

## Removal of bromophenols from water using industrial wastes as low cost adsorbents

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### Abstract

A comparative study of the adsorbents prepared from several industrial wastes for the removal of 2-bromophenol, 4-bromophenol and 2,4-dibromophenol has been carried out. The results show that maximum adsorption on carbonaceous adsorbent prepared from fertilizer industry waste has been found to be 40.7, 170.4 and 190.2 mg g<sup>-1</sup> for 4-bromophenol 2-bromophenol and 2,4-dibromophenol, respectively. As compared to carbonaceous adsorbent, the other three adsorbents (viz., blast furnace sludge, dust, and slag) adsorb bromophenols to a much smaller extent. This has been attributed to the carbonaceous adsorbent having a larger porosity and consequently higher surface area. The adsorption of bromophenols on this adsorbent has been studied as a function of contact time, concentration and temperature. The adsorption has been found to be endothermic, and the data conform to the Langmuir equation. The further analysis of data indicates that adsorption is a first order process. A comparative study of adsorption results with those obtained on standard activated charcoal sample shows that prepared carbonaceous adsorbent is about 45% as efficient as standard activated charcoal in removing bromophenols. To test the practical utility of this adsorbent, column operations were also carried out. The results were found satisfactory in removing bromophenols by column operations. Therefore, the present investigations recommend the use of carbon slurry waste as inexpensive adsorbent for small scale industries of developing/poor countries where disposal of solid waste of various industries and proper treatment of polluted wastewater is a serious problem.

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### 1. Introduction

Among the various aqueous pollutants generally present in wastewaters, phenol and substituted phenols are considered as priority pollutants [1]. The discharge of effluents containing phenolic pollutants from various industries into natural water bodies is an ongoing and serious threat to human health and natural water quality. The ubiquitous nature of phenols, their toxicity even in trace amounts and the stricter environmental regulations make it necessary to develop processes for the removal of phenols from wastewaters. Various methods for the removal of phenols from wastewaters include coagulation, chemical oxidation, solvent extraction, liquid membrane permeation and adsorption [2]. Among these, adsorption onto activated carbon proved to

be one of the efficient and reliable physiochemical treatment methodology in wastewater treatment. In spite of the usefulness of activated carbon as an efficient adsorbent for wastewater treatment, the high cost of activated carbon inhibits its large scale use as adsorbent. Hence, an economical and easily available adsorbent would certainly make an adsorption based process a viable alternative for the treatment of wastewater containing phenolic pollutants. In recent past, considerable attention has been devoted to develop the low cost adsorbents from various materials, but the utilization of agricultural [3,4] and industrial wastes [5,6] is increasingly becoming of vital concern because these wastes represent unused resources and, in many cases, cause serious disposal problems. If these wastes could be used as low cost adsorbents, it will provide a two-fold advantage to environmental pollution. Firstly, the volume of waste materials could be partly reduced and secondly the low cost adsorbent if developed can reduce the pollution of wastewaters at a reasonably cost.

We have carried out recently the comparative studies of adsorbents prepared from the industrial wastes of fertilizer and steel plants [7,8] and have found that carbonaceous adsorbent

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(prepared from fertilizer industry waste) having high organic content adsorbs organic molecules efficiently. In order to further test the applicability of this adsorbent, investigations have been further extended to a number of bromophenols, viz., 2-bromophenol, 4-bromophenol and 2,4-dibromophenol. Further, the results have also been compared with those obtained on standard activated charcoal and adsorbents of inorganic nature prepared from steel industry wastes. The present communication reports these results.

## 2. Experimental

2-Bromophenol (2-BP), 4-bromophenol (4-BP) and 2,4-dibromophenol (2,4-DBP) were procured from Lancaster (England), Spectrochem (India) and Fluka (Switzerland), respectively. The standard activated charcoal sample was obtained from E. Merck. Other reagents used were of AR grade. Double distilled water was used for preparing solutions throughout these investigations.

### 2.1. Preparation of carbonaceous adsorbent

The carbon slurry waste material was procured from National Fertilizer Ltd. (NFL), Panipat (India) and powdered. It was found to consist of small, black and greasy granules and treated [7,9] with  $H_2O_2$  to oxidize the adhering organic material. It was then washed with distilled water and heated at  $200^\circ C$  till the evolution of black soot stopped. The activation of this material was done at different temperatures in muffle furnace for 1 h in the presence of air. After the activation, the ash content was removed by treating the material with 1 M HCl and washed with distilled water and dried. The surface area of samples activated at temperatures 300, 400, 500, 600 and  $700^\circ C$  were found to be 280, 363, 380, 374 and  $367\text{ m}^2\text{ g}^{-1}$ , respectively. Thus, the activation at  $500^\circ C$  imparts maximum surface area and it was also seen that extent of adsorption was maximum for this sample activated at  $500^\circ C$ . Therefore, all studies reported in this paper are on a sample activated at  $500^\circ C$ . The yield of the finished product was found to be  $\sim 90\%$  and it is now called 'carbonaceous adsorbent'. Different mesh sizes were obtained after sieving and kept in desiccator for further use.

### 2.2. Preparation of blast furnace sludge, dust and slag adsorbents

These adsorbents were prepared from wastes obtained from Malvika Steels, Jagdishpur (India) by the method reported elsewhere [7]. The products were sieved and stored in desiccator.

### 2.3. Instrumentation

The spectrophotometric determination of bromophenols was done on Shimadzu 1601 UV-vis spectrophotometer (detection limits were  $0.25\text{ mg L}^{-1}$ ). The pH of solutions was measured with ELICO LI 127 pH meter. Vario EL III, CHNS Elemental Analyzer was used to determine the carbon content of the adsorbents and LEO 435 VP was used for scanning electron

microscopy (SEM). IR spectra of the samples were recorded on a Perkin-Elmer FTIR spectrophotometer model 1600. X-ray measurements were done on a Phillips X-ray diffractometer employing  $Cu\ K\alpha$  radiations.

