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PJBS

ISSN 1028-8880

Pakistan Journal of Biological Sciences

ANSI*net*

Asian Network for Scientific Information
308 Lasani Town, Sargodha Road, Faisalabad - Pakistan

Application of Commercial Powdered Activated Carbon for Adsorption of Carboic Acid in Aqueous Solution

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Abstract: Adsorption studies for Carboic Acid (phenol) removal from aqueous solution on commercial powdered activated carbon were carried out. Batch kinetics and isotherm studies were carried out under varying experimental conditions of contact time, initial phenol concentration, adsorbent dose and pH. Adsorption equilibrium was reached within 6 h for phenolic concentrations 100-500 mg L⁻¹. The adsorption of phenol increases with increasing initial phenol concentration and decreases with increasing the solution pH value. The equilibrium data in aqueous solutions was well represented by the Langmuir and Freundlich isotherm models. Kinetics of adsorption followed a first order rate equation. The studies showed that the palm seed coat carbon can be used as an efficient adsorbent material for the removal of phenolics from water and wastewater.

Key words: Carboic acid, powdered activated carbon, adsorption, isotherm, aqueous solution

INTRODUCTION

Many industrial wastes contain organics which are difficult, or impossible, to remove by conventional biological treatment processes (Rengaraj *et al.*, 2002). Phenols as a class of organics are similar in structure to the more common herbicides and insecticides in that they are resistant to biodegradation. Phenols are widely used for the commercial production of a wide variety of resins including phenolic resins, which are used as construction materials for automobiles and appliances, epoxy resins and adhesives and polyamide for various applications (Banat *et al.*, 2000). In the presence of chlorine in drinking water, phenols form chlorophenol, which has a medicinal taste, which is quite pronounced and objectionable (Mahvi *et al.*, 2004; Aksu *et al.*, 2001; Streat *et al.*, 1995; Lee *et al.*, 1997). Phenolics constitute the 11th of the 126 chemicals which have been designated as priority pollutants by the United States Environmental Protection Agency (Rengaraj *et al.*, 2002). Stringent US Environmental Protection Agency (EPA) regulations call for lowering phenol content in the wastewater to less than 1 mg L⁻¹ (Eahart *et al.*, 1977).

Activated carbon is an effective absorbent primarily due to its extensive porosity and very large available surface area. There are many methods such as oxidation, precipitation, ion exchange and solvent extraction to remove phenolic materials from aqueous solution. However, in water treatment the most widely used method

is adsorption onto the surface of activated carbon (Halhouli *et al.*, 1995). Activated carbons are widely used as an adsorbent for the removal of a wide range of pollutants from various hosting matrices and not those incorporated in the crystal lattice because of their high adsorption capacity, fast adsorption kinetics and ease of regeneration. One of the most important uses of activated carbon is a water treatment process. Several researchers have been reported about the adsorption theory and application of those to the solid phase extraction to remove phenols from water system. Activated carbons are complex and heterogeneous material made of wood, coconut shells, coal, etc with unique adsorptive characteristics mainly influenced by the porous structure, surface area and chemical structure of the surface (Jung *et al.*, 2001; Ania *et al.*, 2002).

Powdered Activated Carbon (PAC) is one type of activated carbon with effective diameter less than 50 µm. PAC is made from a wide variety of materials, including wood, lignite and coal. Its apparent density ranges from 0.36 to 0.74 g mL⁻¹ and is dependent on the type of materials and the manufacturing process. The primary advantages of using PAC are the low capital investment costs and the ability to change the PAC dose as the water quality changes. The latter advantage is especially important for systems that do not require an adsorbent for much of the year (AWWA, 1990).

The objective of the present study is to describe, experimentally, the potential of Commercial Powdered

Activated Carbon (CPAC) (made in Iranian) to adsorb phenolic pollutants using phenol as a model component. Laboratory batch kinetics and isotherm studies were conducted to evaluate the adsorption capacity of CPAC. The influences of various factors, such as initial pH, initial pollutant concentrations on the sorption capacity were also studied. Several models have been published in the literature to describe experimental data of adsorption isotherms. The Langmuir and Freundlich models are the most frequently employed models. In this work, both models were used to describe the relationship between the amount of phenol adsorbed and its equilibrium concentration in solutions at different pH values.

