Pyrolysed Bagasse Char-A Low Cost Effective Effluent System For Pulp And Paper Mill

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ABSTRACT

Pyrolysed bagasse char has been used as cheap carbonaceous adsorbent for treatment of lignin bearing waste water from pulp and paper mill industry. Effect of various parameters like pH, absorbent dose, initial COD concentration, adsorption isotherm, kinetics of removal and colour removal efficiency have been presented. Pyrolysed bagasse was found suitable for treatment of lignin bearing waste water and adsorption capacity was quite comparable to activated carbon.

INTRODUCTION

Indian industry accounts for 6% of total water demand of all sectors of the economy. A sound water management strategy for industry assumes significance when one considers that water requirement of the industry is going to be doubled by 2000 AD and become eight fold by 2025 AD (1). Water consumption in Indian industries is much higher than in developed countries.

Paper industry takes from nature a wide variety of cellulosic and noncellulosic raw materials and consumes large amount of water in various stages of its operation. It generates almost equal quantity of waste water (about 200-350 M^3 per tonne of paper) having high BOD, COD, colour, suspended solids, alkalinity and at times a number of toxic compounds. Characteristics of wastewater and typical generation from large integrated mills, agro based and waste paper based mills given in **Table-1 (2).** With projected demand of 5.0 million tonnes of paper, board and newsprint, Indian paper industry will be requiring about 1250 million cubic meters of water by 2000 AD with generation of equal amount of waste water. Water consumption in Indian paper industry is much higher when compared to that of the United states and several other developed countries. Recycling of waste water has been posing serious problem because of colour, lack of adequate spent liquor recovery system and proper effluent treatment facilities.

Although primary & secondary treatment has been used by Indian paper industry, however, with the existing facilities, many of the paper mills are unable to meet the requirement of MINAS which is given in **Table-2 (3).** Industrial growth during recent years has resulted severe degradation of biosphere. Increasing regulatory pressure warrants the need for treatment of colour bearing effluent in polishing stage. Lime treatment, coagulation, adsorption using activated carbon & polymeric adsorbent, membrane separation processes and biological treatment using white rot fungus etc. have been suggested. However, developing countries like India are finding still difficult to go in for a polishing stage because of poor economic condition. Although biological processes are cost effective, major drawback of lignin biodegradation so far has been its slowness and incompleteness (4).

Adsorption process for water treatment has long productive history and it can deal with compounds that are otherwise difficult to remove by conventional processes (5). Importance of adsorption process can be realized from the fact that world wide sales of adsorbents in more than 500 million dollars (6). During recent years, large number of low cost adsorbents have been investigated (6-16) with a critical review presented by Mall et al. (7). The present paper deals with a low cost effluent treatment technology using pyrolysed bagasse char as adsorbent. Effect of various parameters like adsorbent dose, pH, initial concentration; Effect of various parameters like adsorbent dose, pH, initial concentration; adsorption

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Table-1

Characteristics of Wastewater From Pulp and Paper Mill

Nature of Pollutants	Pollution load
Resin acids : abietic, dehydroabietic isopimaric, palustric, pimaric, sandaracopimaric and neoabietic: Unsaturated fattyacid : Oleic, linoleic, linolenic and palmitoleic acid : Chlorinated resin acid : mono and dichlorodehydroabietic acid, dichlorstearic acid : Diterpene alcohols : pimarol, isopimarol, abienol etc. juvabiones; Lignin and lignin degradation products Fugitive toxicants : Sodium sulphide, hydrogen sulphide; Chlorinated phenolic compounds : 2, 4 6-trichloro phenol 2, 4, 5-trichlorophenol, trichloroguaicol, penta chlorophenol, tetra chloro guaiacol, di-and trichloro catechol, chlorinated vanillin, Chlorinated syringols, chlorinated syringaldehydes, Genotoxic compounds : 1, 3 dichlorome-methyl 5-hydroxy-2 (5H) furanone, chloroacetones, Dyes and pigments.	kg/tonne of paper: Large Integrated Mill: COD: 150-210, BOD : 30-50 Total solids: 100-200 Agro based Paper mill: COD : 500-1200, BOD : 90-300 Total Solids : 100-250 Waste paper based mills: COD : 50-100, BOD : 10-50 Total Solids : 50-80 Waste water generation m^3/tonne of paper Large mills : 200-350 Agro based : 200-350 Waste Paper based : 70-150 Colour kg/tonne of paper: Bleached kraft : 150 Bleached thermomechanical-60

