Detoxification using Low Cost Adsorbents-Removal of Tetrachlorocatechol

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ABSTRACT

Chlorinated cathechols are formed during the chlorination stage of bleaching plant which are toxic. Removal of tetrachlorocatechol by adsorption using bagasse fly ash (BFA), rice husk fly ash (RHFA) and activated carbon (AC) has been investigated. The practical applicability of these adsorbents has been studied in batch operations and effect of various parameters such as initial concentrations of tetrachlorocatechol, adsorbent dose, pH of the solutions have been investigated. The removal kinetics of tetrachlorocatechol shows first order expression and equilibrium adsorption data suited well for both Langmuir and Freundlich isotherms. BFA and RHFA with the AC reveals that use of these adsorbents will be economically viable.

INTRODUCTION

The halogenated organic chemicals, generated from industrial and other human activities, constitute potent source of environmental pollution and health hazards. This group consists of more than 250 individual chemical compounds. Some of the chlorinated organic compounds are highly toxic, carcinogenic, bioaccumulative and persistent to the human body (1). There has been increasing concern over the presence of chlorinated organic compounds in various industrial effluents. Some of the major sources of chlorinated organics are pulp and paper industries, chemical industries, textile industries, tanneries, metal treatment and finishing units, insecticide/pesticide industries, PVC plants, potable water treatment, sewage and municipal effluent etc.

The use of chlorine and chlorine containing compounds as bleaching agents in the production of bleached pulp leads to formation of variety of chlorinated phenolic compounds. Chlorinated catechols are present in bleach plant effluent in appreciable quantity. For individual chlorinated phenolic compounds to form, the linkages with lignin at positions 1 and 4 must be broken. During chlorination stage where both aromatic substitution and oxidation can occur, the most likely compounds to be formed are chlorocatechols by oxidation at two positions (2, 3). Some of the chlorinated catechol identified in bleach plant effluent are 4-chlorocatecol, 3, 4-dichlorocatecol, 3, 6-dichlorocatecol, 4,5-dichlorocatecol, 3,4,5-trichlorocatecol, tetrachlorocatechol (2, 3). Tetrachlorocatechol is present in appreciable quantity in the bleach plant effluent. Concentration of tetrachlocatecol in a typical kraft mill effluent has been reported around 96.9 μg/1 (3). Chlorinated cathechols are toxic and irritant in even very low concentration when present in wastewater. Removal of Chlorinated catechols from the wastewater stream is therefore of vital importance.

Adsorption process offers great potential for the removal of refractory organics, heavy metals and other non biodegradable substances. Although activated carbon is the most effective and commonly used adsorbent, however, high cost has been major deterrent in its utilisation especially in the developing countries. Suitability of the some of the low cost adsorbents has been widely investigated (4-12). A critical review of the use of low cost adsorbents in waste treatment has been presented by Mall et al. and Bailey et al. (11-12).

The present study is in continuation of earlier work for removal of 2, 4-dichlorophenol using low cost adsorbents (13) and deals with the adsorption of tetrachlorocatechol from wastewater onto bagasse fly ash (BFA), rice husk fly ash (RHFA) and activated carbon (AC). The adsorbents bagasse fly ash and rice husk fly ash are produced in large amount by the sugar mills and rice mills respectively.

EXPERIMENTAL

Bagasse fly ash and rice husk fly ash collected from nearby sugar and rice mill were used for removal of tetrachlorocatechol. Analytical grade of activated carbon supplied by Loba-Chemie industrial Co. Mumbai was used for adsorption studies to compare the adsorptive capacity and evaluate the economic viability of the process. Details of the experimental procedure and procedure for estimation of concentration are same as described earlier for 2,4 dichlorophenol (10). Adsorbents were characterised for proximate and chemical analysis, structural and morphological characteristics using X-ray diffraction and scanning electron microscope details of which are given in the earlier paper (10).

RESULTS AND DISCUSSION

Effect of initial concentration of tetrachloro-chatechol

The effect of initial concentration on removal of tetrachlorocatechol by bagasse fly ash, rice husk and activatd carbon is shown in Fig. 1. The percentage adsorption of tetrachlorocatechol decreases with increasing concentration for all adsorbents. However, the amount adsorbed per unit of adsorbents was found to increase with increase in initial concentrations for the three adsorbents. This is because at lower concentration, the ratio of initial number of moles of tetrachlorocatechol to the available surface area is low and subsequently the fractional adsorption becomes independent of initial concentration (7,8). The equilibrium time is independent of initial concentration of tetrachlorocatechol. Removal of more than 90% is possible in the lower concentration range showing the effectiveness of the adsorption in the lower concentration range. However complete removal is possible in two stage treatment.

