Treatment of Small Agro Based Pulp Mill Effluent Using Low Cost Adsorbents

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Agro-based pulp and paper discharges effluent of high COD, BOD and colour. The problem is more severe with mills which are not having chemical recovery system. The present paper deals with removal of COD and colour form agro-based paper mills, utilising straw for paper production, with adsorbents waste carbon (WC), bagasse fly ash (BFA) and activated carbon (AC). WC is produced in fertilizer plants during manufacture of ammonia whereas BFA is available as a waste from bagasse-fired boilers. High surface area, pore volume and pore size observed exhibit potential use of WC and BFA as adsorbent. The COD removal kinetics of agro based pulp mill effluent was found to follow pseudo-second order rate expression. Intraparticle diffusion was found to be rate controlling for adsorption. Equilibrium data were analyzed using Freundlich, Langmuir, Dubinin-Radushkevich and Temkin isotherms. Equilibrium adsorption data fitted best for Freundlich isotherm. Economic considerations, adsorbent characterization, and adsorption capacity of the adsorbents show that use of both BFA and WC could be viable alternative adsorbents for treatment of pulp and paper mill effluent.

INTRODUCTION

Agro based pulp and paper mill effluents present very high pollution load which includes generation of large amount of wastewater containing high COD because of the presence of lignin, dyes and colour. One of the major problems associated with agro-based mills has been lack of viable recovery system especially for mills having low capacity. Due to increasing environmental concern and in order to meet the minimal standard (MINAS) for small paper mills [1], agro based mill will have to go for proper environmental management plan by incorporating recovery system and various treatment technologies. However, removal of lignin and other refractory organics responsible for COD and colour in pulp and paper mill effluent are still causes of major concern.

Various external control measures used for decolourization and removal of non-biodegradable materials include lime treatment, coagulation, ozonation, adsorption, membrane filtration etc. Adsorption is one of the most versatile technology suitable for the removal of broad range of organic pollutions, and other non-biodegradable material. Activated carbon is most commonly used adsorbent, however, its high initial cost has been major deterrent in its utilisation in developing countries. During recent years low cost adsorbents like coal fly ash, bagasse fly ash, bottom ash etc, have been investigated to provide economically viable adsorbents for removal of phenols, heavy metals, pyridine, picoline, dyes, COD from pulp and paper mill effluents etc. [2-5]. A critical review of this has been presented by Mall et al. [6] and Srivastava [7].

This paper deals with adsorptive treatment of combined effluent of an agro-based pulp and paper mill using waste carbon (WC) and bagasse fly ash (BFA) which are available as wastes from fertilizer plant and bagasse fired boilers, respectively. Economical evaluation of the process has been also presented.

Availability of waste carbon and bagasse fly ash

WC is produced in ammonia plants during the manufacture of synthesis gas by partial oxidation of fuel oil and other heavy hydrocarbons. About 1.4 kg of WC

per tonne of ammonia is produced, and normally dumped as waste by fertilizer plants. India is the largest consumer and second largest producer of sugar in the world. Sugar industry is amongst the largest agro processing industries in India. Total sugar cane crushed is about 17.66 million tonnes with 436 sugar mills located through out the country. During production of sugar about 0.33 tonne of bagasse is produced per tonne of sugarcane crushed. About 90-95% of the bagasse produced in India is being utilised by the sugar mills for steam and cogeneration. A wide variety of bagasse-fired boilers are being used in the sugar industry with efficiency varying from 60-80%. With overall 80% collection efficiency the availability of fly ash from the bagasse fired boiler the uncontrolled emission of fly ash is estimated to be about 0.60 million tonnes.

Experimental Programme

Combined effluent of an agro-based paper mill using straw as raw material was used as adsorbate for the removal of its COD and colour in present investigation. WC collected from National Fertilizer Ltd. (NFL) Panipat, Haryana, India and BFA collected from nearby sugar mill were used as adsorbent without any pretreatment except sieving of very fine particle in case of BFA. Physico-chemical analysis of the adsorbents was carried out as per IS standards [8-9]. Analytical grade of activated carbon (AC) was used comparative batch study. Batch experiments were conducted to study the effect of important parameters like initial concentration, contact time etc. To study of the effect of the initial COD and colour concentration on removal, the original effluent concentration was rated as 100 percent and desired concentrations were obtained by successive dilution.

Paper mill effluents contain lignin, which is an amorphous, branched polydispersed macromolecular substance having several functional groups, notably phenolic, hydroxyl benzylic hydroxyl and carbonyl and aliphatic carboxylic groups. Marton [10] reported that the lignin behaves like a hydrocolloid and precipitates as the pH is lowered (in the acidic region) with simultaneous protonation of the acidic groups in the lignin. Lignin precipitation is higher below pH 3, and so the filtrate (or supernatant) has lower COD and colour concentration in this pH range [7]. Therefore, all the experiments were performed at pH 3 to achieve maximum lignin precipitation and thus COD removal.

Each experiment was run with 50 ml of effluent with

predetermined optimum amount of the adsorbent (100 mg for AC and BFA, and 50 mg for WC) in a 100 ml stopped conical flask [11]. This adsorbate-adsorbent mixture was agitated in a temperature controlled shaking water bath at a constant speed of 150 revolutions per minutes (rpm) at 25 ± °C. This mixture was agitated for 4 hours to attain equilibrium while other parameters like temperature, pH and agitation speed were kept constant. The wastewater containing adsorbent was centrifuged using Research Centrifuge (Remi Instruments, Mumbai) at 10,000 rpm for 20 minutes and the supernatant solution obtained were analysed through colourimetry of double beam spectrophotometer (Schmadzur, Japan) to find out the residual colour concentration. Residual COD of the supernatants of effluent was also determined. The percentage COD and colour removal of the effluents were determined at different time intervals with adsorbents till the equilibrium was achieved.

