

Adsorption of p-Nitrophenol by Surface Modified Carbons from Aqueous Solution

Meenakshi Goyal[♦]

(Department of Chemical Engineering & Technology, Panjab University, Chandigarh, India

[♦]e-mail: meenakshi_chem@yahoo.co.in

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Abstract

Adsorption isotherms of p-nitrophenol from its aqueous solutions on two samples of activated carbon fibres and two samples of granulated activated carbons have been determined in the concentration range 40–800 mg/L (ppm). The surface of these carbons was modified by oxidation with nitric acid and oxygen gas, and by degassing the carbon surface under vacuum at temperatures of 400°, 650° and 950°C. The oxidation of carbon enhances the amount of carbon-oxygen surface groups, while degassing decreases the amount of these surface groups. The adsorption of p-nitrophenol does not depend upon the surface area alone but appears to be influenced by the presence of oxygen groups on the carbon surface. The adsorption decreases on oxidation while the degassing of the carbon surface enhances the adsorption. The decrease in adsorption depends upon the strength of the oxidative treatment being much larger in case of the oxidation with nitric acid, while the decrease in adsorption on degassing depends upon the temperature of degassing. The results show that while the presence of acidic surface groups which are evolved as CO₂ on degassing suppress the adsorption of p-nitrophenol, the presence of non acidic surface groups which are evolved as CO on degassing tend to enhance the adsorption. Suitable mechanisms compatible with the results have been presented.

Keywords : Adsorption, Activated carbons, Carbon-oxygen surface groups

1. Introduction

Phenol compounds, when present in water can cause objectionable taste and odour and can exert adverse effects on various biological processes. Some of the phenolic compounds are carcinogenic even when present in small amounts and cause several different ailments. Many of these phenolic compounds originate from natural sources by the decay of vegetation which releases phenol in water while others are obtained from the effluents of several industries such as plastics, dyes, coal gasification and petrochemical units. These phenolic compounds if not managed properly cause long-term contamination of both surface and ground waters.

Several methods have been investigated for the removal of phenolic compounds, which include aerobic and anaerobic biodegradation [1], chemical oxidation with ozone [2, 3] and adsorption on activated carbons. However, adsorption on activated carbons appears to offer the best technology for overall treatment especially for the effluents with moderate and low concentrations [4-6], because these carbon materials have a high adsorption capacity.

Diciano and Weber [7] studied the adsorption of phenol, p-nitrophenol, 2, 4, dinitrophenol and the anions of these three species and observed that the anions showed a much lower adsorption affinity for activated carbons than the neutral molecules. Gain and Snoeynik [8] also observed the same

effect when studying the adsorption of p-nitrophenol and p-bromophenol, sodium benzenesulphonate and their anions on Filtrasorb 400. Gonzalez-Martin and coworkers [9, 10] observed that the adsorption of p-nitrophenol from aqueous solutions depended upon the surface area and occurred in narrow pores. Wolborska [11], while investigating the adsorption of p-nitrophenol from water using a fixed bed of activated carbon, derived an equation describing the initial stage of the adsorption dynamics and the concentration distribution in the bed on the low concentration portion of the breakthrough curve by a three stage model. Calleja *et al.* [12] studied the adsorption kinetics of phenol and p-nitrophenol from aqueous solutions using activated carbon. Three different adsorption kinetic models were tried to explain the results. The pore diffusion model was found to give best fit to the kinetic data.

Puri and coworkers [13], while studying the adsorption of phenol and p-nitrophenol on activated carbons and carbon blacks with different surface areas and containing varying amounts of carbon oxygen surface groups, observed that the adsorption was a function of surface area when carried out at moderate concentrations. Marsh and Campbell [14] and Hu *et al.* [15] found that the adsorption of phenol and p-nitrophenol at low concentrations on PF and PVC, and coconut shell activated carbons was extremely sensitive to the microporous structures of these materials. The adsorption

isotherms were similar to those of N₂ and CO₂. The adsorption of p-nitrophenol at low relative concentrations could be used to compare the microporosities of these carbons. The surface areas calculated from adsorption of p-nitrophenol were smaller than the N₂ surface areas which were attributed to differences in the efficiencies of packing of micropore and transitional pore volumes and to the effect of the solvent during building up of layers of the adsorbate molecules in transitional porosity.

