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Column operation studies for the removal of dyes and phenols using a low cost adsorbent

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ABSTRACT: Fertilizer plant waste carbon slurry has been investigated after some processing used as efficient adsorbent for the fast removal and rapid adsorption of dyes and phenols using columns. The results reveals that the adsorbent developed from carbon slurry is carbonaceous in nature and having appreciable surface area (380 m²/g) can remove dyes both cationic (meldola blue, methylene blue, chrysoidine G, crystal violet) as well as anionic (ethyl orange, metanil yellow, acid blue 113), and phenols (phenol, 2-chlorophenol, 4-chlorophenol and 2,4-dichlorophenol) fruitfully from water. The column type continuous flow operations were used to obtain the breakthrough curves. The breakthrough capacity, exhaustion capacity and degree of column utilization were optimized and evaluated from the plots. The results obtained revealed that the degree of column utilization for dyes falls in range from 60 to 76% while for phenols was in the range 53-58%. The exhaustion capacities were quite high as compared to the breakthrough capacities and were found to be 217, 211, 104, 126, 233, 248, 267 mg/g for meldola blue, crystal violet, chrysoidine G, methylene blue, ethyl orange, metanil yellow, acid blue 113, respectively and 25.6, 72.2, 82.2 and 197.3 mg/g for phenol, 2-chlorophenol, 4-chlorophenol and 2,4-dichlorophenol, respectively.

KEYWORDS: Adsorption; Breakthrough curve; Column; Dyes; Low cost adsorbent; Phenols

INTRODUCTION

Present era of modernization, development and industrialization provided us a vast number of facilities but on other hand our environment paid a lot for this. Water pollution is one of the serious issues resulting from these activities and influx of the various pollutants are damaging our living biosphere thereby making the clean drinking water a big challenge for present world. Among pollutants especially pertaining to water, dyes and phenols occupy an important place and ought to remove from water. Dyes production has increased tremendously in past years due to their requirement in textiles and other industrial areas. It was found that

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more than 100,000 dyes are available in the world with different chemical structures and out of them 10-15% enters in water from different industries (Christie 2007, Hai, *et al.*, 2007). Dyes are mutagenic, toxic, allergenic, carcinogenic, non-degradable, stable towards light and oxidizing agents and resistant to aerobic digestion thereby creating serious problem (Golka, *et al.*, 2004, Christie 2007, Das, *et al.*, 2009). Similar to dyes, phenol and its derivatives are also present in waste waters especially from pesticide, paper and pulp industries and chemical solvent, coal-conversion, phenol-production, plastics, dyes, paint, pesticides, insecticides, iron-steel, and wood preserving pharmaceutical, rubber-proofing, petrochemical and oil refining industries (Hu and Vansant 1993, Domínguez-Vargas, *et al.*, 2009). Phenols and its derivatives even at their low concentration are health hazards; the US

Environmental Protection Agency has fixed 1mg/L as a limit for phenol in the waste water (Ioannou and Simitzis 2009). Phenol causes various adverse effects on brain, eye, heart, skin and other part of body and is considered as carcinogenic (Jia and Lua 2008, Lorenc Grabowska and Rutkowski 2014). Besides this, oral exposure of phenol causes paralysis, coma, headache, loss of coordination, muscle weakness and other mental problems (Nabais, *et al.*, 2009) and are therefore ought to be removed from water.

A wide spectrum of treatment technologies are being used for treatment of wastewaters and adsorption especially using activated carbons (Bansal and Goyal 2005, Carrott, *et al.*, 2008) is one of the process giving promising results as it can be used to remove different types of the coloring materials as well as phenols, thereby, providing an attractive treatment technology (de Oliveira Brito, *et al.*, 2010). Literature (Suhās, *et al.*, 2007, Gupta, *et al.*, 2009, Gupta and Suhās 2009) shows that though activated carbons are good materials for the removal of different types of dyes and phenols in general but their use is sometimes restricted owing to the cost and the additional expenses associated to the regeneration, if required, thereby prompting the researchers working in the field of waste management and pollution control to look for alternative adsorbents (Babel and Kurniawan 2003, Crini 2006, Ali and Gupta 2007, Gupta, *et al.* 2009, Gupta and Suhās 2009) such as industrial wastes in addition with some less utilized renewable resources for this purpose, which can be of low cost than activated carbons.

In order to treat waste waters using activated carbons or Low Cost Adsorbents (LCAs) the batch experiments were generally carried out in research labs; the treatment of tiny quantity of waste water but are less conveniently used on the industrial scale where large volumes of wastewaters are generated for instance in industries (Zhang, *et al.*, 2011). The column operations are therefore preferred in industries owing to their distinct advantages over static treatment (Li, *et al.*, 2011) and to obtain breakthrough curves.