RESULTS AND DISCUSSION

### Characterisation of effluent

Various characteristics of combined pulp and paper effluent were COD (mg/L) 1960, BOD (mg/L) 560, pH 7.4, conductivity (μ mhos) 1.57, turbidity (NTU) 47.7 and total solids (g/L) 6.42.
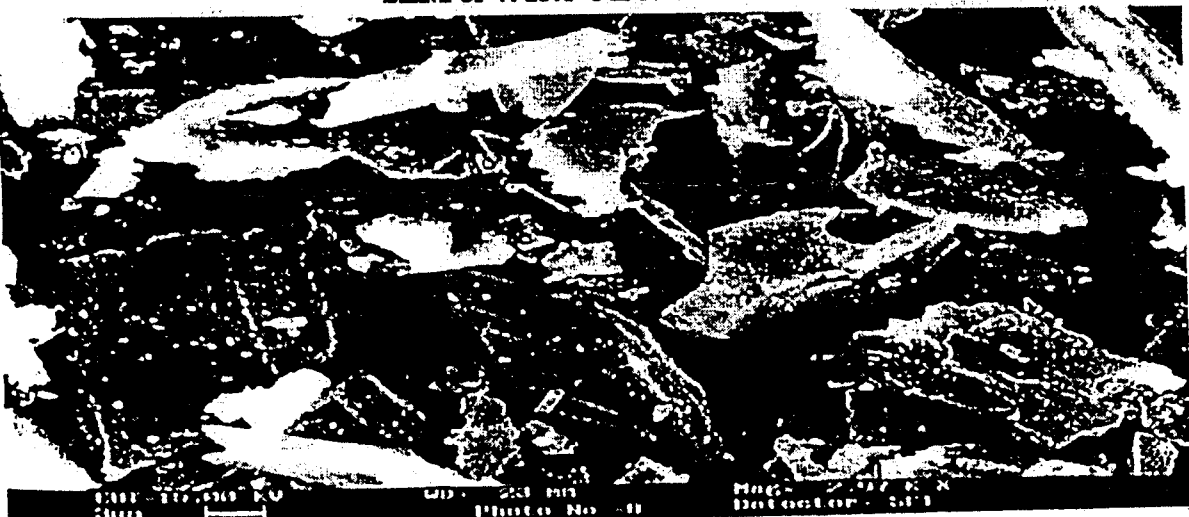
Characterisation of adsorbent

Particle size analysis and physicochemical properties, XRD and SEM, of the WC, BFA and AC are given in Table 1, and Figure 1, [4-5]. From the XRD patterns (not shown), major components identified in BFA were $CaSiO_3$, Al_2O_3, and $Ca_8Si_5O_{18}$, whereas AC mainly contained $CaSiO_3$, Al_2O_3, $Fe_2(SO_4)_3.9H_2O$, $Pb_5Cl(AsO_3)_3$, $PbSO_4$. Diffraction peaks corresponding to crystalline carbon were not observed in WC, BFA and AC. The other peaks indicated the presence of Fe_2O_3, MgO and CaO. The broad peak in WC and BFA were due to presence of silica. Scanning Electron Microscope SEM Figure 1. of WC and AC shows that the particles of AC are comparatively larger than that of WC; and there are pores between particles in both WC and AC. The SEM of BFA shows fibrous structure with large pore size with strands in each fibre. The SEM of AC also shows similar structure due to inherent fibre structure of the original raw material for its manufacture, however, the sizes of the fibre and inter-fibre space are smaller in comparison to BFA, The SEM of WC shows very fine particle size to the order of a micrometer or less. BFA had the lowest bulk density among the adsorbents Table 1. Amount of fixed carbon was also low in BFA in

SEM of Bagasse Fly Ash
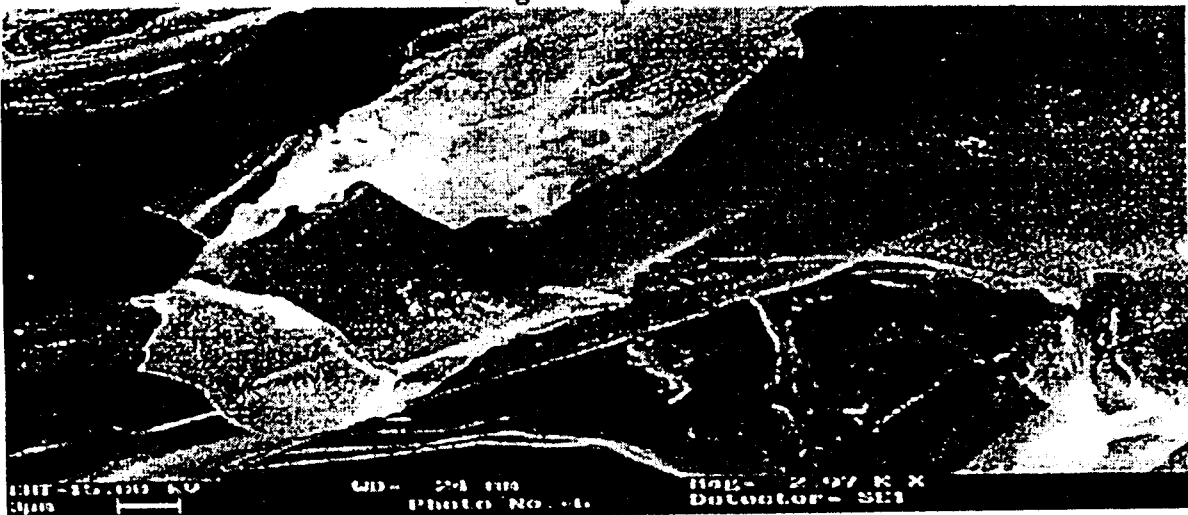
SEM of Waste Carbon

