Treatment of Methyl Violet Bearing Wastewater From Paper Mill Effluent Using Low Cost Adsorbents

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ABSTRACT: The present work examines the removal of methyl violet bearing wastewater in batch and column system using bottom ash from coal fired boiler of two paper mills. It has been found that low concentration, higher pH and speed of agitation favours the removal of methyl violet. Langmuir and Freundlich isotherms have been used to represent the equilibrium data at different temperature. Kinetics of removal has been described by first order rate expression. Intraparticle transport of dye within pore of bottom ash was found to be rate limiting step. Breakthrough time was found to increase with increase in bed heights and decrease in flow rates. The bed depth and service time data fitted well with the BDST model.

INTRODUCTION

Paper has become an essential ingredient of civilised life. However, at the same time paper industry causes large scale pollution of water, air and ecosystem and is amongst the highly polluting industries in India. Because of the public resentment for the coloured water, decolourisation of paper mill effluent has been cause of major concern. Lignin and dyes are two sources of colour in pulp and paper mill effluent and paper industry is still looking for viable treatment method for the treatment of lignin and dyes bearing wastewater. In small paper mills which are not having pulping units, dyes bearing wastewater is main source of colour and decolourisation of dye bearing wastewater is of prime importance. Apart from its aesthetic aspect the coloured effluent impede light penetration and upset the biological process. Some of the dyes has been found carcinogenic also [1-3]. During the manufacture of violet poster and match box paper about 8-10 kg of methyl violet per tonne of paper is consumed and highly coloured effluent is discharged and causes lot of problem in treatment and recyling of wastewater.

Adsorption process have received considerable interest during recent years for the removal of phenolic compounds, heavy metals, dyes and colour, refractory organics and other unbiodegradable materials. Although activated carbon is the most commonly used adsorbent, however, because of its high cost and 10-15% loss in regeneration, application of activated carbon in the developing countries has been restricted for only specialised purposes. Low cost adsorbents like fly ash, saw dust, bagasse pith, wood, agricultural residues have been extensively tried [4-15]. Present paper deals with utilisation of bottom ash from coal fired boilers which is available in huge quantity in the paper itself. Paper mills consumed about 3.0 - 4.0 tonnes of coal per tonne of paper and about 1.0 - 1.6 tonnes of coal ash per tonne of paper is produced. Utilisation of bottom ash will provide a promising substitute for activated carbon.

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Batch and column studies have been carried out to see the suitability of the bottom ash for the treatment of the methyl violet bearing waste.

EXPERIMENTAL

Bottom ash from a large integrated paper mill based on bamboo, hardwood and waste paper (Bottom Ash I) and small paper mill using agricultural residues and waste paper (Bottom Ash II) were used as adsorbent. The ash was grounded and Bottom ash I and Bottom ash II of 28.0 and 15.6 micron size were used for the batch studies to see the effect of initial concentration, pH, speed of agitation and for adsorption isotherms and kinetics of removal. In batch experiments 50 cc of methyl violet bearing wastewater was contacted with 0.25 g of bottom ash at $30 \pm 0.5^{\circ}C$ and constant speed of agitation of 150 rpm. In the column studies the methyl violet bearing waste water was treated in 20 mm downflow column. The concentration of the dye was analysed using Bausch and Lomb spectrophotometre.

Bottom ash samples were characterised for their physico-chemical characteristics. Proximate and chemical analysis was done as per IS-1984. Particle size analyzer and sieve shaker were used for the particle size of the fine and the coarse bottom ash samples. X-ray diffractometre and scanning electron microscope were used for the morphology. Surface area analyzer (Flow Sorb II) was used for the surface area measurement. Methyl violet bearing synthetic waste water was characterised for its COD, pH and conductivity.