The adsorption of phenolic compounds from aqueous solutions has also been found to be influenced by the presence of associated oxygen on the carbon surface [16, 17]. The adsorption has been found to be partly irreversible and involved strong bonding between the adsorbate and the surface oxygen groups. Mattson *et al.* [18] and Epstein *et al.* [19] suggested that the adsorption was favoured when the surface contained quinone groups.

Moreno-Castilla *et al.* [20] studied the adsorption of several phenols from aqueous solutions on activated carbons obtained from original and demineralised bituminous coal and found that the adsorption capacity depended upon the surface and the porosity of the carbon, the solubility of the organic compound and the hydrophobicity of the substituent. The adsorption was attributed to the electron donor-acceptor complexes formed between the basic sites on the carbon surface and the aromatic ring of the phenol.

Above perusal of the literature indicates that activated carbons are good adsorbents for the removal of p-nitrophenol from waste water. It has also been indicated that the presence of carbon-oxygen groups on the carbon surface influences the adsorption of p-nitrophenol. However, the influence of each surface group separately has not been systematically investigated. The present work was therefore undertaken.

In the present paper, the adsorption of p-nitrophenol from aqueous solutions on activated carbons having different surface areas and associated with varying amounts of different types of carbon-oxygen surface groups has been studied. The adsorption has also been carried out after enhancing the carbon-oxygen surface groups by oxidation and after eliminating increasing amounts of these groups by degassing at different temperature.

2. Experimental

Two samples of granulated activated carbons (GAC-S and GAC-E) obtained from Norit N.V. the Netherlands and two samples of activated carbon fibers (ACF-307 and ACF-310) obtained from Ashland Petroleum Company, Kentucky USA have been used in these investigations. The as-received activated carbons have been oxidised with nitric acid and gaseous oxygen at 350°C to enhance the amount of carbon-oxygen surface groups. The oxidised carbons have been degassed at 400°, 650° and 950°C to gradually eliminate

varying amounts of these surface oxygen groups. The procedure for degassing has been described elsewhere [21-25] but a brief description is given here.

2.1. Oxidation with nitric acid

5 g of each as-received activated carbon sample was heated with 150 ml. of pure nitric acid in a borosil beaker of 250 ml. capacity in a water bath maintained at about 80°C. When all but about 10 ml of the acid had evaporated, the contents of the beaker were cooled, diluted with water and transferred over a filter paper. The carbon sample was washed exhaustively with hot distilled water until the filtrate was free of nitrate ions. The washed carbon sample was dried first in air and then in an electric oven at 120°C and the dry carbon was stored in stoppered glass bottles.

2.2. Oxidation with oxygen gas

5 g as-received activated carbon sample was spread in a platinum boat. The mouth of the boat was covered with a platinum lid having holes so that oxygen gas could make contact with the carbon. The boat containing the carbon sample was placed in a resistance tube furnace. The temperature of the furnace was maintained at 350°C. Pure and dry oxygen was passed over the sample at the rate of 2 L/hr for 4 hrs. The sample was then cooled in oxygen and transferred to stoppered reagent bottle.

2.3. Degassing of the carbon

About 5 g of the activated carbon sample was spread in thin layers about 5 inches long in a tube furnace. It was kept in position by means of porous copper gauge plugs. The tube furnace was connected to a Hyvac. Cenco vacuum pump capable of giving a vacuum to the order of 3×10^{-2} mmHg. The temperature of the furnace was raised to the required level slowly. The gases begun to be evolved soon after. The temperature was allowed to rise gradually and before it was raised by another 50°C complete elimination of the gases, at the proceeding temperature was ensured. After degassing at the required temperature, the sample was allowed to cool in vacuum to room temperature to avoid reformation of the carbon-oxygen surface groups and was then transferred to stoppered bottles flushed with nitrogen. These samples are referred to as 'degassed samples' in the text.

The oxidized activated carbon samples were degassed at different temperatures between 400°C and 950°C to gradually eliminate varying amounts of the carbon-oxygen surface groups. The amounts of the carbon-oxygen surface groups present on each as-received, oxidised and degassed carbon sample were determined by evacuating each sample at gradually increasing temperatures upto 950°C and analysing the gases (CO₂, CO and H₂O) evolved. The details of the procedures are already published [26, 27].