SEM of Activated Carbon

Figure 1. Scanning electron micrograph of various adsorbents

**Table 1.** Characteristics of adsorbents

Proximate analysis

Adsorbent	Inherent Moisture(%)	Ash (%)	Volatile Matter (%)	Fixed Carbon (%)	Bulk Density (kg/m³)
WC	4.85	5.1	13.33	76.62	308.03
BFA	3.63	73.36	2.34	20.67	185.51
AC	10.56	2.96	48.64	37.84	455.04

Chemical analysis

Adsorbent	Insoluble Residue(%)	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)
WC	90.3	79.13	9.56	4.22	2.67	2.5
BFA	86.16	84.96	6.29	1.75	2.05	2.08

Physical characteristics

Adsorbent	BET surface area (m²/g)	Pore volume (cm³/g)	Average pore diameter (A°)	Average particle size (μm)	Calorific value (KJ/kg)
WC	357.32	0.579	64.83	167.35	22279.8
BFA	168.83	0.101	23.97	167.35	4631.6

CHN analysis

Adsorbent	Carbon (%)	Hydrogen (%)	Nitrogen (%)
WC	66.75	2.38	10.90
BFA	16.36	9.77	2.55

comparison to AC and WC. High surface area, pore volume and pore size observed from the analyses for BFA and WC exhibit their potential for use as adsorbents.
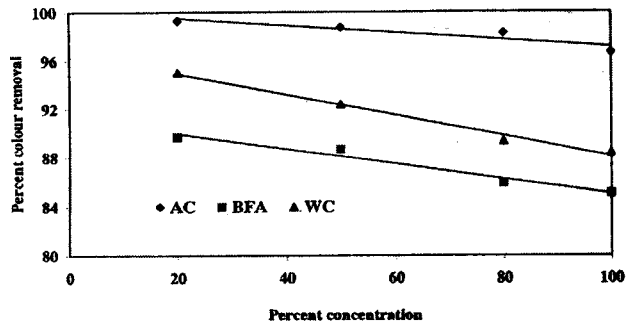
Effect of initial concentration and contact time

A given mass of adsorbent can adsorb only a fixed amount of adsorbate, so the initial concentration of adsorbate solution is very important. Effect of initial concentration on the removal of COD and colour is given in Figure 2. and 3. From the figures, it is evident that percentage removal of COD and colour decreased for all the adsorbents with the increase in initial COD and colour concentration.

The contact time between the pollutant and the adsorbent is of significant importance in the wastewater treatment by adsorption. A rapid uptake of pollutants and establishment of equilibrium in a short period signifies the efficacy of that adsorbent for its use in wastewater treatment. In physical adsorption most of the adsorbate species are adsorbed within a short interval of contact time. However, strong chemical binding of adsorbate with adsorbent requires a longer contact time for the attainment
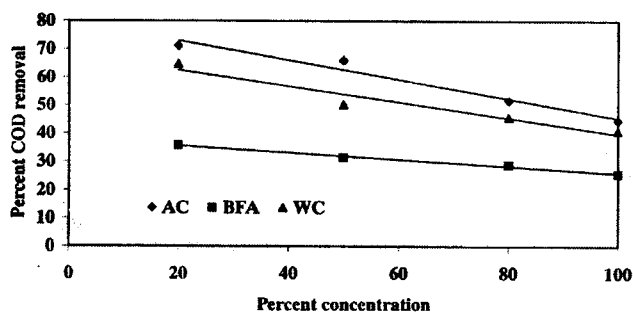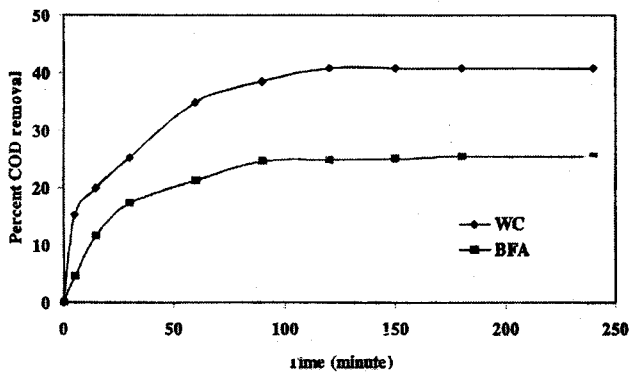