RESULTS AND DISCUSSION

Characteristics of the Bottom ash and Methyl Violet

Physico-chemical characteristics of the bottom ash samples are given in Table 1. Silica, alumina and carbon are the major constituents in both the bottom ashes. X-ray diffractogram of both the bottom ashes (Fig. 1) show the presence of quartz, crystobalite, illite, mullite and magnetite as the main constituents [17-18]. In the SEM the alumino silicate appears as an nonporous continuous phase with sphere attached to it. Broad peak characteristic of silica in amorphous phase were observed in the X-ray diffractogram. No peaks of any form of crystalline carbon was observed. The COD conductivity, pH, of synthetic waste water and the

W-Weak, S-Strong, VS-Very strong, VVS-Very very strong

Fig.1: X-Ray Diffractogram of Bottom Ash
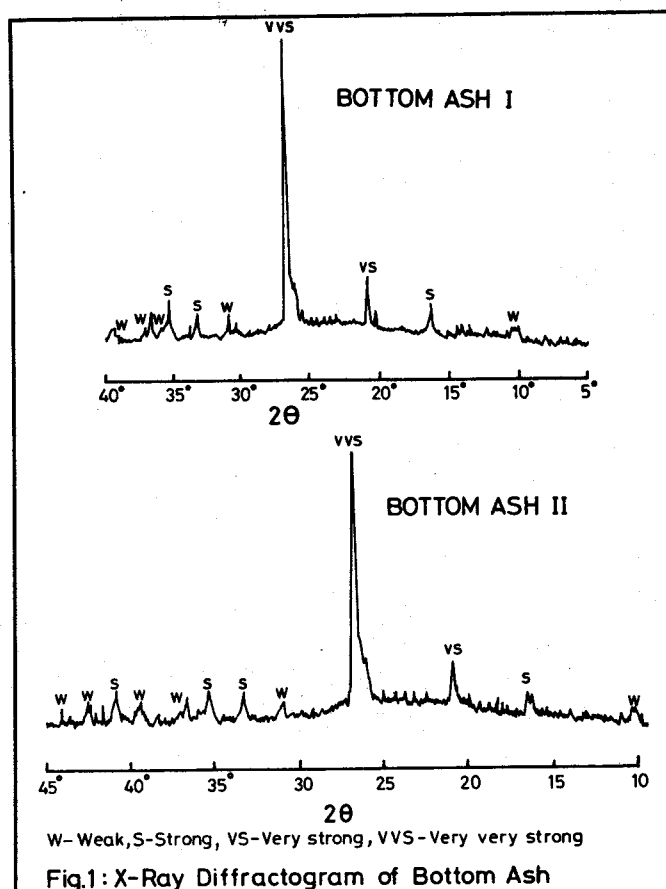
consumption of methyl violet per tonne of paper is given in the Table 2. The molecular structure of the dye is given in the Fig. 2.

Table-1

Characteristics of Adsorbents Used in the Present Investigation

Characteristics	Bottom ash I	Bottom ash II
Bulk density kg/m^3	1169.00	1158.00
Surface area m^2/g	18.00	12.40
Proximate Analysis:		
% Ash	83.20	84.20
% Volatile Matter	3.01	3.38
% Fixed Matter	13.79	12.42
Chemical Analysis:		
(% Composition)		
Loss on Ignition	16.80	15.80
Silica (SiO$_2$)	47.92	48.50
Alumina (Al$_2$O$_3$)	26.80	27.45
Fe$_2$O$_3$	6.17	6.90
CaO	1.92	0.98
MgO	0.36	0.35
Others	0.03	0.02