isotherms, kinetics of removal and economic evaluation of the process have been presented for treatment of lignin bearing waste water obtained from black liquor of kraft pulp mill. COD and colour removal from pulp and paper mill combined effluent and chlorination stage waste water from a large integrated paper mill has also been presented.

AVAILABILITY OF BAGASSE FLY ASH

During production of sugar 30-33% wet bagasse (with 50% moisture) is produced. With the target of 20 million tonnes of sugar and 350 million tonnes of sugarcane by 2001 AD, the availability of bagasse is estimated to be about 100 million tonnes (with 50%) moisture. Taking 10% surplus bagasse from sugar mills it is expected that about 10 million tonnes (with 50% moisture) of bagasse will be available for other uses.

EXPERIMENTAL

Pyrolysed bagasse prepared by carbonising the bagasse at about 450°C in a furnace was used as such for treatment of waste water prepared from black liquor (Waste water I), combined waste water from a large integrated mill (Waste water II) and chlorination stage effluent (Waste water No III). For evaluating the effect of various parameters affecting adsorption, Waste water I was used. Characteristics of pyrolysed bagasse char and various waste water used in the investigation are given in **Table 3 and 4.** Batch experiments were conducted by shaking known amount of pyrolysed bagasse char and activated carbon with various waste water in a constant temperature shaking water bath at a speed of 150 rpm. For evaluation of various parameters affecting adsorption, COD of the treated effluent was analyzed as per standard method and the colour using spectrophotometer (Model: Schimadzu, Japan) UV 210 A). Results obtained with pyrolysed bagasse char were also compared with that of with activated carbon.

RESULTS AND DISCUSSION

Effect of pH on COD removal

Waste water treatment using conventional and non conventional adsorbents is highly dependent on pH of the waste water under treatment as it may effect the surface charge of adsorbents as well degree of ionization and the rate of adsorption of adsorbate species in aqueous media. Change of pH affects the adsorptive process through dissociation of functional groups on the adsorbate and adsorbent. The effect of pH on removal of COD from Waste water I by pyrolysed bagasse and activated carbon is shown in **Fig.1**. It may be observed that COD removal increases with increase in pH from 2 to 5 and then it starts decreasing with increase in pH.

Table-2

MINAS for Pulp and Paper Mills

MINAS for Small Pulp and Paper Mill.

Parameter	*Discharged on to surface water*	*Disposal on land*
pH	5.5-9.0	5.5-9.0
Suspended Solids, mg/l	100	100
BOD, mg/l	30	100

MINAS for Large Pulp and Paper Mills Capacity > 24,000 Tonnes/annum

Parameter	*Concentration*
pH	7.5-8.5
Suspended Solids, mg/l	50
BOD, mg/l	30
COD, mg/l	350
TOCl, kg/T	2

Total waste water generation per tonne of paper.

For capacity above 24000 tonnes/annum:

200 cubic metre (100 cubic metre for mills established after 1992).

For capacity below 24,000 tonnes per annum:

Agro based: 200 cubic metre (150 cubic metre for mills established after 1992)

Waste paper based: 75 cubic metre (50 cubic metre for mills established after 1992)

MINAS for caustic chlorine plant

Parameter	*Concentration*
pH	5.5-9.0
Mercury in the final effluent, mg/l	0.01
Mercury bearing waste water generation	10 kilo-litre/tonne of caustic produced

