Utilisation of Bagasse Fly Ash and Carbon Waste from Fertiliser Plant for Treatment of Pyridine and 3-Picoline Bearing Wastewater

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Abstract: The present work explores the possibility of utilizing sugarcane bagasse fly ash and carbon waste obtained from sugar mills and nitrogenous fertilizer plants, respectively for the removal of pyridine and 3-picoline from waste water. The adsorbing capacity of both adsorbents has been compared with that of activated carbon. Batch studies were conducted to see the effect of contact time, adsorbent dose, initial concentration and pH on the removal of pyridine and 3-picoline. Equilibrium data were fitted with Langmuir and Freundlich isotherms. Adsorptive capacities were found to be in the order: activated carbon > carbon waste > bagasse fly ash. Adsorption was found to follow first order kinetics and intra-particle diffusion was found to be rate controlling. Two-stage batch adsorption (using bagasse fly ash and carbon waste) was found

to give 85-100% removal of pyridine. Column studies were also conducted for the removal of pyridine using bagasse fly ash as adsorbent. BDST model was used to analyze the column data.

Keywords: Baggase fly ash; carbon waste; activated carbon; pyridine; 3-picoline; wastewater.

Introduction

Pyridine and its alkyl derivative picoline are the parent of a series of important medicinal, agricultural and industrial chemicals. These are used in the synthesis of vitamins and drugs, etc. They are highly toxic, and intensely odorous compounds, and are detectable at very low concentrations. Pyridine and 3-picoline manufacturing plants are plagued with the problem of intense odour emanating either from the waste water or from the handling and storage facilities. Removal of pyridine and picoline from wastewater stream is therefore of vital importance. In a typical industrial effluent pyridine and its alkyl derivative, 3-picoline in are present in trace amounts [in the range: pyridine – 0.01% to 0.05% and 3-picoline range– 0.0002%]

Activated carbon has for long been used as an adsorbent for the removal of organics and other non-biodegradable materials from waste water. Kumar et al. [1995] have studied the removal of pyridine from pyridine bearing wastewater using activated carbon. High cost and loss in regeneration are, however, seen as a major deterrents in the use of activated carbon in developing countries. In view of this factor, low cost alternate adsorbents have received considerable attention for use as adsorbents [1-7]. Mall et al. [1] and Bailey et al. [2] have critically reviewed the use of such adsorbents.

About 0.6 million tonnes/year of sugarcane bagasse fly ash is available from the sugar industry in India. The surface area of the bagasse fly ash is generally found to be in the range 160-360 m^2/g. In nitrogenous fertilizer plants, the fine carbon particles produced during the partial oxidation of heavy fuel oil are scrubbed from the gas stream producing an aqueous carbon slurry containing 2-3 % carbon. It is estimated that production of carbon waste (CW) is about 1.45 kg per tonne of ammonia produced. The carbon waste has the surface area in the range of 300- 400 m^2/g.

The present paper aims at exploring the possibility of utilizing bagasse fly ash and carbon waste for the removal of pyridine and 3-picoline from waste water.

Experimental

Materials: Bagasse fly ash (BFA) obtained from Deoband Sugar Mill (U.P, India), carbon waste (CW) from NFL (Panipat, Haryana, India,) and laboratory grade activated carbon (AC) procured from M/s E. Merck India were used in the present investigation.

Instrumental: Proximate analysis and Chemical analysis of three adsorbents, namely BFA, CW and AC were performed using standard procedures. Bulk densities of the adsorbents were determined using MAC bulk density meter. Particle size analysis of bagasse flyash was done using standard sieve analysis, where as those of carbon waste and activated carbon were determined by Malvern particle size analyser. Carbon, hydrogen and nitrogen analysis was done using Perkin Elmer CHN elemental analyser. X-Ray diffraction (XRD) analysis have been carried out using Phillips diffraction unit (Model PW 1140/90) using copper target with nickel as filter media , and K radiation maintained at 1.542 Å. Goniometer and chart speed were maintained at 1° min^{-1} and 1 cm min^{-1}, respectively. Scanning Electron Micrographs (SEM) were obtained by using LEO 435 VP Scanning electron microscope. BET surface area, pore volume distribution and pore diameter of the adsorbents were determined using Flow sorb 2300 surface area analyser. UV spectrophotometer (Perkin Elmer Lambda 35) was used to determine the concentration of pyridine and 3-picoline in the synthetic water samples.

