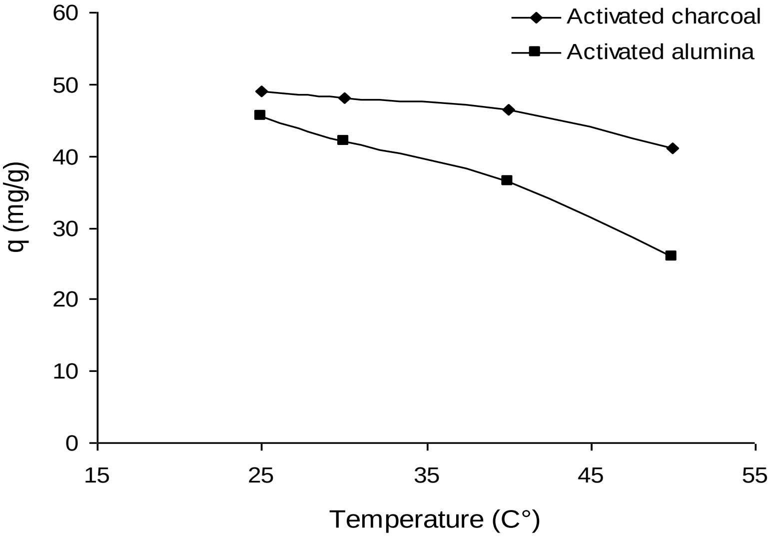

Figure 4: Effect of temperature on *p*-cresol removal by AC and AA. C_0 = 50mg/L, R = 1g/L for AA and 0.7 g/L for AC, pH = 7, contact time = 2 h, speed agitation = 100 rpm.

The enthalpy (ΔH°) and entropy (ΔS°) of adsorption were estimated from the slope and intercept of the plot of ln K_D versus $1/T$ yields, respectively.

$$\text{Ln} K_D = -\frac{\Delta G°}{RT} = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{R} \qquad (9)$$

The adsorption enthalpies, adsorption free energies, and adsorption entropies of *p*-cresol adsorbed onto AC and AA are presented in Table 3. From the table it can be concluded that the adsorption was exothermic (ΔH° = -71.87 kJ/mol for AC and -68.59 kJ/mol for AA). In particular, the absolute value of the adsorption enthalpy for

AC is a little greater than for AA, displaying the interaction of the *p*-cresol with AC is a little stronger. Also, the magnitude gives information on the type of adsorption, which could be chemical in nature involving strong forces of attraction [26]. The negative adsorption free energies imply the process is favorable. Moreover, the adsorption free energies for AC are a little more negative than for AA, displaying the more favorable process for AC. The reaction was accompanied by a decrease in entropy (ΔS° = -209.30 J/K.mol for AC and - 211.41 J/K.mol for AA). The negative Δ*S*° value suggests a decrease in the randomness at the solid/solution interface during the adsorption.

Table 3: Thermodynamic parameters calculated for the adsorption of *p*-cresol by AC and AA.

	T(°C)	K_D	$\Delta G°$ (J/mol)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (J/K.mol)
Activated charcoal	25	49.01	-3365.1	- 71.87	- 209.30
	30	24.20	-2911.4		
	40	13.29	-2472.0		
	50	4.56	-1117.4		
Activated alumina	25	10.11	-5729.44	-68.59	- 211.41
	30	5.25	-4175.30		
	40	2.70	-2587.04		
	50	1.08	-214.84		

3.5. Effect of $NaNO_3$ on the p-cresol adsorption

Owing to the coexistence of inorganic salts with the industrial wastewater containing *p*-cresol at a comparatively high level, the effect of $NaNO_3$ on the ability of AC and AA to remove *p*-cresol in aqueous solution was evaluated. The results are depicted in Figure 5. We note that, the addition of $NaNO_3$ decreases distinctly the adsorption of *p*-cresol by the two adsorbents. This behavior can be attributed to change in the electric double layer surrounding the adsorbents particles in aqueous solutions. Previous studies reported that the thickness of this double layer was compressed by an increase in the ionic strength of the solution [27], which increases the attraction forces between adsorbents surface and *p*-cresol molecules. The observed decrease in adsorption amounts could be attributed either to the increase repulsive attractions *p*-cresol molecules or a competition between the ions electrolytes and the *p*-cresol molecules towards the sites of adsorption.