Table-3				
Characteristics of bagasse fly ash and activated carbon.				
Parameter	*Pyrolysed bagasse char*		*Activated carbon*	
A. Proximate analysis				
Bulk density (kg/m^3)	143.00		620.00	
Moisture (%)	9.31%		16.99%	
Volatile matter (%)	37.51%		11.00%	
Ash (%)	8.93%		13.10%	
Fixed carbon (%)	53.56%		75.90%	
E. Particle Size				
	Micron		mm	
	>600	48.26%	>2.0	14.3
	600-500	20.45%	2.0-1.4	36.8
	500-425	2.09%	1.4-1.18	2.1
	425-355	12.64%	1.18-1.0	19.8
	355-300	6.07	1.0-710 micron	21.2
	300-250	2.71%	<710 micron	5.8
	250-100	5.57%	<1.205	3.2
	< 100	2.21 %		
	<125-<	8.00 %		
	0.75	9.10 %		
	< 0.75			

Effect of Adsorbent Dose

The effect of adsorbent dose on removal of COD from three types of waste waters is given in **Fig.2.** It may be seen that the COD removal efficiency increases with increase in adsorbent dose upto a level of 15 g/l. Howerver, with any further increase in the adsorbent dose, there is no appreciable increase in COD removal.

Effect of Initial Concentration and Contact Time

In the adsorption process, initial concentration of pollutants plays an important role because the resistance to the uptake of solute from the solution decreases with the increasing concentration. (17). The effect of initial concentration on the removal of COD from Waste water I by pyrolysed bagasse char and activated carbon is give in **Fig.3** It may be seen that equilibrium time is about 4 h. Percentage removal was found to decrease with increase in initial COD

Table-4			
	Characteristics of waste water		
Parameters		***Characteristics***	
	Waste water I	***Waste water II***	***Waste water III***
Colour	Dark brown	Pale yellow	Brown
pH	9.8	2.5	8.2
COD, mg/l	1200	825	700
BOD, mg/l	450	165	142
Total solids, mg/l	3025	1585	1605
Suspended solids, mg/l	1010	185	1500
Dissolved solids, mg/l	2015	1400	1500

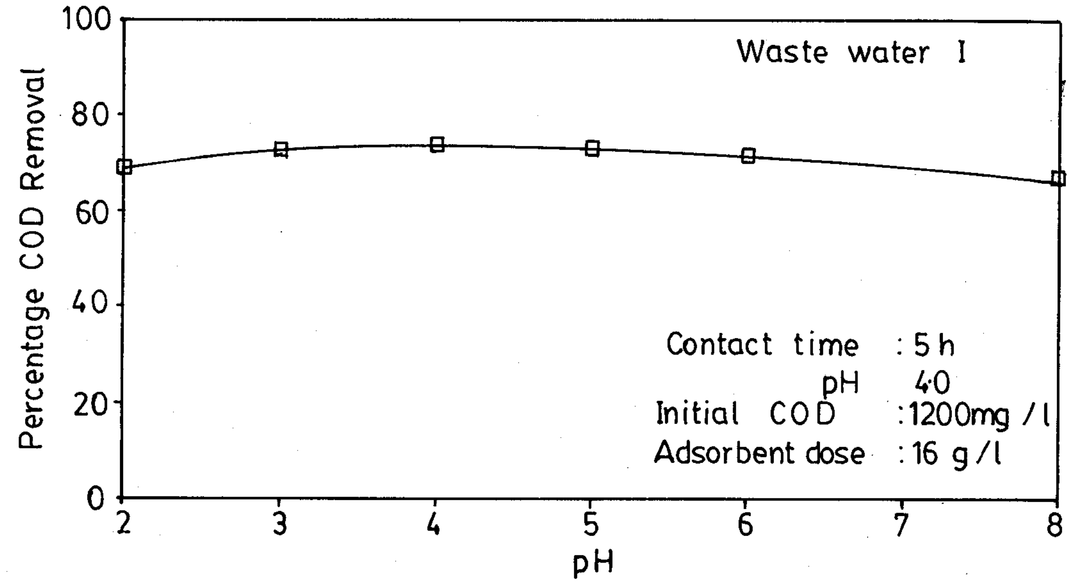

FIG. 1 EFFECT OF pH ON COD REMOVAL

concentration. However, COD removal per unit weight of the adsorbate was found to increase with increase in COD concentration. Percentage removal for initial concentration of 300 mg/l was 72% and 91% for pyrolysed bagasse char and activated carbon, respectively for a adsorbent dose of 15 g/l.