Figure 2. Effect of initial COD concentration of effluent on percent COD removal by different adsorbents (original COD concentration = 1960 mg/L, pH=3.0, temperature = 25°C, contact time = 240 min , AC dose = 50 mg/50 ml, BFA dose = 50 mg/50ml, WC dose = 25 mg/50ml)

of equilibrium. Available adsorption results reveal that the uptake of adsorbate species are fast at the initial stages of the contact period, and thereafter, it becomes slower near the equilibrium. In between these two stages of the uptake, the rate of adsorption is found to be nearly constant. This is obvious from the fact that a large number of vacant surface sites are available for adsorption during the initial stage, and after a lapse of time, the remaining
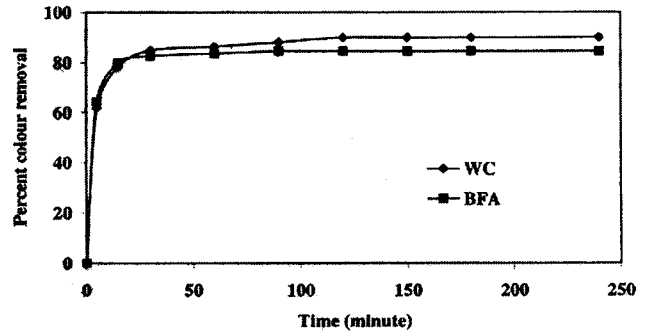
Figure 3. Effect of initial colour concentration of effluent on percent colour removal by different adsorbents (pH = 3.0, temperature = 25°C, contact time = 240 min AC dose = 50 mg/50 ml, BFA dose = 50 mg/50 ml, WC dose = 25 mg/50ml.

Figure 5. Effect of contact time on colour removal of effluent by different adsorbents (pH=3.0, temperature=25°C, BFA dose = 50 mg/50ml, WC dose=25 mg/50ml)

vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules of the solid and bulk phases. Figures 4 and 5, respectively, present the plot of percent COD and colour removed versus contact time for WC and BFA at adsorbent concentration of 1 and 0.5 g/L, respectively and the initial COD concentration of 1960 mg/L. The adsorption curves of contact time indicate the formation of mono-later coverage at the outlet interface of the adsorbents. The curved portion cf these graphs is due to surface mass transfer and final linear part to intraparticle diffusion. It is observed that the percent removal of COD and colour is very rapid during the initial period of time. Maximum COD gets removed in first 90 minutes whereas maximum colour removal occurs in first 30 minutes. Equilibrium is attained in 180 minutes for COD removal and in 120 minutes for colour removal for both WC and BFA. Accordingly all the batch experiments were conducted

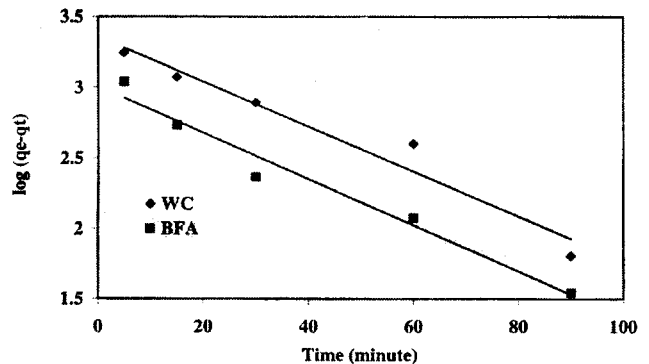with a contact time of 4 hours (240 minutes) under vigorous shaking conditions to attain the equilibrium.

Adsorption kinetic study

The kinetics of adsorption is very important from the point of view that it controls the process efficiency. In the present study, kinetic modeling of the COD removal from effluent has been done for WC and BFA as adsorbents by pseudo-first-order model, pseudo-second-order model, intraparticle diffusion model and Bangham's model.

Pseudo-first-order model: The pseudo-first-order equation is

$$\frac{dq_t}{dt} = k_f (q_e - q_t) \tag{1}$$

Where q_t is the amount of adsorbate adsorbed at time t (mg/g), q_e is the adsorption capacity in equilibrium (mg/g), k_f is the rate constant of pseudo-first-order model (min

Figure 4. Effect of contact time on COD removal of effluent by different adsorbents (original COD concentration = 1960 mg/L, pH = 3.0, temperature = 25°C, BFA dose = 50mg/50ml, WC dose=25mg/50 ml)

Figure 6. Pseudo first-order kinetic plots for COD removal of effluent by different adsorbents (original COD concentration = 1960 mg/L, pH=3.0, temperature=25°C, BFA dose = 50 mg/50 ml, WC dose = 25 mg/50ml)

Table 2. Kinetic parameters for the COD removal of effluent by different adsorbents

Pseudo-first-order-constants

Adsorbent	$k_f (min^{-1})$	$q_e (mg/g)$	$R1^2$(linear)	$R2^2$ (non-linear)
WC	0.0366	2287.523	0.9552	0.9774
BFA	0.0378	1019.0030	0.9772	0.9850

Pseudo-second-order constants

Adsorbent	h (mg/g min)	k_s (g/mg min)	R_1^2 (linear)	R_2^2 (non-linear)
Wc	609.8905	4.5549×10^{-5}	0.9953	0.9990
BFA	175.3634	7.6268×10^{-5}	0.9978	0.9977

Intra-particle diffusion constants

Adsorbent	K (mg/g min)	R_1^2 (non-linear)	$k_{id'2}$ (mg/g min)	R_2^2 (non-linear)
WC	244.0732	0.9862	15.0966	0.9987
BFA	268.0212	0.9927	20.2296	0.9968

^{1}), and t is the time (minute). After definite integration by applying the initial conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, the equation becomes [12].
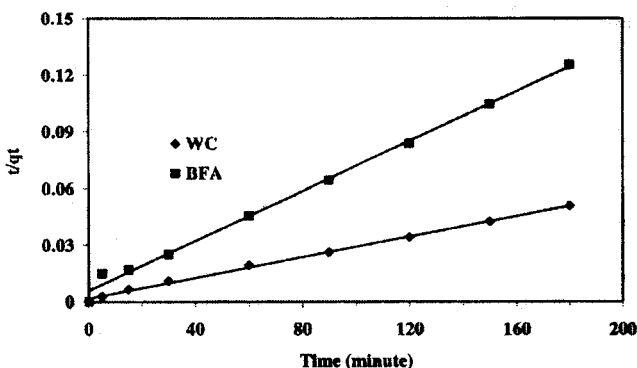
$$\log(q_e - q_t) = \log q_e - \frac{k_f}{2.303}t \qquad (2)$$

The plot of log(qe − qt) vs t gives straight-line Figure 6. The values of rate constant have been presented in table 2. These values indicate that the adsorption rate was very fast at the beginning of adsorption.