Batch and Column Studies: Batch experiments were conducted to study the effect of important parameters like adsorbent dose, initial concentration, pH, contact time etc. For each experimental run, synthetic solutions of pyridine and 3-picoline of known concentration and pH were used for different adsorbents. The synthetic solution-adsorbent mixture was agitated in a temperature controlled shaking water bath at a constant speed of 145 revolutions per minutes (rpm) at 30 ± 1°C. In case of pyridine 20kg of bagasse fly ash, 18kg of carbon waste 5kg of activated carbon per cubic meter of the wastewater was used, while in case of picoline 4kg of carbon waste and 1.1kg of activated carbon per cubic meter of wastewater was used. Samples were withdrawn at appropriate time intervals, filtered and analysed for residual pyridine, and 3-picoline concentrations. For adsorption isotherms, water samples of different concentrations were agitated with known amounts of adsorbents till the equilibrium was achieved. Two stage adsorption studies were also carried out for the removal of pyridine using BFA and CW. Filtrate obtained from the first stage (after shaking for stipulated time) was again treated with fresh adsorbent and the removal efficiency for two stage treatment was determined. A plexiglass column of 25mm diameter and 1000mm length was used for packed column adsorption test using BFA. Pyridine solution having initial concentration of 200 mg/l was used for column studies with bed heights of 150 mm, 300 mm and 600 mm and flow rate of 2.2 l/hr.

Results and Discussions

Characterization of adsorbents: The characteristics of the adsorbents are sbown in Tables 1-2. XRD and SEM analyses for BFA, CW and AC are presented in Figs 1, 2 and 3 respectively. BFA has the lowest bulk density among the adsorbents. Amount of fixed carbon is also low in BFA in comparison to AC and CW. High surface area, pore volume and pore size observed from the analyses for BFA and CW exhibit their potential for use as adsorbents. 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. The sizes of the fibre and inter-fibre space are smaller in comparison to BFA. The SEM of CW shows very fine particle size to the order of a micrometer or less. From the XRD patterns major components in BFA are identified as $CaSiO_3$, Al_2O_3, and $Ca_8Si_5O_{18}$, whereas $CaSiO_3$, Al_2O_3, $Fe_2(SO_4)_3.9H_2O$, $Pb_5Cl(AsO_3)_3$, $PbSO_4$ in AC(Powder Diffraction Files, 1979). Diffraction peaks corresponding to crystalline carbon were not observed in BFA and AC. The other peaks indicate the presence of Fe_2O_3, MgO and CaO. The broad peak in BFA and CW are due to presence of silica.

Table 1 : Proximate Analysis of Adsorbents

S. No.	Adsorbent	Surface Moisture (%)	Inherent Moisture (%)	Ash %	Volatile Matter (%)	Fixed Carbon (%)	Bulk Density (kg/m^3)
1	Bagasse Fly ash	0.11	3.63	73.36	2.34	20.67	185.51
2	Carbon Waste	10.74	4.85	5.2	13.33	76.62	308.03
3	Activated Carbon	10.68	10.56	2.96	48.64	37.84	455.04

Bagasse fly ash : Surface area (m^2/g): 168.83; Pore volume (cm^3/g): 0.101;Average pore dia (Å): 23.97
Average particle size (μ): 167.35; Calorific value (kJ/kg): 4631.6

Carbon waste: Surface area (m^2/g): 357.32; Pore volume (cm^3/g): 0.579;Average pore dia (Å): 64.83
Average particle size (μ): 167.35; Calorific value (kJ/kg): 22279.8