Adsorption Isotherms

Langmuir and Freundlich isotherms which are represented by following expression were used for analysing the equilibrium data.

$$Q = \frac{Q_m K_a C_e}{1+K_a C_e}$$

$$Q = K_f C^{1/n}$$

Where Q is the mass of the adsorbate per unit

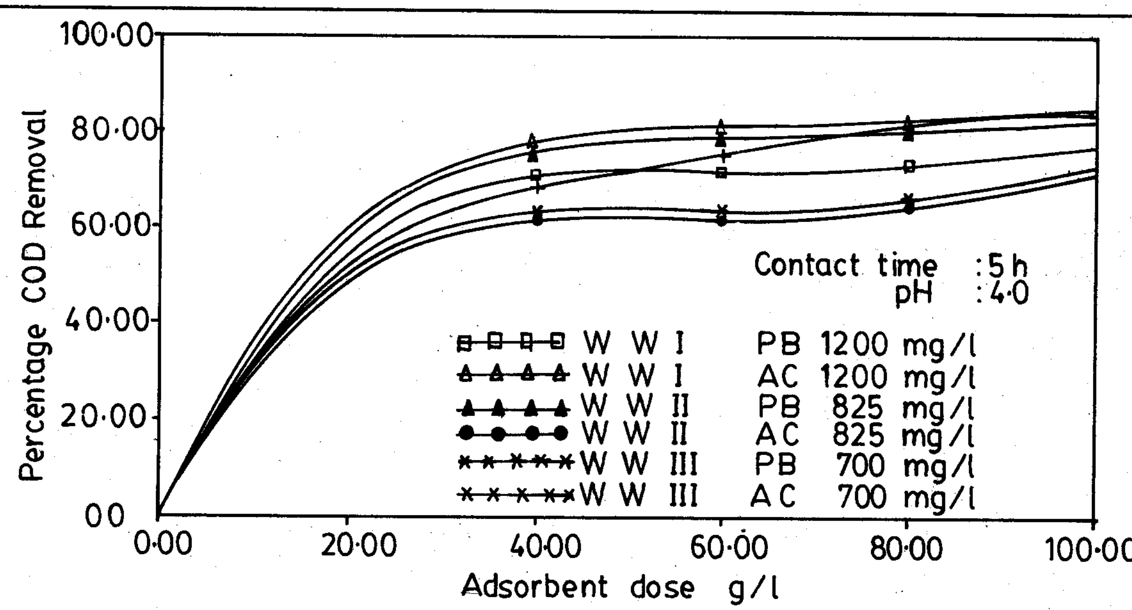

FIG. 2 EFFECT OF ADSORBENT DOSE ON COD REMOVAL

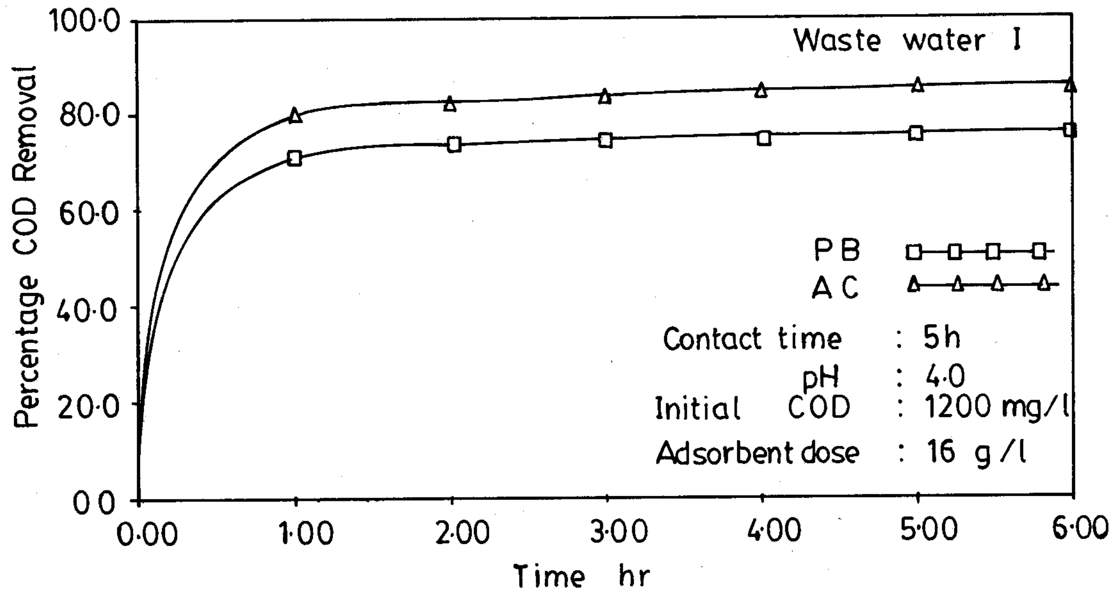

FIG. 3 EFFECT OF CONTACT TIME ON COD REMOVAL

mass of the adsorbent; Q_m is the mass of the adsorbate adsorbed per unit mass of the adsorbent for complete monolayer; C_e is the concentration of the adsorbate in solution at equilibrium; K_a is Langmuir isotherm constant related to enthaply of adsorption, K_f and n are the Freundlich Constant. The equilibrium data fitted in well with the Freundlich Isotherm (**Fig.4**). However, the data did not fit with Langmuir isotherm model. The Freundlich isotherm constant is given in **Table 5.**

