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Bagasse fly ash as novel adsorbent for ionic dyes

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ABSTRACT

Colored waste water contamination in natural resources due to natural and anthropogenic activities is becoming a world wide problem now a days. The toxic nature of several dyes is a serious threat to human health. Among several treating technologies adsorption has been recognized as a effective tool for color removal. In the present study Bagasse fly ash is evaluated for its adsorption efficiency towards model cationic, anionic and zwitterionic dyes. The equilibrium and kinetic experiments were performed in batch mode. The equilibrium data was fitted with Langmuir and Freundlich models. Several operation variables such as adsorbent dosage, contact time, initial pH, and temperature on the removal of dyes were investigated. The removal efficiency increased with increase in adsorbent dosage. The adsorption process followed pseudo second order kinetics. Thermodynamic parameters like ΔH° , ΔS° and ΔG° were analyzed. The processes were spontaneous for the ionic dyes. These results suggest that bagasse fly ash is a potential low cost industrial waste for textile industry waste water treatment containing ionic dyes.

Key words: Adsorption; Ionic dyes; Kinetics; Thermodynamics

INTRODUCTION

In developing nations like India the conventional effluent treatment technologies are not affordable. Rapid industrial growth has brought economical revolution in all the parts of world and industrial waste water treatment is an important task due to environmental concerns. Thousands of dyes are prepared for printing and dyeing industries from coal tar based hydrocarbons such as benzene, anthracene, naphthalene, xylene, toluene etc. Dyes are used in industries like paper, textile, cosmetics, rubber, food, drug and plastics[1]. According to an estimate 10,000 different types of commercial dyes are present and 7X10⁵ tones of dyes are produced annually worldwide[2]. This is observed that aerobic biodegradation has very less color removal efficiency. Most of the treatment technologies work on biological treatment processes. Other physical and chemical methods like coagulation [3], oxidation[4], membrane separation[5] and adsorption are in practice. Adsorption is a procedure of choice due to its simplicity, efficiency and cost efficacy[6]. Activated carbon is the best adsorbent but its higher cost and difficult regeneration has encouraged many workers for the research of new adsorbents. Ionic dyes have been removed by the use of adsorbents like orange and banana peels [7], almond shells[8], corn cob [9], de-oiled soya[10], shale oil ash[11], Sugar cane bagasse [12],coir pith[13], hazelnut shells[14], rice husk[15], wheat husk[16], sewage sludge[17], bark [18] etc. The present work reports the results of adsorption studies of ionic dyes model anionic dye, acid orange-7 (AO-7) and model cationic dye, basic red 12(BR-12), and a zwitterionic dye basic violet-10 (BV-10) on sugar industry waste bagasse fly ash after minimal chemical treatment. Thermodynamic and kinetics of the adsorption process is studied along with the mechanism of adsorption using FTIR analysis of the adsorbent.

MATERIALS AND METHODS

Materials

Bagasse fly ash (BFA) was collected from Rana sugar mills, Dhilwan Punjab.10.0 g BFA was dipped in 10% v/V of 20 V H₂O₂ for 24 hours to oxidize the organic matter. This was then filtered and washed with distilled water several times till the washings attain neutral pH and negligible conductance. This was then dried in a hot air oven at 80° for 12 hours and sieved to get the particle size less than 250 µm and was stored in an air tight container for further use. The dyes i.e. AO-7, BR-12, and BV-10 were procured Thomas Baker Co. The structures of dyes are given in Figure 1. 1000 ppm stock solution of dyes was prepared by dissolving in double distilled water (DDW). Dye solutions were prepared by dissolving appropriate amount of dye in DDW and stored in dark colored bottles and diluted by adding suitable amount of water to the stock solution as per requirement. The dye concentration before and after adsorption was determined by using Systronics 2201spectrophotometer. A standard plot is drawn for known concentrations and the concentration of dyes was determined by converting the optical density to corresponding concentration. The residual dyes were analyzed at their respective λ max. The FTIR of BFA was carried out in the range 400-4000 cm⁻¹ using Shimadzu spectrophotometer. The adsorbent is mixed with anhydrous KBr to make a pellet and scans are carried out to give the average FTIR scan. The adsorbent samples were also characterized by powder X-ray diffractometry using an X'PERT PRO PANalytical with Cu-K_a radiation. The phases of crystalline and mesoporous BFA was determined. SEM is carried out by using ZEOL scanning electron micrograph. The micro porous structures of the BFA were studied. BET surface area measurement is carried out by using micromeritics surface area analyzer. This also gave monolayer volume of N_2 and pore volume of the adsorbents. The pH of dye solutions and pHzpc were determined by using pH meter by Toshvin (TMP-85). An auto arranging conductivity meter TCM+15, provided with temperature compensator made by Toshnival, India was used for determination characteristics and nature of the filtrate of BFA washings. The weighing was carried out on a digital weighing balance of accuracy up to 0.1 mg by citizen Co.

