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Column Studies for the Adsorption of Brilliant Green, Fast Green FCF and Phenol Red Dyes on De-Oiled Soya and Bottom Ash

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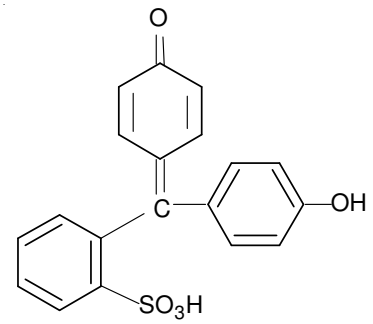
The adsorption of the brilliant green (BG), fast green FCF (FCF) and phenol red (PR) dyes over waste materials like bottom ash (BA) and de-oiled soya (DOS) was investigated. Subsequent desorption was carried out using a suitable eluent. The eluent emerging out of the column was analyzed spectrophotometerically. The percentage saturation of the columns were found to be brilliant green (99.39 and 99.43 %) phenol red (99.14 and 99.16 %) and for fast green FCF (98.94 and 98.38 %), for bottom ash and de-oiled soya, respectively. Percentage recovery in case of brilliant green-bottom ash and brilliant green-de-oiled soya was 76.22 and 88.89 %, which was about 64.09 and 98.02 % for fast green FCF-bottom ash and fast green FCF-de-oiled soya and 91.40 and 98.02 % recovery phenol red-bottom ash ad phenol red-de-oiled soya, respectively.

Key Words: Brilliant green, Fast green FCF, Phenol red, Column studies, Desorption, Column studies.

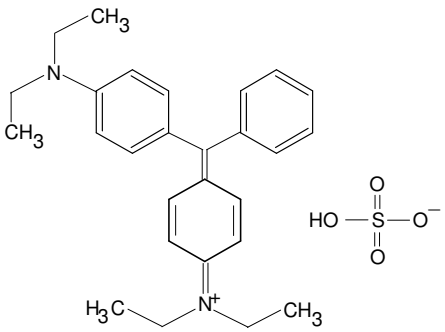
INTRODUCTION

The number of textile industries is considerably increasing in today's scenario. Many dyestuffs present in the effluents pose a great threat to the aquatic life and human beings possibly due to their toxic and carcinogenic nature[1,2]. Most of the dyes have complex molecular structures with synthetic origin, specifically designed to be resistant to microbial attack, light and pH[3]. Therefore the presence of colour contaminants (dyes) is the main point of concern for the researchers. Considering the toxicity, carcinogenetic and the non-biodegradable nature of the dyes their elimination from the water bodies becomes essential.

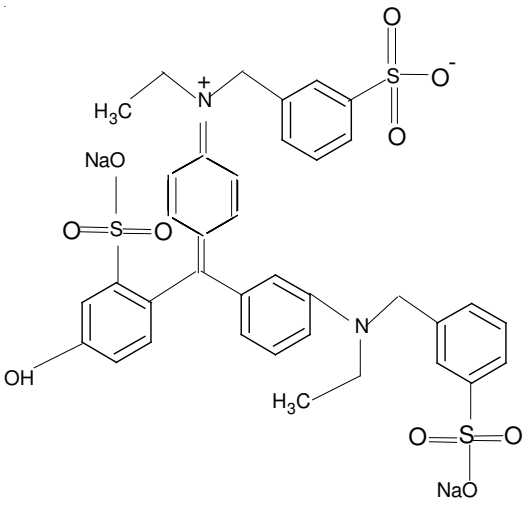
Several methods for the removal of these toxic contaminants have been carried out in which adsorption process has an edge over the others. This process is gaining advantage primarily due to its efficiency, simplicity and cost effectiveness[4]. Waste materials proving to be low cost adsorbents for the removal of hazardous substances from waste water, are more and more coming into play[5-7]. The present research is an attempt to explore two such waste materials bottom ash (BA) and de-oiled soya (DOS) as adsorbents for the removal of brilliant green (BG) (Fig. 1b), fast green FCF (FCF) (Fig. 1c) and phenol red (PR) (Fig. 1a) dyes and to investigate their behaviour in column studies.