Pseudo-second-order model

The pseudo-second-order model can be represented in the following form [13].

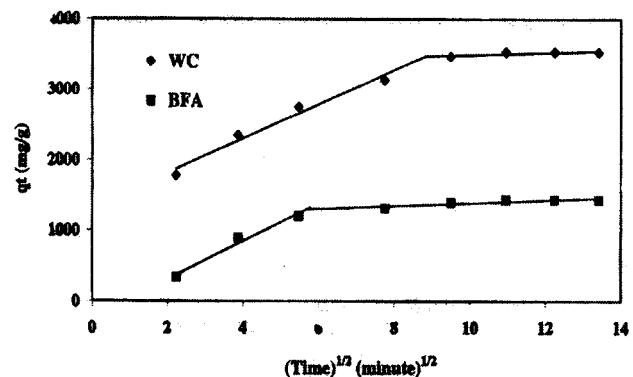$$\frac{dq_t}{dt} = k_s (q_e - q_t)^2 \qquad (3)$$

where k_s is the rate constant of pseudo-second-order model (in g/mg min). After integrating eq. (3) for boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, following form of equation can be obtained :

$$\frac{t}{q_t} = \frac{1}{k_s q_e^2} + \frac{1}{q_e}t \qquad (4)$$

the initial sorption rate, h (mg/g min), as $t \to 0$ can be defined as

$$h = k_s q_e^2 \qquad (5)$$

The initial sorption rate (h), the equilibrium adsorption capacity (q_e), and the pseudo-second order constant k_s can be determined experimentally from the slope and intercept of plot of t/q_t versus t (Figure 7.). Calculated

Figure 7. Pseudo second-order kinetic plots for COD removal by different adsorbents (original COD concentration = 1960 mg/L, pH=3.0, temperature = 25°C, BFA dose = 50 mg/50 ml, WC dose = 25mg/50ml)

Figure 8. Weber and Morris intraparticle diffusion plot for COD removal by different adsorbents (original COD concentration = 1960 mg/L, pH=3.0, temperature=25°C, BFA dose = 50mg/50ml, WC dose=25 mg/50ml
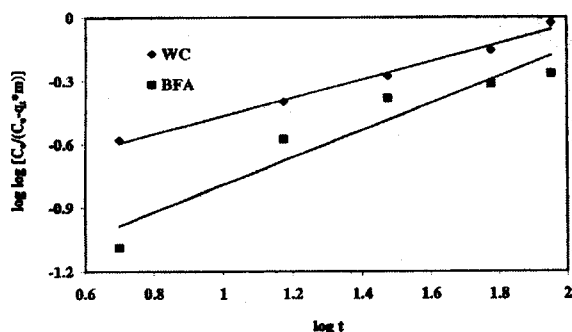
Figure 9. Bangham plot for COD removal by different adsorbents (original COD concentration = 1960 mg/L, pH=3.0, temperature=25°C, BFA dose=50mg/ml, WC dose=25mg/50ml)
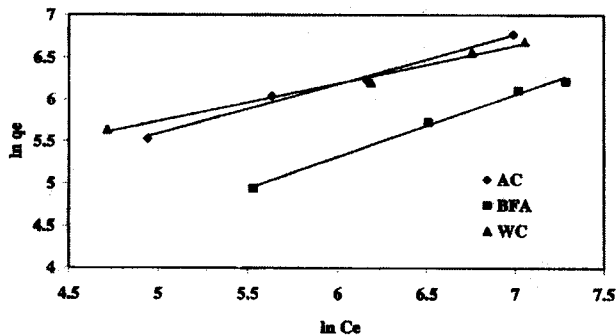

Figure 10. Frendulich isotherm plot for COD removal by different adsorbents (pH=3.0, temperature=25°C, contact time = 120 min. AC dose = 50 mg/50ml, BFA dose =50mg/50ml, WC dose=25mg/50ml.

correlation coefficients for pseudo-first-order model and pseudo-second-order model by using linear regression procedure for WC and BFA are shown in Table 2. As calculated correlation coefficients are closer to unity for pseudo-second-order kinetics model than the pseudo first-order kinetic model, therefore the sorption reaction could be better approximated by pseudo-second-order kinetics model. The k_s and h values as calculated from the Figure 7 are listed in Table 2. It can be seen that the h values for sorption on WC is higher than that on BFA.