## 2.4. Adsorption studies

### 2.4.1. Batch studies

The adsorption of bromophenols on prepared adsorbents was studied at room temperature ( $25 \pm 2^\circ C$ ) by employing the batch method. Known volume (10 mL) of bromophenols solution of varying initial concentrations, taken in 50 mL glass tubes, was shaken with a fixed dose of adsorbent (0.01 g) for a specified period of contact time in a thermostated shaking assembly. The glass tubes were tightly stoppered (covered) to avoid vaporization losses of bromophenol from the aqueous solution. After equilibrium, the concentration of the adsorbate in the residual solution was determined spectrophotometrically at  $\lambda_{\text{max}}$  of 274.0 nm for 2-bromophenol, 280.0 nm for 4-bromophenol and 286.0 nm for 2,4-dibromophenol, respectively. The reproducibility during concentration measurements was ensured by repeating the experiments at least three times under same conditions and average values are reported. Standard deviations were found to be within  $\pm 5.0\%$ . Furthermore, the error bars for the figures were smaller than the symbols used to plot the graphs and hence are not shown.

The amount of bromophenols adsorbed ( $q$  in  $\text{mg g}^{-1}$ ) was determined as follows

$$q = (C_0 - C_f) \frac{V}{m} \quad (1)$$

where  $C_0$  and  $C_f$  are the initial and final concentrations of the adsorbate in solution ( $\text{mg L}^{-1}$ ),  $V$  the volume of solution (L) and  $m$  is the mass of the adsorbent (g).

The pH of the solutions was adjusted using 0.1N HCl and 0.1N NaOH solutions. pH of the solutions was measured before and after the equilibration and a slight change in pH was observed. The initial pH value of all bromophenols solutions was from 5.8 to 6.8 before experiments. After the experiments, the pH value was observed from 5.5 to 6.5 for all the bromophenols. However, after adjustment of the pH of adsorbent-adsorbate system, no further change was observed. The adsorption was studied as a function of contact time, initial concentration and temperature.

### 2.4.2. Column studies

In the present investigations, a glass column (50 cm  $\times$  1.05 cm) was fully loaded with adsorbent on a glass-wool support. Double distilled water was used to rinse the adsorbent and to remove any bubbles present. A bromophenol solution or wastewater containing mixtures of phenols and other materials was poured over the column and the column effluent was allowed at a flow rate of  $2.5\text{ mL min}^{-1}$ . A definite amount of the column effluent (10 mL) was taken and the concentration of the solute (pollutants under investigation) determined from time to time by spectrophotometric method. This process has continued until the concentration in the column effluent started

increasing and finally becomes constant. The plots of concentration of the adsorbate in the column effluent and volume of the effluent provide breakthrough curves.

### 3. Results and discussion

#### 3.1. Characterization of the prepared adsorbents

The BF sludge, dust and slag were chemically analyzed by standard methods [10] and it was found that BF slag is inorganic in nature, i.e. it contains mainly inorganic constituents like silica (32.7%), calcium oxide (31.7%), magnesium oxide (6.8%) and  $R_2O_3$ ;  $R = Fe, Al$  (22.8%). On the other hand, silica,  $R_2O_3$  (mainly iron oxide) and carbon (due to the presence of coke particles) are the prominent components of BF dust and sludge. Although, the inorganic constituents like silica (15.8% and 12.7%),  $R_2O_3$  (44.9% and 35.4%), MgO (4.2% and 3.0%) and CaO (4.7% and 3.5%) in BF dust and sludge, respectively, are present in major amounts, but the presence of appreciable carbon content imparts partial organic character to BF sludge and dust. Of course, partial organic character of BF sludge (carbon content = 35.0%) is more than that of BF dust (carbon content = 21.7%). We may therefore, say that BF sludge and dust character is of mixed type with inorganic nature predominating organic. However, as compared to slag, dust and sludge, the analysis of carbon slurry indicates 0.9% of ash and 89.8% carbon. Thus, due to the presence of high carbon content, the carbon slurry may be treated as organic in nature. Thus it was expected that carbonaceous adsorbent will show greater porosity as compared to other three adsorbents. In order to confirm this, the scanning electron microscopy (SEM) photographs of all the prepared adsorbents were taken and are shown in Figs. 1–4. It is seen from these photographs that carbonaceous adsorbent is highly porous whereas BF slag is least porous. The decreasing order of porosity as seen from SEM photographs is, carbonaceous adsorbent > BF sludge > BF dust > BF foamed slag. The porosity imparts higher surface area to the adsorbents. In order to confirm the expected relationship between surface area and

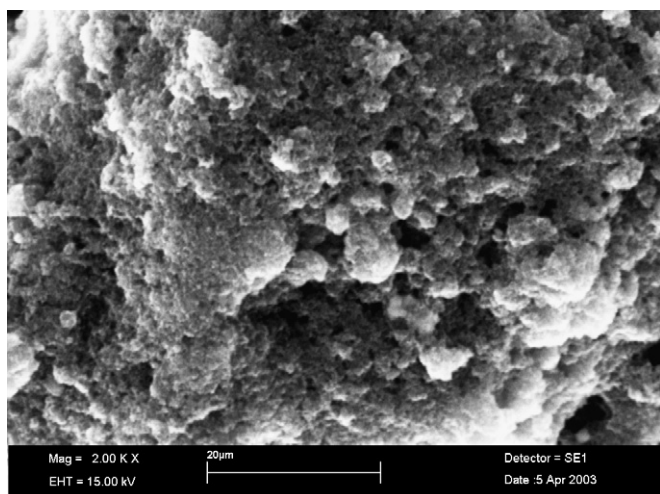


Fig. 1. Scanning electron micrograph (SEM) of activated carbonaceous adsorbent.

