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Single and Tertiary System Dye Removal from Aqueous Solution Using Bottom Ash: Kinetic and Isotherm Studies

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Abstract: This paper investigates the ability of Bottom ash to adsorb three cationic dyes from aqueous solution in single and tertiary systems. Crystal Violet (CV), Methylene Blue (MB) and Malachite Green (MG) were used as cationic dye models. The surface characteristics of Bottom ash were investigated using Fourier Transform Infrared (FTIR). Pseudo second order model was fitted better than Pseudo First order model for all system of MG, MB and CV. From the isotherm study, the adsorption capacity increased in the order of MB< MG<CV for single and MB<CV<MG for tertiary system. It may be concluded that the adsorption capacity of Bottom ash decreases in tertiary system as compared to single system. Langmuir and Freundlich isotherm models were fitted for all system of dyes. Freundlich isotherm model found to be the best fit for all systems.

INTRODUCTION

The use of dyes by many industries, such as textile, paper and plastics is a common activity. Since these industries also use substantial amount of water in their processes, this results in highly colored effluent of these industries which is generally colored due to the presence of these organic chemicals [1]. The discharge of highly colored effluents into natural water bodies is not only aesthetically displeasing, but it also impedes light penetration. Thus it will affect biological processes within a stream. In addition, many dyes are toxic to some organisms. Some dyes can cause allergic dermatitis, skin irrigation, cancer and mutation in man. Recent estimates indicate that, approximately, 12% of synthetic textile dyes used each year is lost during manufacture and processing operation and 20% of these dyes enter the environment through effluents that result from the treatment of residual industrial waters [2].

Removal of many dyes by conventional waste treatment methods is difficult since these are stable to light and oxidizing agents and are resistant to aerobic digestion. Possible methods of color removal from textile effluents include chemical oxidation, froth flotation, adsorption, coagulation, etc. Among these, adsorption currently appears to offer the best potential for overall treatment and it can be expected to be useful for a wide range of compounds, more so than any of the other listed processes [3]. Even though activated carbon showed advantages, the main drawback of the activated carbon is the cost and difficulty in regeneration [4]. Therefore, in recent years, this has prompted a growing research interest in the production of activated carbons from renewable and cheaper precursors which are mainly industrial and agricultural by-products [5]. There are several industrial waste were used as low cost adsorbent. Coal fly ash [6], bagasse fly ash [7], Red Mud [8] etc are some examples.

This study is an aim in the same direction in exploring the use of an industrial by-product namely Bottom ash for treating three basic dyes (Crystal Violet, Methylene Blue and Malachite Green) in single and tertiary system. The Bottom ash is a coarse, granular, incombustible by-product of power plants, obtained after combusting

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coke. It is an undesired collected material, whose disposal has always been a matter of concern to the station authorities, as the dumped ash makes the land infertile [9]. Malachite green is a broadly used dye in the textile industry that has properties that make it difficult to remove from solutions. It is also used in leather industries and distilleries for coloring purposes [10]. The dye has found wide applications in the aquaculture industry, as it is relatively cheap, effective and easy to obtain. Its use in the aquaculture practice in many countries has not been regulated. Many adverse effects from the consumption of the dye due to its carcinogenic and mutagenic properties in animal studies have been reported [11]. Crystal violet, also known as Basic Violet 3, is a well-known cationic dye being used for various purposes: a biological stain, a dermatological agent, a veterinary medicine, an additive to poultry feed to inhibit propagation of mold, intestinal parasites and fungus etc. It is also extensively used in textile dyeing and paper printing. It is a mutagen and mitotic poison [12]. Methylene Blue is a thiazine (cationic) dye, which is most commonly used for coloring paper, temporary hair colorant, dyeing cottons, wools and so on. Although MB is not considered to be a very toxic dye, it can reveal very harmful effects on living things. After inhalation, symptoms such as difficulties in breathing, vomiting, diarrhea and nausea can occur in humans [13].

MATERIALS AND METHODS

Adsorbent: The thermal power plant waste material, 'Bottom ash' (particle size less than 75 μm) was used as a potential adsorbent in this study. The adsorbent was obtained from Neyveli Lignite Corporation Limited, Neyveli.

