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Effect of Surface Oxygen Complexes of Activated Carbon on the Adsorption of 2,4,6-Trinitrophenol

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ABSTRACT

The adsorption isotherms for 2,4,6-trinitrophenol (picric acid) on five samples of coconut-based activated carbons (ACs) with varying surface area have been studied. The results obtained show that adsorption depends upon surface area but is not linearly related to it. The adsorption increases on oxidation with ammonium persulphate ($(NH_4)_2 S_2 O_8$) as well as on degassing at 600 °C. The results have been explained on the basis of the existence of surface carbonyl groups, where the O_2 of the carbonyl group interacts with π electrons of the benzene ring of picric acid.

1 INTRODUCTION

The presence of nitrophenols in waste water is of great environmental concern. These compounds are usually found in effluent wastes from explosive industries, textile industries and by photodegradation of pesticides, etc. Adsorption studies of phenols, nitrophenols and some of their derivatives from aqueous solutions using different adsorbents are well-documented¹⁻⁵. However, adsorption on activated carbon (AC) is the most widely used technique for the removal of phenolic compounds from waste water. Some workers⁶ have observed enhancement in the adsorption of phenols in the presence of combined surface O_2 on AC. Coughlin⁷, *et al.* reported negative influence of chemisorbed surface O_2 on the adsorption of

phenols. Gao and coworkers⁸ also observed change in adsorption behaviour of phenol with change in the surface chemical properties of AC brought about by oxidation with HNO_3 and reduction with H_2 .

This paper presents adsorption isotherms of picric acid on five different grades of indigenously available coconut based ACs. The effects of surface area and surface O_2 complexes created by various oxidative and degassing treatments have been discussed.

2. EXPERIMENTAL DETAILS

2.1 Materials

Five grades of commercially available coconut-based ACs with surface area ranging

from 650 to 1300 m²/g were used during the studies. ACs were dried at 120 °C for 3 hr before use. All chemicals used were of AR quality and double-distilled water was used for preparing solutions and rinsing.

2.2 Modification of Activated Carbons

As-received *C* samples were oxidised with (NH₄)₂S₂O₈ and H₂O₂ and degassed at 400, 600 and 1000 °C by methods commonly used for the purpose⁹.

2.3 Study of Adsorption Isotherms

Carbon dosages were in the range 0.2-2.0 g/l, whereas the initial concentration of picric acid was kept at 300 mg/l. Isotherm experiments were carried out at 30 ± 1 °C by various methods.

3. RESULTS & DISCUSSION

Adsorption isotherms of picric acid on different samples of ACs having different surface areas in the range 650-1300 m²/g with varying *C* doses are shown in Fig. 1. The plots are concave to concentration axis, indicating a rapid rate of adsorption in the beginning. The adsorption data correlate well with Langmuir adsorption modes. Values of Langmuir adsorption constants, *Q_m*, the maximum adsorption at monolayer saturation and the constant, *b*, as calculated from linear Langmuir isotherms for different *C* samples, are given in Table 1.

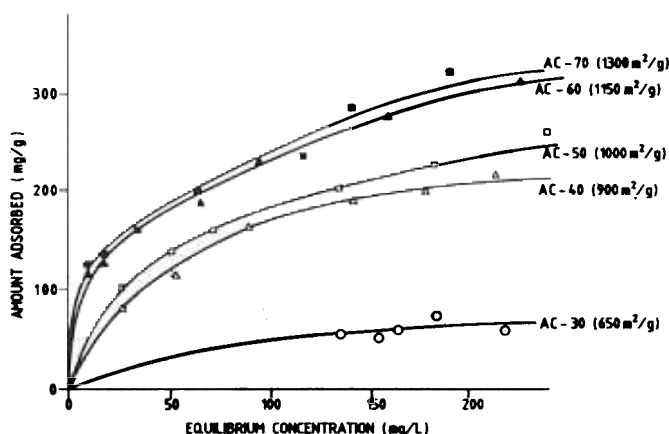


Figure 1. Adsorption isotherms for trinitrophenol on activated carbons of different surface areas. Temperature 30 ± 1 °C, contact time 24 hr, initial concentration 300 mg/l and carbon dose 0.2-2.0 g/l.