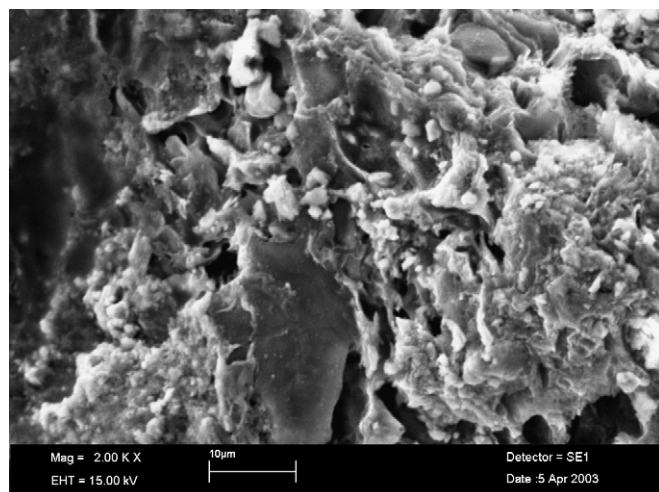


Fig. 2. Scanning electron micrograph (SEM) of activated blast furnace sludge.

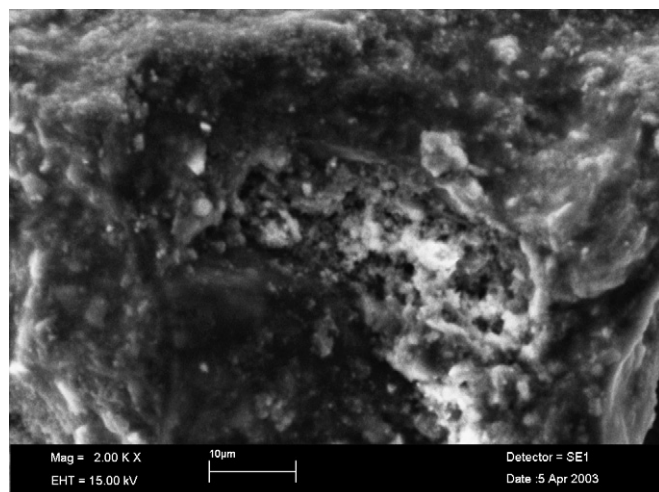


Fig. 3. Scanning electron micrograph (SEM) of activated blast furnace dust.

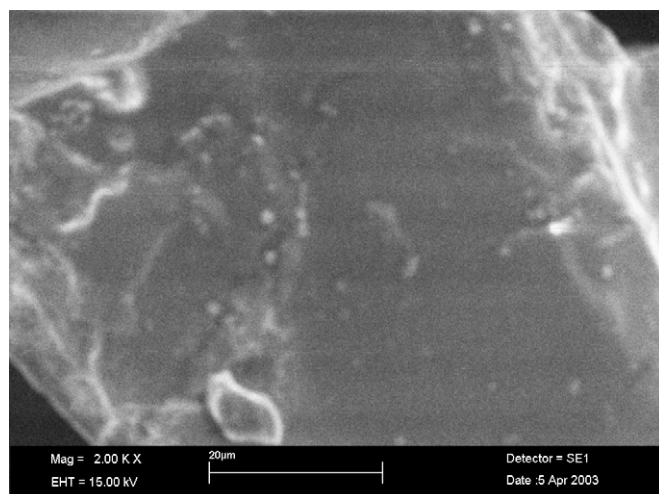


Fig. 4. Scanning electron micrograph (SEM) of activated blast furnace slag.



Table 1  
Characteristics of adsorbents used

	Standard activated charcoal	Carbonaceous adsorbent	BF sludge	BF dust	BF slag
Surface area ( $\text{m}^2 \text{g}^{-1}$ )	710	380	28	13	4
Methylene blue no.	198	90	6	3	2
Iodine no.	635	330	24	11	3

porosity, the surface area of the adsorbents was determined by  $\text{N}_2$ -gas adsorption and given in Table 1. It is seen from the table that carbonaceous adsorbent has maximum surface area of  $380 \text{ m}^2 \text{ g}^{-1}$  whereas BF slag has the least ( $4 \text{ m}^2 \text{ g}^{-1}$ ). The surface area decreases in the order, carbonaceous adsorbent > BF sludge > BF dust > BF foamed slag, which is also the order of decreasing organic/carbon content. Further, the surface area order is parallel to porosity order.

Two other important parameters which are normally used to indicate adsorptive property are methylene blue and iodine numbers. These two numbers were also determined by standard procedures [11] and are given in Table 1. It is seen that these two numbers decrease in the order, carbonaceous adsorbent > BF sludge > BF dust > BF foamed slag. These numbers reflect that extent of adsorption is parallel to surface area of adsorbents. Thus, it is expected that adsorption capacity of carbonaceous adsorbent would be much greater as compared to other three adsorbents.

The samples of carbonaceous adsorbent, slag, dust and sludge were stirred with deionized/distilled water (pH 6.9) for 2 h and left for 24 h to see any interaction. It was seen that in case of BF slag, dust and sludge, an enhancement of pH of deionized/distilled water was observed indicating alkaline hydrolysis of inorganic constituents. In case of carbonaceous adsorbent, the pH of water was lowered, which indicates that carbonaceous adsorbent, as per Steenberg classification [12], comes under "L" type carbon. X-ray spectra of carbonaceous adsorbent does not show any peak, thereby indicating its amorphous nature. The X-ray diffraction peaks in the spectra of BF sludge and dust are due to iron oxides while in case of BF slag indicates the presence of silicates of calcium and aluminum and quartz. The IR spectra of the sample of carbonaceous adsorbent taken indicates the presence of two prominent bands lying at  $1605$  and  $3340 \text{ cm}^{-1}$ . The first peak may be assigned to the presence of carbonyl group and the latter one to OH group.

### 3.2. Effect of contact time and concentration

In order to establish equilibration time for maximum uptake and to know the kinetics of adsorption process, the adsorption of bromophenols on carbonaceous adsorbent was studied as a function of contact time and results are shown in Fig. 5. It is seen that the rate of uptake of all the bromophenols is rapid in the beginning and 50% adsorption is completed within 2 h. Fig. 5 also indicates that the time required for equilibrium adsorption is 8 h. Thus, for all equilibrium adsorption studies, the equilibration period was kept 10 h. The effect of concentration on the equilibration time was also investigated as a function of initial

bromophenols concentration and the results are shown in Fig. 6 (in case of 2-bromophenol). Similar plots were also obtained for other two bromophenols. It was found that time of equilibrium as well as time required to achieve a definite fraction of equilibrium adsorption is independent of initial concentration. These results indicate that the adsorption process is first order, which is confirmed by Lagergren's plots discussed later under dynamic modelling.