Both batch as well as columns play important role in obtaining parameters for designing adsorption experiments and to obtain key parameters (Song, *et al.*, 2011). Adsorption using column is one of the most common and efficient way for removal of pollutants from water. However, it worth to note that it may be helpful that before evaluating the feat of adsorbent in fixed-bed adsorber, adsorption isotherm studies such

as batch experiments were conducted to calculate the maximum adsorption capacity of the adsorbent (Al-Degs, *et al.*, 2009). Columns have an advantage over batch since a continuous flow is maintained over a fixed bed thereby increasing the adsorbent capacity contrary to batch where the concentration gradient between adsorbent and adsorbate decreases with time (Andersson, *et al.*, 2012). The present work aims to investigate and elucidate the adsorption behavior of a LCA (carbon slurry from fertilizer plant) for the removal of several dyes cationic (mordant blue, methylene blue, chrysoidine G, crystal violet), anionic (ethyl orange, metanil yellow, acid blue 113) and phenols (phenol, 2-chlorophenol, 4-chlorophenol and 2,4-dichlorophenol) in continuous fixed-bed operation (columns) is evaluated and compared with batch adsorption capacities reported elsewhere (Jain, *et al.*, 2003a; 2003b; 2003c; 2004).

This study has been performed in the Department of Chemistry, Indian Institute of Technology Roorkee 247667, India during January to July 2015.

MATERIALS AND METHODS

The anionic dyes, ethyl orange was procured from Riedel–deHaën and metanil yellow and acid blue 113 from Aldrich, Cationic dyes viz. chrysoidine G, crystal violet, methylene blue and mordant blue were procured from fluka, spectrochem (India), LOBA chemicals and Sigma, respectively. Phenol, 2-chlorophenol, 4-chlorophenol and 2,4-dichlorophenol were procured from Spectrochem (India). Carbon slurry was procured from National Fertilizer Limited (NFL), Panipat, India. Double distilled water was used throughout for the preparation of solutions. All reagents used in the present study were of analytical grade.

The raw material a waste (carbon slurry) used in this study was mainly of organic in nature because of high carbon content. It was processed in the following manner so that can be used as adsorbents. Carbon slurry waste was procured from NFL Plant, Panipat and was treated with hydrogen peroxide (Jain, *et al.*, 2003a; 2003b) to oxidize the adhered organic matter, which was later followed by washing with distilled water and dried in oven. The obtained material was further activated at several temperatures in muffle furnace for 1 h in air atmosphere and the activated material developed (carbonaceous adsorbent) was passed through different British Standard Sieves (BSS) and fractions corresponding to 50-100, 100-150, 150-

200 and 200-250 mesh were collected and stored in desiccator. The optimum temperature of activation was found to be 500 °C.

Dyes and phenols were determined spectrophotometrically on Shimadzu 160A UV-Vis spectrophotometer and the pH of solutions was measured with an ELICO LI 127 pH meter.

Column experiments were conducted in a glass column cross-sectional area: 0.9 cm² and adsorbent mass: 0.5 g. Carbonaceous adsorbent particle sizes of 50-200 BSS mesh were used in the column with a bed height 3.1 cm on a glass wool support. The dyes/phenols containing influents with concentrations (chrysoidine G - 6.0×10^{-4} m; meldola blue- 7.5×10^{-4} m; crystal violet- 6.0×10^{-4} m, methylene blue- 3.0×10^{-4} m, acid blue 113- 5.0×10^{-4} m; metanil yellow, 6.0×10^{-4} m, ethyl orange, 6.0×10^{-4} m, Phenol- 6.0×10^{-4} m; 2-chlorophenol- 6.0×10^{-4} m; 4-chlorophenol- 6.0×10^{-4} m and 2,4-dichlorophenol- 1.0×10^{-3} m) were passed in the down flow mode through the column with linear flow rates of 1.5 mL/min. The effluent samples were collected at regular time interval and analysed without previous filtration spectrophotometrically. Breakthrough and exhaustion were defined at relative effluent concentration C/C_0 of 0.01 and 0.90, respectively.

Theoretical background of column operation studies

In order to remove pollutants from water using adsorption methodology generally two techniques are used batch or column. The batch technique (Jain, *et al.*, 2003a; 2003b; 2003c; 2004) is selected because of its simplicity and ease of evaluating the parameters (Song, *et al.*, 2011) influencing adsorption process. On the other hand, the practical value of adsorbent in adsorbing the noxious pollutants from wastewater is known mainly carried out using column study. Column (Weber, 1972; Andersson, *et al.*, 2012) operation creates a continuous concentration gradient and the adsorbent is constantly in contact with spanning new solution. It is worth to note that as the adsorption continues the concentration of aqueous solution in contact with the adsorbent layer is relatively constant in the column operation while it decreases steadily in batch method. Thus the batch method is less effective than the column operation.

To understand the efficiency of column operations, the breakthrough curves are plotted. A breakthrough curve is a plot of the column effluent concentration as a function of either volume treated or the time of

treatment or the number of bed volumes (BV) treated. The important features of a breakthrough curve (Snoeyink and Summers 1999) are breakthrough capacity (BC), exhaustion capacity (EC) and degree of column utilization (DOC). The definition of breakthrough capacity is the mass of adsorbate eliminated by the adsorbent at breakthrough concentration, which in turn is defined as utmost acceptable (desired) concentration. When the effluent concentration touches this value, at that time the developed adsorbent may be replaced. The DOC utilization may be defined as the ratio of mass adsorbed at breakthrough to the mass adsorbed at complete saturation i.e. when effluent concentration becomes equal to or nearly equal to influent concentration. The EC is defined as the mass of the adsorbate removed by one unit weight of the adsorbent at the point of saturation.