Intraparticle diffusion study

The overall adsorption process may be controlled either by one or more steps, e.g. film or external diffusion, pore diffusion, surface diffusion and adsorption on the pore surface, or a combination or more than one step. In a rapidly stirred batch adsorption, the diffusive mass transfer can be related by an apparent diffusion coefficient which will fit the experimental sorption-rate data. A functional relationship common to most of treatments of intraparticle transport is that uptake varies almost proportionally with the square root of time, $(t^{1/2})$, rather than time, (t), itself [14].

$$q_t = k_{id} t^{1/2} \qquad (6)$$

where k_{id} is the intra-particle diffusion rate constant. Therefore, in Figure 8 plot of mass of COD adsorbed per unit mass of adsorbent, q_t vs $t^{1/2}$ is presented for two adsorbents viz., WC and BFA. It is evident form Figure 8 that adsorption follows two phases, viz. (I) a linear phase in which instantaneous extremely fast uptake takes place, and (II) a quasi-stationary state. In phase I, about 70% of the COD is uptaken by WC within a $t^{1/2}$ value of 5.5 min and manifests an average rate of uptake of about 500 mg/

g min$^{1/2}$. This is attributed to the instantaneous utilisation of the most readily available adsorbing sites on the adsorbent surface. In the case of BFA, about 62% of the COD is uptaken within a $t^{1/2}$ value of 5.5 min and manifests an average rate of uptake of about 220 mg/g min$^{1/2}$. Phase II may be attributed to a very slow diffusion of the adsorbates from the surface film into the micropores which are the least accessible sites of adsorption. This also stimulates a very slow rate of migration of adsorbates from the liquid phase on to the adsorbent surface. The values of intra-particle diffusion rate parameters are given in Table 2.

Bangham's equation

Kinetic data were further used to know about the slow step occurring in the present adsorption system using Bangham's equation [15].

$$loglog = \left(\frac{C_0}{C_0 - q_t m} \right) = log \left(\frac{k_0 m}{2.303 V} \right) + \alpha log(t) \qquad (7)$$

where C_0 is the initial concentration of adsorbate in solution (mg/L), V is the volume of solution (mL), m is the weight of adsorbent per liter of solution (g/L), q_t (mg/g) is the amount of adsorbate retained at time t, and $\alpha(<1)$ and k_0 are constants. The double logarithmic plot (Figure 9.) according to above equation yielded perfect linear curve for COD removal by WC showing that the diffusion of adsorbate into pores of the sorbent basically controls the adsorption process [16]. However, for BFA the curve is not perfect linear hinting that pore-diffusion may not be the only rate-controlling step.

Adsorption Isotherm

For better understanding, determination of feasibility of

Table 3. Isotherm parameters for COD removal by bagasse fly ash

Freundlich constants

Adsorbent	$K_F (mg/g)/(mg/L)^{1/n}$	$1/n$	R_1^2(linear)	R_2^2 (non-linear)
WC	32.4579	0.4517	0.9890	0.9945
BFA	2.3069	0.7464	0.9939	0.9970
AC	14.0267	0.5901	0.9882	0.9941

Langmuir constants

Adsorbent	$K_L (L/mg)$	$q_m(mg/g)$	R_L	R_1^2 (linear)	R_2^2(non-linear)
WC	0.0025	1037.472	0.1678	0.9515	0.9754
BFA	0.0006	1139.046	0.4771	0.9851	0.9925
AC	0.0014	1394.632	0.2611	0.9479	0.9736

Redlich-Peterson constants

Adsorbent	$K_R (L/mg)$	a_R	β	R_1^2 (linear)	R_2^2 (non-linear)
WC	232.8499	6.9856	0.5517	0.9924	0.9962
BFA	0.6629	0.0016	0.8601	0.9924	0.9962
AC	5.4237	0.1414	0.5330	0.9764	0.9881

Dubnin-Radushkevich constants

Adsorbent	$q_s (mg/g)$	$E(KJ/mol)$	R_1^2(linear)	R_2^2(non-linear)
WC	672.3191	0.0165	0.8393	0.9161
BFA	453.9435	0.0063	0.9298	0.9643
AC	655.1076	0.0124	0.7945	0.8913

Temkin constants

Adsorbent	$K_T (L/mg)$	B_1	R_1^2 (linear)	R_2^2 (non-linear)
WC	0.0283	218.0959	0.9460	0.9726
BFA	0.0074	209.1481	0.9876	0.9938
AC	0.0149	296.9471	0.9551	0.9772

adsorbing system, selection of adsorbents and evaluation of dose of adsorbents, etc. It is necessary to study the modeling of equilibrium data. Various adsorption isotherm models have been studied in the present study.

Freundlich and Langmuir isotherms

The Freundlich [17] isotherm was derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface. Whereas in the Langmuir [18] theory the basic assumption was that sorption takes place at specific homogenous sites within the adsorbent. The adsorption data of were correlated with Freundlich and Langmuir models, which are represented by the following equations:

Freundlich isotherm $\ln q_e = \ln K_F + 1/n \ln C_e$ (8)

Langmuir isotherm $\dfrac{C_0}{q_e} = \dfrac{C_e}{q_m} + \dfrac{1}{K_L q_m}$ (9)

where K_F is Freundlich constant (L/mg), $1/n$ is the heterogeneity factor, K_L is the langmuir adsorption constant (L/mg) related to energy of adsorption and qm signifies adsorption capacity (mg/g). Freundlich (ln q_e vs ln C_e) and Langmuir (C_e/q_e vs C_e) plots at 25°C are given in Figures 10 and 11 respectively for the COD removal by AC, BFA and WC. The values of Langmuir and Freundlich constants along with calculated correlation coefficients for COD removal of effluent at 25°C are shown in Table 3. As seen, Freundlich isotherm yielded better fit to the experimental data as compared to Langmuir isotherm for all the adsorbents used in the study. The essential characteristics of a Langmuir isotherm can
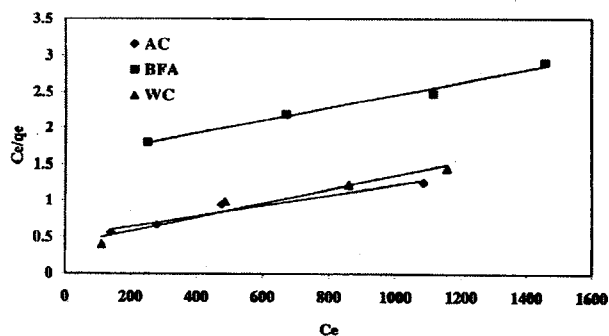
Figure 11. Langmuir isotherm plot for COD removal by different adsorbents (pH=3.0, temperature=25°C, contact time=120 minutes, AC dose=50mg/50ml, BFA dose=50mg/50ml, WC dose = 25 mg/50 ml)

expressed in terms of a dimensionless separation factor, R_L [19] which describes the type of isotherm and is defined by

$$R_L = 1/(1+K_L C_0) \qquad (10)$$

where K_L is a Langmuir constant which indicates the nature of adsorption and indicates the shape of the isotherm accordingly. C_0 is the initial concentration of adsorbate.