FIG. 2-Effect of Initial Concentration on Removal of Methyl Violet

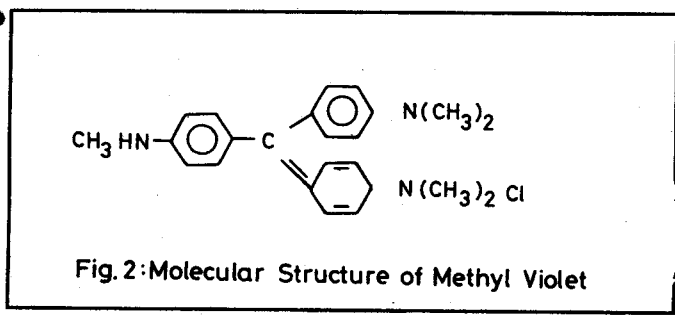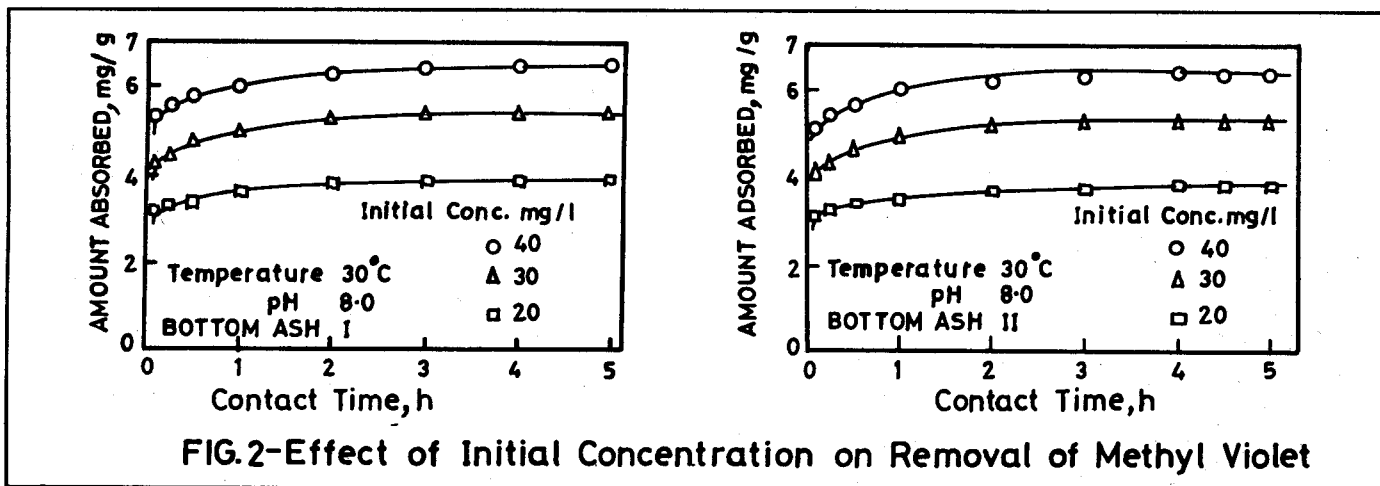Fig. 2: Molecular Structure of Methyl Violet

Table-2

Characteristics of Methyl Violet

Name of the dye	Consumption of dyes kg/tonne of pulp	Colour	Type of dye	λmax	Characteristics of 20 mg/l dye solution		
					pH	COD mg/l	Conductivity, mho
Methyl Violet	8.0-9.0	Violet	Basic	580	6.90	16.00	0.016

**Effect of Initial concentration and contact Time**

Fig. 3 show the effect of initial concentration and contact time on the removal of methyl violet. It may be observed that about 85% of the dye is removed during the first 30 minute and is characterised by initial steep and almost straight part of the curve which may be due to the external surface reaction followed by gradual decrease in removal. About 96% removal of dye was observed at the initial concentration of 20 mg/l. However, 100% removal was observed at the initial concentration below 20 mg/l. The equilibrium time was about 4 h for the both adsorbents and was found independent of the initial concentration of methyl violet.

FIG. 3-Effect of pH on Removal of Methyl Violet
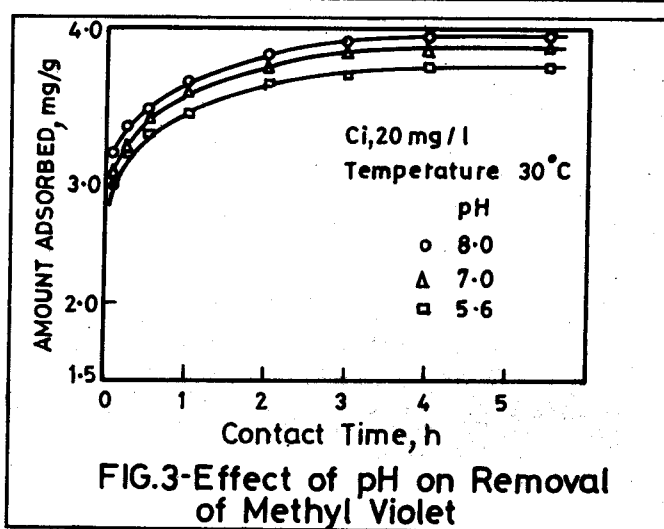
Removal of methyl violet per unit weight of adsorbents was found to increase with the increase in initial concentration while the percentage removal decreased with the increasing initial concentration of the dye. Similar observation has been reported by other investigators also [6, 12, 13].