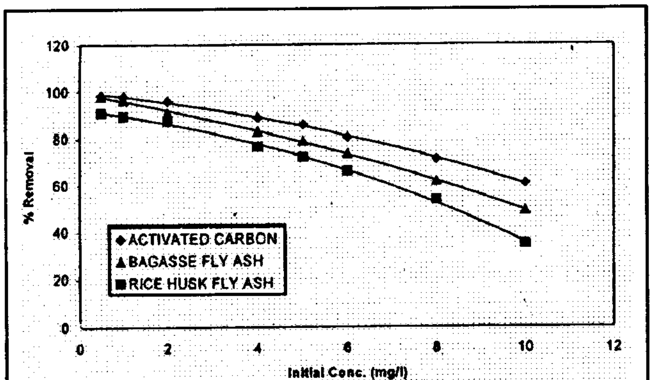

Fig. 1 Effect of initial concentration on removal of tetrachlorocatechol
Quantity = 50 ml, Adsorbent conc. = 20 g/l
Contact time = 6 hr, Temperature = 30°C

Effect of adsorbent dose

The effect of adsorbent dose on removal of tetrachlorocatechol using different adsorbents is presented in Fig. 2. It may be observed that on increasing of adsorbent dose, the percentage removal of tetrachlorocatechol increases upto certain dose, however, by increasing the adsorbent dose further no increase in the percentage removal of tetrachlorocatechol takes place. Initially the percentage removal increases with increase in adsorbent dose as more surface area is available for adsorption. The plot of unit adsorption versus dose reveals that the unit adsorption was high at low doses than at high doses.

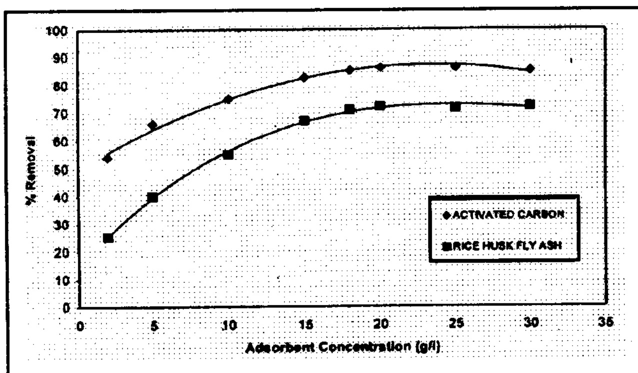

Fig. 2 Effect of Adsorbent dose on removal of tetrachlorocatechol
Initial conc. = 5 mg/l, Quantity = 50 ml,
Contact time = 6 hr, Temperature = 30°C

Effect of pH

The removal of pollutants from wastewater by adsorption is highly dependent on pH of the solution

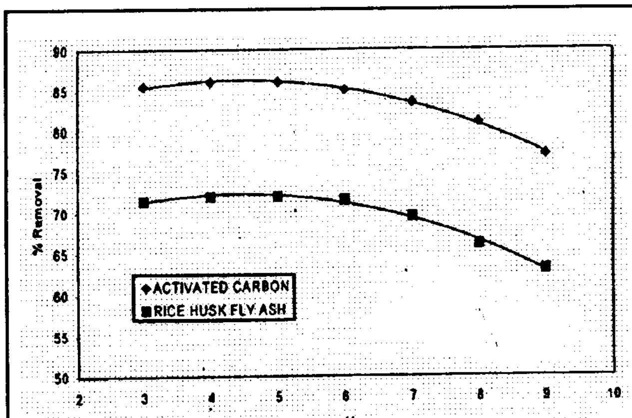

Fig. 3 Effect of pH on removal of tetrachlorocatechol
Initial conc. = 5mg/l, Adsorbent conc. = 20g/l,
Quantity = 50 ml, Contact time = 6 hr,
Temperature = 30°C