MATERIALS AND METHODS

This study was conducted at Kurdistan University of Medical Sciences in 2006. The CPAC used in this study was purchased from local company in Tehran, Iran. The CPAC was used in the batch experiments. Prior to use, the carbons were washed several times with deionised water. Afterward they were dried in an oven at 110°C for 24 h and stored in a desiccator until used. The characteristics of the activated carbon are presented in Table 1.

Batch adsorption experiments were carried out by allowing an accurately weighted amount of CPAC to reach equilibrium with phenol solutions of known concentrations (based on earlier studies and our pretest results). Initial concentrations of phenol were held between 100 and 500 mg L⁻¹. The pH was adjusted using dilute HCl or NaOH solutions. Known weights of CPAC (0.3 mg) were added to glass backer bottles each containing 100 mL solution. The backers were agitated on a shaker at an 80 rpm constant shaking rate at 25°C for 24 h to ensure equilibrium was reached. At the end of the equilibrium period the contents of the backers were filtered, centrifuged for 10 min at 5000 rpm using a 4124 Bestell centrifuge (Haraeus-Christ, Germany) and the supernatant was subsequently analyzed for residual concentration of phenol. The concentration of phenol was determined with photometric method (APHA, 1995). At

the end, after the preparation of samples according to the standard methods, the residual phenol concentrations were measured using spectrophotometer equipment (spectrophotometer DR-2000, HACH). The absorbance of the colored complex of phenol with 4-aminoantipyrine was read at 500 nm (APHA, 1995). Finally the suitability of the Freundlich and Langmuir adsorption model to equilibrium data were investigated for phenol-sorbent system in three different pH. All experiments were run in duplicates to ensure reproducibility.

RESULTS AND DISCUSSION

Effect of pH: The adsorption of phenol by CPAC was studied at various pH values. Different initial concentrations of phenol were prepared based on the researches concerning the phenol concentration in industrial effluents (Kartal *et al.*, 2001) in the range of 100-500 mg L⁻¹ and adjusted to different pH values of 5, 7 and 11. CPAC was added to make its concentration 30 mg L⁻¹ and sorption was carried out until equilibrium. The results are displayed in Fig. 1. As was expected, the adsorbed amount decreases with increasing the pH value (Fig. 1). This can be attributed to the dependency of phenol ionization on the pH value. The ionic fraction of phenolate ion (ϕ_{ions}) can be calculated from (Banat *et al.*, 2000):

$$\phi_{\text{ions}} = \frac{1}{[1 + 10^{(\text{pK}_a - \text{pH})}]}$$

Obviously, ϕ_{ions} increases as the pH value increased. Accordingly, phenol, which is a weak acid (pK_a = 10), will be adsorbed to a lesser extent at higher pH values due to the repulsive forces prevailing at higher pH values. Similar behavior has been reported by Halhouli *et al.* (1997) for the adsorption of phenol by activated carbon (Banat *et al.*, 2000). In the higher range phenol forms salts which readily ionize leading negative charge on the phenolic group. At the same time the presence of OH-ions on the adsorbent prevents the uptake of phenolate ions (Rengaraj *et al.*, 2002; Mahvi *et al.*, 2004).

Effect of contact time: The results show that the equilibrium time required for the adsorption of phenol on CPAC is 6 h. It is also seen that the remaining concentration of phenol becomes asymptotic to the time axis after 6 h of shaking (Fig. 2). However, for subsequent experiments, the samples were left for 24 h to ensure equilibrium. These results also indicate that the sorption process can be considered very fast because of the largest amount of phenol attached to the sorbent within the first 3 h of adsorption. The equilibrium time was

Table 1: Properties of the commercial powdered activated carbon

Property	Unit	Value
Density	g cm ⁻³	0.495
Ash	wt. %	4
Moisture	wt. %	2.8
Solubility in water	wt. %	0.37
Solubility in acid	wt. %	1.2
Solubility in methanol	wt. %	0.26
Volatile matter	wt. %	7.1
Surface area	m ² /g	540
Iodine number	mg/g	500
Nominal size	µm	38-75
pH	-	8.1

