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Column Studies of Phenols and Dyes Removal from Aqueous Solutions Utilizing Fertilizer Industry Waste

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Abstract: The use of carbonaceous adsorbent-packed columns has been tested to remove a number of phenols (methylated and halogenated) and dyes (cationic and anionic) from aqueous solutions. The breakthrough capacity, exhaustion capacity and degree of column utilization have been evaluated from breakthrough curves. The results obtained indicated that breakthrough capacity is about 7-30% less than the batch capacity (results from previous studies). Further, degree of column utilization was found to lie in the range 63-70%. The results of present investigations indicate that carbonaceous adsorbent-packed columns can be fruitfully used to remove pollutants from industrial effluent and is a suitable alternative of standard activated charcoal in view of its cheaper cost.

Key words: Carbon slurry waste, dyes, phenols, homogenous column, breakthrough-curves

Introduction

Waste Management is becoming one of the key problems of the modern world, an international issue that is intensified by the volume and complexity of waste discarded by society's domestic and industrial activities. Among the various forms of pollution, water pollution is of great concern since water is the prime necessity of life and extremely essential for the survival of all living organisms. But since last few decades, the demand for water has increased tremendously to meet the requirements of various activities. This has resulted in the generation of large amount of wastewater (Lehr *et al*., 1980; Nemerrow, 1978) which causes adverse affect on the aquatic ecosystem and human life. As a result, stringent regulations have come into force with regard to wastewater discharge. This has forced industries to look for cost effective technologies for treating their wastewater before mixing them with good quality water of natural water-bodies.

A number of methods exist to treat industrial effluents with varying degree of success. However, the adsorption process is widely used for pollutants removal and activated carbon is used as adsorbent for this purpose. The use of activated carbon in pollution control is sometimes hindered due to its higher cost. As such attempts have been made by various workers to prepare low cost adsorbents. Excellent reviews have been published since last few years by different researchers on the topic (Pollard *et al*., 1992; Bailey *et al*., 1999; Babel and Kurniawan, 2003).

Use of industrial waste materials is of great interest as these are available almost free of cost and cause major disposal problems. If the solid 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. Therefore, a number of waste materials from different industries (Akgerman and

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Zardkoohi, 1996; López-Delgado *et al*., 1998; López *et al*., 1998; Calce *et al*., 2002) have been investigated with or without treatment as low cost adsorbents for the removal of pollutants from wastewaters. However, these materials have not shown promising adsorption characteristics in comparison to activated carbon. Further, in most cases, only batch capacities were determined of such adsorbents. However, the practical utility of an adsorbent in removing pollutants from wastewaters is judged mainly by column operations. Very little data is available dealing with column studies of low cost adsorbents. Therefore it is still important to develop efficient low cost adsorbents alternatives to activated carbon and to perform column operations besides batch studies.

Carbon slurry waste of fertilizer industry has been explored by Jain *et al*. (2001), Jain *et al*. (2002), Jain *et al*. (2004) and Bhatnagar and Jain (2005) for the removal of different classes of dyes and phenols from aqueous solutions. The evaluation of performance of carbonaceous adsorbent as compared to standard activated charcoal sample in our batch studies indicates that it is 40-45% and 80-90% as efficient as the standard activated charcoal in removing phenols and dyes, respectively.

In order to apply carbonaceous adsorbent to industrial scale usage, it is necessary to investigate the column studies in detail. In the present study, the performance of carbonaceous adsorbent-packed columns has been tested and the breakthrough curves of the adsorption of phenols and dyes were obtained. The results from column studies were compared with batch capacities determined by us in previous experiments.

Materials and Methods

Materials and Solutions

Four methyl-phenols viz., 2-methylphenol (2-MP), 4-methylphenol (4-MP), 2,4-dimethylphenol (2,4-DMP) and 2,4,6-trimethylphenol (2,4,6-TMP) were procured from SRL (India), Merck (Germany), Eastman Kodak Company (New York) and Fluka (Switzerland), respectively. The two halogenated phenols viz., 2-fluorophenol (2-FP) and 2-iodophenol (2-IP), were procured from E. Merck (Germany) and Lancaster (England), respectively. Brilliant blue G dye was procured from SRL (India) and the other three dyes viz. methyl orange, rhodamine B and bismarck brown R were procured from s.d. fine-chem. Limited (India).