(a) Structure of phenol red (m.w. 354.38)



(b) Structure of brilliant green (m.w. 482.63)



(c) Structure of fast green FCF (m.w. 808.85)

Fig. 1. Structures of different dyes

EXPERIMENTAL

Adsorbents and instrumentation: bottom ash samples were collected from thermal power station of (TPS) of M/s Bharat Heavy Electrical Limited (BHEL), Bhopal (India) and de-oiled soya from M/s Sanwaria Agro Oils Ltd. The pH adjustment of the dye solution was done with the help of microprocessor-based pH meter Model HI 8424 (M/s Henna Instruments, Italy). Further the difference in the amount of the dye present in the solution before and after adsorption, was measured with the help of UV-VIS spectrophotometer, Model 117, M/s Systronics, Ahemdabad (India). Quantasorb Model QS-7 surface analyzer was used to calculate the surface of the adsorbent particles. Scanning electron microscopic studies of the two adsorbents were carried out using Philips SEM 501 electron microscope while the recording of the IR spectrum of the adsorbent was done on a Perkin-Elmer FTIR Model Spectrum-One. X-Ray measurements were carried out by a Philips X-ray diffractophotometer.

Adsorbates: The adsorption of three dyes of the class triarylmethane *viz.*, brilliant green (m.f. $C_{27}H_{34}N_2O_4S$ and m.w. 482.63, fast green FCF (m.f. $C_{37}H_{34}N_2O_{10}S_3Na_2$ and m.w. 808.85) and phenol red (m.f. $C_{19}H_{14}O_5S$ and m.w. 354.38), is studied in the present research. All the three dyes (brilliant green, fast green FCF and phenol red) were procured from M/s Merck. The dye solutions used in the experimentation were prepared from the stock solution.

Development of adsorbent: A pretreatment of the two adsorbents was done by washing, dipping in hydrogen peroxide (30 % v/v) for 24 h (for decomposition of the organic impurities), again washing in double distilled water and drying at 100 ºC for 0.5 h. This was then followed by activation of the adsorbent bottom ash at 500 ºC for 15 min in order to develop more activation sites for adsorption.

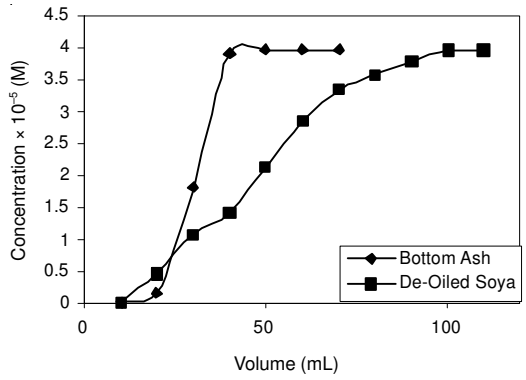
Thereafter sieving of the adsorbents was carried out to various mesh sizes *viz.*, 36, 100 and 170 BSS mesh, which were finally stored in a dessicator.

Column studies: The practical applicability of the two adsorbents was ascertained by column studies. Column studies are usually carried out in order to estimate the bulk amount of the dye continuously from the running wastewater. In these studies the dye solution remains incessantly in contact with the column bed[8-10]. Column studies were aimed at studying the effect of various process parameters like inlet flow rate, initial dye concentration, bed height at various volumes *etc.*[11,12].

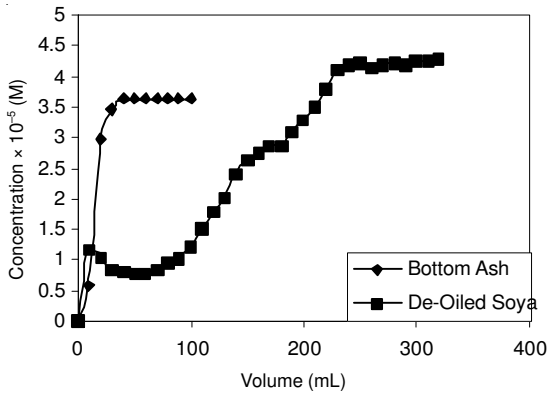
For column studies Perspex column of length 30 cm and internal diameter 1 cm was prepared. A layer of glass wool was made the first layer at the bottom of the column, over which slurry of a weighed amount of the adsorbent was poured, over heal of water, avoiding any possibility of air entrapment in the column. Generally adsorbents of large mesh sizes were used in order to avoid chocking of the colum flow (36 BSS mesh).

The research deals with two broad aspects *i.e.*, adsorption and desorption of the three dye brilliant green, fast green FCF and phenol red solutions over the two adsorbents bottom ash and de-oiled soya.