Batch Experiments

The series of experiments were conducted by placing 50 ml of dye solution in an Erlenmeyer flask and adding the required amount of adsorbent to that in an incubator shaker. The pH of different solutions was adjusted with 0.1 N HCl and 0.1 N NaOH. After attainment of equilibrium the aqueous phase was analyzed for residual dye concentration using UV visible spectrophotometer. From the absorbance data $q_e (mg g^{-1})$ was determined using equation 1.

$$q_e = \frac{(C_0 - C_e)V}{W}$$

Where C_0 is initial dye concentration, C_e is final dye concentration and V is volume of dye in liters and W is mass of adsorbent in g. Duplicate experiments were performed to get concordant results. The kinetics of dye removal was studied using optimum dye concentration. The samples were withdrawn at regular intervals and residual concentration was analyzed after centrifugation using ultracentrifugation at 1000 rpm. The isotherms were studied by using 50 ml of dye solution within suitable concentration range at 303 K, 313 K and 323 K. The pHzpc (pH zero point charge) was determined by the method reported earlier [19].

RESULTS AND DISCUSSION

Characterization of BFA.

Surface chemistry of the BFA such as specific surface area, pore volume distribution, and pore diameter were measured using nitrogen gas adsorption technique with micromeritics surface area analyzer. The acidity and basicity of the adsorbent were determined by the Boehm titration method [20, 21] as reported elsewhere. For morphological uniqueness, scanning electron micrograph of BFA was carried out. SEM is widely used to study the morphological features and surface characteristics of the adsorbent materials. SEM of BFA discloses uneven and spongy surface texture. SEM of BFA and its derivatives have been shown in Figure 2. The X-ray diffraction analysis of the BFA was carried out and shown in Figure. 3, revealed the crystalline nature of BFA. EDAX studies reveal that BFA is mainly composed of up of SiO₂, Al₂O₃ and CaO FTIR spectra (Figure. 4) revealed that the adsorbent mainly shows Al-O streching [22] as a prominent band is observed at 1072 cm⁻¹. The presence of SiO₂ is also inferred[23] by a peak at 775 cm⁻¹. A prominent band at 467 cm⁻¹ indicates Ca-O stretching [24]; Hence BFA contains Al₂O₃, SiO₂ and CaO as main components. The characteristics of BFA are given in Table 1.

(1)

Table 1- Physicochemical properties of BFA

Surface area (m ² g ⁻¹)	18.641
Monolayer volume(cm ³ /g)	4.282
Bulk density (g mL ⁻¹)	0.338
Pore volume $(m^3 g^{-1})$	0.0094
Zero point charge (pHpzc)	7.91
Total surface acidity (mmol g ⁻¹)	0.691
Total surface basicity (mmol g ⁻¹)	3.720

Table 2-Freundlich and Langmuir parameters for adsorption of BR-12, BV-10 and AO-7 over BFA at different temperatures