Various factors (Weber, 1972; Snoeyink, 1999) effects the breakthrough curves like adsorbate nature and adsorbent nature, pH, concentration of solute, adsorption mechanism (Rate limiting step), equilibrium conditions, size of particle, column geometry and operating condition. At extremely high adsorption rate and favorable adsorption isotherm the point of breakthrough and the point of exhaustion coincide practically and the breakthrough curve becomes sharp (Shang, *et al.*, 2012). Mass transfer rate effect the sharpness of the breakthrough curves, as the transfer of mass are finite breakthrough curve, which are diffuse and S shaped. For most adsorption operations in water and wastewater treatment, breakthrough curves exhibit a characteristic S shape but with varying degree of steepness (Weber, 1972).

The relationship between the breakthrough curves and fixed bed adsorber was well elucidated by Weber and by Snoeyink (Weber, 1972, Snoeyink and Summers, 1999) and is presented in the Fig. 1. When the column operation begins, the starting/upper layers adsorb the solute/pollutant to be removed in a short time. As can be seen from the Fig. 1, that the topmost layers are indeed in touch with the aqueous solution at its highest concentration level, C_0 (denotes the influent concentration) and a little quantity of solute which escape adsorption in the first few layers of the adsorbent is then adsorbed in the lower strata of the bed, and therefore practically no solute/pollutant escapes from the column initially (effluent concentration, $C=0$). The Fig. 1 shows that the top or

influent end of the column represents the active adsorption zone. With the continuous flow of pollutant to the column, the upper layer of the adsorbent become fully saturated with the pollutant/solute and they become ineffective for further removal of pollutant and the active adsorption zone moves downward towards the freshly prepared adsorbent layers. The wavelike progress of this region (Weber, 1972), accompanied due to the movement of influent concentration front, and occurs at a rate which is generally much slower than the speed of the wastewater. It is clear from the Fig. 1 that downward movement of the active adsorption zone causes large volume of the solute to escape in the effluent. In Fig. 1, C/C_0 versus volume/time for constant flow rate represent that the movement of the adsorption zone downward causes increase in the ratio of the effluent to influent concentration. It is worth to state that there exists a correlation between the shape of the curve and method chosen for the operation of the fixed bed adsorber. The estimation of BC, EC and DOC utilization were done utilizing the areas in Fig. 1 and described elsewhere (Weber, 1972,

Snoeyink and Summers, 1999) by a computer program developed.

The portion of breakpoint on the breakthrough curve (Fig. 1) to give breakthrough capacity has been adopted differently by various workers. Mollah and Robinson (Mollah and Robinson, 1996) while doing adsorption and desorption experiments for pentachlorophenol on granular activated carbon, considered the breakpoint on the breakthrough curve as the point at which C/C_0 became equal to 0.5 i.e. effluent concentration was 50% of the influent concentration. Sotelo *et al.* (2012) while studying the removal of atenolol and isoproturon on granular activated carbon considered the breakpoint on breakthrough curve when $C/C_0=0.15$ whereas in adsorption study of methylene blue on jackfruit leaf powder Tamez Uddin *et al.* (2009) considered the breakthrough point when the dye concentration in the effluent reached 5mg/L which correspond to ~16% of the influent concentration. Das *et al.* (2009) in their work on the adsorption of malachite green on surfactant-modified alumina consider the breakpoint

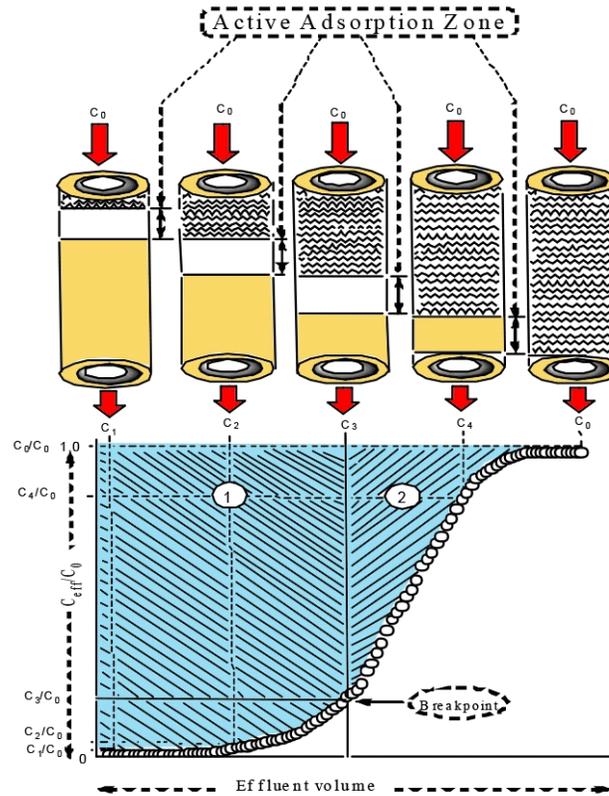


Fig. 1: Adsorption zone movement in a column and a resultant breakthrough curve

corresponding to $C/C_0 = 0.020$, when effluent concentration becomes 2% of the influent concentration. Other workers (Karunaratne and Amarasinghe, 2013) have considered the breakpoint at which $C/C_0 = 0.2$ i.e. when effluent concentration is 20% of the influent concentration. Some other workers (Srivastava, et al., 1997) have considered the breakpoint, at which C/C_0 become approximate equal to 0.02, i.e., effluent concentration is 2% of influent concentration.