If :   > 1   unfavourable

        = 1   linear

R_L — 0<   <1   favourable

        = 0   irreversible

The values of R_L for COD removal of effluent are given in Table 3. The value of R_L was found to be less than 1 for all the three adsorbents so adsorption using these adsorbents
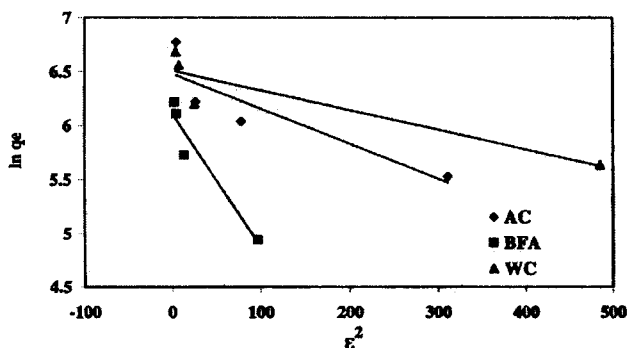

Figure 12. Redlich-Peterson isotherm plot for COD removal by different adsorbents (pH=3.0, temperature=25°C, contact time=120 minutes, AC dose = mg/50mg/50ml, BFA dose=50mg/50ml, WC dose=25mg/50ml)

was favorable.

The values of 1/n were also found to be less than 1 [20]. So, it again proves adsorption to be favourable.

Redlich-peterson isotherm

Redlich and Peterson [21] model combines elements from both the Langmuir and Freundlich equation and the mechanism of adsorption is a hybrid and does not follow ideal monolayer adsorption. The Redlich-Peterson isotherm has a linear dependence on concentration in the numerator and an exponential function in the denominator. The R-P equation is a combination of the Langmuir and Freundlich models. It approaches the Freundlich model at high concentration and is in accord with the low concentration limit of the Langmuir equation. Furthermore, the R-P equation incorporates three parameters into an empirical isotherm, and therefore, can be applied either in homogenous or heterogeneous

Figure 13. Dubnin-Radushkevich isotherm plot for COD removal by different adsorbents (pH=3.0, temperature=25°C, contact time=120 min   AC dose=50mg/50ml, BFA dose=50mg/50ml, WC dose=25 mg/50ml)
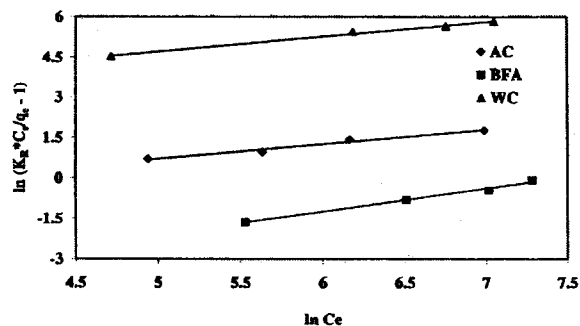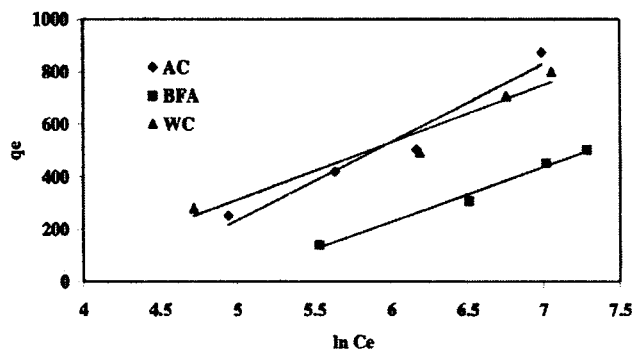

Figure 14. Temkin isotherm plot for COD removal by different adsorbents (pH=3.0, temperature=25°C, contact time=120 min   AC dose=50mg/50ml, BFA dose=50mg/50ml, WC dose=25mg/50ml)

Table 4. Removal of COD and Colour from Different Effluents

Adsorbents	Adsorbent dose, Kg/m³	Percent Removal		Adsorbent cost, Rs/tonne	Treatment cost, Rs/tonne of paper produced	Treatment cost, Rs/kg of COD removed
		COD	Colour			
AC	1	44.59	97.67	30,000-40,000	1800-2800	15000-20000
BFA	1	25.64	86.05	5000*	300-350	2500
WC	0.5	40.89	88.39	5000*	150-175	1250

* handling charges of adsorbents

Basis : Initial COD of effluent = 1960 mg/L

Effluent generated/tonne of paper produced = 60 − 70 m³.

systems due to the high versatility of the equation.