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Temperature(K)	K _F	n	$Q_{\rm o}({\rm mol/g})$	b(L/mol)
BR-12				
303	0.3626	1.755	27.469	17.713
313	2.4706	1.601	34.411	17.392
323	2.1072	1.349	48.883	12.446
BV-10				
303	1.6627	1.547	4.404	66.708
313	10.765	2.608	4.333	97.356
323	10.995	2.678	4.243	96.858
AO-7				
303	0.0379	1.043	15.458	0.812
313	0.9062	1.232	8.835	1.914
323	1.0853	1.328	6.641	3.622

Table 3-Values of thermodynamic parameters for adsorption of BR-12, BV-10 and AO-70ver BFA at different temperatures

Temperature(K)	$\Delta G^{o}(\mathrm{KJ} \mathrm{mol}^{-1})$	$\Delta H^{o}(\mathrm{KJ} \mathrm{mol}^{-1})$	$\Delta S^{o}(J \text{ mol}^{-1} \text{ K}^{-1})$
BR-12			
303	-7.241		
313	-7.432	18.969	83.437
323	-6.711		
BV-10			
303	-10.581		
313	-11.913	-40.075	-91.003
323	-12.28		
AO-7			
303	0.523		
313	-1.689	-100.1	314.88
323	-3.456		





Figure 1. Structure of ionic dyes(a) BR-12(b) AO-7(c) BV-10

Table-4-Pseudo second order rate constants for the removal of BR-12, BV-10 and AO-70ver BFA at 303 K

	$k_2(g m g^{-1} m i n^{-1})$	$qe(mg g^{-1})$	R
BR-12	0.0166	15.702	0.9998
BV-10	0.0259	3.175	0.9914
AO-7	0.0245	2.673	0.9922



Figure 2. SEM of BFA



Effect of adsorbent dose.

The effect of adsorbent dose was investigated by adsorption of dyes on variable dose of BFA. The experiments were conducted with adsorbent dose between 2.5 g/100 ml to 20.0 g/100 ml at 303 K and it was found that with an increase in the dose, the adsorption increases for all types of dyes. The optimum adsorbent dose for BR-12, AO-7 is 1.25g/ 100 ml and for BV-10 is 5.0g/100ml. The given mass of BFA can adsorb only fixed amount of dye and the this amount depends upon the charge on the dye molecule and its surface area for diffusion across the boundary of BFA. This may be attributed to the reason as at lower adsorbent dosage the number of dye molecules is relatively higher as compared to availability of active adsorption sites. Further, the nature of functional groups on the surface decides the maximum adsorption capacity of the dyes on the surface. In view of this it is justified that with the increase in adsorbent dose 100% dye removal takes place. The results are shown in Figure 5.

Effect of pH

The dye adsorption is affected by solution pH and in the present study the effect of pH was studied in the range of 2-9 while initial concentration of 100 ppm was used for BV-10 and AO-7, adsorbent dose (1.25g/100 ml) for AO-7 and (5.0g/100 ml) for BV-10 is maintained at 303 K, while for BR-12 initial concentration of 250 ppm at adsorbent

dose of 1.25g/100 ml were kept constant at 303 K.. The effect of initial pH on the dye removal is shown in Figure 6. The adsorption capacity increases when the pH increases for BR-12 while the adsorption of AO-7 decrease with the increase of pH, while towards BV-10 the adsorption capacity of BFA almost remains unchanged, the above fact can be explained by assuming that the oxides of aluminium, silicon and calcium undergo hydroxylation forming M-OH bonds in aqueous medium. The pHzpc of SiO_2 , Al_2O_3 and CaO is 2.2, 8.3 and 11 respectively [25]. The pHzpc measured for BFA was 7.91 suggesting that the different proportions of SiO₂, Al₂O₃ and CaO decides the nature of BFA towards ionic dyes in aqueous medium. The pK values measured for different ionic dyes suggests that pK value for BR-12, BV-10 and AO-7 is 5.5, 7.0 and 4.5 respectively and beyond pHzpc negative charge develops on the surface so cationic dyes are best adsorbed above their pHzpc. The oxides are protonated at pH lesser than 2.2, The electrostatic forces of attraction increases among the adsorbent and anionic dye at this pH but with the increase of pH of the medium, deprotonation of protonated oxides takes place causing negative charge on the adsorbent and increasing the removal of cationic dye. At high pH the competitive adsorption of anionic dye and OH⁻ ions takes place causing decrease of adsorption of anionic dye. Percentage of anionic dye removal decrease with the increase of pH and cationc dye increases with increase of pH. The zwitterionic dye is protonated at pH 2.0, the adsorbent is also protonated at this pH, hence the electrostatic repulsion takes place between dye and adsorbent surface, while at higher pH the dye and adsorbent both are deprotonated carrying negative charge creating repulsive interactions. Further experiments were carried out at pH 2 for AO-7 BV-10 and pH 5 for BR-12.