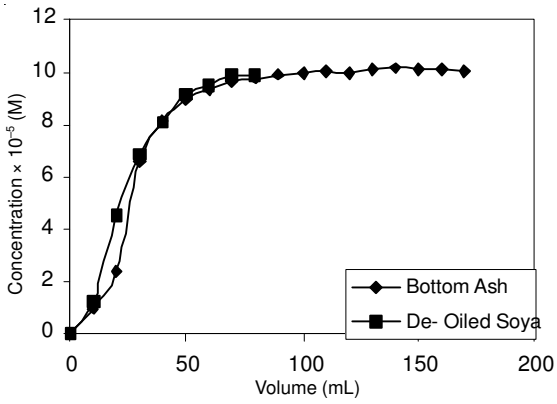
Adsorption studies: Adsorption experiments were carried out by passing the dye solutions of known concentration at regulated flow rate[13] over the adsorbent bed through the column. A difference in the concentration of the dye solutions before and after emerging out through the column were noted and breakthrough curves were plotted which give the concentration of the eluent (dye solution) as a function of time or volume. The characteristic shape of the breakthrough curve depends on the inlet flow rates, concentration and other properties such as column diameter and bed height *etc*. The general position of the breakthrough curve along the volume axis depends on the capacity of the column with respect to the feed concentration, flow rate and bed height. Generally 'S' shaped breakthrough curves are obtained for almost all adsorbate-adsorbent systems (Fig. 2a-c).



(a) Brilliant green



(b) Fast green FCF



(c) Phenol red

Fig. 2. Breakthrough curves for column studies

Dye solution of concentration 4×10^{-5}, 5×10^{-5} and 10×10^{-5} M, were used for column operations in case of brilliant green, fast green FCF and phenol red, respectively. In all the three cases the flow rate for the dye percolation was maintained as 0.5 mL/min. The amounts of the bottom ash used was 0.5 g (36 BSS mesh) for brilliant green and fast green FCF columns, whereas 0.25 g for phenol red column. On the other hand 0.25 g of de-oiled soya (36 BSS mesh) was used for all the three dye columns.

The dye effluent was collected at the bottom through a 2 mm diameter orifice. Samples of the outlet bulk solution were collected at definite intervals of time and examined for dye concentration spectrophotometrically at definite wavelength (λ_{max}- 626 nm, 622-626 nm, 435 nm, for brilliant green, fast green FCF and phenol red, respectively), corresponding to the particular dye. When the dye solution has moved through the whole column and the exit becomes equal to the feed concentration, at this stage the column is considered to be exhausted, since complete adsorption has occurred. The flow through this column is then stopped at this point followed by desorption and regeneration of the column. Various parameters calculated from the breakthrough studies[14] are as under:

$$t_x = \frac{V_x}{F_m} \quad (1)$$

$$t_\delta = \frac{V_x - V_b}{F_m} \quad (2)$$

$$\frac{\delta}{D} = \frac{t_\delta}{t_x - t_f} = \frac{t_\delta}{t_x + t_\delta(f-1)} = \frac{(V_x - V_b)}{V_b + f(V_x - V_b)} \quad (3)$$

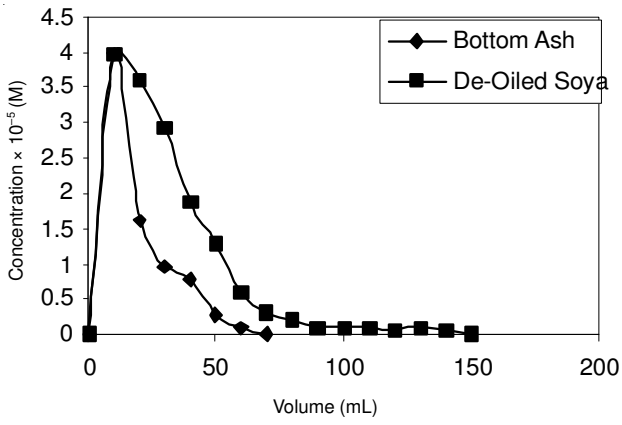
$$f = 1 - \frac{t_f}{t_\delta} = \frac{M_s}{(V_x - V_b)C_o} \quad (4)$$