### 3.3. Adsorption isotherms

In order to evaluate the efficacy of the prepared adsorbents, the equilibrium adsorption of all the bromophenols was studied as a function of concentration. The adsorption isotherms of

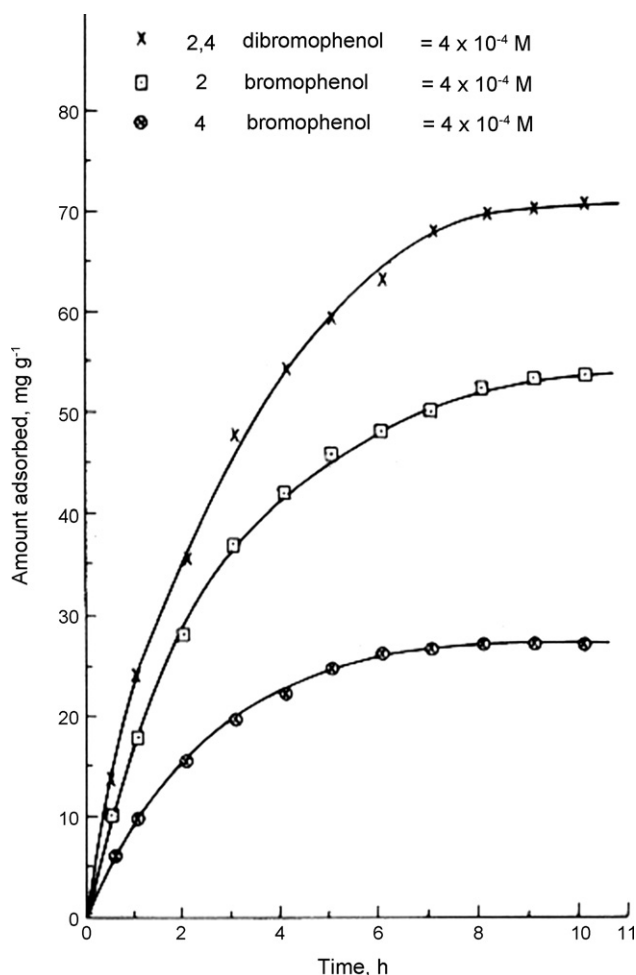


Fig. 5. Effect of contact time on uptake of bromophenols on carbonaceous adsorbent (temperature:  $25^\circ\text{C}$ ; particle size: 200–250 mesh).

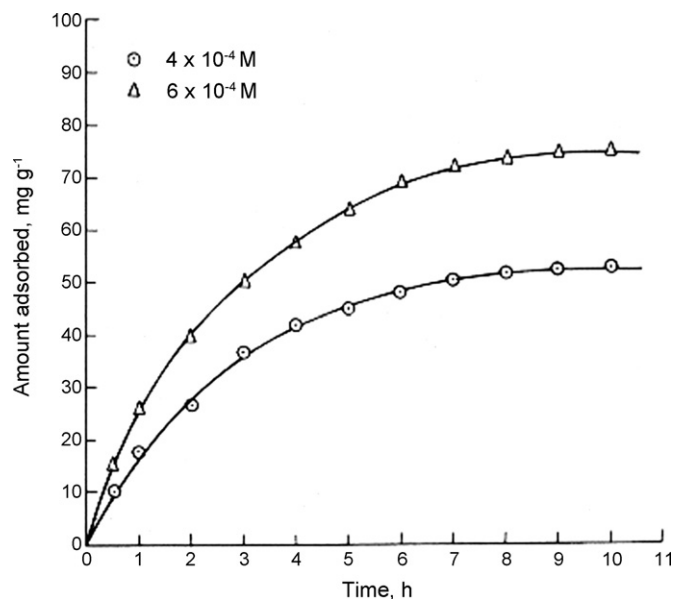


Fig. 6. Effect of contact time on uptake of 2-bromophenol on carbonaceous adsorbent at different initial concentrations (temperature: 25 °C; particle size: 200–250 mesh).

2-bromophenol on various adsorbents are shown in Fig. 7. Similar adsorption isotherms were also obtained for the other two bromophenols. The maximum adsorption from these adsorption isotherms has been calculated and compiled in Table 2. It is seen from Table 2 that order of adsorption in terms of amount adsorbed (mg/g) on different adsorbents is: carbonaceous adsorbent > BF sludge > BF dust > BF slag. The adsorption on BF sludge and dust is small whereas on BF slag negligible. This appears due to inorganic nature of these three adsorbents which causes poor porosity and surface area resulting in small adsorption of bromophenols. Thus, these three inorganic adsorbents are not good materials for the removal of bromophenols from wastewaters.

On the other hand, carbonaceous adsorbent which has higher carbon content, more porosity and high surface area as compared to these three adsorbents tends to adsorb all bromophenols in amounts appreciably larger. This is because adsorption of phenols on carbonaceous adsorbent is purely a surface phenomenon where van der Waals forces operate to some extent. The adsorption of phenols could also be occurring to some extent due to their interaction through hydrogen bonding with hydrophilic sites or groups formed on carbon surface at the time of activation.

It is further seen from Table 2 that the extent of adsorption of all bromophenols on different adsorbents follow the order: 2,4-dibromophenol > 2-bromophenol > 4-bromophenol. It has been