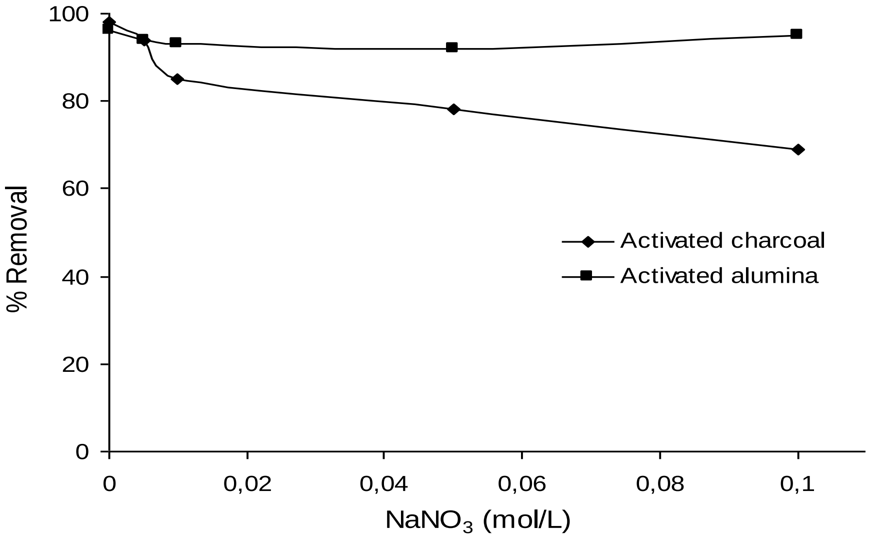

Figure 5: Effect of ionic strength on *p*-cresol removal by AC and AA. C_0 = 50mg/L, R = 1g/L for AA and 0.7 g/L for AC, pH = 7, temperature = 25°C, contact time = 2 h, speed agitation = 100 rpm.

3.6. Adsorption isotherms

The effect of initial concentration on the adsorption of *p*-cresol was studied in the range of 10-70 mg/L. Figure 6 shows that *p*-cresol removal is highly concentration dependent. The equilibrium sorption capacity increased with a rise in initial concentration. This increase in adsorption capacity with solution concentration is probably due to a high driving force for mass transfer [28]. In fact, high concentration in solution implicates high adsorbat molecules fixed at the surface of the adsorbent. The isotherms form was type L in Giles classification [29]. These types of isotherms are usually associated with ionic solute adsorption with weak competition with the solvent molecules [30]. The Langmuir and Freundlich models were applied for the analysis of equilibrium sorption data obtained. The Langmuir isotherm model [31] is valid for a monolayer sorption onto a surface of a finite number of identical sites.

The Langmuir model is given by Eq. (10):

$$q_\mathrm{e} = \frac{q_\mathrm{m} K_\mathrm{L} C_\mathrm{e}}{1 + K_\mathrm{L} C_\mathrm{e}} \qquad (10)$$

Where q_e (mg/g) is the absorbed amount at equilibrium, C_e is the equilibrium concentration (mg/L), K_L is Langmuir equilibrium constant (L/mg) and q_m the maximum adsorption capacity (mg/g).

The empirical Freundlich isotherm [32] is obtained on the assumption that the adsorption takes place on a heterogeneous adsorbent surface, where the adsorption energy distribution decreases exponentially. This equation is also applicable to multilayer sorption and is expressed by the following equation:

$$q_\mathrm{e} = K_\mathrm{F}\, C_e^{1/\mathrm{n}} \qquad (11)$$

Where K_F ($mg^{1-1/n}\ g^{-1}\ L^{1/n}$) is the Freundlich constant and n is the heterogeneity factor. The K_F value is related to the adsorption capacity; while $1/n$ value is related to the adsorption intensity.