Table 2 : Chemical Analysis of adsorbents

S. No.	Adsorbent	Insoluble residue (%)	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)
1	Bagasse Fly ash	86.16	84.96	6.29	1.75	2.05	2.08
2	Carbon waste	90.3	79.13	9.56	4.22	2.67	2.5

CHN analysis:
Bagasse fly ash: C= 16.36%, H: 9.77% , N: 2.55%; carbon waste : C= 66.75%, H: 2.38, N: 10.90%

Batch Adsorption Studies

Effect of Adsorbent Dose and pH: Increase of the adsorbent dose (BFA and CW) increases the percentage removal of pyridine and 3-picoline up to a value and there after the percentage removal remains almost constant. For larger concentration of adsorbent the adsorption sites are more and the adsorbate molecules have to travel considerable distance in order to reach these sites. Therefore, no effect on adsorbate removal is observed on further increase in adsorbent dose. A typical plot for pyridine is shown in Fig. 4. The pH of the solution affects the surface charge of the adsorbents as well as the degree of ionisation and speciation of different components. Basic pH range facilitates the removal of pyridine. Effect of pH on removal of pyridine is shown in Fig. 5. Maximum removal is found at pH 8.0.

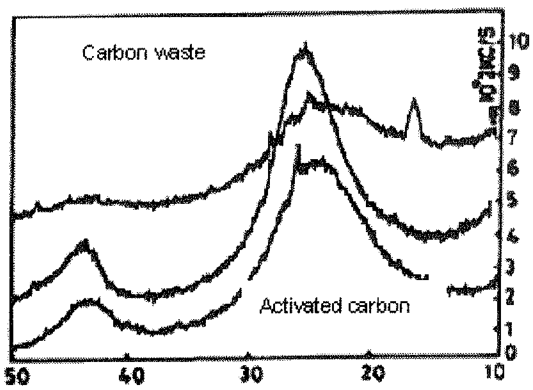

Fig. 1 X-ray Diffraction

Fig. 2 SEM of Bagasse Flyash

Fig. 3 SEM of Carbon waste

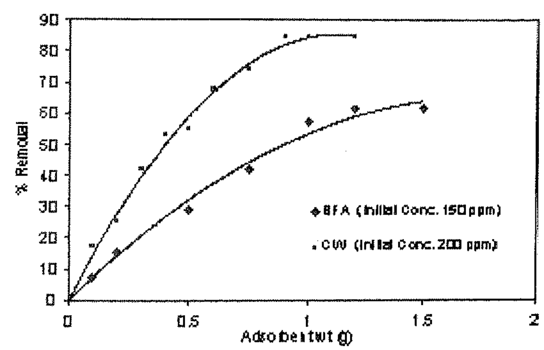

Fig. 4: Effect of Adsorbent Dose on Removal of Pyridine

Effect of Contact Time and initial concentration: The contact time between the pollutant and the adsorbent is of significant importance. A rapid uptake of components and establishment of equilibrium in a short period signifies the efficacy of that adsorbent for its use in wastewater treatment. Figs 6 shows the typical plot for 3-picoline. A similar though sluggish removal pattern was observed for pyridine using BFA. It is found that the rate of removal is very rapid during initial 30-50 minutes and, thereafter, it starts decreasing. No significant change is observed after 180 minutes. This can be explained on the basis of the fact that a large number of vacant surface sites are available for adsorption during the initial stage, and after some time, the remaining vacant surface sites are difficult to occupy due to repulsive forces between the solute molecules in the solid and the bulk phase.

The initial concentration of pyridine and 3-picoline on adsorption is found to follow the usual pattern i.e. percentage removal decreases with the increasing initial concentration of adsorbate solution. Fig. 6 shows a typical plot of 3-picoline - CW system. Adsorption studies revealed that the removal efficiency of adsorbents were in the following order: Activated carbon > Carbon waste > Bagasse fly ash.