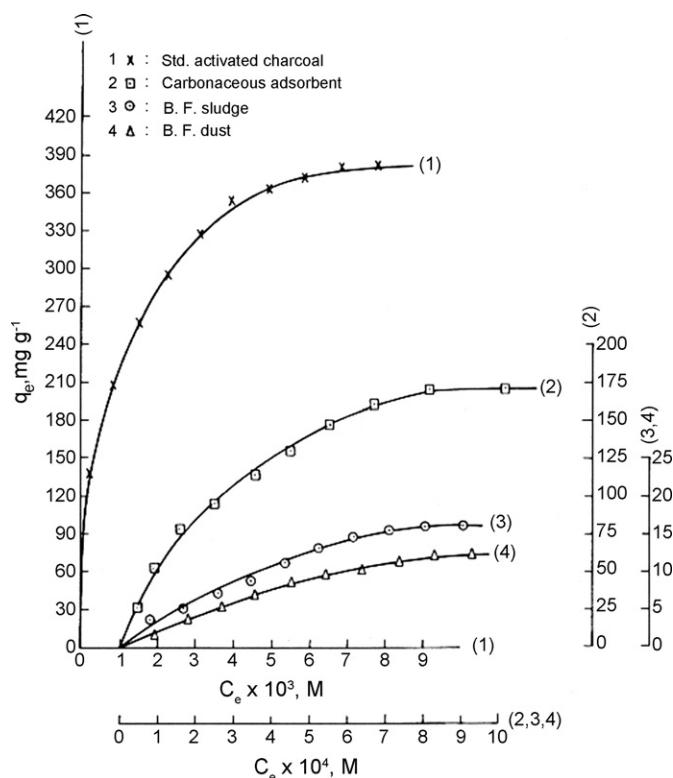


Fig. 7. Adsorption isotherms of 2-bromophenol on different adsorbents at 25 °C.

reported that in the adsorption of phenols on carbon surface, the role of donor–acceptor complex mechanism [13] involving carbonyl oxygen groups of the carbon surface acting as electron donor and the aromatic ring of the adsorbate as acceptor is important. Thus, it is expected that electron withdrawing groups which deactivate the ring would promote adsorption through complex formation occurring via donor–acceptor mechanism. The order of deactivation of the ring would be, 2,4-dibromophenol > 2-bromophenol ≈ 4-bromophenol, and consequently the adsorption via donor–acceptor mechanism would follow this order. As a result of higher deactivation of the ring in 2,4-dibromophenol, there would be higher tendency of adsorption through a donor–acceptor complex mechanism resulting in maximum adsorption.

Besides this, the solubility and pK<sub>a</sub> of solute is also expected to affect adsorption to a great extent. A decrease in both solubility and pK<sub>a</sub> of the solute is associated with an increase in adsorption capacity [4]. The solubility data and pK<sub>a</sub> values of bromophenols are given in Table 2 which indicates that the pK<sub>a</sub> [14,15] and solubility of bromophenols [16,17] decreases in the order, 4-bromophenol > 2-bromophenol > 2,4-dibromophenol. A com-

Table 2  
pK<sub>a</sub>, solubility and adsorbability of bromophenols (mg/g) on various adsorbents at 25 °C

Phenols	pK <sub>a</sub>	Solubility in water (g liter <sup>-1</sup> )	Adsorbability (mg g <sup>-1</sup> )			
			Standard activated charcoal	Carbonaceous adsorbent	BF sludge	BF dust
4-Bromophenol	9.37	14.0	90.0	40.7	12.7	9.5
2-Bromophenol	8.45	2.2	380.0	170.4	16.5	12.1
2,4-Dibromophenol	7.79	1.9	415.0	190.2	18.9	13.8

parison of  $pK_a$  and solubility and adsorbability/adsorption capacity (Table 2) clearly indicates that there exists an inverse relationship between the extent of adsorption and solubility and  $pK_a$  of solute. The bromophenols which have lower  $pK_a$  as well as smaller solubility (lesser affinity for water) would obviously have higher tendency to get adsorbed at solid–liquid interface. Thus, 2,4-dibromophenol having least solubility and least  $pK_a$ , is adsorbed to maximum extent and 4-bromophenol having maximum solubility and greater  $pK_a$ , is adsorbed to smaller extent. Thus, all these factors, i.e. the tendency to form more donor–acceptor complex at carbon surface, low  $pK_a$  and low solubility lead to same order of adsorption of bromophenols (2,4-dibromophenol > 2-bromophenol > 4-bromophenol). Therefore, it may be concluded that combined effects of all these factors, viz., solubility,  $pK_a$  of solute and tendency to form more donor–acceptor complexes play an important role during adsorption of bromophenols on the surface of carbonaceous adsorbent.

Of these two effects, i.e. donor–acceptor complex mechanism and solubility effect, the effect of solubility appears to be much more. This is evident from the fact that the adsorption of 2-bromophenol is much larger as compared to 4-bromophenol on carbonaceous adsorbent. This cannot be explained on the basis of deactivation because the deactivation of the ring in case of 2-bromophenol and 4-bromophenol is almost similar and extent of adsorption on this basis should have been almost same. However, the solubility of 2-bromophenol is much smaller than that of 4-bromophenol. This smaller solubility of 2-bromophenol leads to its higher adsorption. Thus, it is reasonable to conclude that solubility factor plays a major role in affecting adsorption of aromatic solutes at a solid–liquid interface.

As the carbonaceous adsorbent is the best, its performance was further assessed by comparing its results with those on standard activated charcoal. The results on adsorption of these bromophenols on standard activated charcoal are also incorporated in Table 2. It is seen that carbonaceous adsorbent is  $\approx 40$ –45% as efficient as standard activated charcoal in removing bromophenols and therefore, can be employed for effluent treatment. As the carbonaceous adsorbent appears to be promising material with high adsorption efficiency, all further studies were done with it only.

### 3.4. Effect of temperature

In order to understand the effect of temperature on the adsorption of bromophenols, experiments were also conducted at 45 and 65 °C and results are shown in Fig. 8 (at 45 °C). A comparison of adsorption isotherms at 25 and 45 and 65 °C shows that adsorption increases with increase in temperature indicating that the process is apparently endothermic. Similar results were also obtained by other workers [18,19]. It seems that at higher temperatures, dissociation of phenol molecule occurs. However, the effect of temperature can mainly be explained on the basis of hydrogen bonding [20]. In aqueous solutions of phenols, there exists extensive hydrogen bonding between the phenol molecule and water resulting in appreciable solubility. These hydrogen bonds get broken at higher temperatures and this would cause phenols to be less soluble and therefore, exhibit higher tendency