RESULTS AND DISCUSSION

The carbonaceous adsorbent prepared from carbon slurry has appreciable surface area ($380 \text{ m}^2/\text{g}$), reported elsewhere (Jain, et al., 2003a, Jain, et al., 2004) with a porous surface as confirmed from the SEM image and the previous batch studies discussed elsewhere (Jain, et al., 2003a, Jain, et al., 2003b, Jain, et al., 2003c, Jain, et al., 2004, Ali and Gupta, 2006) confirmed the fact that this material can be fruitfully utilized for the removal of dyes and phenols.

Column operation for dyes

The column operation carried out using synthetic solution of cationic and anionic dyes on columns of carbonaceous adsorbent at a flow rate of 1.5 mL/min. These column operations could not be satisfactorily carried out on adsorbent particles of size 200-250 mesh

because of column getting choked due to the delicacy of the adsorbent particle. Therefore, column operations were carried out with particles having size of 50 to 200 mesh. As a result of mixing of larger size of particles with smaller particles, the column did not get choked and influent flowed freely over a period of 8–10 hours involving a total outflow of 600-900 mL of dye solution. The effluent was sampled in ten 10 mL aliquot and analyzed for the dye content. This process was sustained till the concentration of the dye in the aliquot of effluent sustained reached nearly 90% of the C_0 , i.e., $C/C_0 \sim 0.9$. The results obtained have been plotted in terms of C/C_0 against volume of the effluent. The breakpoint on these figures has been considered when C/C_0 attains a value of 0.01. The breakthrough plots are given in Figs. 2-4.

The BC, EC and DOC utilization was investigated from the figures plotted using a computer program developed and the obtained values are presented in Table 1. It is seen that BC is about 10-20% less than the batch capacity. This appears due to (i) lesser time of contact of the solute with adsorbent and (ii) larger size of particles (50 to 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 fast removal of chlorophenols by the developed bituminous shale.

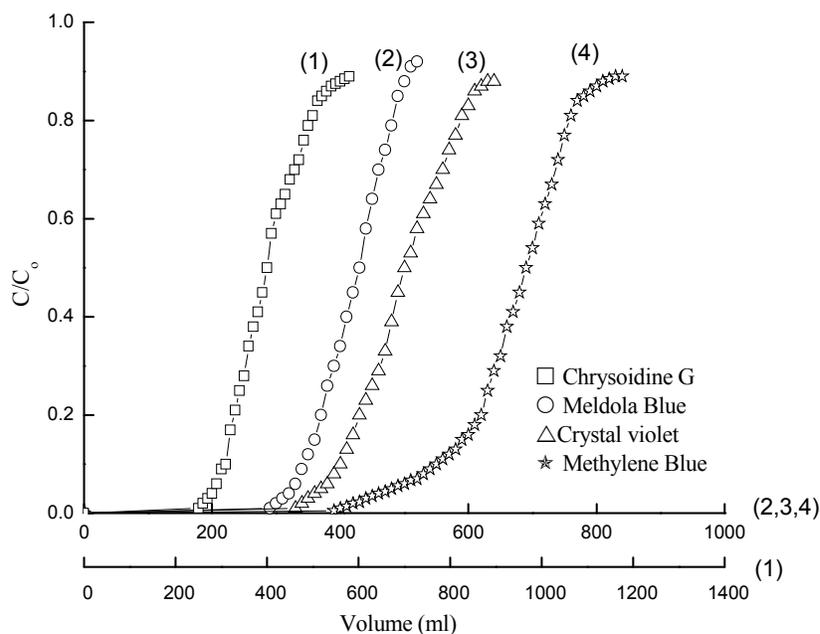


Fig. 2: Breakthrough curves of cationic dyes on carbonaceous adsorbent (chrysoidine G - 6.0×10^{-4} M; meldola blue- 7.5×10^{-4} M; crystal violet- 6.0×10^{-4} M and methylene blue- 3.0×10^{-4} M)

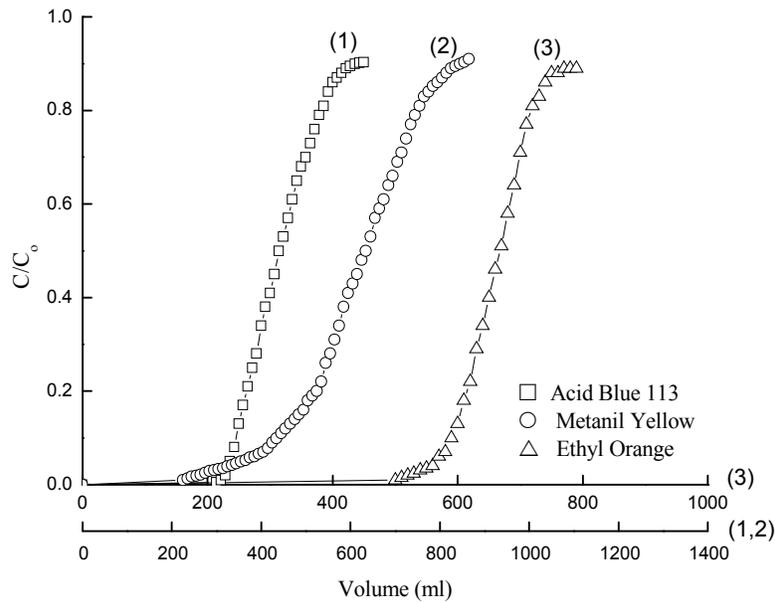


Fig. 3: Breakthrough curves of anionic dyes on carbonaceous adsorbent (acid blue 113- 5.0×10^{-4} M; metanil yellow, 6.0×10^{-4} M and ethyl orange, 6.0×10^{-4} M)