Figure 4. Effect of Adsorbent dose on dye removal, dye concentration 250 ppm BR-12, 100ppm AO-7 and and BV-10, 303 K, 200 rpm



Figure 5. FTIR spectra og BFA



Figure 6. Effect of pH on dye removal, dye concentration 250 ppm BR-12, 100ppm AO-7 and and BV-10, 303 K, 200 rpm



Figure 7.Effect of contact time on percentage dye removal, dye concentration 250 ppm BR-12, 100ppm AO-7 and and BV-10, 303 K, 200 rpm

Effect of contact time

The effect of contact time was investigated in the batch mode at optimum dye concentration and adsorbent dose for AO-7, BR-12 and BV-10. The results have been shown in Figure. 7 which suggests that the adsorption capacity of dyes increases with increasing contact time. To begin with the rate of dye removal is higher due to high concentration gradient which decreases steadily due to decrease of dye concentration in the medium and obstruction of active sites of the adsorbent. The equilibrium adsorption capacity is 6.87, 4.27, 4.88 mg/g for BR-12, AO-7 and BV-10 respectively. The adsorption capacity of cationic dye is highest anionic dye is lowest while for amphoteric dye is medium. The adsorption is rapid for BR-12 is highest because deprotonated oxygen of alumina and silica makes electrostatic attractions feasible between cationic dye and anionic oxides. The protonated oxygen atoms causes attraction between anionic dye and positively charged surfaces of BFA. The behaviour of BV-10 is in between these two extremes. The equilibrium is attained in 6h for all the dyes in a constantly stirred batch reactor. The driving force is concentration gradient between solid containing functional group and aqueous layer. This seems that the dye molecules first encounter the boundary layer effect and then follow the diffusion film mechanism. When a charged surface is present it takes relatively longer time for diffusion due to repulsive interaction of dye molecules with the surfactant on the surface. The dye molecules tend to arrange themselves as a least energetic conformation with minimum repulsions and maximum attractive forces before diffusion through the surface. The presence of

different charges on the surface of BFA at different pH makes the process happening gradually. This seems that the processes are electrostatic complexation driven.



Figure 8c Langmuir plot for adsorption of AO-7over BFA

Figure. 9a Freundlich plot for adsorption of BR-12 over BFA

Figure 9b Freundlich plot for adsorption of BV-10 over BFA

Figure 9c Freundlich plot for adsorption of AO-7over BFA

Figure 10 First order kinetic model for the adsorption of BR-12, BV-10 and AO-7 on BFA at 303 K

Figure 11 Pseudo second order kinetic model for the adsorption of of BR-12, BV-10 and AO-7 on BFA at 303 K

Adsorption isotherms

The Freundlich, Langmuir and redlich peterson isotherm models have been successfully applied to all of the above system at various temperatures 303 K, 313 K and 323 K and thermodynamic parameters calculated accordingly. For the equilibrium concentration of adsorbate (Ce) and amount of dye adsorbed at equilibrium (qe), the following linear forms of Langmuir[26] and Freundlich[27] isotherms were studied.