The carbon slurry was procured from National Fertilizer Limited (NFL), Panipat, India. Double distilled water was used throughout these investigations.

Preparation of Carbonaceous Adsorbent

In India, carbon slurry is produced as a waste in fertilizer plants using fuel oil/ LSHS as a feed stock (Fig. 1). This waste slurry is available at a very cheap rate (US $ 7 ton^{-1}) and can be a good adsorbent for pollutants in view of its porous nature. This slurry produced in plants is dumped in huge tanks and allowed to dry. The dried cake material was procured from NFL, Panipat (India) and powdered. It was found to consist of small, black and greasy granules and treated (Fig. 2) with H_2O_2 to oxidize the adhering organic material (Jain *et al*., 2001; Srivastava *et al*., 1987). It was then washed with distilled water and heated at 200°C till the evolution of black soot stopped. The activation of this material was done at different temperatures in muffle furnace for one hour 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 yield of the finished product was found to be ~ 90% and it is now called carbonaceous adsorbent. Different mesh sizes were obtained after sieving and kept in desiccator for further use. It was found after preliminary adsorption studies that the activation at 500°C imparts

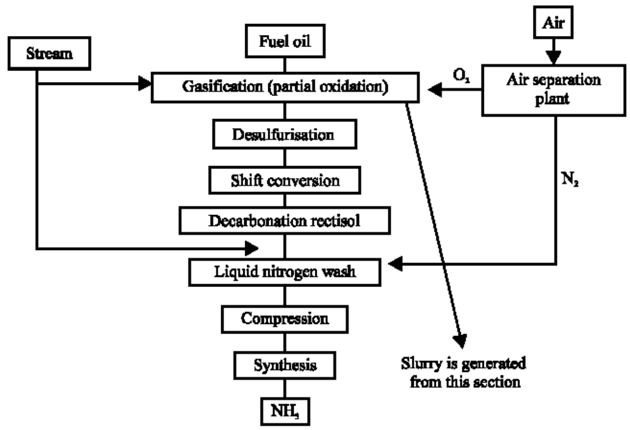

Fig. 1: Process sequence for Ammonia production using fuel oil partial oxidation process in National Fertilizer Limited (NFL), Panipat

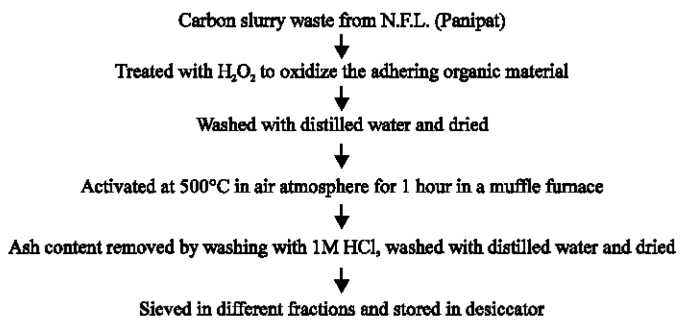

Fig. 2: Flow diagram of the preparation of carbonaceous adsorbent

maximum adsorption characteristics (Jain *et al*., 2001) and therefore, all investigations were carried out on the samples activated at this temperature only.

Homogenous Column

In the present investigations, a glass column (50×1.05 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. The column operations were carried out using solutions of all the six phenols and four dyes on columns (cross sectional area: 0.9 cm^2; height: 3.1 cm; mass: 0.5 g) of carbonaceous adsorbent at a flow rate of 2.5 mL min^{-1}. The adsorbent has to be granular with sufficient particle size, otherwise the column becomes choked in no time. Therefore, particles having size of 50-200 mesh were used for column operations. A definite amount of the column effluent was taken and the concentration of the solute (pollutants under investigation) determined from time to time by spectrophotometric method. This process has continued till 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. These investigations provide information regarding the optimum mass, height and area of the column and the rate of the effluent flow which will permit best treatment of industrial effluents.