Characterization of Adsorbent: The pH value of the adsorbents were determined by mixing 2 g of adsorbent with 100 mL of distilled water and recording pH at every 1 h interval for a period of 24 h. The loss on ignition (LOI) was determined by heating a pre-weighed dry sample (left at 105°C in an oven and then cooled in desiccators) to 600°C over a period of 1 h [14]. Fourier Transform Infra Red (FTIR) spectroscopic techniques were utilized to identify the functional groups of adsorbent. FTIR spectra of the samples were also recorded on PerkinElmer Model System 2000 using KBr pellet method.

The Point of Zero Charge (PZC) was determined using the solid addition method [15] viz: a series of 100mL conical flasks, 45mL of 0.1M KNO_3 solution was transferred. The pH_0 values of the solution were roughly adjusted from 2 to 10 by adding either 0.1N HNO_3 or

NaOH. The total volume of the solution in each flask was made exactly to 50mL by adding the KNO_3 solution. The pH_0 of the solutions were then accurately noted. Adsorbent (1g) was added to each flask and securely capped, immediately. The suspension was then manually agitated. The pH values of the supernatant liquid were noted. The difference between the initial and final pH (pH_f) values ($\Delta pH = pH_0 - pH_f$) was plotted against the pH_0. The point of intersection of the resulting curve at which pH_0 gave the PZC.

In order to provide a better understanding of the environmental impacts of adsorbent utilization, the solubility characteristics of various chemical species associated with Bottom ash were examined. One gram sample of adsorbent were equilibrated with 200 mL of distilled water for 2 h [14]. After filtration, the major chemical constituents in the filtrate were measured. The measurement of heavy metal concentration was done by using an S Series Atomic Absorption Spectrophotometer (AAS). Elemental analysis was determined by wet chemical method and measurement of elemental concentration was done by using an AAS supplied by PerkinElmer, USA, Model AAnalyst 700.

Adsorbate: The dyestuffs were used as the commercial salts. 1. Methylene Blue (C.I. 52015, λ_{max} = 663 nm, M.W =373.9 g/mol, M.F = $C_{16} H_{18} Cl N_3 S \cdot 3H_2O$), 2. Malachite Green (C.I. 42000, λ_{max} = 518 nm, M.W =364.911 g/mol, M.F =$C_{23}H_{25}ClN_2$), 3.Crystal Violet (C.I.42555, λmax =579 nm, M.W =407.99 g/mol, M.F = $C_{25} H_{30}Cl N_3$) (Note: C.I = Colour Index, λ_{max} = Peak wavelength, M.W= Molecular weight; M.F = Molecular Formula). The dyes (Adsorbates) and their chemical structures (Fig. 1) utilized in this study are listed below.

Equipments: A UV/Vis spectrophotometer (Lambda 25, PerkinElmer, USA) was used for measurement of dye concentration. The pH measurements were carried out using an Orion EA 940 (USA) expandable ion analyzer. An IHC- 3280 Orbital shaking incubator (Mumbai, India) was used for all adsorption experiments. Centrifuge was done by TC 650 S Multispin centrifuge (Mumbai, India).

Batch Study: Adsorption studies were carried out by batch process for individual system (MG, MB and CV) and tertiary system (MG+CV+MB). Batch kinetic experiments were carried out at constant pH of 8.0 with initial concentration of 10 mg/L. Kinetic study was conducted with the known dosage of adsorbent (Bottom ash 0.05 g) for the 50 mL of dye solution.
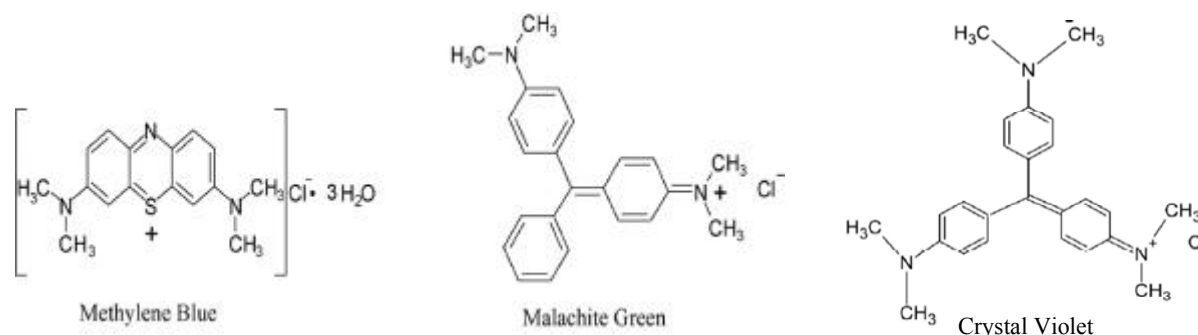
Fig. 1: Chemical Structures of Dyes

The mixture (dye + adsorbent) was shaken well in an orbital shaking incubator at an agitation rate of 150 rpm at a temperature of 30°C. The samples were withdrawn at suitable time intervals and analyzed for effluent concentration. Effect of adsorbent dosage was carried out by shaking a series of bottles containing different amounts of adsorbents (0.01 to 0.1 g) in 50 mL of dye solution and kept in the shaker for constant duration (equilibrium contact time). The sorbent solution mixtures were then centrifuged at 3600 rpm for 5 minutes and the supernatant was analyzed for the dye concentration.