Kinetics of COD removal

The contact time data for removal of COD is shown in **Fig.4.** From the figure, it may be interpreted that the sorption kinetics comprises of three phases. The first phase shows instantaneous sorption

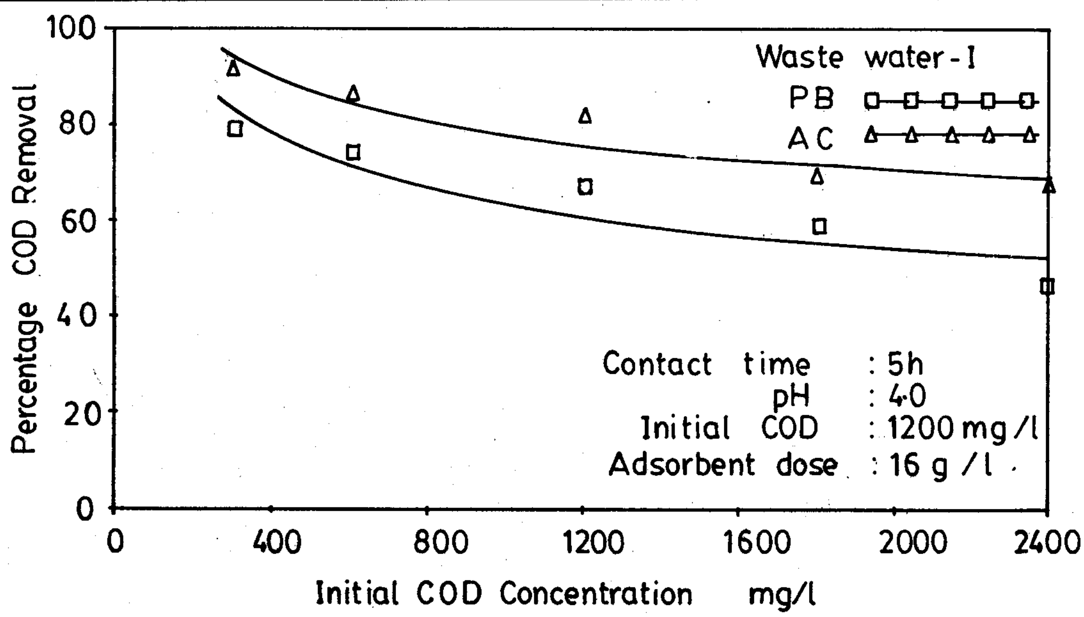

FIG. 4 EFFECT OF INITIAL CONCENTRATION ON COD REMOVAL

Table-5		
Langmuir and Freundlich isotherm constants for removal of COD		
Adsorbent	*Freundlich constants*	
	1/n	K_F
Pyrolysed bagasse char	0.459	17.78 x 10^{-3}
Activated carbon	0.487	19.95 x 10^{-3}

characterized by initial linear but steep rise in percent removal. This phase occurs within the first 30 min. During the later phases, adsorption rate and percent removal gradually decreases and levels off as equilibrium is established.

