CAPACITY OF ACTIVATED CARBON FOR REMOVING CHLORINATED PHENOLS FROM DRINKING WATER

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ABSTRACT

Little is known about the adsorptive capacity of activated carbon in removing chlorinated phenols, particularly when they are present in mexture. The present work determined the adsorption capacity for pentachlorophenol, 2, 4, 6-trichlorophenol, 2, 4-dichlorophenol, 2-chlorophenol and phenol as a function of chlorine substitution.

Results have showed that the more highly substituted with chlorine the phenol molecule is, the better the adsorption of the undissociated molecule.

In multisolute systems, competitive adsorption resulted in mutual inhibition of the adsorption capacity of each solute. However, the total adsorption capacity of carbon at equilibrium was higher for multisolute systems.

INTRODUCTION

Chlorinated phenols are known to be present in drinking water, resulting either from contamination of raw water sources or from chlorination of water containing phenolic compunds. Phenols may be present in raw water owing to the discharge of wastewaters from coke distillation plants, the petrochemical industry and numerous other industries. When water containing phenl itself is clorinated, the main reaction products are 2- and 4- chlorophenols, 2,4-dichlorophenol and 2,4,6-trichlorophenol. In addition, some halogenated phenols are used as biocides. Pentachlorophenol is used extensively as a wood preservative. Its occurrence in natural aquatic environment as reported by Wegman et al. (1979), is almost ubiquitions.

Chlorophenols removal is necessary because their presence is the cause of many complaints of odor in finished water in addition to their uncertain public health implications.

One of the best available techniques for removing halogenated phenols is by adsorption on activated carbon (Murin et al. 1979). According to Weber and Smith (1986), adsorption is a partitioning process in which activated carbon is the most common solid phase or adsorbent used in water and wastewater treatment. Morris and Weber (1964) and (1966),

have reported considerable amount of data on the adsorption of phenols. They found that increasing molecular weight had a favorable effect on carbon adsorption. Also, total organic carbon removal for a mixture was enhanced compared with that expected from simple solute data. As stated by Singer and Yen (1980), the adsorptive capacity of carbon for aromatic compounds is influenced by substitution in the ring structure. Introduction of substituent groups to phenols results in increased adsorbability. The position of the substituents seems to have no effect on adsorbability. Aly and Faust (1972) , found that adsorption is enhanced when the number of substituents on the phenol molecule is increased.

Little is known about the adsorbtive capacity of activated carbon in removing chlorinated phenols particularly when they are present in mixture. The main objective of this work is to detrmine the activated carbon adsorption capacity for each of the chlorinated phenolic compounds as function of chlorine substitution and assess the effect of solubility on the competitive adsorption of these compounds when coexisting in mixture.

MATERIALS AND METHOD

Compounds selected for the present investigation were used as received from the supplier (Supelco) in their neat form without correction for purity. The selection of the compounds to be studied was based on the following criteria:
1- Occurrence in drinking water as a product of chlorination for disinfection.
2- Solubility.
3- Number of chlorine substituents on the phenol molecule.
4- Public health implication.

The selected compounds were as follows:
1- Phenol
2- Chlorophenol
3- 2,4- dichlorophenol
4- 2,4,6- trichlorophenol
5- Pentachlorophenol

Filtrasorb 300 granular activated carbon, a product of Calgon Corporation was used as adsorbent.

The analytical method used for the determination of the compounds of interest is the standard USEPA method 604 (Longbottom and Lichtenberg 1982). All analysis were performed on a Varian 6000 GC. equipped with a flam ionization detector, and a 60 meter, 0.75 mm ID opentubular Supelco SPB5 column. Helium was used as a carrier at 10 ml/min flow, while the make-up gas flow was set at 20 ml/min. The injection temperature

was 250°C while the detector heating block was set at 280°C. The oven temperature was programmed at 105°C for 10 min., then increased by 8°C/min. up to 225°C.

All compounds were added to one liter distilled organic free water in stoppered bottles and left to equilibrate on a shaker for 3 days at room temperature (20° + 2C). At the end of each run, samples were filtered, extracted, and then stored in a cooler for GC analysis. All compounds were spiked at around 20 mg/1. The stock spiking solutions were prepared in 2- propanol. The assumption made was that 2- propanol will not affect the adsorption capacity of the compounds of interest. Similar assumptions were verified by Dobbs and Cohen (1980), where ethanol had no effect on the adsorption capacity of 2- chlorophenol. For multisolute systems, about 4 mg of each compound was added to 1 liter of organic free water and left to equilibrate under similar conditions as for single solute systems.