RESULTS AND DISCUSSION

Characterization of Adsorbent: The Bottom ash used in the batch experiments were analyzed for various physical and chemical properties. The main physical properties of adsorbent are given in Table 1. The solubility concentration of some elements in water from adsorbent is given in Table 2. The composition of Bottom ash is given in Table 3. From Table 3, it can be observed that the SiO_2 and Al_2O_3 contents make up about 89% of the Bottom ash.

The results of the zero point of charge of the Bottom ash (pH_{PZC} =6.2) is presented in Fig. 2. This shows that at pH less than 6.2 the surface of the Bottom ash is predominated by positive charges while at pH greater than 6.2 the surface is predominated by negative charges. The FTIR spectrum of Bottom ash is shown in Fig. 3. Composition, PZC and FTIR spectrum of Bottom ash is also given in our previous work [16]. From Fig. 3, it was found that Bottom ash have peaks at 953, 1098, 1638, 3451 cm^{-1}etc. The broad band around 3446 cm^{-1} was attributed to the surface hydroxyl groups, adsorbed water and amine groups. The O-H stretching vibrations occurred within a broad range of frequencies indicating the presence of "free" hydroxyl groups and bonded O-H bands of carboxylic acids [5]. C-H stretching bands from aliphatic

Table 1: Properties of bottom ash

Property	Values
Point of zero charge	6.2
pH	1.547
Specific gravity	38.15 %
Los on ignition(LOI)	6.2

Table 2: Soluble Concentration of Some Elements in Water from Bottom ash

Metal ions	Concentration (mg/g)
Cu^{+2}	5.5×10^{-3}
Na^+	05×10^{-2}
Al^{+3}	BDL
K^+	1.625×10^{-2}
Cd^{+2}	5×10^{-4}

(BDL: Below Detectable Level)

Table 3: Composition of Bottom ash [16]

S.No	Element oxide	Weight (%)
1.	Calcium Oxide (CaO)	2.11
2.	Alumina (Al_2O_3)	23.49
3.	Silica (SiO_2)	65.22
4.	Iron Oxide (Fe_2O_3)	3.59
5.	Magnesia (MgO)	0.60
6.	Sodium Oxide (Na_2O)	0.21
7.	Others	4.78

compounds occur in the range 2850 -3000cm^{-1}. The main adsorption band for Bottom ash is at 1000-1200 cm^{-1} reflects the siloxane (-Si-O-Si-) group and the bands at 786 and 714 cm^{-1} represent SiO-H vibration [17].

Effect of Contact Time: In order to study the kinetics of adsorption of MB, MG and CV, adsorption experiments were carried out at different contact time at constant initial concentration of dye and Bottom ash dosage. The removal efficiency of dyes increased with increase in contact time and reached a maximum value.
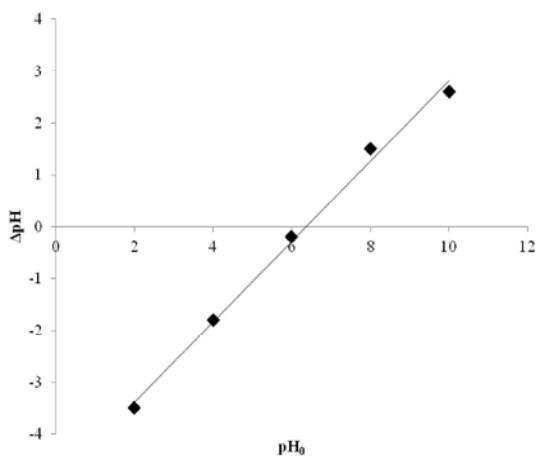
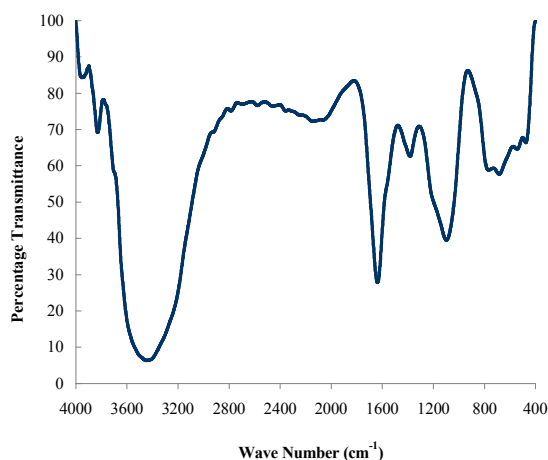Fig. 2: Point of Zero Charge for Bottom ash [16]