2.4. Adsorption of p-nitrophenol

A known weight (0.200 mg) of each carbon sample dried at 120°C in an electric oven was mixed with a known volume (20 ml) of p-nitrophenol solutions of different concentrations in stoppered borosil glass bottles. The bottles were placed in an air thermostat maintained at $30 \pm 1^\circ\text{C}$. The suspensions were shaken occasionally for 24 hrs. After which the concentration of the supernatant liquid was determined spectrophotometrically at a wavelength of 318 nm.

3. Results and Discussion

3.1. Adsorption Isotherms

Adsorption isotherms of p-nitrophenol on the four samples of activated carbons from aqueous solutions in the concentration range 40-800 mg/L are presented in Fig. 1. The isotherms are similar in shape and appear to be Langmuirian in character. All the four carbons adsorb appreciable amounts of p-nitrophenol although the amount adsorbed is different in different carbons. In general, the amount adsorbed is larger in case of the activated carbon fibres ACF-307 and ACF-310 compared to the adsorption in case of the granulated activated carbons GAC-E and GAC-S. The amount adsorbed varies between 20-25% in case of the fibrous carbons and between 10-12% in the case of granulated carbons. The adsorption of p-nitrophenol can not be related to surface area since ACF-307 which has smaller surface area ($910 \text{ m}^2/\text{g}$) than GAC-S ($1256 \text{ m}^2/\text{g}$) adsorbs larger amounts of p-nitrophenol at all concentrations. It appears that the adsorption of p-nitrophenol can not be explained on the basis of surface

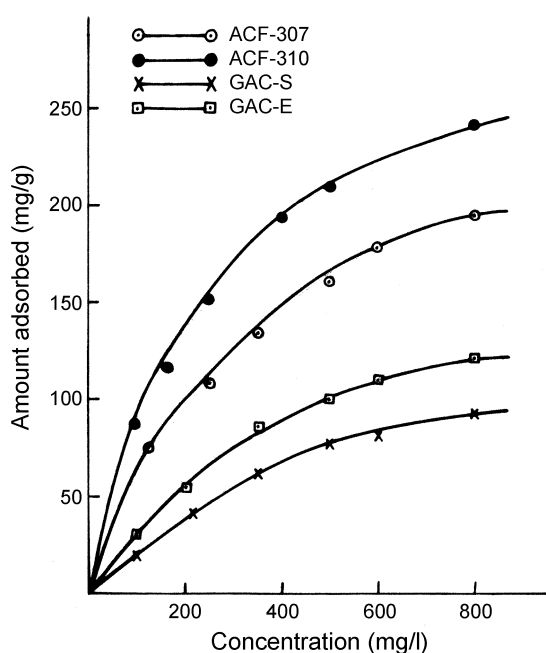


Fig. 1. Adsorption Isotherms of p-nitrophenol on different as-received activated carbons.

area alone. It is probable that the adsorption of p-nitrophenol is also influenced by the chemical nature of the carbon surface. As these carbons have been prepared using different raw materials and using different procedures, the chemical nature of their surfaces is likely to be different.

The adsorption of phenols by activated carbons has been interpreted differently. While Mash and Campbell [14], Hu *et al.* [15], Puri and coworkers [13] and Gonzalez-Martin and coworkers [9, 10] observed that the adsorption of phenol and p-nitrophenol from aqueous solutions at low and moderate concentrations depended upon the microporous nature and the surface area of the activated carbon, Mattson *et al.* [18], Graham [26] and Coughlin *et al.* [27], presented the view that the associated oxygen present on the carbon surface also influences the adsorption of phenols through the formation of a bond with the oxygen surface groups. As the data presented in this paper does not show any direct relationship between the adsorption of p-nitrophenol and the surface area, it was thought of interest to examine the influence of carbon oxygen surface group on the adsorption of p-nitrophenol.

3.2. Influence of Carbon Oxygen Surface Groups on the Adsorption of p-nitrophenol

It is well known that associated oxygen on the carbon surface is present in the form of two types of surface groups: first which are evolved on evacuation as CO_2 in the temperature range $350\text{-}750^\circ\text{C}$ and the second which are evolved as CO on evacuation in the temperature range $500\text{-}950^\circ\text{C}$ [21, 22]. The former groups are acidic in character and are postulated as carboxyls and lactones [23, 24, 28, 33], while the latter groups are non-acidic and have been postulated as quinones [24, 28, 31]. These groups make the carbon surface hydrophobic. The amounts of carbon-oxygen surface groups, present on the activated carbons used in these investigations, were determined by degassing the carbons at gradually increasing temperatures upto 950°C . The results have been recorded in Table 1. It is seen that the fibrous activated carbons ACF-307 & ACF-310, are associated with larger amounts of total oxygen compared to the granulated activated carbons GAC-E & GAC-S. However, the disposition of the total oxygen into the two types of surface groups is different.

