

ADSORPTION OF PHENOLS FROM AQUEOUS PHASE ONTO ACTIVATED CARBONS: EFFECT OF SURFACE OXYGEN COMPLEXES AND pH OF THE SOLUTION

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Introduction

Phenols are among the most common water pollutants. Removal of phenolic pollutants is necessary because of its toxicity and slightly pungent odor, several methods are available for treatment of pollutants in order to detoxify water, and among them one is adsorption over suitable adsorbents. Several materials possess adsorption capabilities, but active carbon is the most widely used owing to its high adsorption potential coupled with cost effectiveness. Moreover, activated carbon shows an amphoteric character in aqueous solution; that is, their surface charge density depends on the solution of weak electrolytes because these are attracted or repelled by the surface of the activated carbons, according to pH. The adsorption of phenolic compounds from aqueous solution by activated carbons has been studied essentially phenol and p-nitrophenols and oriented essentially to the influence of carbon porosity and the surface oxygen complexes present on the activated carbon[1]. The main objective of the present work is to investigate the adsorption behavior of phenols of different acidities, and molecular weights on activated carbons having different physicochemical nature, studying the influence of the solution pH, the surface oxygen complexes and the type of substituent of the phenolic compounds on the adsorption process.

Experimental

Activated carbon used in this work was obtained from M/S Active Carbon India Ltd., Hyderabad of coconut shell origin and steam activated, with particle size of 12x30 BSS. The samples were oxidized with HNO_3 , H_2O_2 and $(\text{NH}_4)_2\text{S}_2\text{O}_8$. These oxidized samples will be referred to as GN, GH, GS and whereas the original sample referred as OG respectively. The detail of these procedure has been reported elsewhere [2]. These activated carbon samples were characterized by N_2 adsorption at 77K. Apparent surface area was obtained by applying BET and DR equations to the N_2 adsorption data. The surface acidity was determined by using Boehm method.

The adsorption processes from aqueous solution of the different phenolic compounds, phenol, p-nitrophenol, p-chlorophenol and p-aminophenol on the activated carbons were carried out at 300K. Adsorption isotherms were determined by using stoppered flasks containing 0.1g of carbon/ 50 cc of solution. They were kept in a thermostat shaker bath at 300K for 2days, after which the equilibrium concentration was determined spectro-

photometrically using a Perkin Elmer Lambda 3B, spectrophotometer. In order to avoid the introduction of a new electrolyte in the system, all the adsorption studies were carried out without adding any buffer to control the pH. However, since the adsorption capacity of an activated carbon depends on pH of the solution[1]. Some of the samples were selected to study this relationship. These experiments were carried out under the same conditions as those of the adsorption isotherms, but using an initial concentration of the phenolic compound of 200 mg/L. The different pHs of the solutions was obtained by adding either HCl or NaOH.

Results

The adsorption isotherms of phenols i.e., phenol, p-chlorophenol, p-nitrophenol, and p-aminophenol on the activated carbon are of type I of the BET classification showing a rapid adsorption at lower concentration and tending to level off at higher concentrations. These isotherms are well fitted by the langmuir equation. The adsorption capacity value for the different phenols increase with increase in the surface area and porosity of the activated carbons and decrease with the amount of surface oxygen complexes on the activated carbon. Thus, activated carbon OG with highest surface area, most developed porosity and lowest amount of surface oxygen complexes has the highest adsorption capacity. The adsorption capacity of a given activated carbon for the different phenols is, in general, related to their solubility in water and to the hydrophobic character of their solubility in water and to the hydrophobic character of their substituents. Thus, in general, p-nitrophenol possessing very low water solubility is adsorbed on the activated carbons to a greater extent than the other phenols. However, p-nitrophenol and p-chlorophenol, which have a hydrophobic group are also adsorbed to a greater extent than p-aminophenol and phenol both which has hydrophilic groups. The adsorption capacity or the relative affinity of the phenols toward the surface of the adsorbents increases with decrease in surface oxygen content of the activated carbon. Thus, adsorption capacity of oxidized samples is decrease with increase in the surface oxygen surface of acidic type. Incidentally the carbon sample oxidized with nitric acid has the maximum amount of acidic surface groups while the sample oxidized with H_2O_2 has the minimum amount of the acidic oxygen surface groups. The amount of surface groups on the surface of activated carbon samples was changed by

degassing the activated carbon sample at higher temperature. Thus there is a considerable change in phenol uptake capacity of the oxidized sample degassed at 600 °C.