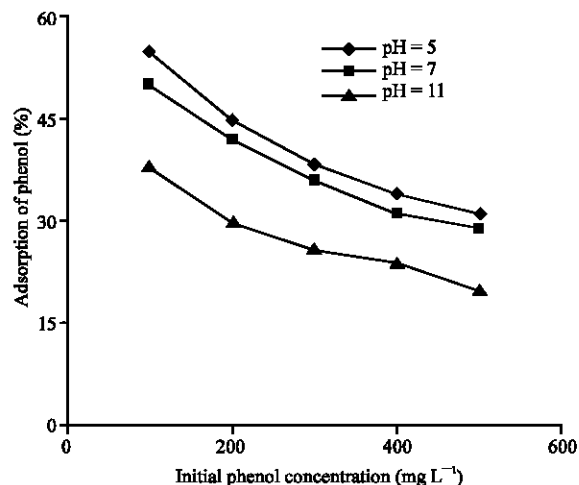


Fig. 1: Relationship between initial phenol concentration and its percent adsorption for various pH values

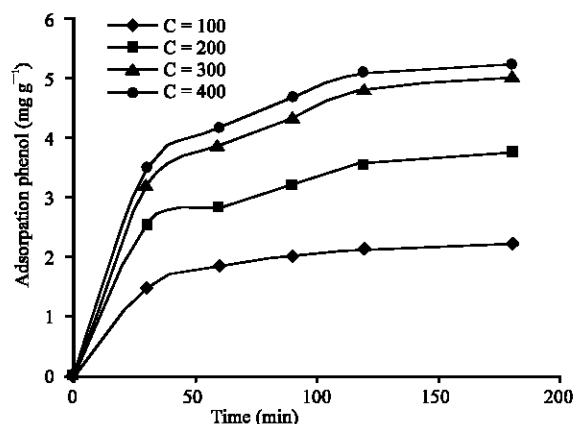


Fig. 2: Effect of contact time for the removal of phenol by CPAC in various phenol concentration

independent of initial concentration of phenol. The phenol removal versus time curves is single, smooth and continuous leading to saturation, suggesting the possible monolayer coverage of phenol on the surface of the adsorbents (Banat *et al.*, 2000).

Initial phenol concentration: As has been shown previously (Fig. 2) the adsorption of phenol by CPAC increases as the initial phenol concentration increased. This is also inconsistent with the results of Fig. 3. Increasing the initial phenol concentration would increase the mass transfer driving force and therefore the rate at which phenol molecules pass from the bulk solution to the particle surface. Hence a higher initial concentration of phenol enhances the sorption process. This would results in higher adsorption (Banat *et al.*, 2000). On a relative

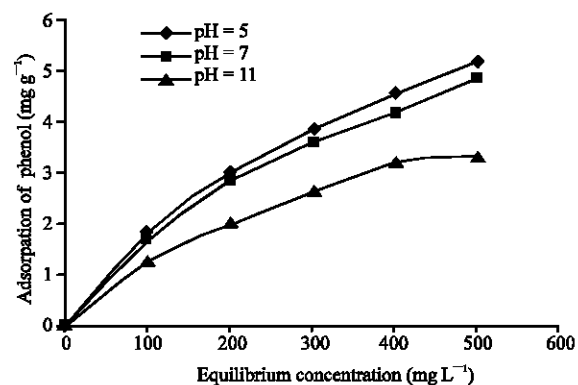


Fig. 3: Relationship between equilibrium phenol concentration and its percent adsorption for various pH values

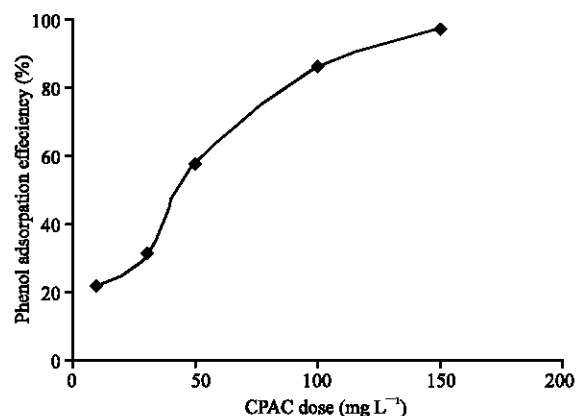


Fig. 4: Effect of carbon dosage on the removal of phenol by CPAC

basis, however, the percentage adsorption of phenol decreases (Fig. 1) as the initial phenol concentration increases. Similar results reported by other researcher (Banat *et al.*, 2000).