Table 1. Surface areas and gases evolved on degassing different as-received activated carbons at 950°C

Sample identification	BET(N_2) Surface area (m^2/g)	Oxygen evolved as (g/100 g)			
		CO_2	CO	H_2O	Total
ACF-307	910	1.00	5.30	1.30	7.60
ACF-310	1184	1.90	4.20	1.40	7.50
GAC-S	1256	2.10	1.05	1.24	4.39
GAC-E	1190	2.13	1.66	1.33	5.12

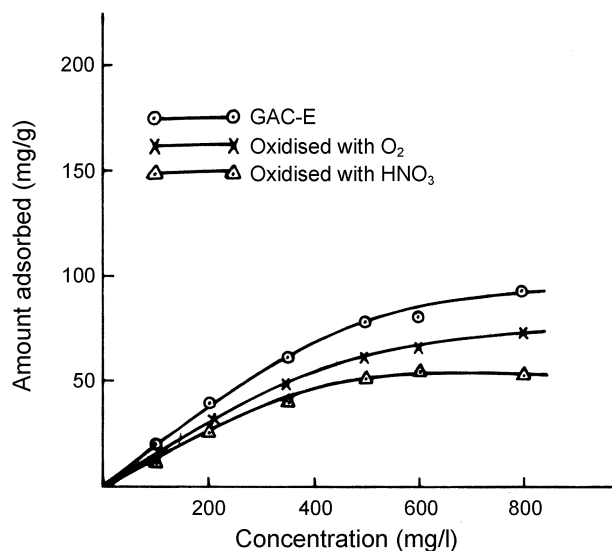


Fig. 2. Adsorption isotherms of p-nitrophenol on GAC-E before and after oxidation.

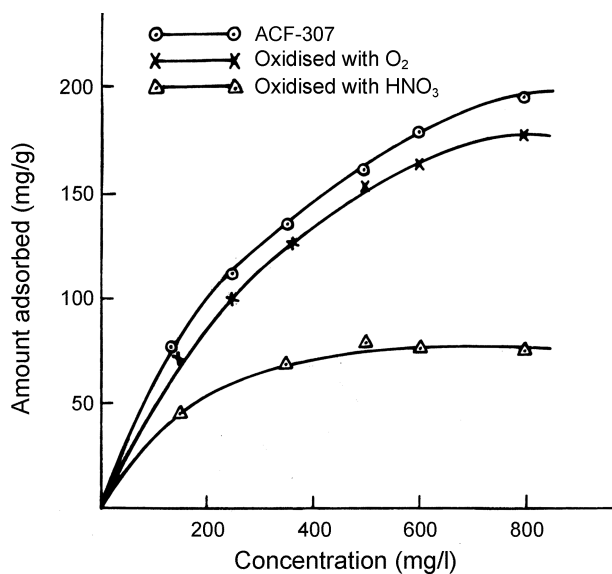


Fig. 3. Adsorption isotherms of p-nitrophenol on ACF-307 before and after oxidation.

While the fibrous activated carbons have smaller amounts of acidic surface groups, the granulated carbons have smaller amounts of non acidic surface groups. Thus it cannot be clearly inferred whether it is the total oxygen associated with the carbon surface or the fraction of it disposed off as acidic or non acidic surface groups which influences the adsorption of p-nitrophenol.