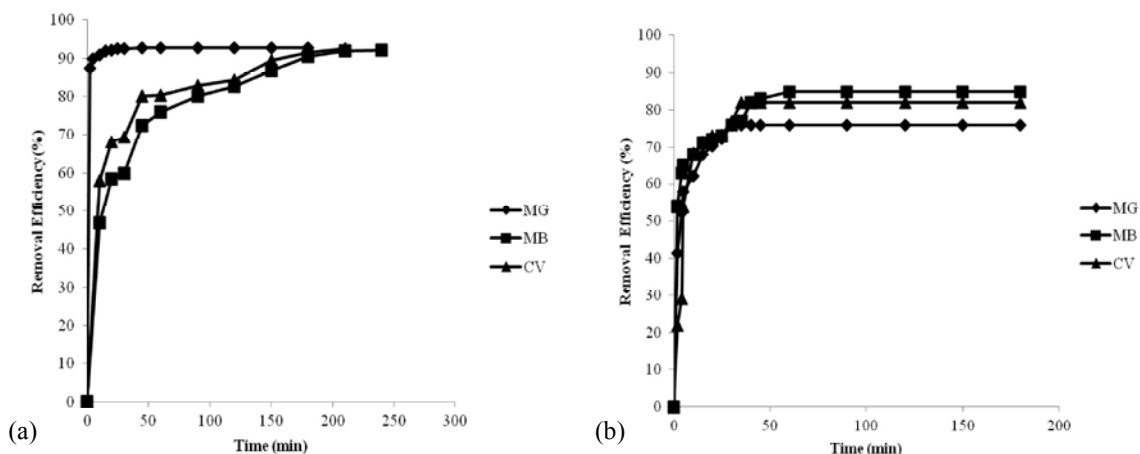
Fig. 3: FTIR Spectrum of Bottom ash [16]

Fig. 4: Effect of Contact Time (a) Single System (b) Tertiary System

Fig 4 (a) and (b) shows the effect of contact time on the removal of single and tertiary system of basic dyes (MG, MB and CV). It was very clear from the figure that the rate of removal of color was rapid initially. After that the rate decrease gradually and reaches an equilibrium value. From the Fig. 4(a), it was observed that dye uptake in single system was rapid for first 4 min incase of MG, 5 min for MB and 7 min for CV and thereafter it proceeded at a slower rate and finally reached saturation. The uptakes of MG, MB and CV for an initial concentration of 10mg/L were found to be 92.75%, 91.95% and 92% at 15 min, 210 min and 180 min respectively. The initial rapid phase may be due to an increase in the number of vacant sites available at the initial stage [18]. From the Fig. 4(b), it was observed that dye uptake for tertiary system was rapid for the first 7 min incase of MG, 10 min for MB and 8 min for CV and thereafter it proceeded at a slower rate and ?nally reached saturation. The uptakes of MG, MB and CV were found to be 76%, 85% and 82% at 60 min for an initial

concentration of 10mg/L. Fig. 4 shows that the uptake of dyes were rapid and efficient than that of single system. Similar results were reported by Ong *et al*. [19] and Wong *et al*. [20] for binary systems. Ong *et al*. [19] reported that Methylene Blue removal increases from 90.3 to 90.8% by natural rice husk from single and binary systems. Similarly percentage uptake of Reactive Orange 16 by ethylenediamine tetraacetic acid modified rice husk has a sharp increase in binary system than that in single system. Wong *et al*. [20] reported that Basic Blue 3 removal on sugar cane bagasse was 77.65 and 82.16 % in single and binary systems respectively.