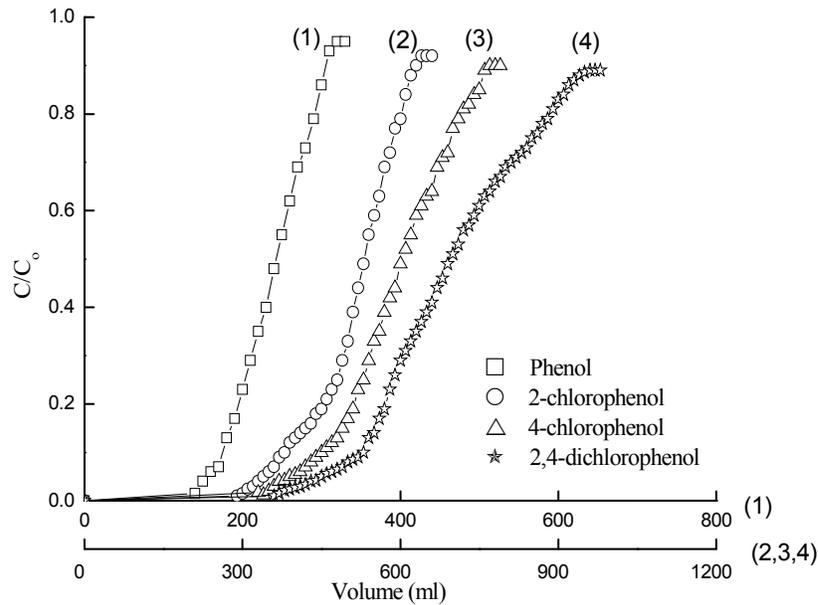


Fig. 4: Breakthrough curves of phenols on carbonaceous adsorbent (phenol- 6.0×10^{-4} M; 2-chlorophenol- 6.0×10^{-4} M; 4-chlorophenol- 6.0×10^{-4} M and 2,4-dichlorophenol- 1.0×10^{-3} M)

It is further seen from Table 1, that the exhaustion capacity of column is relatively higher than the batch adsorption capacity. This appears due to organization of incessantly superior concentration gradients at the boundary zone as the pollutant influent crosses

throughout the column. The gradient concentration in general remains maintained because of the fresh inflow of influent, while, in case of batch experiments, the concentration gradient incessantly decreases with time resulting in smaller adsorption capacity. Further, Table

1 show that the DOC utilization lies in the range 60 to 76%. Among the cationic and anionic dyes, the value of degree of column utilization is maximum for meldola blue and ethyl orange, respectively. These higher values are in conformity with higher rate constants of these dyes as reported elsewhere (Jain, *et al.*, 2003a, Jain, *et al.*, 2003b, Jain, *et al.*, 2003c) for batch adsorption process. The higher rate constant obviously leads to slightly better utilization of column capacity in a given time. Thus these results have shown that the columns can be used to remove dyes from aqueous solutions (meldola blue, 7.5×10^{-4} M; crystal violet, 6.0×10^{-4} M; chrysoidine G, 6.0×10^{-4} M; methylene blue, 3.0×10^{-4} M; ethyl orange, 6.0×10^{-4} M; methanil yellow, 6.0×10^{-4} M and acid blue 113, 5.0×10^{-4} M) quite efficiently. Thus 1 kg of adsorbent can treat a total volume of dye solution from 500 L to 1,000 L of the above concentration, respectively.

Column operation for phenols

The investigations on the removal of phenols by carbonaceous adsorbent, already reported (Jain, *et al.*, 2004) have shown that adsorption capacity of carbonaceous adsorbent is significant and therefore, it can be used for their removal from wastewater. As such, in order to test the practical utility of the prepared adsorbents, the column operations were done. The operations were carried out using columns (cross-sectional area: 0.9 cm^2 ; height: 3.1 cm; mass: 0.5 g) of carbonaceous adsorbent of particles of size 50 to 200 mesh, at a flow rate of 1.5 mL/min for influent solutions

of phenol, 2-chlorophenol, 4-chlorophenol and 2,4-dichlorophenol. A 10 mL aliquot of the effluent was collected and analyzed for phenol content. This process was continued till the concentration of the phenol in the effluent aliquot collected reached 90% of the influent concentration. As usual, the breakthrough curves were drawn by plotting C/C_0 against volume of effluent and shown in Fig. 4. The breakthrough point was taken at $C/C_0 = 0.01$. The values of BC, EC and DOC utilization have been calculated and are given in Table 2. It is seen from Table 2 the BC is about 15-20% less and the column EC about 40-50% more than batch capacity. These observations are almost similar as observed with column operations with dyes and explained the preceding paragraphs. The same explanation holds good for the column operations of phenols also. It can be supplementary seen from the Table 2 that DOC utilization is maximum in case of phenol and lowest for 2,4-dichlorophenol. This is consistent with highest rate constant of phenol for batch adsorption process (Jain, *et al.*, 2004). The phenol, having higher rate constant was adsorbed at a faster rate in column thus leading to better degree of column utilization.