The carbon adsorption data generated were plotted according to the Freundlich equation. According to Weber (1972), the equation is emperical, however, it is widely used and has been found to describe the adsorption process in dilute solution. The Freundlich equation was applied in its logarithmic form as follows :

$$\log x / M = \log K + 1/n \log Cf$$

where, X = The amount of compound adsorbed from a given volume of solution.

M = The weight of activated carbon.

Cf = The amount of compound remaining in the treated water.

K and 1/n are emperical constants characteristic of the compound and carbon used in the test. Graphically, K is the X/M intercept of the isotherm plot at Cf = 1 and 1/n is the slope of the line when the equation is plotted on logarithmic paper. The intercept is an indicator of adsorption capacity and the slope of adsorption intensity.

RESULTS AND DISCUSSION

At equilibrium, adsorption and desorption will attain an equal rate state. Figure 1 illustrates the fact that equilibrium was acheived for all studied compounds following the 3 days contact time. This illustration represents the amount of solute adsorbed per unit of adsorbent as a function of the equilibrium concentration in bulk solution at constant temperature. The adsorption isotherms obtained for phenol, 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, and pentachlorophenol are typical for adsorption by activated carbon from dilute aqueous solutions where adsorption does not proceed beyond the monomolecular layer. This confirms results obtained by Waber (1972) and El-Dib et al. (1975).

The Freundlich adsorption isotherm model was used to investigate the
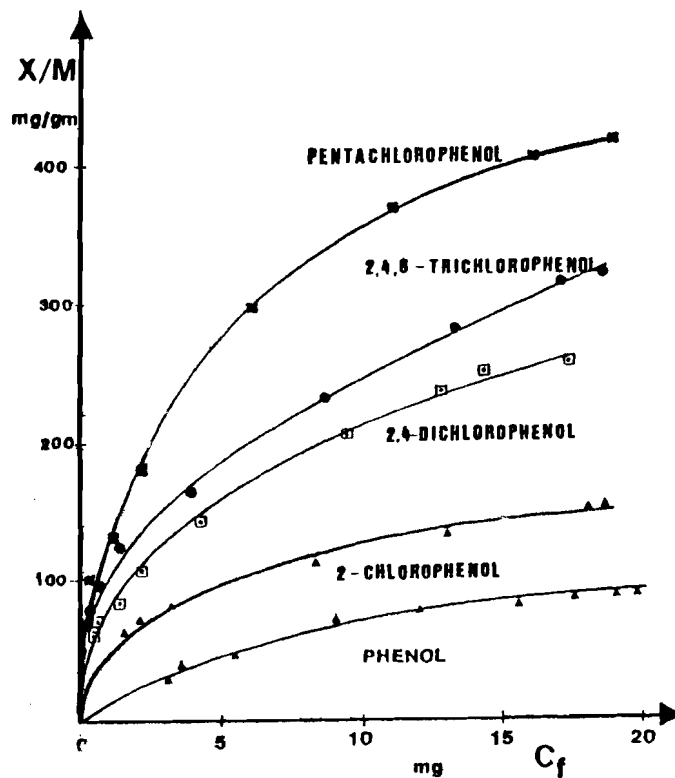
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Fig. (1)
Adsorption of chlorinated phenols on
activated carbon at equilibrium.

extent and intensity of adsorption for each contaminant when present
in single solute system. The results indicated that the compounds under
investigation complied with the Freundlich equation which provided the
most straighforward best fit to the experimental data. Figure 2 illustrates
the extent and intensity of adsorption for each contaminant when present
in single solute system. Variation in the adsorption capacity of carbon
for the studied compounds is reflected in the values of X/M at which the
plateau-like region of the isotherm is reached. Such values together with
that of K indicate that adsorption increases in the order pentachlorophenol
> 2,4,6- trichlorophenol > 2,4,-dichlorophenol > 2-chlorophenol > phenol.
This trend agrees with that reported by Alý and Faust (1972).