$$\text{Saturation}\ (\%) = \frac{D + \delta(f-1)}{D} \times 100 \quad (5)$$

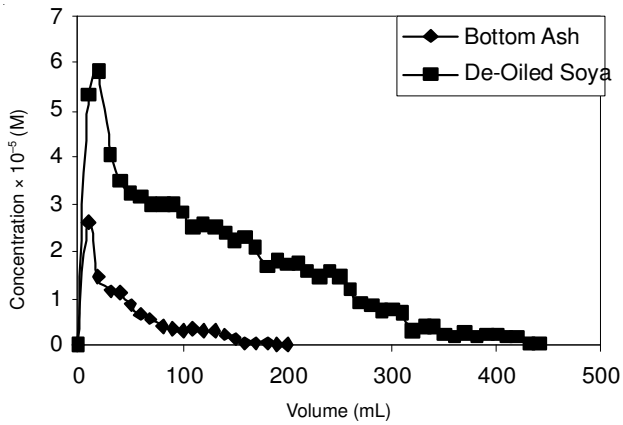
here δ (cm) is length of the primary adsorption zone, t_x (min) is time involved for the establishment of primary adsorption zone, t_δ (min) is time for the primary adsorption zone to move down its length, t_f (min) is time for initial formation of primary adsorption zone, f is fractional capacity of the column, C_o (M) is initial concentration of adsorbate, C_x (M) is concentration of effluent during exhaustion, C_b (M) is concentration of effluent at the break point, V_x (mL) is volume of effluent during exhaustion, V_b (mL) is volume of effluent at break point, V (mL) eluted volume of the dye, F_m (mg/cm^2/min) is mass rate flow of the dye solution and D (cm) is length of column bed.

Desorption studies: Retrieving the original adsorbent and reusing the exhausted column after the complete adsorption process is one of the factors of utmost importance. Regeneration of the used adsorbents and recycling is helpful also if the adsorbents are costly materials, moreover it also plays a prime role in regaining the adsorbate.

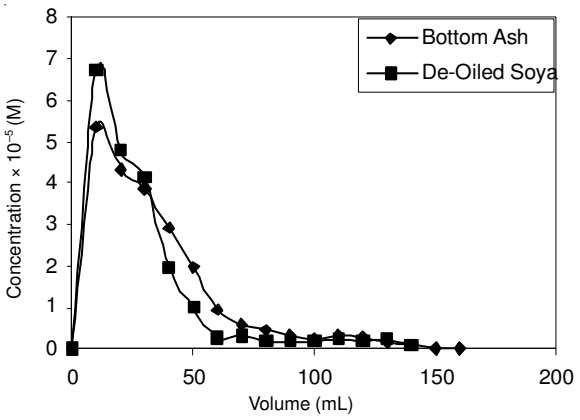
Therefore keeping the above into consideration desorption experiments of the used column were carried out and the adsorbate solutions were obtained using a suitable eluent (Fig. 3a-c). Different categories of eluents have been used by several researchers like sulphuric acid, acetone, acetic acid sodium hydroxide *etc*. However in certain cases distilled water of appropriate pH was also used as an eluent[15]. Therefore the regeneration of the exhausted bottom ash and de-oiled soya columns were carried out by passing sulfuric acid of pH 3 for brilliant green, NaOH solution of pH 9.5 for fast green FCF and acidic water of pH 2, for phenol red dye. As in the case of the adsorption process, the flow rate of 0.5 mL/min was maintained in all the cases. The eluent was flown through the saturated columns with a controlled flow rate (0.5 mL/min) and the concentrations of the aliquots of collected dye solutions were monitored spectrophotometrically, till absorbance of the solution was nullified.



(a) Brilliant green



(b) Fast green FCF



(c) Phenol red

Fig. 3. Desorption of dyes from exhausted bottom ash and De-Oiled soya columns

Desorption process was followed by through washing of the column bed with hot distilled water, thereby regenerating it.

RESULTS AND DISCUSSION

Adsorption: The column studies utilize 70 mL of brilliant green[16], 100 mL of fast green FCF[17] and 170 mL of phenol red[18] dye solutions for exhaustion of bottom ash column and 110, 330 and 80 mL of dye solutions for de-oiled soya column, respectively.

As evident from the breakthrough curves, in case of brilliant green out of 1.35 mg dye in 70 mL of the dye, 0.48 mg was adsorbed over 0.5 g bottom ash and out of 2.12 mg of the dye in 110 mL solution, 0.83 mg was adsorbed over 0.25 g de-oiled soya. Similarly in the case of fast green FCF 0.36 mg was adsorbed over 0.5 g of bottom ash, out of 4 mg dye in 100 mL solution and 6.13 mg was adsorbed over 0.25 g of de-oiled soya, out of 13.32 mg of the dye in 330 mL solution. On the other hand 0.25 g of bottom ash adsorbed 0.84 mg of the phenol red dye from 6.02 mg of the dye present in 170 mL solution whereas 0.25 g of de-oiled soya adsorbed 0.74 mg of the dye out of 2.83 mg of it in 80 mL dye solution (Fig. 2a-c).