Table 1. Langmuir constants and fraction of surface area utilised for adsorption of trinitrophenol

Carbon type	Surface area (m ² /g)	Fraction of area utilised	<i>Q^{max}</i> (mg/g)	<i>b</i>
AC-30	650	0.180	54	0.3242
AC-40	900	0.457	190	0.0314
AC-50	1000	0.465	210	0.0313
AC-60	1150	0.486	258	0.0316
AC-70	1300	0.448	269	0.0282

It is seen that maximum adsorption of picric acid (269 mg/g) took place on AC-70 (1300 m²/g) which has the largest surface area; minimum adsorption (54 mg/g) was on AC-30 (650 m²/g) having the smallest surface area (Table 1). However, no linear relationship between adsorption and surface area was observed in the present study. Fraction of unit surface area covered by picric acid at monolayer increases with increase in BET area up to 1000 m²/g and becomes more or less constant thereafter (Fig. 2). This may be attributed to the molecular dimension of picric acid (9.08 Å) which restricts the entry of picric acid molecules on carbons having higher fraction of ultra microporosity.

It is well-known that the amount adsorbed is not entirely controlled by the specific surface area but is also influenced by the chemical structure of

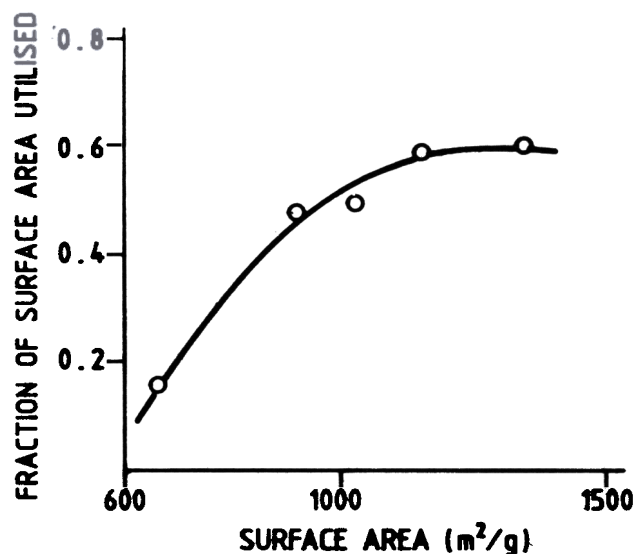


Figure 2. Fraction of surface area utilised for monolayer adsorption of trinitrophenol on activated carbons.

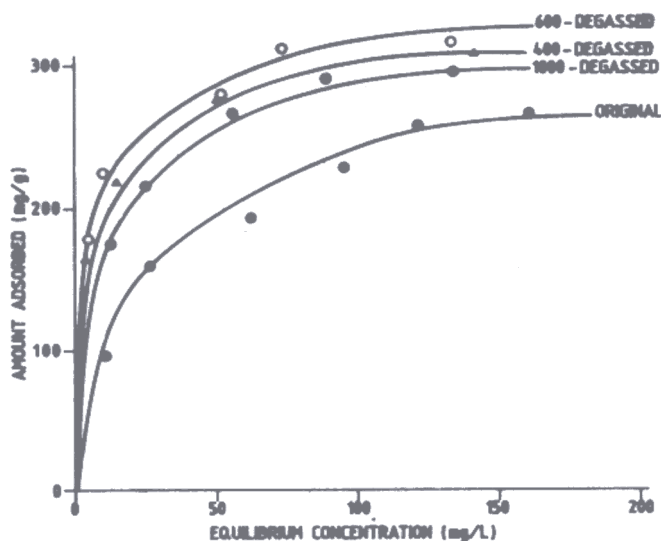


Figure 3. Freundlich adsorption isotherms for trinitrophenol on activated carbon AC-60 (1150 m²/g) before and after outgassing at different temperatures. Temperature 30 ± 1 °C, contact time 24 hr, initial concentration 300 mg/l, and carbon dose 0.2-2.0 g/l.

C surface. To assess their influence, adsorption isotherms were determined by modifying the carbon-oxygen surface complexes by oxidation with (NH₄)₂S₂O₈ and H₂O₂ and by degassing at 400, 600 and 1000 °C. The amounts of carbon-oxygen surface complexes given out as CO₂ and CO, and the amount adsorbed are shown in Table 2. It is seen that the oxidation enhances the amount of O₂ surface complexes, whereas degassing reduces it. The adsorption isotherms of picric acid on AC-60(1150 m²/g), original and outgassed at different temperatures are shown in Fig. 3.