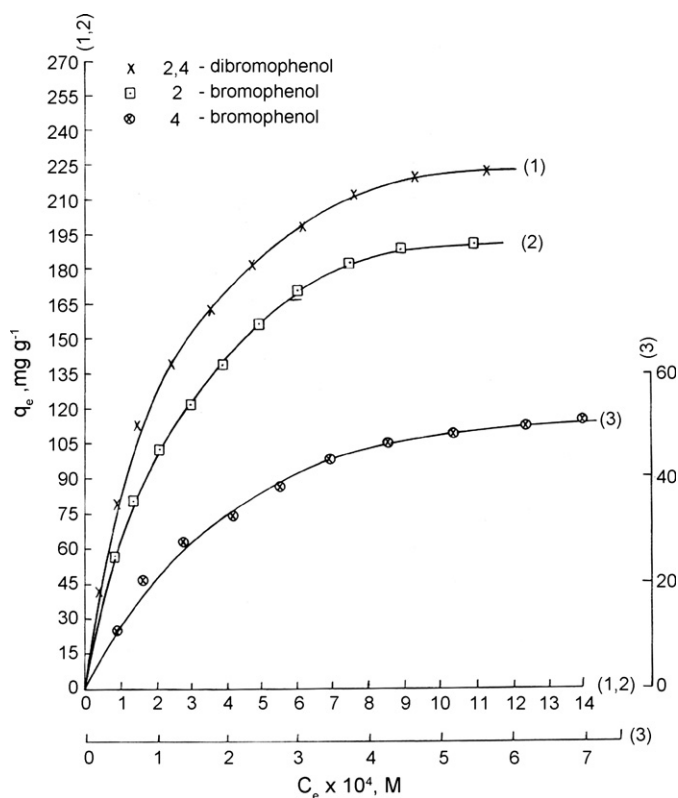


Fig. 8. Adsorption isotherms of bromophenols on carbonaceous adsorbent at 45 °C.

to go to the adsorbent surface and get adsorbed rather remaining in the solution. This would result in more adsorption at higher temperature [20]. Few researchers [5] also described this phenomenon (more adsorption at higher temperatures) on the basis of “active surface centers” (presence of free hydroquinone and quinone groups on the carbon surface which could constitute the active surface centers for the adsorption of phenols by hydrogen bonding). They suggested that number of active surface centers available for sorption increase with increasing temperatures resulting higher adsorption of phenols.

The adsorption data was further analyzed to Freundlich and Langmuir models and found to conform best to following Langmuir equation with good correlation coefficients ( $R^2 = 0.999$ – $0.991$ ):

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m b C_e} \quad (2)$$

where  $q_e$  ( $\text{mg g}^{-1}$ ) is the amount adsorbed at equilibrium concentration  $C_e$  ( $\text{mol L}^{-1}$ ),  $q_m$  ( $\text{mg g}^{-1}$ ) the Langmuir constant representing maximum monolayer capacity and  $b$  is the Langmuir constant related to energy of adsorption. The plots between  $1/q_e$  and  $1/C_e$  for the adsorption of 2-bromophenol are drawn in Fig. 9. Similar plots were also obtained for other bromophenols. The values of monolayer capacity ( $q_m$ ) and equilibrium constant ( $b$ ) have been evaluated from the intercept and slope of these plots and given in Table 3. It is seen from Table 3 that monolayer capacity ( $q_m$ ) of the adsorbent for the bromophenols is comparable to the maximum adsorption (Table 2) obtained

Table 3  
Langmuir constants and separation factor for the adsorption of phenols on carbonaceous adsorbent at different temperatures

Phenols	Temperature (°C)	$q_m$ (mg g <sup>-1</sup> )	$b$ ( $\times 10^3$ L mol <sup>-1</sup> )	$R_L$ ( $\times 10^{-1}$ )
4-Bromophenol	25	58.8	3.7	3.8
	45	74.1	4.5	3.4
	65	81.4	5.1	3.1
2-Bromophenol	25	192.3	4.1	2.3
	45	204.1	5.3	1.9
	65	211.6	6.2	1.4
2,4-Dibromophenol	25	217.4	4.3	2.2
	45	238.1	6.1	1.8
	65	253.7	7.5	1.1

from adsorption isotherms. As  $b$  values reflect equilibrium constant for the adsorption process, it reflects the affinity of the adsorbent for phenol. Thus,  $b$  values indicate that the adsorbent has maximum affinity for 2,4-dibromophenol and minimum for 4-bromophenol.

The influence of adsorption isotherm shape has been discussed [21] to know whether adsorption is favorable or not in terms of  $R_L$ , a dimensionless constant referred to as separation factor or equilibrium parameter.  $R_L$  is calculated using the following equation:

$$R_L = \frac{1}{1 + bC_0} \quad (3)$$

The values of  $R_L$  calculated as per above equation are incorporated in Table 3. All the  $R_L$  values lie between 0 and 1 confirming that the adsorption isotherm is favorable [21].

The free energy change ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) were calculated using following equations:

$$\Delta G^\circ = -RT \ln(b) \quad (4)$$

$$\ln\left(\frac{b_2}{b_1}\right) = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad (5)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (6)$$

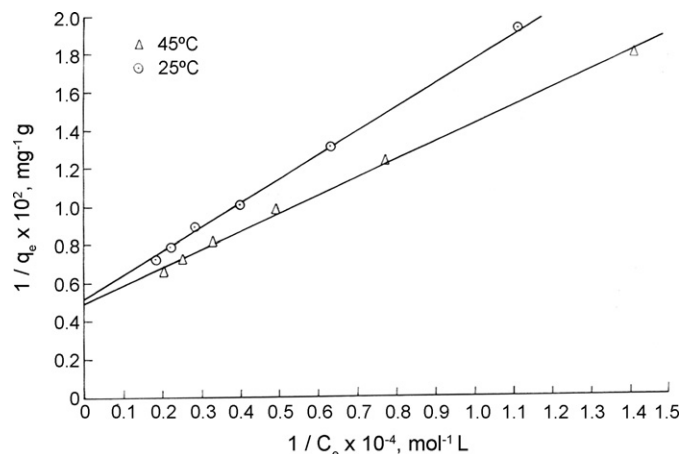


Fig. 9. Langmuir adsorption isotherms of 2-bromophenol on carbonaceous adsorbent at different temperatures.

for adsorption process in order to know the nature of adsorption and are summarized in Table 4. The  $\Delta H^\circ$  values are positive due to the effect of temperature on breaking of hydrogen bonds which resulted in increased adsorption. Thus, the pre-adsorption step (breaking of hydrogen bonds between phenol and water molecules at higher temperatures) gives rise to positive  $\Delta H^\circ$ . These positive  $\Delta H^\circ$  values are only apparent heat of adsorption. As a matter of fact,  $\Delta H^\circ$  values reflect the combined effect of endothermic hydrogen bond breaking process and exothermic adsorption process. The endothermic process predominates the exothermic adsorption process giving rise to positive  $\Delta H^\circ$ . Further, negative  $\Delta G^\circ$  values indicate spontaneous process.  $\Delta S^\circ$  values were found positive which indicate the affinity of adsorbent for bromophenols and suggests an increased randomness at the solid–solution interface during adsorption process.