In order to examine the influence of these different carbon-oxygen surface groups on the adsorption of p-nitrophenol more clearly, two of the carbon sample viz ACF-307 and GAC-E were oxidised with nitric acid and oxygen gas. These treatments are known to enhance the amounts of these

Table 2. Gases evolved on degassing different as-received and oxidised activated carbons at 950°C

Sample Identification	Oxygen evolved as (%)			
	CO ₂	CO	H ₂ O	Total
ACF-307				
As-received	1.00	5.30	1.30	7.60
HNO ₃ -oxidised	12.90	7.47	2.40	22.77
O ₂ -oxidised	3.11	7.71	1.20	12.02
GAC-E				
As-received	2.13	1.66	1.33	5.12
HNO ₃ -oxidised	12.40	6.20	1.92	20.52
O ₂ -oxidised	3.17	5.97	1.26	10.40

carbon-oxygen surface groups [23, 24, 25, 28]. The adsorption isotherms on the oxidised ACF-307 and GAC-E samples are shown in Fig. 2 and 3. The adsorption isotherms on the as received samples are reproduced in these figures for easy comparison. It is seen that the uptake of p-nitrophenol decreases on oxidation of the carbons with nitric acid as well as with oxygen gas. Furthermore, the magnitude of decrease in adsorption is different in the two oxidative treatments in both the carbons. The decrease in adsorption is smaller in case of the oxidation with oxygen gas and much larger on oxidation with nitric acid. Incidentally, the treatment with nitric acid is a much stronger oxidative treatment and results in the fixation of considerably larger amounts of oxygen on the surface of both the carbons. (cf Table 2). The amount of associated oxygen increases from 5-7% for as-received carbons to between 20~22% on oxidation of the two carbons with nitric acid and only to between 10~12% on oxidation with oxygen gas. This will indicate that the oxygen associated with the carbon surface inhibits the adsorption of p-nitrophenol.

A careful examination of Table 2, however, shows that the disposition of the chemisorbed oxygen into acidic and non-acidic surface groups is different in case of the two oxidative treatments. It is interesting to note that for a given oxidised activated carbon such as ACF-307 or GAC-E the non-acidic oxygen groups which are evolved as CO have similar values while the amounts of acidic surface groups evolved as CO₂ are widely different. In fact, the oxidation of carbons with nitric acid enhances the acidic surface groups by 6~13 times of its value in the as-received samples while the increase on oxidation with oxygen gas is comparatively much lower. This indicates that it is not the total oxygen but the acidic oxygen associated with the carbon surface which inhibits the adsorption of p-nitrophenol. It appears that the acidic surface groups which have been postulated as carboxyls and lactones [23, 24, 28] being bulky molecules and block entrances into some of the narrow micropores for adsorption of relatively larger p-nitrophenol molecules.

This receives support from the adsorption isotherms on the

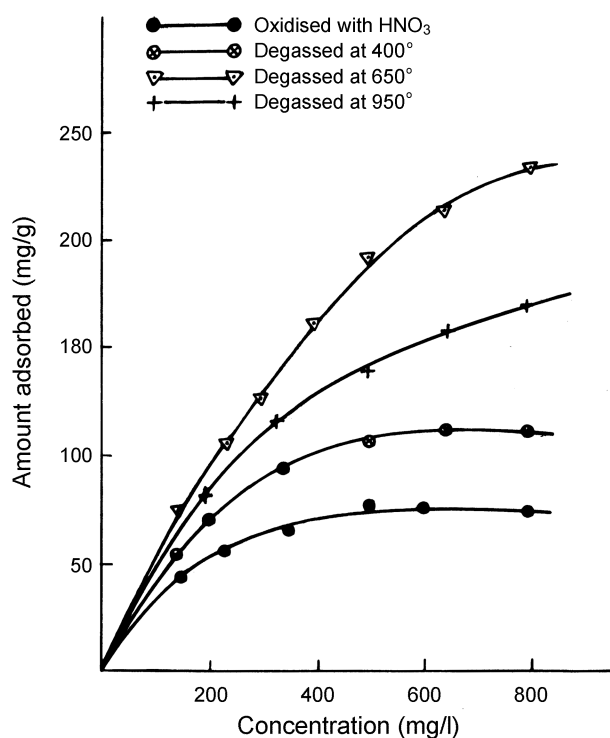


Fig. 4. Adsorption isotherms of *p*-nitrophenol on ACF-307 oxidised with nitric acid before and after degassing.

oxidised samples ACF-307 and GAC-E after degassing these samples at 400, 650 and 950°C. The degassing of the carbons at increasing temperatures results in the removal of varying amounts of the two types of carbon-oxygen surface groups, depending upon the temperature of degassing. The adsorption isotherms on the degassed samples are shown in Figs. 4-7. It is seen that the adsorption of *p*-nitrophenol increases on degassing at all temperatures and in both the carbons. However, the increase in adsorption is maximum in case of the samples degassed at 650°C.