Treatment of wastewater from local dyeing unit and paper and pulp mill

The investigation on the rapid adsorption of dyes having positive and negative charge on prepared adsorbents as already reported have shown that carbonaceous adsorbent has a good adsorption

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

Dye	Batch capacity* (from adsorption isotherms) (mg/g)	Breakthrough Capacity (mg/g)	Exhaustion capacity (mg/g)	Degree of column utilization (%)
Meldolabue	170	152	217	69.9
Crystal violet	161	142	211	67.5
Chrysoidine G	75	66	104	63.3
Methylene blue	92	76	126	60.3
Ethyl orange	198	178	233	76.5
Metanil yellow	211	184	248	74.4
Acid blue 113	219	190	267	71.3

*Source (Jain *et al.*, 2003a; Jain, Gupta *et al.*, 2003b; Jain *et al.*, 2003c)

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

Phenols	Batch capacity* (from adsorption isotherms) (mg/g)	Breakthrough capacity (mg/g)	Exhaustion capacity (mg/g)	Degree of column utilization (%)
Phenol	17.2	14.8	25.6	57.8
2-chlorophenol	50.3	40.7	72.2	56.3
4- chlorophenol	57.4	46.5	82.2	56.6
2,4-di chlorophenol	132.5	103.7	197.3	52.6

*Source (Jain *et al.*, 2004)

capacity and It can be efficiently used for the rapid removal of noxious dyes from wastewater. The use of this developed adsorbent in rapid removal of dyes has been shown by carrying out column studies of water solutions of pure dyes. As these operations have been found to be successful, it has been considered as desirable material to treat noxious waste solution obtained from an industrial effluent.

The noxious outcome was obtained from an industrial outlet using several marketable dyes for the dyeing purposes of several textiles. The dye wastewater obtained contains a number of dyes and was brownish in color. It had a pH of 9.1 with a COD of 980 mg/L. The absorption spectra shows that the dye wastewater has two λ_{\max} values at 456.5 and 580.5 nm, with total absorbance of 27.8 and 27.06 at 456.5 and 580.5 nm, respectively. This handling of the noxious dye solution for dyes removal was carried out using a column (cross-sectional area: 0.9 cm²; height: 6.2 cm; mass: 1000 mg) of carbonaceous adsorbent, of particles size 50 to 200 mesh at a flow rate of 1.5 mL/min. The concentration of the dye wastewater after passing through the column was monitored spectrophotometrically at the λ_{\max} of the solution. It was found that noxious dye coming out of the column had almost nil absorbance at both the λ_{\max} values up to a total volume of 110 mL. Later than, the dye color starts appearing and absorbance value increases. The breakpoint observed from the breakthrough curve (not shown) obtained after transient this dye wastewater through carbonaceous adsorbent column showed that a column of 1 g of carbonaceous adsorbent, as used by us can treat 110 mL of dye wastewater. The COD of the treated dye wastewater was within acceptable limits. Thus the results show that 1 kg of the prepared carbonaceous adsorbent can treat 110 L of the noxious dye solution. Hence it can be concluded that the prepared adsorbent can be efficiently employed as an alternative low cost adsorbent for treating dye wastewater.

The studies on adsorption of phenols have shown that carbonaceous adsorbent has significantly high adsorption capacity for phenols and can be used for their removal. The column operations worked satisfactorily and it was possible to remove phenols from their aqueous solutions prepared in the laboratory. Thus the carbonaceous adsorbent is likely to succeed in the treatment of wastewater containing phenol and similar compounds. In order to evaluate the potentiality of this adsorbent for the treatment of an industrial effluent, an

untreated black liquor waste from a paper and pulp mill was used as effluent. The color of this untreated waste is dark brown and it is discharged in significant amounts. This waste black liquor generally contains besides phenols, many other organic compounds such as lignins, degraded products of cellulose and hemicellulose, saponified fatty acids etc. This effluent has a pH 12.1 and a high COD value and possesses foul smell besides the dark color. These characteristics make it imperative that it be treated before discharging into any natural water body. The treatment of this waste black liquor was done on the column of carbonaceous adsorbent using particles of size 50 to 200 mesh at a flow rate of 1.5 mL/min. The effluent after passing through column was monitored and the monitoring was done by measuring the COD value. It was seen that 3 mL of solution collected initially leads to a reduction of 90% in COD value and neither any color observed nor any foul smell. After 3 mL, the COD started increasing and as well as color started appearing slowly and slowly. A second column operation using a fresh adsorbent load was done to further reduce the COD of the colorless effluent obtained. This second column operation could decrease the COD to an almost 1% of the initial value. As the wastewater from the paper and pulp mill was highly polluted, the adsorbent is required in larger amounts to treat it fully. The results show that 1 kg of adsorbent can be used to treat 3 L of the pollutant successfully. This is a large amount of the adsorbent and makes the process difficult on practical grounds. As such, it should be used to treat paper and pulp mill waste in conjunction with other treatment processes.