Effect of CPAC dose: Figure 4 shows the removal of phenol as a function of carbon dosage by CPAC at the solution pH of 7. Carbon dosage was varied from 10 to 150 mg L⁻¹. It is evident that for the quantitative removal of 400 mg L⁻¹ of phenol in 100 mL, a minimum carbon dosage of 150 mg L⁻¹ CPAC is required for 97% removal of phenol. The data clearly shows that the CPAC is effective for the removal of phenol. The results also clearly indicate that the removal efficiency increases up to the optimum dosage beyond which the removal efficiency is negligible (Rengaraj *et al.*, 2002).

Adsorption isotherms: The three equilibrium curves that were obtained at the three pH values in this study are well

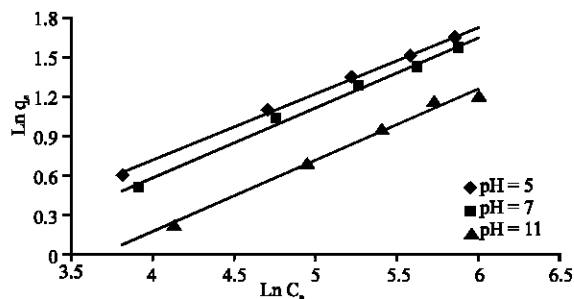


Fig. 5: Freundlich adsorption isotherm for phenol with CPAC at various pH values

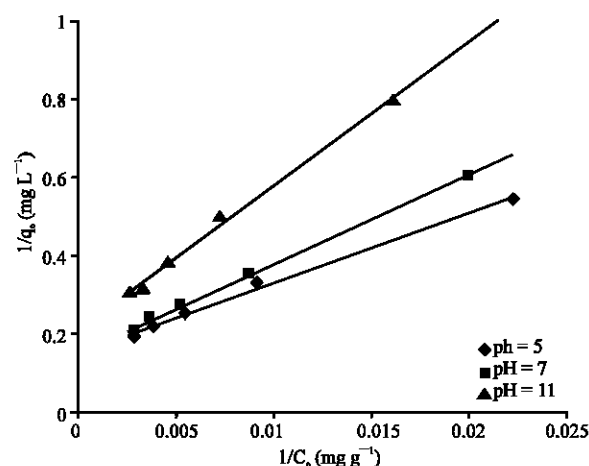


Fig. 6: Langmuir adsorption isotherm for phenol with CPAC at various pH values

Table 2: Parameters of Freundlich and Langmuir isotherm models

pH	Freundlich constants			Langmuir constants		
	K	1/n	R ²	Q ⁰	b	R ²
5	0.27	0.51	0.998	6.41	0.009	0.993
7	0.21	0.53	0.993	6.39	0.007	0.997
11	0.14	0.54	0.989	4.7	0.006	0.992

represented by the Freundlich isotherm model (Fig. 5). When the Langmuir isotherm model was applied to these data, a very good fit was obtained at all pH values (Fig. 6).

The Langmuir constants Q^0 and b and Freundlich constants k and $1/n$ at various pH values are displayed in Table 2. It is obvious that the parameters Q^0 (6.41 at pH of 5 to 4.7 at pH of 11) and k (0.27 at pH of 5 to 0.135 at pH of 11), which are related to the sorption capacity, increase with a decrease in the pH values (Banat *et al.*, 2000; Mahvi *et al.*, 2004; Aksu *et al.*, 2001). This is consistent with the experimental observation. R^2 values, which are a measure of goodness-of-fit (Table 2), show that both the Langmuir and Freundlich isotherm models can adequately describe the adsorption data.

CONCLUSIONS

In this study, the ability of commercial Powdered Activated Carbon to adsorb phenol from aqueous solution was investigated as a function of pH and initial phenol concentration. CPAC adsorption capability was strongly dependent on the pH of the solution. The adsorption capacity was increased with a decrease in the pH and an increase in the initial phenol concentration. The results clearly showed that the CPAC has a linear effect for the removal of phenol. The adsorption of phenol was increased with increasing contact time and became almost constant after 6 h. The sorption phenomenon of phenol to CPAC was expressed by the Langmuir and Freundlich adsorption models. Consequently, the experimental data showed that both the Langmuir and Freundlich isotherm models can adequately describe the adsorption data.

This study shows the potentialities of activated carbon in water and wastewater treatment. Adsorption with CPAC can be an alternative treatment method for those pollutants resistant to conventional methods. Therefore, it can be used for complete decomposition of phenol.

ACKNOWLEDGMENT

This study was conducted in the Department of Environmental Health, Kurdistan University of Medical Sciences, Iran. The authors like to thank to students for their assistance in the handling of experiments.

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