The amounts of the two types of carbon oxygen surface groups associated with these carbons are shown in Table 3 for the carbon sample ACF-307 and in Table 4 for GAC-E. It is evident that the 400°C-degassed samples have lost only a small portion (18-20%) of the acidic surface groups and retain most of their non-acidic surface groups. The 650°C-degassed samples, on the other hand, have lost most (~80%) of their acidic surface groups and only a small part of their non-acidic surface groups. The 950°C-degassed samples are almost free of all the oxygen surface groups. Thus a small increase in the adsorption of *p*-nitrophenol in case of the 400°C-degassed carbon samples may be attributed to a small decrease in the amount of acidic surface groups. The adsorption of phenol is the largest in case of the 650°C-degassed samples because these samples have lost most of their acidic surface groups although they still retain a larger portion of their non-acidic surface groups. It is apparent, therefore, that

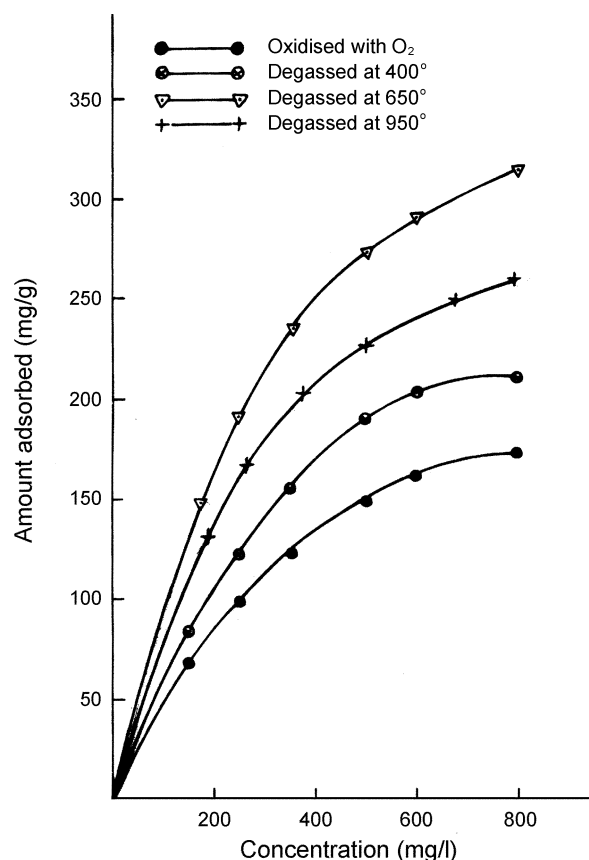


Fig. 5. Adsorption isotherms of *p*-nitrophenol on ACF-307 oxidised with oxygen gas before and after degassing.

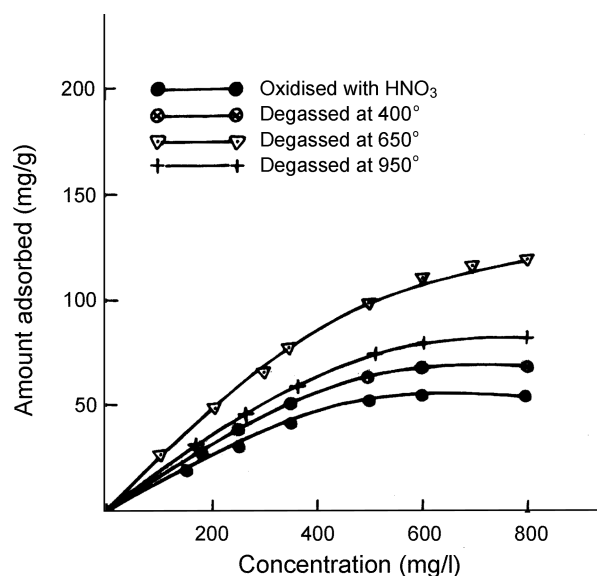


Fig. 6. Adsorption isotherms of *p*-nitrophenol on GAC-E oxidised with nitric acid before and after degassing.

the acidic surface groups tend to suppress the adsorption of *p*-nitrophenol and their removal, and the dominance of non