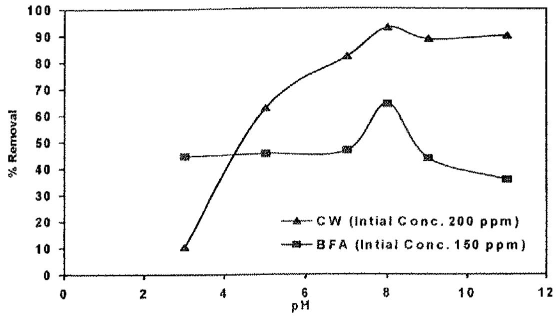

Fig. 5: **Effect of pH on Removal of Pyridine**

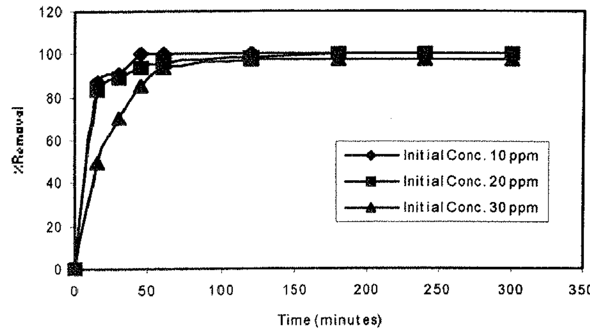

Fig. 6: **Effect of Contact Time and initial concentration(Ci) on Removal of 3-Picoline using carbon waste as adsorbent**

Kinetics of adsorption : The Lagergren equation has been used by a number of investigators [4,5,7] to study the adsorption kinetics:

$$\log(q_e - q) = \log q_e - \frac{k}{2.3}t$$

where q_e = amount of adsorbate adsorbed at equilibrium, (mg/g); q = amount of adsorbate adsorbed at time t, (mg/g); k = adsorption rate constant, (min^{-1}) and t = time, (min).

A plot of log (q_e – q) against time is shown in Fig. 7. The straight-line plots show the validity of Lagergren equation. Table 3 gives the value of adsorption rate constant (k) for different adsorbates with different adsorbents.

Intra-particle diffusion study: A functional relationship commonly used to describe the intra-particle transport is the plot between mass of solute adsorbed per unit mass of adsorbent (q) and square root of contact time ($t^{0.5}$). The linear nature of the plot shows that the controlling mechanism for adsorption is intra-particle diffusion [1]. The plots for pyridine and 3-picoline are shown in Fig. 8.

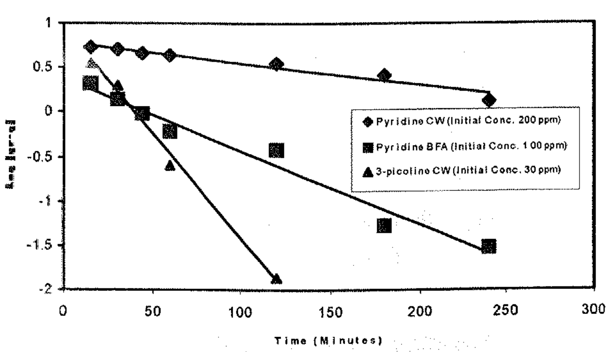

Fig. 7: Lagergren Plot for Removal of Pyridine and 3-Picoline

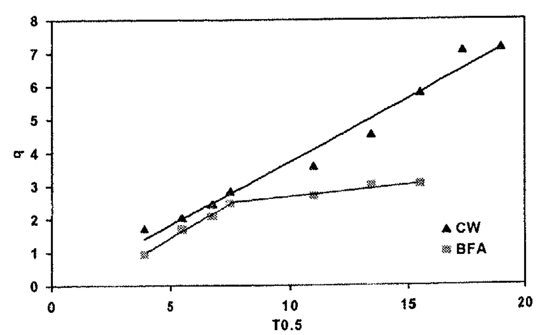

Fig. 8: Weber and Morris Intra-particle Diffusion Plot for Removal of Pyridine

The plots are found to be linear for a wide range of contact time for CW-pyridine system. However, the plots of BFA-pyridine system and CW- 3-picoline system showed two different linear regions. The initial portion of the plot shows the dominance of due to external mass transfer followed by the region showing intra-particle diffusion dominance. This indicates that the controlling mechanism is intra-particle diffusion. The values of intra-particle diffusion rate parameters are given in Table 3.