Results and Discussion

Characterization of Carbonaceous Adsorbent

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. The surface area of the carbonaceous adsorbent was found 380 $m^2 g^{-1}$ by N_2-gas adsorption. In order to see the morphology of carbonaceous adsorbent, SEM photographs were taken and shown in Fig. 3 which confirms the very well developed porous structure developed in carbonaceous adsorbent. The sample of carbonaceous adsorbent was stirred with deionized water for 2 h and left for 24 h to see any interaction. It was seen that the pH of water was lowered which indicates that carbonaceous adsorbent, as per Steenberg classification (Mattson and Mark, 1971) 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. IR spectra provides to some extent information about these groups. The IR spectra of the sample of carbonaceous adsorbent taken indicates the presence of two prominent bands lying at 1605 and 3340 cm^{-1}. The first peak may be assigned to the presence of carbonyl group and the latter one to OH group.

Effect of Flow Rate

The studies were also undertaken to understand the effect of flow rate on the breakthrough of carbonaceous adsorbent column of phenols and dyes adsorption. Three flow rates viz., 2.5, 5.0 and 10.0 mL min^{-1} 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. The lower the flow rate, the longer the contact time and hence the greater the interaction between adsorbate and adsorbent. This should lead to a higher removal rate of dyes and phenols.

Breakthrough Curves

A breakthrough curve is obtained by plotting column effluent concentration versus volume treated or the time of treatment or the number of bed volumes (BV) treated. Breakthrough curves of phenols