The kinetics of removal of COD from waste water prepared from black liquor by pyrolysed bagasse char and activated carbon were analyzed using Lagergren first order rate expression (16)

$$\log (Q_e - Q) = \log Q_e - (K_d/2.303)\ t$$

Where Q and Q_e are the amount of COD removal per unit weight of adsorbent at time t and equilibrium: K_d is the adsorption rate constant. The plot of log (Q_e - Q) versus time for removal of COD by pyrolysed bagasse char and activated carbon are shown in **Fig.5.** The straight line plots show the validity of the Lagergren equation. The rate constant K_d is 0.016 min^{-1} and 0.0192 min^{-1} in case of pyrolysed bagasse char and activated carbon respectively.

Colour Removal

Decolourisation of pulp and paper mill effluent has been a cause of major concern due to the complexity of the colour constituent present in the wastewater, industry has been looking for a viable treatment method. The summary of the findings of the experiments carried out with pyrolysed bagasse char and activated carbon for removal of colour are given in **Table 6.** It may be seen that removal of COD colour to the extent of 64% and 80% has been possible by bagasse char and activated carbon respectively.

ECONOMICS OF THE PROCESS

The adsorption capacities of pyrolysed bagasse char and activated carbon and the economics of the treatment process has been presented in **Table 7.** It may be seen that adsorption capacity of activated carbon is higher than pyrolysed bagasse char. However, the overall cost of treatment with pyrolysed char will be much cheaper as cost of activated carbon is

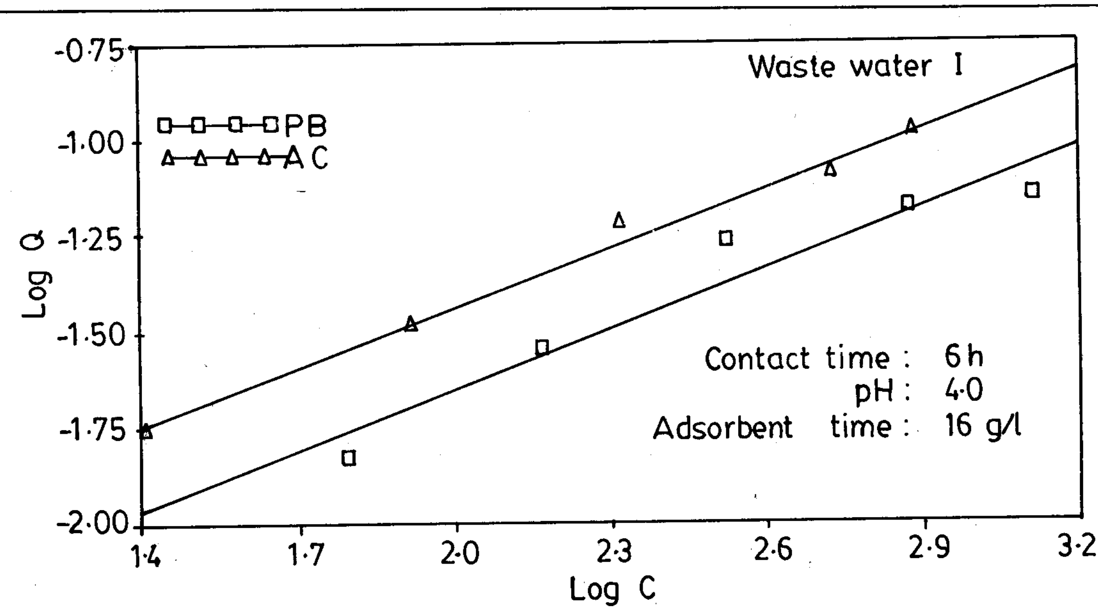

FIG. 5 FREUNDLICH ISOTHERM FOR REMOVAL OF COD

Table-6					
Summary of results on COD, BOD and colour removal from various effluents experimented					
Type of waste water	*Initial COD mg/l*	*Pyrolysed bagasse % Removal*		*Activated carbon % Removal*	
		COD	*Colour*	*COD*	*Colour*
Waste water I	1200	73.5	70.0	82.5	80.0
Waste water II	825	65.1	68.0	80.0	79.0
Waste water III	700	68.2	64.0	81.2	70.0