Table (1) lists the Freundlich adsorption isotherm parameters. The
given data confirm the fact that adsorption of organic contaminants from

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TABLE (1)
Freundlich adsorption parameters

Single solute systems

Contaminant	Cl substitutes	Solubility mg/l	Slope	K mg/gm
Phenol	0	93,000	0.51	20.5
2-chlorophenol	1	28,000	0.35	56.0
2,4-dichlorophenol	2	4,500	0.40	82.0
2,4,6-trichlorophenol	3	850	0.58	97.0
Pentachlorophenol	5	20	0.40	125.0

Multisolute system

Contaminant	Slope	K mg/gm	% Reduction in Adsorption Capacity
Phenol	0.27	11.0	53.6
2-chlorophenol	0.18	27.0	84.2
2,4-dichlorophenol	0.19	32.0	39.0
2,4,6-trichlorophenol	0.10	44.0	45.4
Pentachlorophenol	0.38	66.0	52.8

aqueous systems increases as their solubilities decreases (Weber 1972, and Aly and Faust 1980). Figure (3) illustrates the effect of the number of chlorine substitution on the adsorption capacity of single systems. Phenols with higher chlorine substitution have lower solubility which in turn contributed to a better adsorption capacity. This phenomenon can be interpreted by the fact that a higher solubility indicates a strong solute-solvent affinity, and the extent of adsorption is expected to be low (case of phenol) because of the necessity of breaking the solute-solvent bond before adsorption can occur.

For mixed solute solution, the adsorption parameters given in table 1 indicate that the uptake of each compound was substantially reduced. However, figure (4) illustrates the fact that the order of adsorption (preference) was the same as for single solute systems. Since adsorption from solution is usually monolayer, multisolute adsorption involves competition between different compounds for the available sites on the
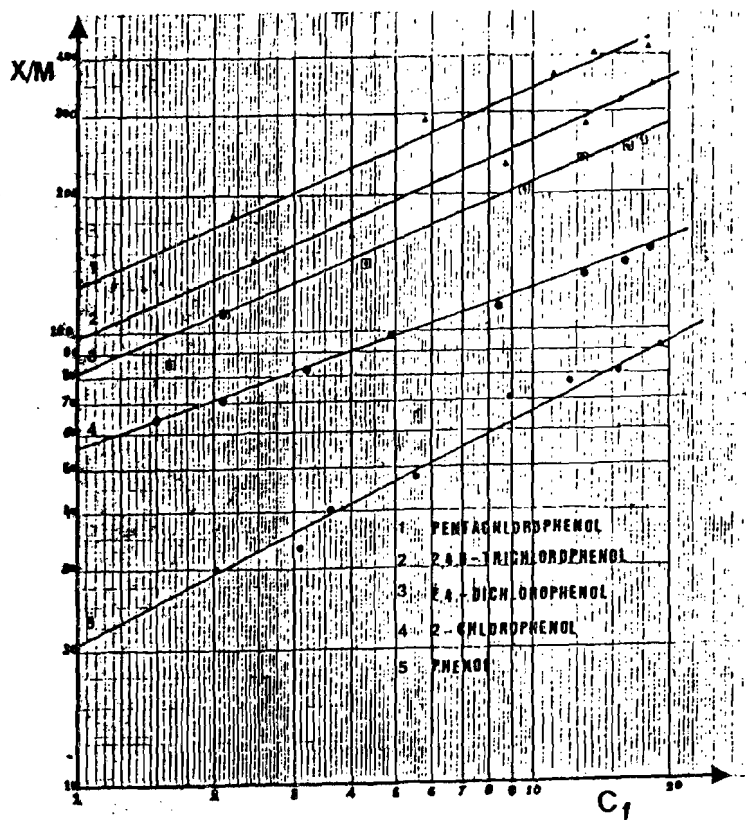
Fig. (2)
Freundlich adsorption isotherm for chlorinated
phenols in single solute systems.

carbon surface. Previous studies have confirmed the fact that competitive
adsorption generally results in mutual inhibition of the adsorption capacity
of each solute (Weber 1972); (Singer et at. 1980); and (Faust et al. 1972).
In multisolute systems, the percent reduction in adsorption capacity for
individual compounds ranged from 39 % to 53.6 %. However, the total
adsorption capacity of carbon at equilibrium was noticed to be higher
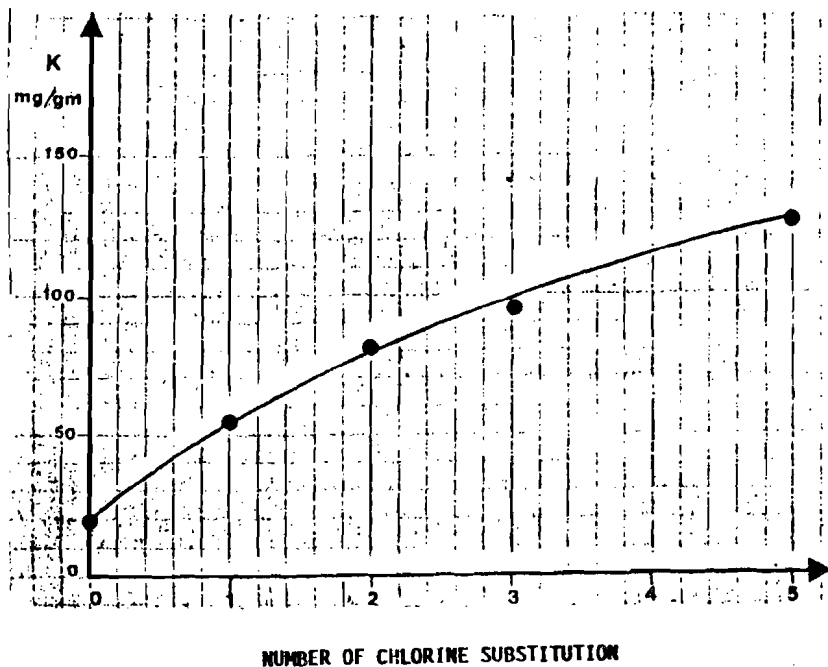for multisolute systems as compared to single solute systems. When