CONCLUSION

The column type continuous flow operations were used to obtain the breakthrough curves and to perform adsorption studies. Column studies have shown that carbonaceous adsorbent developed from industrial waste can fruitfully remove dyes both cationic as well as anionic and phenols too. The breakthrough capacities were found to be less than the batch adsorption capacities whereas the exhaustion capacities were quite higher than the batch as well as breakthrough capacities. The carbonaceous adsorbent prepared thus can be suitable for the removal of toxic substances from effluents. The exhaustion capacities were quite high as compared

to the breakthrough capacities and were found to be 217, 211, 104, 126, 233, 248, 267 mg/g for meldola blue, crystal violet, chrysoidine G, methylene blue, ethyl orange, metanil yellow, acid blue 113, respectively and 25.6, 72.2, 82.2 and 197.3 mg/g for phenol, 2-chlorophenol, 4-chlorophenol and 2,4-dichlorophenol, respectively.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

REFERENCES

- Al-Degs, Y.S.; Khraisheh, M.A.M.; Allen S.J.; Ahmad, M.N., (2009). Adsorption characteristics of reactive dyes in columns of activated carbon. *J. Hazard. Mater.*, 165(1-3): 944-949 (6 pages).
- Ali, I.; Gupta, V.K., (2007). Advances in water treatment by adsorption technology. *Nat. protoc.* 1: 2661-2667 (7 pages).
- Andersson, K.I.; Eriksson, M.; Norgren, M.; (2012). Lignin removal by adsorption to fly ash in wastewater generated by mechanical pulping. *Ind. Eng. Chem. Res.* 51(8): 3444-3451 (8 pages).
- Babel, S.; Kurniawan, T.A., (2003). Low-cost adsorbents for heavy metals uptake from contaminated water: A review. *J. Hazard. Mater.*, 97(1-3): 219-243 (25 pages).
- Bansal, R.C.; Goyal, M., (2005). Activated carbon adsorption. Boca Raton, Taylor and Francis Group.
- Carrott, P.J.M.; Suhas; Carrott, M.M.L.R.; Guerrero, C.I.; Delgado, L.A., (2008). Reactivity and porosity development during pyrolysis and physical activation in CO₂ or steam of kraft and hydrolytic lignins. *J. Anal. Appl. Pyrol.*, 82(2): 264-271 (8 pages).
- Christie, R.M. (2007). Environmental aspects of textile dyeing. Cambridge, Woodhead ; Boca Raton.
- Crini, G., (2006). Non-conventional low-cost adsorbents for dye removal: A review. *Bioresource Tech.* 97(9): 1061-1085 (25 pages).
- Das, A.; Pal, A.; Saha, S.; Maji, S.K., (2009). Behaviour of fixed-bed column for the adsorption of malachite green on surfactant-modified alumina. *J. Environ. Sci. Health, Part A* 44(3): 265-272 (8 pages).
- de Oliveira Brito, S.M.; Andrade, H.M.C.; Soares, L.F.; de Azevedo, R.P., (2010). Brazil nut shells as a new biosorbent to remove methylene blue and indigo carmine from aqueous solutions. *J. Hazard. Mater.*, 174(1-3): 84-92 (25 pages).
- Domínguez-Vargas, J.R.; Navarro-Rodríguez, J.A.; de Heredia, J.B.; Cuerda-Correa, E.M., (2009). Removal of chlorophenols in aqueous solution by carbon black low-cost adsorbents. Equilibrium study and influence of operation conditions. *J. Hazard. Mater.*, 169(1-3): 302-308 (7 pages).
- Golka, K.S.; Kopps S.; Myslak Z.W.,(2004). Carcinogenicity of azo colorants: influence of solubility and bioavailability. *Toxicol. Lett.*, 151(1): 203-210 (8 pages).
- Gupta, V.K.; Suhas, (2009). Application of low-cost adsorbents for dye removal: A review. *J. Environ. Manage.*, 90(8): 2313-2342 (30 pages).
- Gupta, V.K.; Ali, I.; Suhas; Saini, V.K., (2006). Adsorption of 2,4-D and carbofuran pesticides using fertilizer and steel industry wastes. *J. Colloid. Interface. Sci.* 299(2): 556-563 (8 pages).
- Gupta, V.K.; Carrott, P.J.M.; Carrott, M.M.L.R.; Suhas, (2009). Low-Cost adsorbents: Growing approach to wastewater treatment: A review. *Crit. Rev. Env. Sci. Tec.*, 39(10): 783-842 (60 pages).
- Hai, F.I.; Yamamoto, K.; Fukushi, K., (2007). Hybrid treatment systems for dye wastewater. *Crit. Rev. Env. Sci. Tec.*, 37(4): 315-377 (63 pages).
- Hu, Z.; Vansant, E.F., (1993). Adsorption of phenol and chlorophenols from aqueous solution by modified elutrilithes. *Catalysis Today* 17(1-2): 41-51 (11 pages).
- Ioannou, Z.; Simitzis, J., (2009). Adsorption kinetics of phenol and 3-nitrophenol from aqueous solutions on conventional and novel carbons. *J. Hazard. Mater.*, 171(13): 954-964 (11 pages).
- Jain, A.K.; Gupta, V.K.; Bhatnagar, A.; Suhas, (2003b). A comparative study of adsorbents prepared from industrial wastes for removal of dyes. *Sep. Sci. Tech.*, 38(2): 463-481 (19 pages).
- Jain, A.K.; Gupta, V.K.; Bhatnagar, A.; Suhas, (2003c). Utilization of industrial waste products as adsorbents for the removal of dyes. *J. Hazard. Mater.*, 101(1): 31-42 (12 pages).
- Jain, A.K.; Gupta, V.K.; Bhatnagar, A.; Jain, S.; Suhas, (2003a). A comparative assessment of adsorbents prepared from industrial wastes for the removal of cationic dye. *J. Indian Chem. Soc.*, 80(4): 267-270 (4 pages).
- Jain, A.K.; Gupta, V.K.; Jain, S.; Suhas, (2004). Removal of chlorophenols using industrial wastes. *Environ. Sci. Tech.*, 38(4): 1195-1200 (6 pages).
- Jia, Q.; Lua, A.C., (2008). Effects of pyrolysis conditions on the physical characteristics of oil-palm-shell activated carbons used in aqueous phase phenol adsorption. *J. Anal. Appl. Pyrol.*, 83(2): 175-179 (5 pages).
- Karunarathne, H.D.S.S.; Amarasinghe, B.M.W.P.K., (2013). Fixed bed adsorption column studies for the removal of aqueous phenol from activated carbon prepared from sugarcane bagasse. *Energy Procedia*, 34: 83-90 (8 pages).
- Li, W.; Yue, Q.; Tu, P.; Ma, Z.; Gao, B.; Li, J.; Xu, X., (2011). Adsorption characteristics of dyes in columns of activated carbon prepared from paper mill sewage sludge. *Chem. Eng. J.*, 178(0): 197-203 (7 pages).
- Lorenc-Grabowska, E.; Rutkowski, P., (2014). High basicity adsorbents from solid residue of cellulose and synthetic polymer co-pyrolysis for phenol removal: kinetics and mechanism. *Appl. Surf. Sci.*, 316: 435-442 (8 pages).
- Mollah, A.H.; Robinson, C.W., (1996). Pentachlorophenol adsorption and desorption characteristics of granular activated carbon-II. Kinetics. *Water Res.*, 30(12): 2907-2913 (7 pages).
- Nabais, J.M.; Gomes, J.A.; Suhas; Carrott, P.J.; Laginhas, C.; Roman, S., (2009). Phenol removal onto novel activated carbons made from lignocellulosic precursors: influence of surface properties. *J. Hazard. Mater.*, 167(1-3): 904-910 (7 pages).
- Shang, G.; Shen, G.; Wang, T.; Chen, Q., (2012). Effectiveness and mechanisms of hydrogen sulfide adsorption by camphor-derived biochar. *J. Air Waste Manage. Assoc.*, 62(8): 873-879 (7 pages).
- Snoeyink, V.L.; Summers, R.S., (1999). Adsorption of organic compounds. Water quality and treatment: a handbook of community water supplies. R. D. Letterman and A.W.W. Association, McGraw-Hill.