Table-7		
Economics of the treatment process		
Adsorbent	**adsorption capacity mg/g**	**Cost per tonne of adsorbent**
Pyrolysed bagasse char	24.59	Rs. 3000/-
Activated carbon	46.75	Rs. 30,000/-
NB. Additional saving through sale of briquettes		

about 30,000/- per tonne against the cost of pyrolysed char which will be about Rs. 3000 per tonne. Pyrolysed bagasse char may also be used for making fire briquettes as its carbon content is high and adsorbed organic matters will increase the heating value of the char. The revenue generated from the sale of briquette will compensate the cost of pyrolysing bagasse.

The whole process seems to be very attractive and economically feasible. The various equipments used in the manufacture of fire briquettes are mixer for mixing binder and pyrolysed char, briquetting equipment and drying trays etc.

CONCLUSIONS

Pyrolysed bagasse char has been found as an

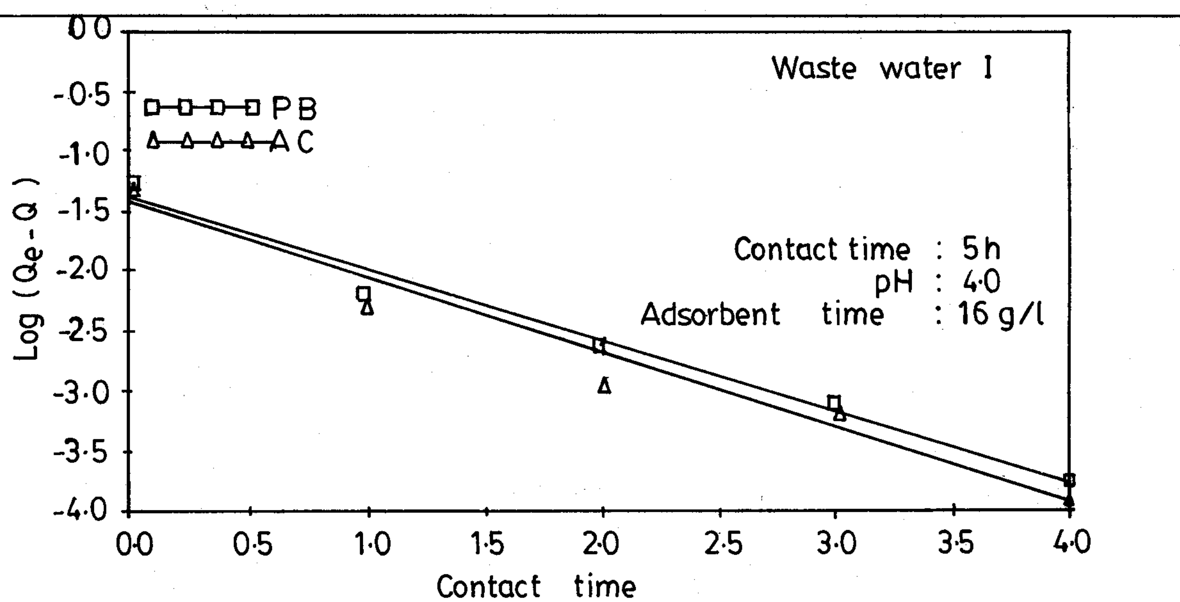

FIG. 6 - LAGERGREN PLOT FOR REMOVAL OF COD

effective adsorbent for the removal of COD from pulp and paper mill effluent in the polishing stage. The overall cost of treatment will be lower than that of activated carbon due to the high cost and the resulting loss of activated carbon during its regeneration and reduction in adsorption capacities. The pyrolysed bagasse char having high carbon content and calorific value, after the treatment can be utilized for making fire briquettes, thus avoiding disposal problem. The process is believed quite attractive for the integrated sugar-mill complexes.

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