Kinetic Modelling: The study of adsorption dynamics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface [21]. The kinetics and dynamics of adsorption of dyes by Bottom ash have been studies by applying the following kinetic equations:
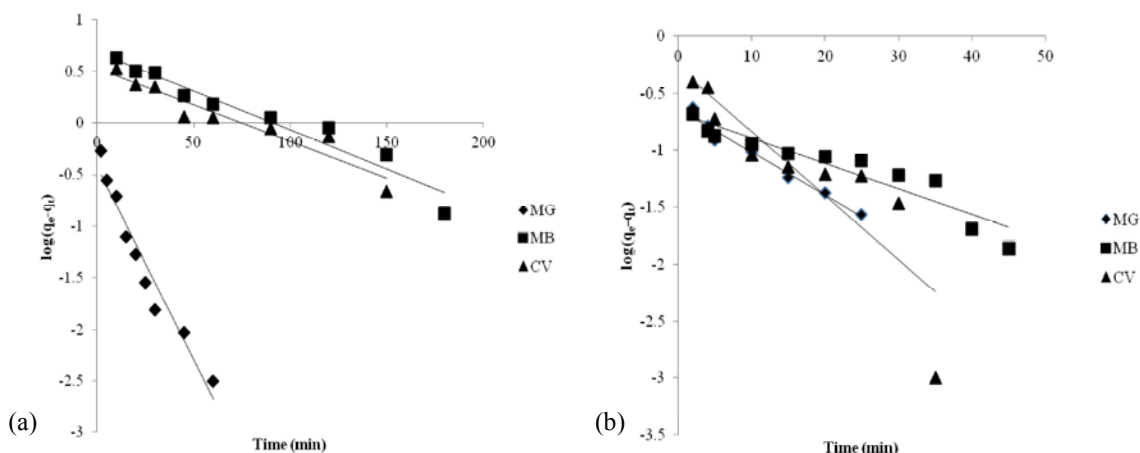
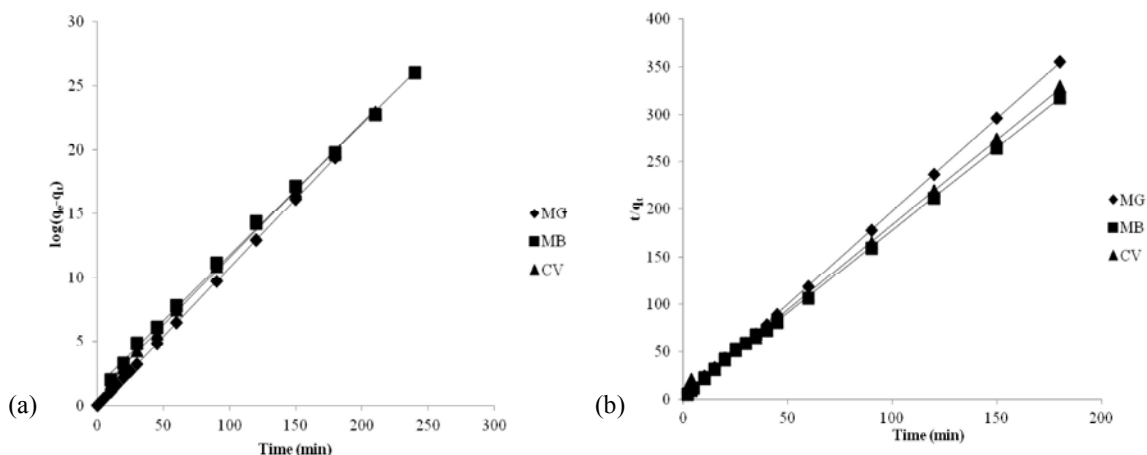Fig. 5: Pseudo 1ˢᵗ Order Kinetics (a) Single System (b) Tertiary System

Fig. 6: Pseudo 2ⁿᵈ Order Kinetics (a) Single System (b) Tertiary System

- Pseudo first-order equation given by Lagergren [22].

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \qquad (1)$$

Where q_e and q_t are the amounts of the MB adsorbed (mg/ g) at equilibrium and at time t (min), respectively and k_1 the rate constant adsorption (h^{-1}).

- The pseudo second-order equation based on equilibrium adsorption [23].

$$\left(\frac{t}{q_t}\right) = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}(t) \qquad (2)$$

Where k_2 is the rate constant of pseudo second-order adsorption (g/mg/min).

- Intraparticle diffusion model Weber and Morris equation [24].

$$q_t = k_{id}t^{1/2} + C \qquad (3)$$

Where C is the intercept and k_{id} is the intraparticle diffusion rate constant (mg/g min⁰·⁵), which can be evaluated from the slope of the linear plot of q_t versus $t^{1/2}$.