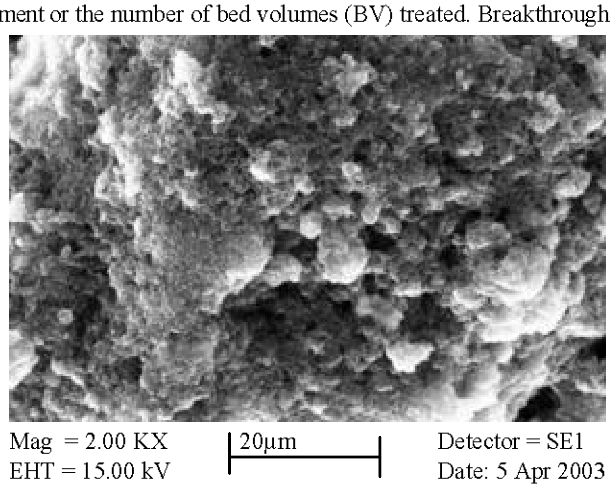

Fig. 3: Scanning Electron Micrograph (SEM) of activated carbonaceous adsorbent

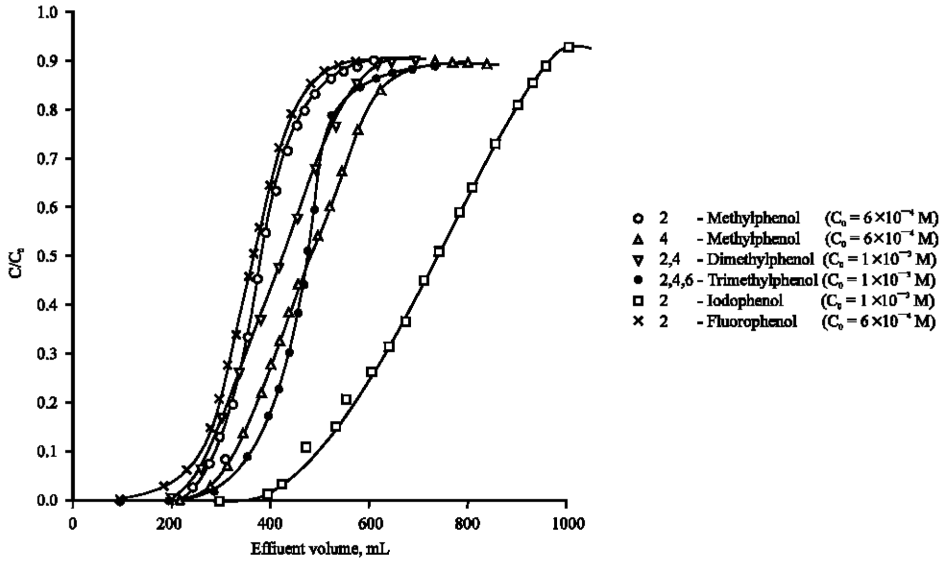

Fig. 4: Breakthrough curves of phenols on carbonaceous adsorbent

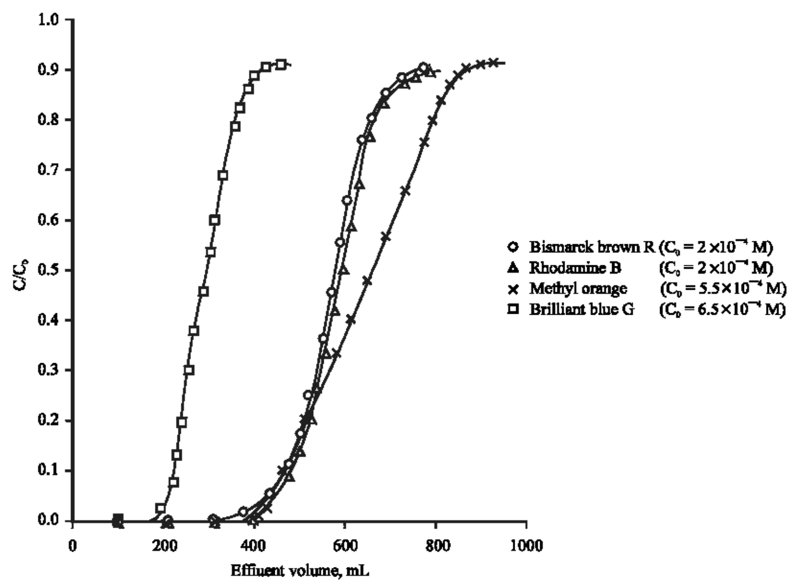

Fig. 5: Breakthrough curves of dyes on carbonaceous adsorbent

and dyes are shown in Fig. 4 and 5, respectively. Various factors influence the breakthrough curves such as nature of the adsorbate and adsorbent, the column geometry and operating conditions. Favourable adsorption isotherms and extremely high adsorption rates would result in virtually coinciding of breakthrough point and exhaustion point and the breakthrough curves would thus approach a straight vertical line. As the mass transfer rates are decreased, breakthrough curves become less sharp. Since mass transfer rates are finite, the breakthrough curves are diffuse and exhibit an

Table 1: Comparison of batch and column capacities and degree of column utilization for phenols

Phenols	Batch capacity (mg g^{-1}) (from adsorption isotherms)	Breakthrough capacity (mg g^{-1})	Exhaust capacity (mg g^{-1})	Degree of column utilization (%)
2-MP	37.3[+]	29.8	44.6	66.8
4-MP	40.5[+]	34.7	54.1	64.1
2,4-DMP	65.9[+]	53.6	83.9	63.9
2,4,6-TMP	88.5[+]	72.9	114.5	63.7
2-FP	35.3[#]	28.1	40.2	69.9
2-IP	235.5[#]	184.8	285.0	64.8

Source: [+]Jain *et al.* (2002); [#]: Jain *et al.* (2004)

Table 2: Comparison of batch and column capacities and degree of column utilization for dyes