Effect of pH

The effect of pH on the removal of methyl violet is shown in the Fig. 4. It may be seen that the removal of the methyl violet increases with the increasing pH. Higher removal of basic dye at higher pH has been reported by other workers also. The basic dyes yield coloured cations in solution and hence sorption patterns follows cationic sorption resulting in higher removal at higher pH. Higher removal of basic dyes in alkaline pH range has been reported by other workers also [19, 20].

FIG.4-Effect of Agitation Speed on Removal of Methyl Violet
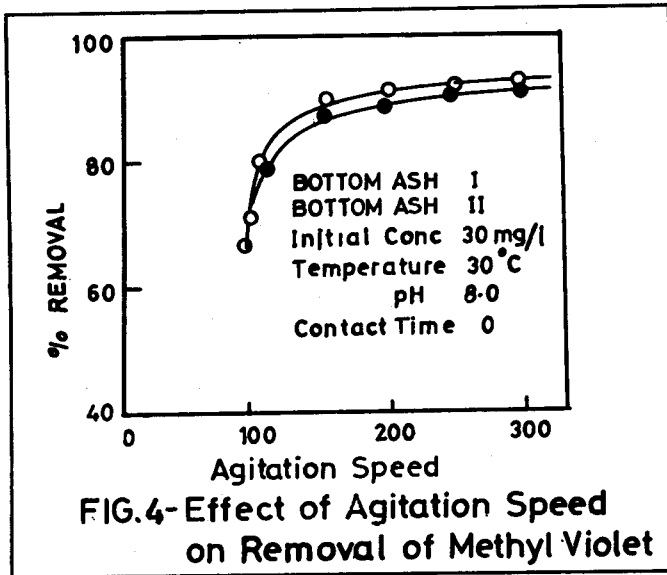
Speed of Agitation

Effect of agitation speed on the removal of methyl violet is shown in Fig. 5. It may be seen that the removal of dye increases with increasing agitation speed. The higher removal by increasing agitation speed