The values of percentage saturation as calculated from the eqn. 5 was found to be brilliant green (99.39 and 99.43 %) *ca.* phenol red (99.14 and 99.16 %) > fast green FCF (98.94 and 98.38 %). As depicted in the order fast green FCF shows the least value of percentage saturation whereas these values are comparable for fast green FCF and phenol red. The possible reason being the bulky nature of fast green FCF in comparison to brilliant green and phenol red. Several other parameters calculated from the column studies are potrayed in Tables 1 and 2. Similarly the order of the mass flow rates fast green FCF > brilliant green > phenol red, can be attributed again to the greater molecular weights of fast green FCF and brilliant green and the lighter nature of phenol red. It is to be noted here that the mass flow rates in case of brilliant green and fast green FCF is not substantial.

Desorption: A percentage recovery of 76.22 and 88.89 % was observed for brilliant green-bottom ash and brilliant green-de-oiled soya, which was about 64.09 and 98.02 % of the dye fast green FCF-bottom ash and fast green FCF-de-oiled soya and 91.40 and 98.02 % recovery phenol red-bottom ash ad phenol red-de-oiled soya, respectively. In the case of the first adsorbate brilliant green, out of 4.88×10^{-4} g of the total dye adsorbed over bottom ash, about 3.56×10^{-4} g of the dye could be desorbed, whereas out of the 8.33×10^{-4} g dye adsorbed over de-oiled soya, 6.00×10^{-4} g of the dye was desorbed, using 40 mL of dilute sulphuric acid (pH 3). For fast green FCF, the second adsorbate, 80 mL of NaOH was sufficient to desorb 7.11×10^{-4} g of the dye out of adsorbed 1.36×10^{-3} g of the dye in case of bottom ash. On the contrary initial 150 mL of NaOH desorbed about 3.97×10^{-3} g of fast green FCF out of 6.13×10^{-3} g of total adsorbed dye adsorbed over de-oiled soya (Fig. 3a-c). phenol red showed almost 84 % desorption in first 70 mL of the eluent out of the 8.42×10^{-4} g of the dye adsorbed in case of bottom ash, which was 92 % out of 7.42×10^{-4} g of the dye adsorbed for de-oiled soya.

TABLE-1
FIXED BED ADSORBER CALCULATIONS FOR THE BOTTOM ASH COLUMN

Dye	$C_o \times 10^{-5}$ (M)	$C_x \times 10^{-5}$ (M)	$C_b \times 10^{-5}$ (M)	V_x (mL)	V_b (mL)	$t_x \times 10^3$ (min)
Brilliant green	4.0	3.9	0.1	50	20	4.0
Fast green FCF	5.0	3.6	0.6	50	10	1.9
Phenol red	10.0	9.7	1.1	130	20	5759.3
Dye	$t_\delta \times 10^3$ (min)	t_f (min)	f	δ (cm)	F_m (mg/cm^2/min)	D (cm)
Brilliant green	2.4	40	0.99	0.42	0.02	0.75
Fast green FCF	1.5	20	0.98	0.60	0.01	0.70
Phenol red	4873.2	40	1.0	0.42	0.00002	0.50

TABLE-2
FIXED BED ADSORBER CALCULATIONS FOR THE DE-OILED SOYA COLUMN

Dye	$C_o \times 10^{-5}$ (M)	$C_x \times 10^{-5}$ (M)	$C_b \times 10^{-5}$ (M)	V_x (mL)	V_b (mL)	$t_x \times 10^3$ (min)
Brilliant green	4.0	3.9	0.4	100	20	8.1
Fast green FCF	5.0	4.1	0.9	260	80	10.1
Phenol red	10.0	9.5	1.2	60	10	2.6
Dye	$t_\delta \times 10^3$ (min)	t_f (min)	f	δ (cm)	F_m (mg/cm^2/min)	D (cm)
Brilliant green	6.5	40	0.99	0.40	0.02	0.70
Fast green FCF	6.9	160	0.97	0.50	0.01	0.50
Phenol red	2.2	20	1.0	0.42	0.002	0.50

Conclusion

Thus for the six dye-adsorbent columns various parameters such as fractional capacity, mass flow rate and length of the primary adsorption zone *etc*., have been successfully calculated from the break through curves obtained during column studies. The mass flow rates has been found in the order fast green FCF > brilliant green > phenol red. The percentage saturation calculated from column studies is in the order brilliant green (99.39 and 99.43 %) *ca.* phenol red (99.14 and 99.16 %) > fast green FCF (98.94 and 98.38 %). The recoveries of the dyes from the columns have been made by percolating sulfuric acid of pH 3 in the case of brilliant green exhausted columns, NaOH solution of pH 9.5 for fast green FCF exhausted columns and acidic water of pH 2, for both the columns (bottom ash an de-oiled soya) exhausted by phenol red dye. Therefore, column studies have been found useful for the elimination of all the three dyes (brilliant green, fast green FCF and phenol red) using bottom ash and de-oiled soya as adsorbents.

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