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{bQ_0C_e}$$
(2)

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{3}$$

Where Qo and b are Langmuir constants and K_F and n are Freundlich constants. The Freundlich and Langmuir isotherms gave straight lines and intercepts and slopes were used to determine the values of Freundlich and Langmuir parameters as given in Table 2. The isotherms are shown in Figure 8-9. the thermodynamic parameters which were also calculated from the above data using Equations 4-6.

$$\Delta G^{o} = - RT \ln b \tag{4}$$

$$\Delta H^0 = -R \left(\frac{T_2 T_1}{T_2 - T_1} \right) \ln \left(\frac{b_2}{b_1} \right) \tag{5}$$

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$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} \tag{6}$$

Where b, b_1 , b_2 are Langmuir constants at 303 K, 313 K and 323 K respectively. The values are mentined in Table 3. It is clear from the values of isothem parameters that freundlich isotherm is more applicable than langmuir for adsorption of BV-10 and AO-7 suggesting that the adsorption of these dyes is non ideal and reversible in nature. This empirical model is best explained for non distribution of adsorption heat and affinities over the heterogenous surface [28]. The adsorption of BR-12 over BFA follows both langmuir and freundlich isothems with equal ease suggesting that adsorption is homogenous on heterogenous adsorption sites. The activation energy for all the sites is constant with no transmigration of dye molecules in the plane of surface [29]. The value of freundlich constant 'n' indicates surface hetrogenity and its value ranges between 0-1, while in the present study the n>1 suggesting that the adsorption of ionic dyes on BFA is cooperative adsorption [30]. The net Gibbs free energy, ΔG^{0} was found to be negative at all temperatures, indicating spontaneous process at all the temperatures for all dyes while enthalpy ΔH^{0} , was positive for BR-12 on BFA and is negative for BV-10 and AO-7 suggesting endothermic and physisorption of the process for adsorption of BR-12 on BFA and is negative for BV-10 and AO-7 indicating irreversible chemisorption. The positive value of entropy, ΔS^{0} for BR-12 and AO-7 indicates that adsorption of cationic dye and anionic dye is entropy driven in nature.

Kinetic Studies

The rate of removal of ionic dyes has been studied as a function of time on as can be seen in Figure.7. The equilibrium was attained in 6 h for all the dyes. The adsorption proceeds in three steps; in the first step rapid adsorption of dye takes place on the active sites of adsorbent followed by slow establishment of equilibrium under potential gradient. Adsorption rate constant study was carried out with the famous Lagergran rate equation. (Equation. 7).

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t$$
(7)

The time versus log (q_e - q_t) plots as shown in Figure. 10 was found to be linear for BR-12 and non linear for BV-10 and AO-7 suggesting that the adsorption followed the first order kinetics for BR-12. The slope of the plot gave the value of rate constant $k_1 = 5.38 \times 10^{-3} \text{ min}^{-1}$. Pseudo second order model is applied on the adsorption of BV-10 and AO-7.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{8}$$

The plot of t/q_t vs time is shown in Figure 11 and this is clear that pseudo second order model fitted well the data showing that the dye removal is high at the beginning and gradually slows down near equilibrium, irrespective of the charge on the dye, this is probably due to the reason that there exist strong interactions among dye molecules and the adsorbent at aparticular pH. The slope and intercept gave the value of rate constant k_2 , The value of rate constant for different dyes is given in Table 4.

CONCLUSION

This study shows that ionic dyes can be successfully removed from the simulated effluent by adsorption on BFA which is found to be porous and valuable treatment of colored water. The following conclusions can be drawn from this study: The batch adsorption experiments show that the adsorption of the BR-12, BV-10 and AO-7 over BFA and its derivatives is dependent on pH, amount of adsorbent, concentration, contact time, and temperature, and 100% dye removal at dye concentration <250 ppm for BR-12 and < 100 ppm for BV-10 and AO-7 could be consummate at appropriate pH and adsorbent dose. The thermodynamic parameters obtained in both cases verify the feasibility of the process at each concentration. The Freundlich and Langmuir isotherms fitted the data well signifying homogenous distribution of functional groups on the heterogeneous surface of BFA. The results of kinetic experiments show that the adsorption proceeds via pseudo second order kinetics. The BFA based adsorbents are economical and can be used as praiseworthy adsorbents.

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