may be attributed to the decrease in diffusion layer thickness surrounding the bottom ash particles [21]. However, after 150 rpm no appreciable increase in removal of methyl violet was observed with increasing speed of agitation.
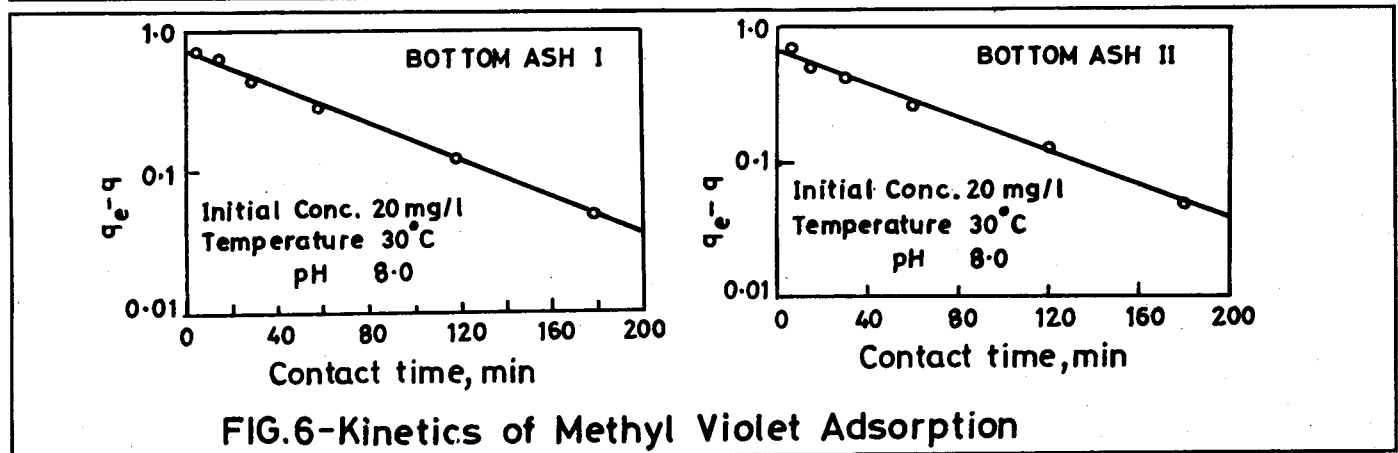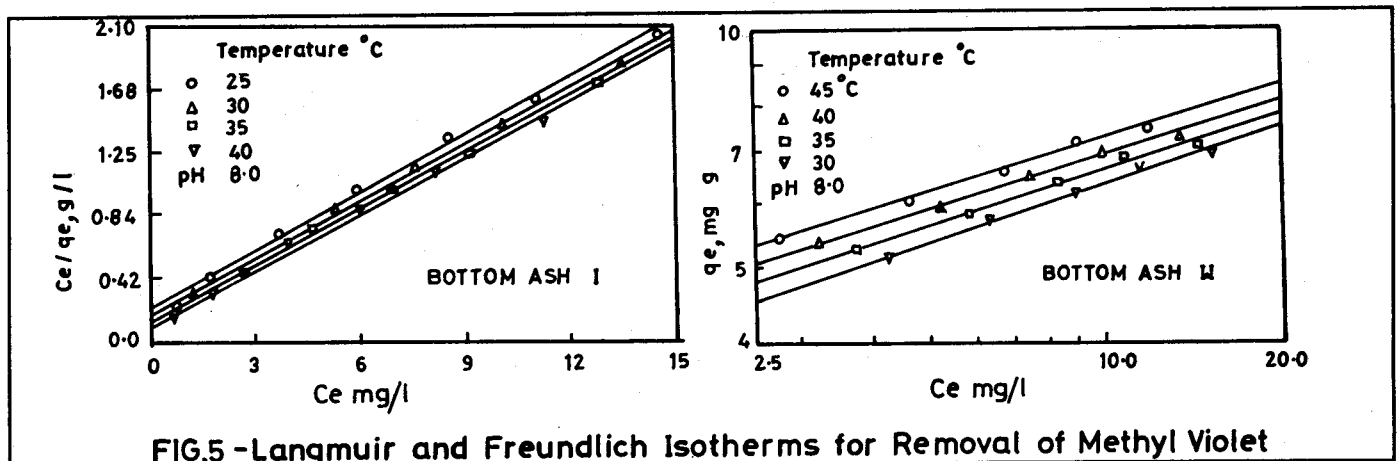
Adsorption Isotherms

Equilibrium data was analysed using Langmuir and Freundlich Isotherms:

$$1/q_e = (1/b\ Q_o)\ 1/C_e + 1/Q_o$$

and $q_e = a_F\ C_e^{1/n}$

Where C_e and qe are the equilibrium concentration and the amount of methyl violet adsorbed per unit weight of the adsorbents: Q_o and b are the Langmuir constants representing sorption capacity and heat of adsorption; a_F and n are Freundlich isotherms representing adsorption capacity and intensity.