### 3.5. Dynamic modelling

Kinetics of adsorption is an important characteristic from the point of view of determining the efficiency of adsorption processes. A number of kinetic models have been used by various workers, where the adsorption has been considered as first order [18,22], pseudo first order [19,23] and pseudo second order process [24]. It has been found that different adsorbent–adsorbate systems conform to different models. Nevertheless, Lagergren's rate equation [25] is most widely used [18,22,26] for the adsorption of adsorbate from a solution. The first order Lagergren's rate equation is

$$\log(q_e - q) = \log q_e - \frac{k_{\text{ads}}}{2.303} t \quad (7)$$

where  $q_e$  and  $q$  are the amount of bromophenol adsorbed at equilibrium and at time  $t$  (mg g<sup>-1</sup>), respectively, and  $k_{\text{ads}}$  is the first order rate constant, and it was applied to the present studies of adsorption of three bromophenols. As such, the values of  $\log(q_e - q)$  were calculated from the kinetic data of Fig. 5 and plotted against time in Fig. 10. The plots are found to be linear with good correlation coefficients ( $R^2 = 0.999$ – $0.990$ ) indicating that Lagergren's equation is applicable to adsorption of bromophenols on carbonaceous adsorbent and the adsorption process is first order process. The first order rate constants calculated from the plots (Fig. 10) and are compiled in Table 5. As the size of 2-bromophenol and 4-bromophenol are nearly same,

Table 4  
Thermodynamic parameters for adsorption of phenols on carbonaceous adsorbent at different temperatures

Phenols	Temperature (°C)	$-\Delta G^\circ$ (kJ mol <sup>-1</sup> )	$\Delta S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta H^\circ$ (kJ mol <sup>-1</sup> )
4-Bromophenol	25	20.4	94.3	7.7
	45	22.2	94.0	
	65	24.6	94.0	
2-Bromophenol	25	20.6	103.4	10.2
	45	22.7	103.5	
	65	25.1	103.2	
2,4-Dibromophenol	25	20.7	115.8	13.8
	45	23.0	115.7	
	65	26.2	115.5	

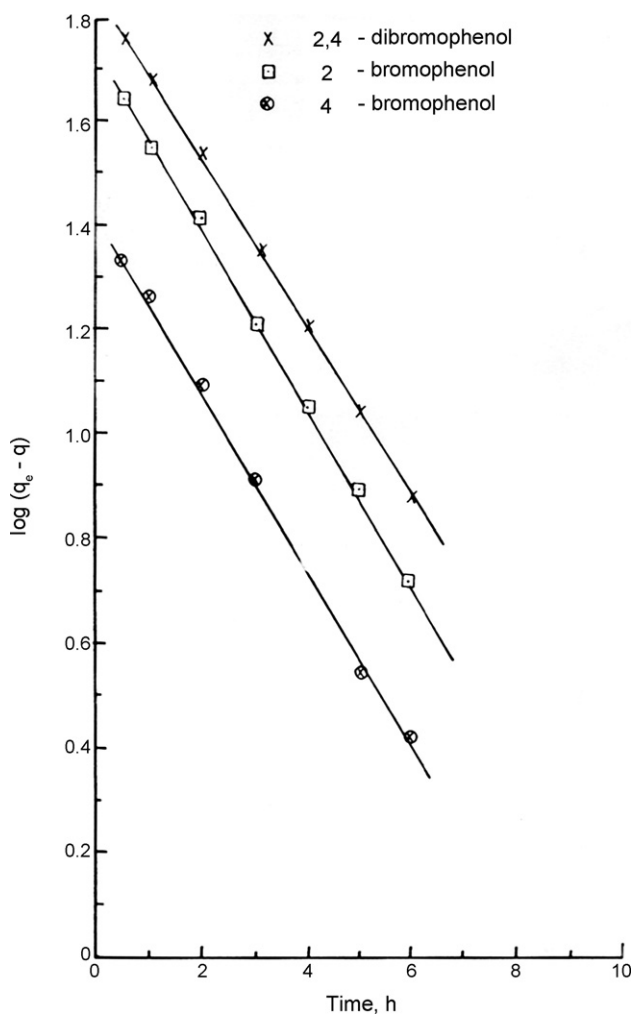


Fig. 10. Lagergren's plot for bromophenols on carbonaceous adsorbent.

Table 5  
Lagergren's first order rate constants ( $k_{\text{ads}}$ ) for the adsorption of bromophenols on carbonaceous adsorbent

Bromophenols	First order rate constants, $k_{\text{ads}}$ ( $\times 10^{-1}$ h <sup>-1</sup> )
2,4-Dibromophenol	3.80
4-Bromophenol	3.86
2-Bromophenol	3.88

their rate constants should also be similar and the experimental rate constants found nearly same (Table 5). 2,4-Dibromophenol being of the largest size has the minimum rate constant.