Dyes	Batch capacity (mg g^{-1}) (from adsorption isotherms)	Breakthrough capacity (mg g^{-1})	Exhaust capacity (mg g^{-1})	Degree of column utilization (%)
Methyl orange	202.3[*]	155.0	227.8	68.0
Brilliant blue G	212.3[*]	198.0	258.6	76.6
Bismarck brown R	71.5[•]	68.3	99.3	68.8
Rhodamine B	82.8[•]	78.6	104.0	75.6

Source[*]: Jain *et al.* (2001) ; [•]: Bhatnagar and Jain (2005)

S shape. The higher concentrations (1×10^{-3} M) were taken for some phenols (2,4-DMP, 2, 4, 6-TMP and 2-IP) because it was not possible to analyse them by UV-VIS having very low concentrations in aliquot of effluent collected. The same phenols were also adsorbed in greater amount during batch method. The reason for adsorbing different phenols in different manners has been explained in our previous reports.

The calculation of breakthrough capacity, exhaustion capacity and degree of column utilization were done and presented in Table 1 and 2 for phenols and dyes, respectively.

The Breakthrough Capacity

The breakthrough capacity is defined as the mass of the adsorbate removed by the adsorbent at breakthrough concentration, which in turn defined as maximum acceptable (desired) concentration. When the effluent concentration attains this value, the adsorbent needs to be replaced. The breakthrough capacities of phenols and dyes on column of carbonaceous adsorbent are shown in Table 1 and 2 and compared with batch capacities (obtained in previous studies). It was observed that breakthrough capacity is about 7-30% less than the batch capacity. This may be due to (i) lesser contact 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 Tutem *et al.* (1998) for the removal of chlorophenols by bituminous shale.

Exhaustion Capacity

The exhaustion capacity is defined as the mass of the adsorbate removed by unit weight of the adsorbent at saturation. It is clear from Table 1 and 2 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.

Degree of Column Utilization

The degree of column utilization is defined as the mass adsorbed at breakthrough point divided by the mass adsorbed at complete saturation i.e., when effluent concentration becomes equal to or nearly equal to influent concentration. Table 1 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 successfully used to remove dyes and phenols. Thus, based on breakthrough capacity, 1 kg of the adsorbent can treat 360 to 840 L solutions of various phenols and dyes from aqueous solution having above concentrations.

Treatment of Industrial Effluent of a Chemical Industry

The effluent was obtained from local chemical factory. This wastewater is characterized by dark brown colour, pH = 11.3 and COD value (890 mg L^{-1}). The treatment of this wastewater for pollutants removal was carried out by passing it through a column (cross sectional area: 0.9 cm^2; height: 3.1 cm; mass: 1.0 g) of carbonaceous adsorbent, of particles of size 50-200 mesh, at a flow rate of 2.5 mL min^{-1}. The monitoring of the column was done spectrophotometrically at λ_{max} values of the solution. For this purpose, 10 mL aliquot was collected and absorbance determined. It was observed that effluent coming out of the column had almost nil absorbance at all the λ_{max} values upto a total volume of 120 mL. After that, the colour starts appearing and absorbance increased. From the breakpoint of this curve, it can be seen that a column of 1 g of carbonaceous adsorbent, as used by us can treat 120 mL of dye wastewater. The COD of the treated wastewater was within acceptable limits. Thus, the results show that 1 kg of prepared carbonaceous adsorbent can treat 120 L of the chemical industry wastewater. It is therefore, reasonable to conclude that the prepared adsorbent can be fruitfully used as an alternative adsorbent for treating industrial effluents.

Conclusions

The present paper highlights the results from a laboratory investigation on the removal of different types of phenols and dyes from water by using columns of carbonaceous adsorbent. The flow rate of 2.5 mL min^{-1} was found optimum to remove all type of pollutants under investigation. The calculation of breakthrough capacity, exhaustion capacity and degree of column utilization were done by using breakthrough curves. The obtained results indicate that columns of carbonaceous adsorbent can be used for treating wastewaters containing organic pollutants (dyes and phenols). Further, low cost (~ US $ 0.1 kg^{-1}) of this material makes it a strong candidate for treating wastewaters.

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