The experimental equilibrium data fitted well both the Langmuir and Freundlich isotherms [Fig. 6, 7]. The
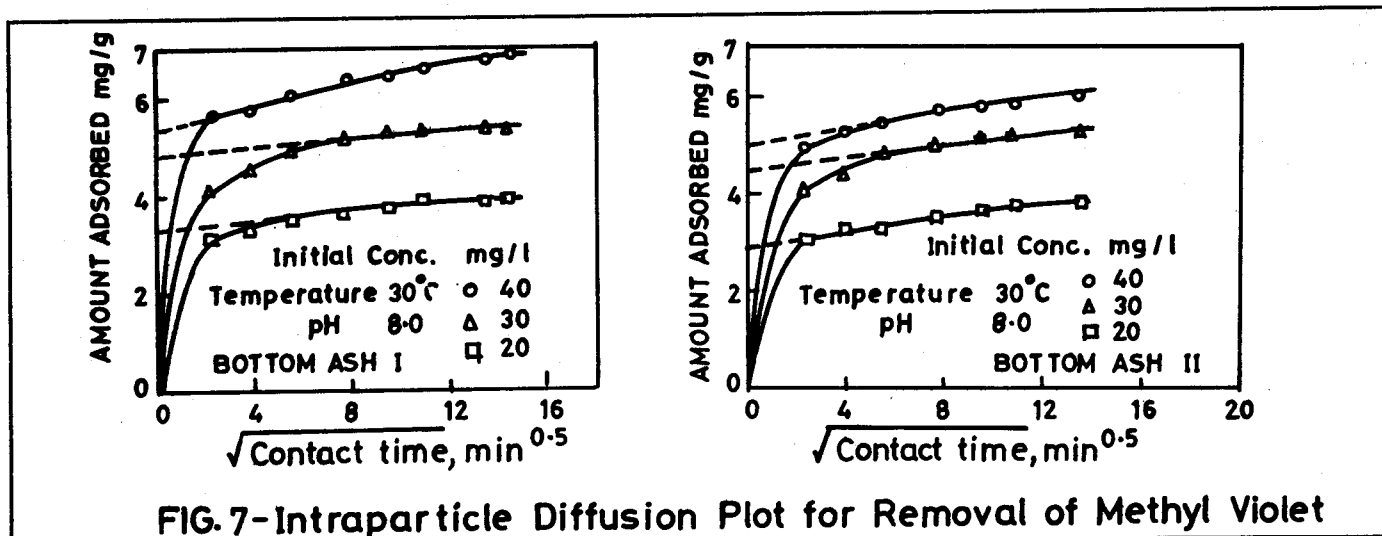

FIG.5 -Langmuir and Freundlich Isotherms for Removal of Methyl Violet

FIG.6-Kinetics of Methyl Violet Adsorption

FIG. 7 - Intraparticle Diffusion Plot for Removal of Methyl Violet

values of the isotherms constants are given in the Table 3. It has been reported that value of n in the range 2-10 represents good adsorption potential [22]. The value of n in the present investigation was in the range 4.1 - 5.8 showing good adsorption potential of bottom ash. The value of equilibrium constant R_L which is defined by $R_L = 1/_1 + bC_o$ (where C_o is the initial concentration) in the range $0 < R_L < 1$ represent good adsorption capacity of the adsorbent [23]. The value of R_L in the range 0.0298 - 0.0704 for both the bottom ash in the present investigation show favourable adsorption.

Table-3

Langmuir and Freundlich Isotherm Constants for Adsorption of Methyl Violet by Bottom Ash

Adsorbents	Temp. °C	Langmuir Constants Q_0, mg g^{-1}	Langmuir Constants 1 mg^{-1}	Freundlich Constants n	Freundlich Constants a_F, mg g^{-1}
	25	4.796	1.618	4.561	3.968
Bottom	30	6.119	1.284	4.786	4.270
Ash I	35	7.920	1.008	5.021	4.572
	40	12.046	0.660	5.810	5.050
	25	4.690	1.615	4.147	3.638
Bottom	30	5.561	1.373	4.308	3.876
Ash II	35	7.869	0.976	4.441	4.111
	40	8.168	0.955	4.466	4.338

Table-4

Values of Equilibrium Parameter R_L for Adsorption of Methyl Violets by Bottom Ash

Adsorbent	Equilibrium Parameter RL x 10^{-2} at temperature °C			
	25	30	35	40
Bottom Ash I	2.99	3.75	4.73	7.04
Bottom Ash II	3.00	3.51	4.87	4.98

The adsorption equilibrium constant b related to heat of adsorption should follow vant' Hoff equation [24].

$$b = b_{oc} - \Delta H/RT$$

Since the adsorption is exothermic (ΔH) negative, b should decrease with increasing temperature. The decreasing value of b with increasing temperature show the exothermic nature of the adsorption [24]. The values of ΔH calculated from linear plot of b vs 1/T is given in Table 5.