Studies carried out by some workers¹⁰, have shown that O₂ complexes evolved as CO₂ on evacuation at 300-700 °C are carboxylic or lactonic groups and those evolved as CO on evacuation at 550-950 °C are quinonic or carbonyl groups. It is seen that adsorption of picric acid increases on C samples outgassed at different temperatures, the increase in adsorption being maximum in the case of 600 °C degassed sample. This can be explained on the basis that 600 °C degassed sample is devoid of a large portion of its CO₂ evolving complexes, while it retains a larger portion of CO-evolving complexes¹⁰. It thus appears that the presence of

CO₂ evolving complexes inhibits the adsorption of picric acid. The decrease in adsorption of phenols due to the acidic groups of carbons was earlier been reported by Puri¹¹ and Oda¹². This finding receives further support from the adsorption isotherm on C samples oxidised with (NH₄)₂S₂O₈, which contains a larger portion of CO-evolving complexes (Table 2). An increase in the 1000 °C degassed sample where both CO₂ and CO groups are negligible may be attributed to widening of some of the microcapillary pores on degassing at such high temperature¹³. In the C sample oxidised with H₂O₂, whereby the CO-evolving complexes increase marginally, a slight increase in adsorption of picric acid has been observed. The increase in adsorption on degassing at 600 °C and on oxidation with (NH₄)₂S₂O₈ can be explained on the basis of

Table 2. Relationship between oxygen evolved on outgassing AC-60 (1150 m²/g) (original and modified) at 1000 °C and amount adsorbed at monolayer on adsorption of trinitrophenol.

C-Type	Oxygen evolved as			Total	Q ^{max} (O ₂)
	CO ₂ (g/100g)	CO (g/100g)	H ₂ O (g/100g)		
Original	0.956	1.202	1.353	3.511	258
H ₂ O ₂ -treated	0.975	1.831	0.997	3.803	266
(NH ₄) ₂ S ₂ O ₈ treated	2.113	2.981	2.532	7.626	290
Degassed at 400 °C	0.748	0.989	1.153	2.890	300
Degassed at 600 °C	0.498	0.888	0.939	2.325	320
Degassed at 1000 °C	-	-	Traces	-	288

interaction between carbonyl oxygen on the C surface and the pi electrons of the benzene ring of picric acid¹¹. The increase in adsorption on (NH₄)₂S₂O₈-treated samples may also be attributed¹³ to interaction of negative charge on nitro-groups of picric acid with partial positive charge on carbonyl or quinonic C atoms (Fig. 4).

It appears from the results of the present study that though the adsorption of picric acid depends on the surface area, it is considerably influenced by the chemisorbed O₂ present on the surface of AC. The presence of CO-evolving surface O₂ complexes

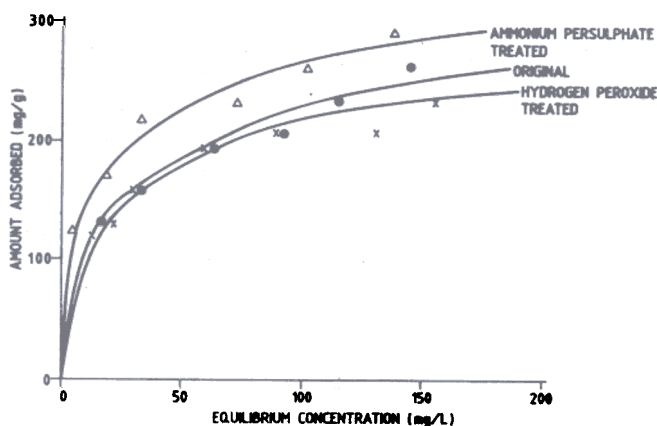


Figure 4. Freundlich adsorption isotherms of trinitrophenol on activated carbon AC-60 (1150 m²/g) before and after surface oxidation. Temperature 30 ± 1 °C contact time 24 hr, initial concentration 300 mg/l and carbon dose 0.2-2.0 g/l.

enhances the adsorption of picric acid, while the presence of acidic CO₂-evolving groups reduces its adsorption.

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