It can be described as follows :

$$q_e = \frac{K_R C_e}{1 + \alpha_R C_e^\beta} \qquad (11)$$

where K_R is R-P isotherm constant (L/g), α_R is R-P isotherm constant (L/mg) and β is the exponent which lies between 1 and 0, where $\beta = 1$

$$q_e = \frac{K_R C_e}{1 + \alpha_R C_e} \qquad (12)$$

It becomes a Langmuir equation. Where $\beta = 0$

$$qe = \frac{K_R C_e}{1 + \alpha_R} \qquad (13)$$

i.e. the Henry's Law equation

Eq. (11) can be converted to a linear form by taking logarithms :

$$\ln\left(K_R \frac{C_e}{q_e} - 1\right) = \ln a_R + \beta \ln C_e \qquad (14)$$

Plotting $\ln (K_R C_e/q_e - 1)$ against $\ln C_e$ to obtain the isotherm constants is not applicable because of the three unknowns, α_R, K_R and β. Therefore, a minimization procedure was adopted to solve equation (14) by maximizing the correlation coefficient between the theoretical data for q_e predicted from equation (14) and experimental data. Therefore, the parameters of the

equations were determined by minimising the distance between the experimental data points and the theoretical model predictions with the solver add-in function of the Microsoft excel.

The linearised form of the R-P isotherm plots for COD removal of effluent onto AC, BFA, and WC are presented in Figure 12. The R-P isotherm constants α_R, K_R and β and the correlation coefficients, R^2, for the R-P isotherm are listed in Table 3. The correlation coefficients as given in Table 3. are significantly higher than both the Langmuir and the Freundlich values. Therefore, Redlich-Peterson was certainly the best fits the isotherm equation of the three isotherms studied so far.

Dubinin and Radushkevich isotherm (D - R)

Another equation used in the analysis of isotherms was proposed by Dubinin and Radushkevish [22].

$$q_e = q_s \exp\left(-B\varepsilon^2\right) \qquad (15)$$

whereas q_s is D-R constant and ε can be correlated :

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \qquad (16)$$

The constant B gives the mean free energy E of sorption per molecule of sorbate when it is transferred to the surface of the solid from infinity in the solution and can be computed using the following relationship [23].

$$E = \frac{1}{\sqrt{2B}} \qquad (17)$$

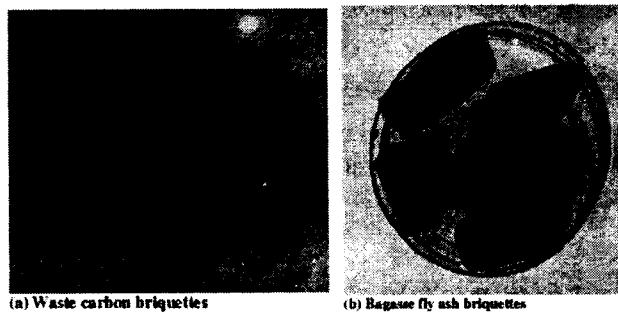Calculated Dubinin-Radushkevich constants for COD

(a) Waste carbon briquettes   (b) Bagasse fly ash briquettes

Figure 15. Waste carbon and bagasse fly ash briquettes

removal by AC, BFA and WC shown in Table 3, the D-R isotherms are plotted against the experimental data points, as shown in Figure 13. From this Figure, it is clear that the sorption energy value is lowest for removal by BFA. The values of correlation coefficients are much lower than the other four isotherms values. In all cases, the D-R equation represents the poorer fit of experimental data than all other isotherms.

Temkin isotherm

Temkin isotherm contains a factor that explicitly takes into account adsorbing species-adsorbate interactions. This isotherm assume that (i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbate-adsorbate interactions, and (ii) adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy [24]. Temkin isotherm is represented by following equation.

$$q_e = \frac{RT}{b} \ln (K_T C_e) \tag{18}$$

Above equation can be expressed in its linear form as :

$$q_e = B \ln K_T + B \ln C_e \tag{19}$$

$$\text{where } B = \frac{RT}{b} \tag{20}$$

A plot of q_e versus $\ln C_e$ enable the determination of the isotherm constants K_T and B. K_T is the equilibrium binding constant (L/mg) corresponding to the maximum binding energy and constant B is related to the heat of adsorption. This isotherm is shown in Figure 14 and parameter values are given in Table 3. This isotherm yields better fit to the experimental data only as compared to Dubinin-

Radushkevich isotherm for all the adsorbents used in the study. In all, Redlich-Peterson isotherm best fits the equilibrium isotherm data of all the isotherms studied.

Economic Analysis

The economic evaluation of the treatment process using AC, BFA and WC is presented in Table 4. Removal efficiency was found in order AC>WC>BFA. Though the percentage removal by AC is higher than that of WC and BFA, the overall cost of treatment with WC and BFA is lower (Table 4.), as these adsorbents are available almost free of cost involving only transportation and handling charges. As the calorific value of both WC and BFA are high (Table 1.), organic matter laden WC and BFA could be used to make fire briquettes. Fire briquettes made from WC and BFA are shown in Figure 15. Revenue generated from briquettes could compensate for transportation and handling charges of WC and BFA.

CONCLUSION

The percent removal of COD and colour was found higher in case of lower concentration. Kinetics of removal followed pseudo-second order rate expression. Intraparticle diffusion was found to be rate controlling mechanism for adsorption. Equilibrium data confirms applicability of Redlich-Peterson adsorption isotherms. Though the amount of removal by activated carbon was higher than that of waste carbon and bagasse fly ash, the overall cost of treatment with waste carbon and bagasse fly ash was lower, as these adsorbents are available almost free of cost involving only handling charges. Economic consideration and adsorbent characterization of the adsorbents show that WC and BFA could be viable alternative adsorbents for treatment of pulp and paper mill effluents.

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