Table 3 : Lagergren constant and Intra-particle diffusion rate parameter

Adsorbate	Lagergren constant K (min^{-1})		Intra-particle diffusion rate parameter k ($mg\ g^{-1}\ min^{-0.5}$)	
	Bagasse fly ash	Carbon waste	Bagasse fly ash	Carbon Waste
Pyridine	0.00313	0.00580	0.4247	0.3784
3-Picoline	-	0.05405	-	0.9220

Adsorption isotherm equations: Various isotherm equations have been used to describe the equilibrium nature of adsorption. Out of these Freundlich and Langmuir isotherm equations are widely used by researchers in the field of environmental engineering.

Freundlich isotherm $q_e = K_F C_e^{1/n}$

The Langmuir isotherm $q_e = \frac{q_m K_A C_e}{1 + K_A C_e}$

The equilibrium data for the removal of pyridine and picolin fitted well both the Langmuir and Freundlich isotherms except in case of BFA -pyridine system. Typical Langmuir isotherm for pyridine and Freundlich isotherm for Picolin is given in Figs 9 and 10 respectively. Langmuir isotherm was not found applicable for pyridine-BFA system.

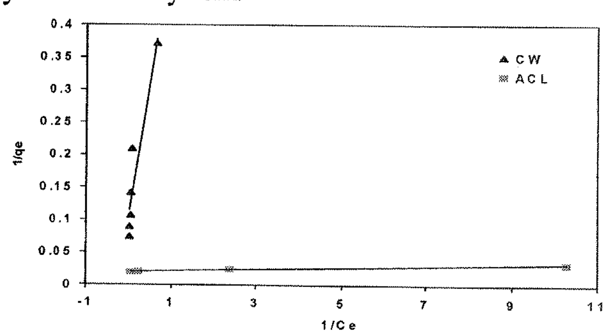

Fig. 9: Langmuir Isotherm for Removal of Pyridine

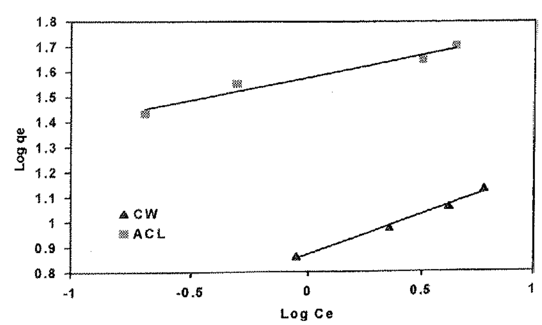

Fig. 10: Freundlich Isotherm for Removal of 3-Picoline

The values of parameters for Freundlich and Langmuir isotherms are given in Table 4. The values of 1/n for Frendulich isotherm were found to be less than 1 showing that adsorption is favourable [8].

Table 4 : Isotherm parameter for different adsorbate-adsorbent system

Adsorbate	Adsorbent	Freundlich Isotherm		Langmuir Isotherm	
		K_F $(mg/l)^{-1/n}$	n	q_m (mg/g)	K_A (mg^{-1})
Pyridine	BFA	2.19	6.51	-	-
	CW	2.00	2.30	34.36	0.01
	ACL	40.40	10.07	49.50	15.54
3-Picoline	CW	7.44	31.37	14.08	1.17
	ACL	37.76	5.56	49.50	6.31

Two Stage Adsorption: Two stage adsorption studies were carried out for the removal of pyridine using BFA and CW. Filtrate obtained from the first stage (after shaking for 5.0 hrs) was again treated with fresh adsorbent and the total removal efficiency of pyridine was found to be 84.28% in case of bagasse flyash and 100% in case of carbon waste, respectively.