### 3.6. Column operations

The column operations were carried out using solutions of all the bromophenols on columns (cross-sectional area: 0.9 cm<sup>2</sup>; height: 3.1 cm; mass: 0.5 g) of carbonaceous adsorbent. The studies were undertaken to understand the effect of flow rate on the breakthrough of carbonaceous adsorbent column of bromophenols adsorption. Three flow rates, viz., 2.5, 5.0 and 10.0 mL min<sup>-1</sup> were selected in our studies. It was found that by reducing the flow rate, the service time increased and hence the volume of adsorbate solutions treated was effectively increased. This flow rate dependence can be explained by the kinetics controlling process [27]. The lower the flow rate, the longer the contact time and hence the greater the interaction between adsorbate and adsorbent. Since, flow rate of 2.5 mL min<sup>-1</sup> shows higher removal rate of bromophenols, therefore, all column studies were done at a flow rate of 2.5 mL min<sup>-1</sup>.

Further, it was not possible to carry out column operations satisfactorily on particles of size 200–250 mesh because of column getting clogged due to the fineness of the adsorbent particles. Therefore, particles having size of 50–200 mesh were used for column operations. The column did not get clogged due to mixing of particles of larger size with smaller ones and influent flowed freely over a period of 6–8 h involving a total outflow of 500–1000 mL of bromophenols solution. This total outflow of bromophenols solutions depended on the adsorption capacity of the adsorbent and the concentration of the solution. This column operation was continued till concentration of bromophenol in the aliquot of effluent collected reached nearly 90% of the influent concentration, i.e.  $C/C_0 \sim 0.9$ . The breakthrough curves were obtained (Fig. 11; in case of 2-bromophenol) by plotting  $C/C_0$  against volume of the effluent. Similar curves were also obtained for other two bromophenols. Those points on these breakthrough curves have been considered as breakpoints at which  $C/C_0$  attains a value of 0.02. The breakthrough capacity, exhaustion capacity and degree of column utilization have been evaluated from these figures and are given in Table 6. It was observed that breakthrough capacity is about 7–30% less than the batch capacity. This may be due to (i) lesser contact



Table 6  
Comparison of batch and column capacities and degree of column utilization

Phenols	Batch capacity (mg g <sup>-1</sup> ) (from adsorption isotherms)	Breakthrough capacity (mg g <sup>-1</sup> )	Exhaustion capacity (mg g <sup>-1</sup> )	Degree of column utilization (%)
4-Bromophenol	40.7	37.4	54.2	69.0
2-Bromophenol	170.4	119.1	175.3	67.9
2,4-Dibromophenol	190.2	176.3	260.0	67.8

time/equilibration time of the solute with adsorbent and (ii) larger size of particles (50–200 mesh), which require longer time for equilibration and thus, inhibiting the utilization of column capacity. Similar results were also obtained by other workers [19] for the removal of chlorophenols by bituminous shale.

It is further seen from Table 6, that the exhaustion capacity of column is relatively higher than the batch capacity. This appears due to establishment of continuously larger concentration gradient at the interface zone as the influent passes through the column. The concentration gradient generally remains maintained because of fresh inflow of influent, whereas, in case of batch experiments, the concentration gradient continuously decreases with time resulting in smaller adsorption capacity. Further, Table 6 shows that the degree of column utilization lies in the range 63–70%. Thus, these results have shown that the columns of carbonaceous adsorbent can be used to remove phenols from wastewaters.

### 3.7. Cost factor

Commercial activated carbons of cheapest variety (generally used for effluent treatment) cost  $\approx$  US\$ 2000 tonnes<sup>-1</sup> in India. The industrial waste materials used in the present

studies are generally available at a very cheap rate  $\approx$  US\$ 5–7 tonnes<sup>-1</sup>. The finished products would cost approximately  $\approx$  US\$ 100–200 tonnes<sup>-1</sup> by adding all expenses (transportation, chemicals, electrical energy, etc.). Since the cost of final adsorbents prepared from industrial wastes is 10 times less than the cost of activated carbons of cheapest variety, it is reasonable to conclude that these materials can be fruitfully used as low-cost adsorbents for the treatment of wastewaters.

## 4. Conclusions

The results of studies carried out on the adsorption of bromophenols on four adsorbents prepared from several industrial wastes lead to the following conclusions:

- A comparative study of the four adsorbents prepared clearly shows that the carbonaceous adsorbent adsorbs bromophenols (organics) in much larger amounts as compared to other three adsorbents leading to the conclusion that the adsorbents having higher porosity and surface area are more appropriate materials for the removal of organic molecules.
- The evaluation of performance of carbonaceous adsorbent as compared to standard activated charcoal sample indicates that it is 40–45% as efficient as the standard activated charcoal in removing bromophenols.
- The adsorption of bromophenols on carbonaceous adsorbent is a first order process.
- As the adsorption potential of the carbonaceous adsorbent in removing organic molecules is appreciable, it can be used as a low cost alternative adsorbent to standard activated carbons.

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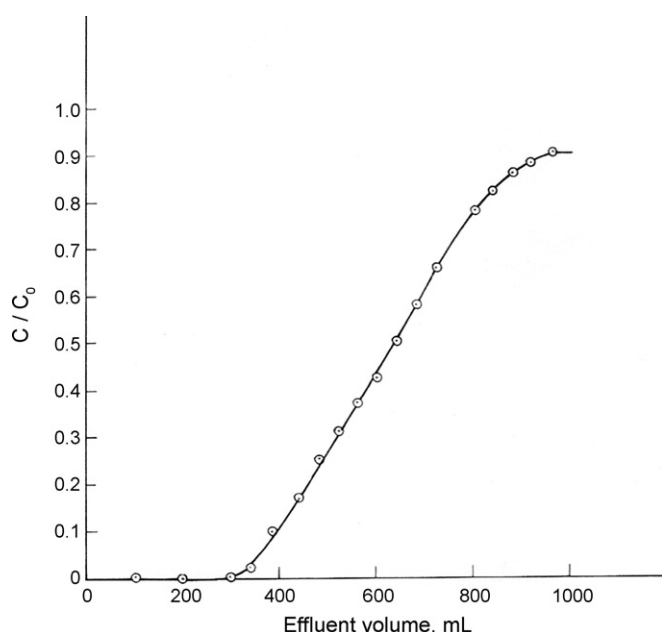


Fig. 11. Breakthrough curve of 2-bromophenol on carbonaceous adsorbent ( $C_0$ :  $1 \times 10^{-3}$  M).

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