Fig. (3)
Effect of chlorine substitution on the adsorption capacity
of chlorinated phenols.

measured as pentachlorophenol, the adsorption capacity of single solute system (X/M) was 125 mg/gm. On the other hand, when all competing species are expressed as pentachlorophenol, the adsorption capacity increased to 180 mg/gm. The lower slope (1/n) observed in multisolute systems, indicates a lower intensity adsorption for all species.

It appears that compounds with lower solubilities are better competetor for empty sites available on activated carbon.
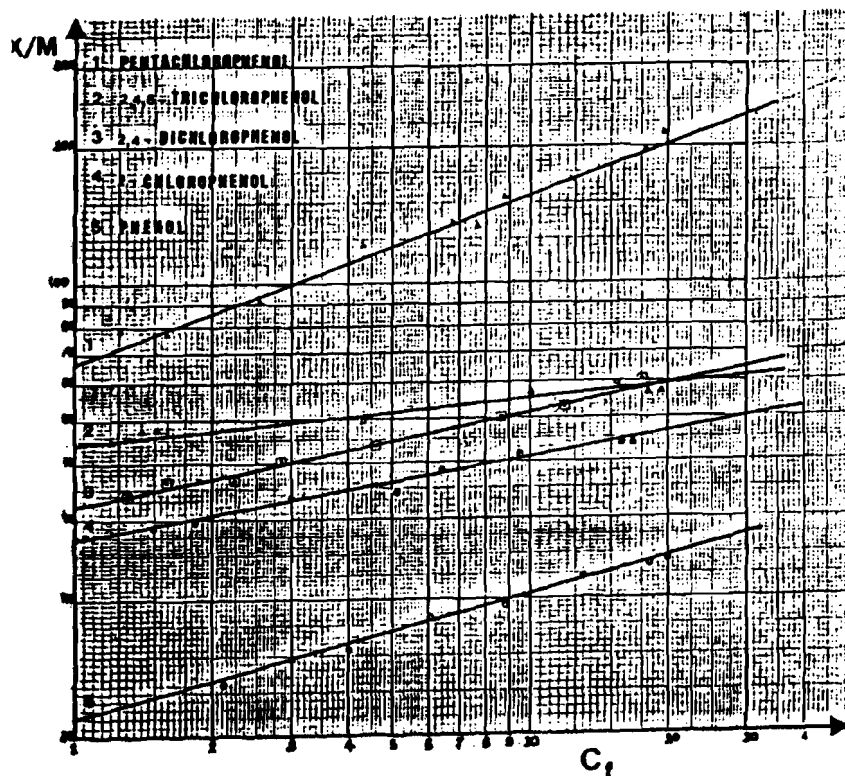
Fig. (4)
Freundlich adsorption isotherms for chlorinated
phenols in multisolute system.

CONCLUSION

Adsorption of chlorinated phenols was found to conform with the Freundlich adsorption isotherm.

The results indicated that the more highly substituted with chlorine the phenol molecule is, the better the adsorption of the undissociated molecule.

For chlorinated phenols, the adsorbility increases in the following order: pentachlorophenol > 2,4,6-trichlorophenol > 2,4-dichlorophenol > 2chlorophenol > phenol.

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Aqueous solubility was found to be the dominant factor determining the adsorbability of phenols in single solute systems.

In multisolute system, competitive adsorption resulted in mutual inhibition of the adsorption capacity of each solute. However, the total adsorption capacity of carbon at equilibrium was higher for multisolute systems. The strength of competition had the same order as in the case of single solute systems.

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