Adsorption of pyridine in the fixed bed of bagasse fly ash: Bohart -Adams Model has been commonly used to predict adsorption capacity of a fixed bed adsorber [9].

$$t = \frac{N_0}{C_{A0}u} Z - \frac{1}{C_{A0}K_a} \ln(\frac{C_{A0}}{C_{Ab}} - 1) \qquad \text{or} \qquad t = m_a Z + C$$

Where C_{Ab} = desired concentration of adsorbate at break through, (mgl^{-1}); K_a = rate constant, (lmg^{-1}); N_0 = adsorptive capacity of the adsorbent, (mgl^{-1}); Z = depth of the adsorbent bed in the column (m); u = linear velocity of the feed solution in the bed (ms^{-1}); t = service time of columns.

Figure 11 presents the breakthrough curves (C/C_o Vs time) for pyridine in a column of bagasse flyash. As the bed height increases the curve becomes less steep. A plot between bed height (Z) and service time (t) that verifies Bohart -Adams Equation is shown in Fig. 12.

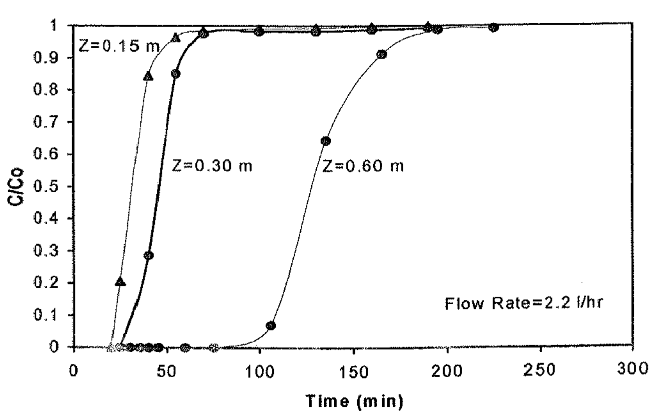

Fig. 11: Breakthrough Curves for Removal of Pyridine by Bagasse Fly Ash

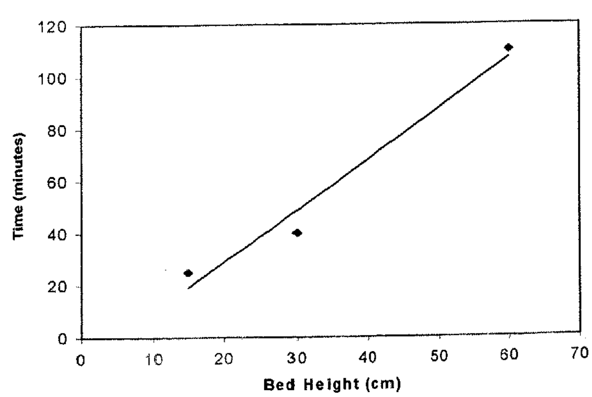

Fig. 12 : BDST Plot for Bagasse Fly Ash

Economic Evaluation of Adsorbents

Economic evaluation of the process has been given in Table 5. It may be seen that cost of bagasse fly ash and carbon slurry is almost available at no cost except handling charges. Hence, we can consider the use of the low cost adsorbents for large scale industrial use which will prove economical.

Table 5 : Economic evaluation based on adsorption capacity of adsorbent (mg/g of adsorbent)

Adsorbate	Adsorption Capacity, mg/g		
	BFA	CW	Activated carbon
Pyridine (150 ppm)	4.55	7.06	29.98
3-Picoline (30 ppm)	-	7.27	27.08
Cost (Rs./tonne)	5000	5000	40,000-50,000

Conclusions

It was observed that bagasse flyash and carbon waste which are the wastes from sugar mills and nitrogenous fertilizer plants are the potential adsorbents for the removal of pyridine and 3-picoline from water streams. About 85-100% removal is obtained for these adsorbates. The adsorption was found to be rapid in the initial stage of contact followed by a slow removal later. Adsorption follows simple first order kinetics. The adsorption equilibrium data could be represented by Langmuir and Freundlich isotherms. BDST model is valid for packed bed adsorption of pyridine on BFA. The adsorption process using bagasse fly ash and carbon waste is economical in comparison to that using AC.

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