Table-5

Adsorption rate constant K_d, Pore diffusion coeff., Intraparticle Diffusion rate constant and H for removal of Methyl violet by bottom ash

Initial Conc., 20 mg/l Temperature 30°C

Adsorbent	Adsorption Rate constant min^{-1}x10^{-3}	Pore diffusion coefficient cm^2/sec	Intraparticle diffusion rate constant	ΔH kcal/ mol
Bottom Ash I	15.39	21.92x10^{-3}	0.066	-11.765
Bottom Ash II	14.38	6.30x10^{-12}	0.071	-7.458

Kinetics of Removal

The rate constant for the kinetics of removal of methyl violet by bottom ash was analysed using Lagergren.model [13].

$$\log (q_e - q) = \log q_e - k_d t / 2.303$$

where q_e and q are the amount of methyl violet removed at equilibrium and time t; k_d is the rate constant. Linear plot of log $(q_e - q)$ versus t show that above first order rate expression is applicable for the removal of methyl violet. The value of k_d are given in Table 5.

Intraparticle Rate study

Intraparticle diffusion parameter k_i can be defined as the linear gradient of q versus $t^{0.5}$. The plot of q versus square root of time [Fig. 9] was linear in wide range of the experimental data showing the intraparticle rate diffusion rate controlling [11]. The initial curved portion may be because of external mass transfer [11, 13].

Pore Diffusion Study

Pore diffusion coefficient D was calculated using the following expression proposed by Helffrich assuming spherical particle [25]:

$$t_{1/2} = 0.03 \, r_0^2 / D$$

$$D = 0.03 \, r_0^2 / t_{1/2}$$

where $t_{1/2}$ is the time for half adsorption, r_0 is the radius of the particle. The value of rate constant is found in the range of 10^{-10} -10^{-12} $cm^2/$ sec indicating that the process is governed by diffusion but pore diffusion is not the only rate limiting step [26].

Fixed Bed study

A series of fixed bed studies have been carried out for the removal of the methyl violet in a downflow 20 mm perspex glass column. Bottom ash I of 517 micron size was used. The break through time was found to increase with increase in the bed heights and decrease in the flow rates. Typical break through curves for the removal of methyl violet by Bottom ash I is

FIG.8-Break Through Curve for Removal of Methyl Violet
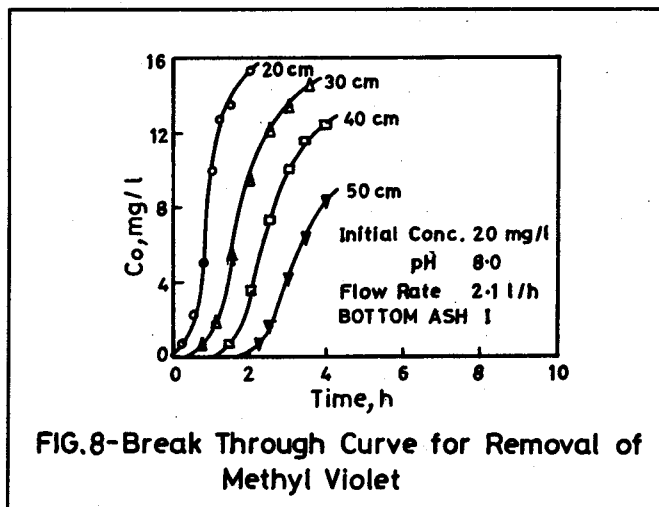
given in Fig. 10. The bed depth service time data fitted well with the BDST model given by Bohrat and Adams [27].

$$t = (N_0/C_0 V) H - \ln [C_0/C_E - 1] K_B C_0$$

The critical bed depth H_0 is calculated from

$$H_0 = V/k_B N_0 \ln [C_0/C_E - 1]$$

where t is break through time, min; C_0 and C_E are initial concentration and the break through concentration, mg/1; H and H_0 are the bed depth and the critical bed depth, cm; k_B is the rate constant, cm^3 min and N_0 is the adsorptive capacity, mg/cm^3. The value of N_0, k_B and H_0 are 0.943, 20.05 and 1.283 respectively.

CONCLUSIONS

The experimental result show that bottom ash have good potential as adsorbent for removal of methyl violet bearing wastewater and the paper mills can utilise the bottom ash for treatment of dye bearing waste water. It is recommended that dye bearing waste water be treated separately rather than treating the combined waste water of the mills.

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