- Song, J.; Zou, W.; Bian, Y.; Su, F.; Han, R., (2011). Adsorption characteristics of methylene blue by peanut husk in batch and column modes. *Desalination*, 265(1-3): 119-125 (**7 pages**).
- Sotelo, J.L.; Ovejero, G.; Rodríguez, A.; Álvarez, S.; García, J., (2012). Removal of atenolol and isoproturon in aqueous solutions by adsorption in a fixed-bed column. *Ind. Eng. Chem. Res.*, 51(13): 5045-5055 (**11 pages**).
- Srivastava, S.; Tyagi, R.; Pal, N.; Mohan, D., (1997). Process development for removal of substituted phenol by carbonaceous adsorbent obtained from fertilizer waste. *J. Environ. Eng.*, 123(9): 842-851 (**10 pages**).
- Suhas, P.J.; Carrott, M.M.R., (2007). Lignin-from natural adsorbent to activated carbon: A review. *Bioresource Tech.*, 98(12): 2301-2312 (**12 pages**).
- Tamez Uddin, M.; Rukanuzzaman, M.; Khan, M.M.R.; Islam, M.A., (2009). Adsorption of methylene blue from aqueous solution by jackfruit (*Artocarpus heterophyllus*) leaf powder: A fixed-bed column study. *J. Environ. Manage.*, 90(11): 3443-3450 (**8 pages**).
- Tutem, E.; Apak, R.; Unal, C.F., (1998). Adsorptive removal of chlorophenols from water by bituminous shale. *Water Res.*, 32(8): 2315-2324 (**10 pages**).
- Weber, W.J., (1972). *Physicochemical processes for water quality control*, Wiley-Interscience.
- Zhang, W.; Dong, L.; Yan, H.; Li, H.; Jiang, Z.; Kan, X.; Yang, H.; Li, A.; Cheng, R., (2011). Removal of methylene blue from aqueous solutions by straw based adsorbent in a fixed-bed column. *Chem. Eng. J.*, 173(2): 429-436 (**8 pages**).

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