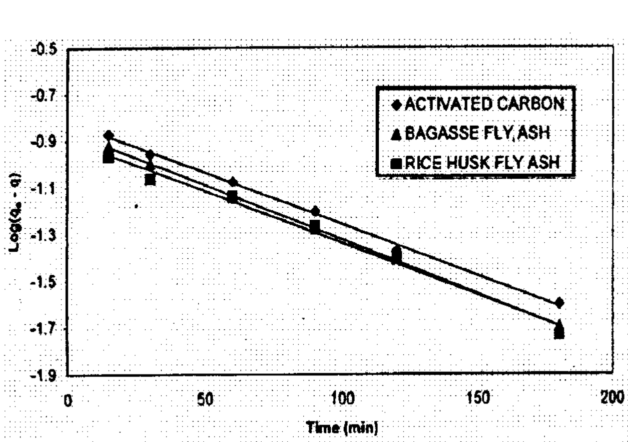

Fig. 4 Lagergren plot for removal of tetrachlorocatechol

which affect the surface charge of adsorbent and the degree of ionisation and speciation of adsorbate (13). Fig. 3 depicts the effect of pH on removal of tetrachlorocatechol. It is clear from the figure that the percentage removal is maximum in the range of pH 3-5 for the bagasse fly ash and rice husk carbon.

Kinetics of Removal of tetrachlorocatechol

Kinetic modeling of the removal of tetrachlorocatechol by the adsorbents has been carried out by using the Lagergren first order rate expression (7,8,10,14)

$$\log (q_e - q) = \log q_e - \frac{k_{ad}}{2.303} t$$

where q and q_e are the amounts of tetrachlorocatechol removed by unit weight of adsorbent at time t and at equilibrium, k is the adsorption rate constant. The straight line plot of log (q_e - q) vs t (Fig. 4) shows validity of the Lagergren first order rate expression for all the three adsorbents. The values of rate constants have been given in Table 1.

Table 1. Lagergren rate constants of tetrachlorocatechol for different adsorbents

Adsorbent	Lagergren constant98; k (min^{-1})
Activated carbone	0.01012
Bagasse fly ash	0.01081
Rice husk fly ash	0.01035

Table 2. Rate parameters k' and k" for Weber-Morris plot

Adsorbent	K'	K"
Activated carbone	0.0116	0.0009
Bagasse fly ash	0.0106	0.0010
Rice husk fly ash	0.091	0.0008

Weber and Moris intraparticle diffusion plot (15, 16) between the solute adsorbed per unit mass of adsorbent (q) and square root of contact time ($t^{0.5}$) has been commonly used to describe the intraparticle transport which is linear in case the controlling mechanism for adsorption is intraparticle diffusion. The linear nature of the plot (Fig. 5) in case of both adsorbents were observed which show that the controlling mechanism for adsorption is intraparticle diffusion. The values of intraparticle diffusion rate parameters are given in Table 2.

Adsorption Isotherm

Modeling of the adsorption equilibrium has been usually done by using Langmuir and Freundlich isotherms which relate the equilibrium solid phase concentration with liquid phase concentration.

Langmuir Isotherm

$$q_e = \frac{Q_0 b C_e}{1 + bC_e}$$

Freundlich Isotherm

$$q_e = K_F C_e^{1/n}$$

where C_e and q_e are the equilibrium concentration mg/L and amount of adsorbate adsorbed per unit weight of adsorbent at equilibrium respectively. b and Q_0 are the Langmuir constants and K_F and n are Freundlich constants. The plots of q_e vs log C_e and $1/q_e$ vs $1/C_e$ for all three adsorbents are given in Fig. 5-6. Straight line of these plots shows the applicability of Langmuir and Freundlich isotherms. The adsorption equilibrium parameters for these two models are given in Table 3. The values of 1/n were found between 0.41 to 0.51 (>1) for all the three adsorbents which show favourable adsorption (17).

The essential characteristics of a Langmuir

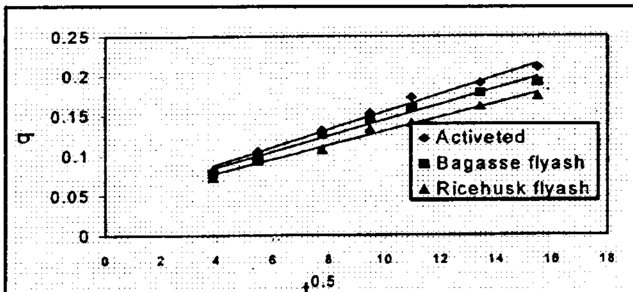

Fig. 5 Weber and Morris intraparticle diffusion plot for removal of tetrachlorocatechol