The Langmuir and Freundlich adsorption constants evaluated from the isotherms with the correlation coefficients are presented in Table 4. The table indicates that the best fit of experimental data was obtained with the Langmuir model with r^2 value close to 1. This result suggests that the Langmuir isotherm may be a suitable model for our data. It was concluded that the removal process of *p*-cresol by AC and AA was monolayer adsorption, and the maximum monolayer adsorption capacity was found to be 56.61 and 55.80 mg/g, respectively for AC and AA.

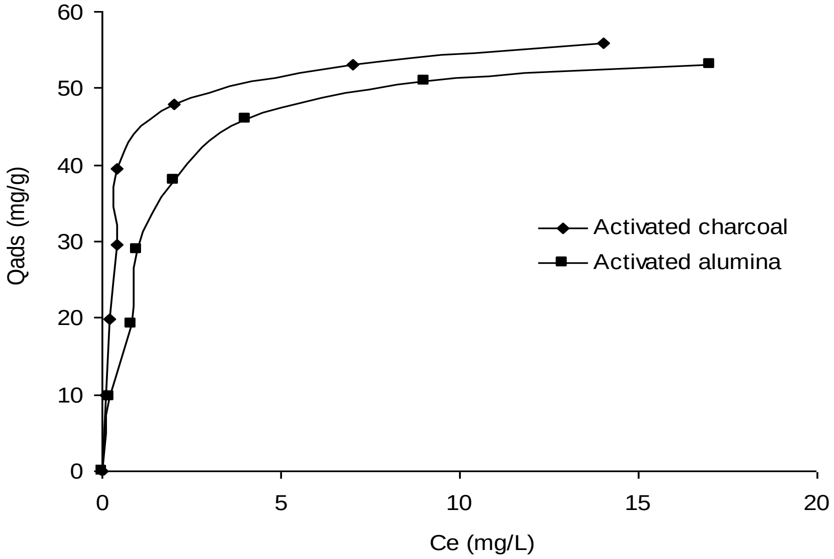

Figure 6: Adsorption isotherms for AA and AC. R = 1g/L, pH = 7, temperature = 25 °C, contact time = 2 h.

Table 4: Langmuir and Freundlich isotherms constants for the adsorption of *p*-cresol by AC and AA.

	Freundlich constants			Langmuir constants		
	K_F ($mg^{1-1/n}\ g^{-1}\ L^{1/n}$)	n	r^2	q_m (mg/g)	K_L(L/mg)	r^2
AC	34.94	4.782	0.880	56.61	3.198	0.971
AA	26.70	3.604	0.924	55.80	0.954	0.989

4. Conclusions

In this study, adsorption experiments for the removal of *p*-cresol from aqueous solutions have been carried out using activated alumina as low-cost adsorbent. It was found that the adsorption is rapid. The increase in mass adsorbents leads to increase in adsorption yield due to increase in number of adsorption sites. The equilibrium uptake was increased with increasing the initial concentration in solution. The adsorption kinetics was well described by the pseudo-first order kinetic model equation. The adsorption isotherms could be well fitted by the Langmuir equation. The adsorption yield was found to decrease with increasing temperature, showing the exothermic nature of the process. The addition of $NaNO_3$ decreases distinctly the adsorption of *p*-cresol by the two adsorbents. Finally, by comparing activated alumina performances to those of activated charcoal, we really found that AA is also suitable adsorbents for the removal of p-cresol from aqueous solution. Further work will be focused on the comparison of adsorption process of cresols isomers such as *o*-, *m*-, and *p*-cresol compound from water environment and industrial effluents using AA as adsorbent.

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