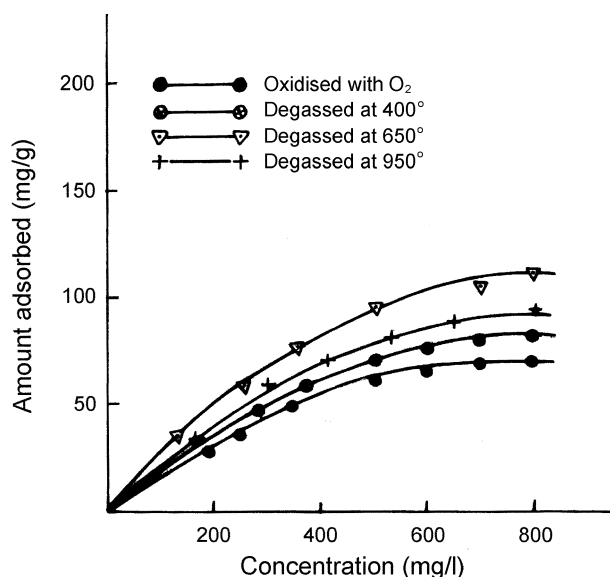


Fig. 7. Adsorption isotherms of p-nitrophenol on GAC-E oxidised with oxygen gas before and after degassing.

Table 3. Gases evolved on degassing different oxidised and degassed ACF-307 carbon samples at 950°C

Sample Identification	Oxygen evolved as (g/100 g)			
	CO ₂	CO	H ₂ O	Total
ACF-307				
HNO₃ oxidised oxidised and then degassed at (°C)	12.90	7.47	2.40	22.77
400	10.85	7.35	0.85	19.05
650	2.15	6.86	0.12	9.13
950	–	Traces	–	–
Oxygen oxidised oxidised and then degassed at (°C)	3.11	7.71	1.20	12.02
400	2.95	8.15	0.82	11.92
650	0.42	7.81	0.21	8.44
950	–	Traces	–	–

acidic surface groups which have been postulated as quinones enhances the adsorption of p-nitrophenol. Further degassing at 950°C results in a decrease in the adsorption of p-nitrophenol because this treatment removes almost completely both the acidic and non acidic surface groups. The adsorption in the 950°C-degassed samples takes place in the pores.

3.3. Mechanism of Adsorption

It is now easy to visualise the mechanism involved in the adsorption of p-nitrophenol by activated carbons. The results presented in this paper clearly show that the oxidation of

Table 4. Gases evolved on degassing different oxidised and degassed GAC-307 carbon samples at 950°C

Sample Identification	Oxygen evolved as (g/100 g)			
	CO ₂	CO	H ₂ O	Total
GAC-E				
HNO₃ oxidised oxidised and then degassed at (°C)	12.40	6.20	1.92	20.52
400	10.85	5.92	1.02	17.79
650	2.15	6.86	0.12	9.13
950	Traces	Traces	Traces	Traces
Oxygen oxidised oxidised and then degassed at (°C)	3.17	5.97	1.26	10.40
400	2.86	5.56	1.00	9.42
650	0.58	4.78	0.62	5.98
950	–	Traces	–	–

carbons with nitric acid which preferably creates carboxylic or lactonic acidic groups suppresses the adsorption of p-nitrophenol. These acidic surface groups, being bulky, block entrances to some of the narrow micropores resulting in a decrease in the adsorption. In addition the water molecules cluster around the polar acidic surface groups again reducing the adsorption capacity. When these acidic surface groups are removed by degassing, the adsorption of p-nitrophenol tends to increase, the extent of increase depending on the amount of acidic groups removed. The adsorption of p-nitrophenol is the highest when the activated carbon surface has lost most of its acidic groups and when carbonyl groups (quinonic) are the dominating surface groups as in the case of the 650°C-degassed sample. In other words, the presence of acidic surface groups inhibits the adsorption while the presence of non acidic surface groups which have been postulated as quinones favour the adsorption of p-nitrophenol [9, 10]. This increase in adsorption of p-nitrophenol can be attributed to the binding of p-nitrophenol by interaction of π (π) electron clouds of the benzene ring system with the partial positive charge on the quinonic carbon atoms. The p-nitrophenol adsorbed could not be recovered completely even on prolonged evacuation at room temperature. This is due to the complexing of p-nitrophenol at the quinonic sites within the micropores.

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