As it is well known, the adsorption of phenolic compounds on activated carbon implies the formation of electron donor-acceptor complexes in which the basic surface oxygen groups act as donors and the aromatic ring of the adsorbate as acceptor[3]. Puri et al.[4] showed that the surface complexes that is acidic and comes off as carbon dioxide preference for water and hence lower adsorbility of phenol while the complex, that comes off as carbon monoxide enhances adsorbility of phenol probably due to interaction of quinonic oxygen with π -electron of benzene ring as well as the -OH group of phenol. Keizo et al. [5] observed that the phenol uptake by porous carbons decreased sharply on surface oxidation and it increases when the chemisorbed oxygen was removed by degassing. For a given activated carbon and for the different phenolic compounds studied, the value of adsorption capacity increases in the following order: p-aminophenol < phenol < p-chlorophenol < p-nitrophenol. This order, found with all carbons, seems to be related to the electron withdrawing or electron donating properties of the substituents of phenol compounds. Thus the electron donating property of the substituents decreases in the above order, which goes from a strong electron, donating group in the benzene ring such as -NH₂ group, to electron-withdrawing groups such as -NO₂, or -Cl. Therefore, electron withdrawal or deactivation of the benzene ring favors the formation of electron donor-acceptor complexes between these rings and basic groups on the surface of the activated carbons increases in that way adsorption capacity value. For a given phenol and for the different activated carbon samples studied, the value of adsorption capacity increase in the following order: GN < GS < GH < GN600 < OG. This order, found with all phenols, seems to be related to the surface oxygen complexes of acidic character. These results show clearly that the adsorption of phenol by activated carbon from aqueous solution is suppressed by the presence of acidic surface groups although these acidic groups can help in the hydrogen bonding. This is due to the fact that this hydrogen bonding can be more easily found between the acidic surface groups and the water molecules which are more polar. In the aqueous solution there is a competition between the phenol molecules and the water molecules. It has been shown by several workers that the acidic surface groups provide sites for the adsorption of water by a mechanism which may involved hydrogen bonding. Furthermore, Mahajan et al.[3] has shown that the adsorption of phenol on acidic surface groups is preferable in non-polar solvents and not in water. Thus the above mentioned order of adsorption is logically justified.

The effect of solution pH on the phenol adsorption capacity of activated carbon was studied using two samples OG and GH. At pH lower than seven the

amount of phenols adsorbed remains constant or increases slightly with the pH, there is a sharp decrease in the value of adsorption capacity which continues to decrease with the increases in pH. These results indicate that the phenolic compounds are preferentially adsorbed on the surface of the activated carbons and continue increasing by acquiring negative charge from the external to the internal surface of the pores as the solution pH increase from to for OG and from to for GH. This variation in the surface charge density of the activated carbons and its affect on their adsorption capacity, is observed essentially when the phenol compounds are dissociated, because the phenolate anions are repelled by the negative charge on the surface of the carbons. However, the amount of phenolic compounds adsorbed depends also on the surface charge of the carbon. Thus in activated carbon OG with a pH_{ZPC} higher than that of activated carbon GH, the decrease in adsorption capacity begins after this pH value. At pH values higher than 10, both the external and internal surface are negatively charged and the phenol compounds are also dissociated. Therefore, the amounts adsorbed above that pH are very low in all the reported cases.

Conclusions

The adsorption capacity of the activated carbons for the phenols studied depends on the surface area, porosity of the carbon and the solubility of the phenolic compounds in water. Thus the adsorption capacity increases with increase in surface area and porosity. The adsorption capacity of the activated carbons depends on the solution pH. At acidic pH the amount adsorbed remains constant or increases slightly with increasing pH. However, at basic pH, the amount adsorbed decreases drastically.

References

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