Table 3. Isotherm parameters for tetrachlorocatechol for different adsorbents

Isotherm equation Parameters	Activated carbon	Bagasse fly ash	Rice husk fly ash
Freundlich isotherm			
K_F	0.23372	0.18009	0.13916
l/n	2.38265	2.42718	1.95274
Langmuir isotherm			
Q_0 (mg.g^{-1})	0.32666	0.27592	0.24540
b (Lmg^{-1})	2.70505	2.29284	1.83898

isotherm can be expressed it terms of a dimensionless constant separation factor R_L (18) which is defind as

$$R_L = \frac{1}{1 + bC_0}$$

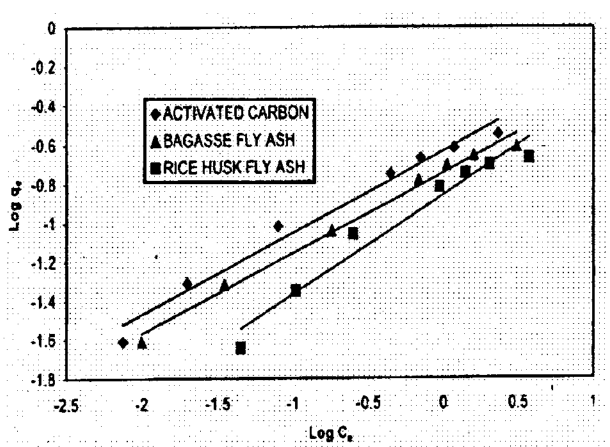

Fig. 6 Freundlich isotherm for removal of tetrachlorocatechol using adsorption

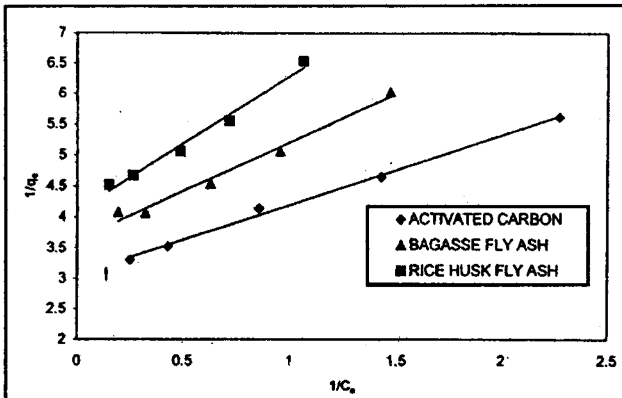

Fig. 7 Langmuir isotherm for removal of tetrachlorocatechol using adsorption

where b is Lagmuir constant and C_0 is the initial concentration of tetrachlorocatechol. The value of R_L less than 1 show highly favourable adsorption. In the present investigation the value of R_L were found in the range 0.04 to 0.52 in case of all the three adsorbents showing favorable adsorption. Adsorption capacity of the adsorbents were in the order: activated carbon>bagasse fly ash>rice husk.

Economic evaluation of the process

The economic evaluation of the treatment process using activated carbon, bagasse fly ash and rice husk fly ash is presented in Table 4. Though the adsorption capacity of activated carbon is higher than that of bagasse fly ash and rice husk fly ash, the overall cost of treatment with bagasse fly ash and rice husk fly ash is lower, as these adsorbents are available almost free of cost involving only handling charges.

Table 4. Economic evaluation of various adsorbents

Adsorbent	Adsorption capacity (mg g^{-1})	Cost of adsorbent (Rs/Tonne)
Activated carbon	0.32666	60,000-70,000
Bagasse fly ash	0.27592	5,000*
Rice husk fly ash	0.24540	5,000*
* Handling charges		

CONCLUSION

Bagasse fly ash and rice husk carbon was studied as adsorbents for the removal of tetrachlorocatechol. Removal was observed to be pH dependent and higher removal was observed in acidic ranges. Percentage removal was found higher in the lower concentration range. Kinetics of removal follow first order expression and removal of tetrachlorocatechol was found to be controlled by intraparticle diffusion. Equilibrium data confirms applicability of Langmuir and Freundlich adsorption isotherms. Adsorption capacity of the adsorbents were in the order: activated carbon >bagasse fly ash rice>husk. Economic evaluation of the process shows that use of bagasse fly ash and rice husk carbon for treatment of tetrachlorocatechol bearing wastewater will be viable.

ACKNOWLEDGEMENT

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