Fig. 5 and 6 shows the plot of the Pseudo First and Pseudo Second Order model for adsorption of single and tertiary system of basic dyes. Experimental and theoretically calculated q_e values and coefficients related to kinetic plots are given in Table 4. From the Table 4 based on the comparison between experimental and theoretically calculated q_e values, it was found that the pseudo second order model fitted better than Pseudo First order model for all system of MG, MB and CV. Fig. 7 shows the plots of the intra particle diffusion model for adsorption of single and tertiary system of basic dyes. The k_{id} values were obtained from the slope of the linear portions of the curve of different dye system and given in Table 5. According to this model, the plot of uptake, q_t, versus the square root of time ($t^{1/2}$) should be linear if intraparticle diffusion is involved in the adsorption process and if these lines pass through the origin then

Table 4: Kinetic Co- efficients

		Pseudo 1st Order Co-efficients			Pseudo 2nd Order Co-efficients			
		---	---	---	---	---	---	---
System	Dyes	q_e (mg/g)	k_1 (1/min)	R^2	q_e (mg/g)	k_2 (g/mg/min)	R^2	$q_e$cal (mg/g)
Single System	MG	0.372	0.086	0.948	9.285	0.983	1	9.145
	MB	928	0.018	0.940	9.756	0.007	0.9984	8.440
	CV	3.367	0.016	0.913	9.506	0.011	0.9983	8.7
Tertiary System	MG	0.212	0.052	0.892	0.561	0.583	0.999	7.600
	MB	0.230	0.087	0.976	0.512	1.466	0.999	8.500
	CV	0.531	0.129	0.762	0.577	0.652	0.9995	8.2

Table 5: Intraparticle diffusion constants for different Dye Systems

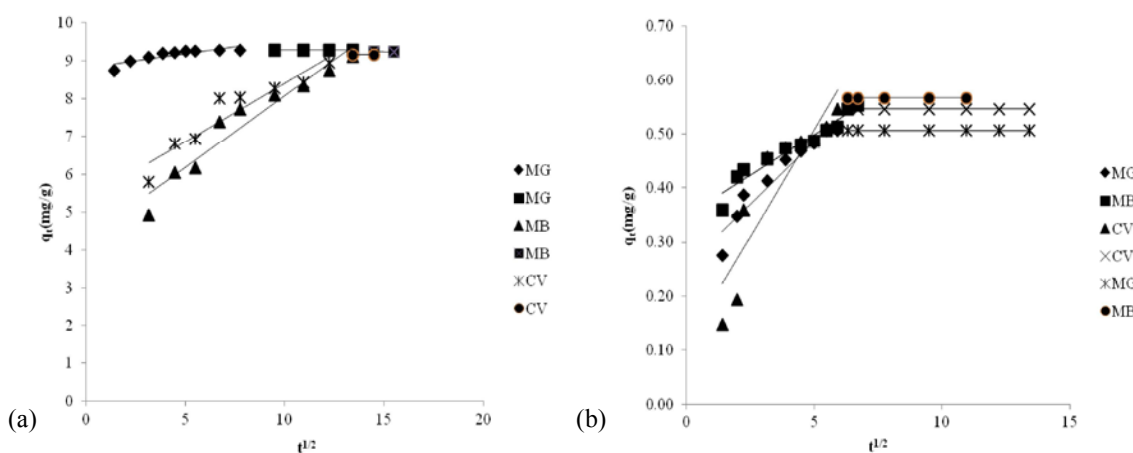| Systems	Dyes	$K_{i,1}$	$K_{i,2}$	C_1	C_2
Single System	MG	0.074	~0	8.811	9.275
	MB	0.378	~0	3.01	9.159
	CV	0.307	0.0028	5.3417	9.274
Tertiary System	MG	0.047	-	0.2531	0.507
	MB	0.03	-	0.3481	0.547
	CV	0.08	-	0.1088	0.567
	CV	1.215	-	0.5453	8.46

Fig. 7: Intraparticle Diffusion Model (a) Single System (b) Tertiary System

intraparticle diffusion is the rate controlling step. When the plots do not pass through the origin, this is indicative of some degree of boundary layer control and these further shows that the intraparticle diffusion is not the only rate-limiting step, but also other kinetic models may control the rate of adsorption, all of which may be operating simultaneously. The values of intercept give an idea about the boundary layer thickness such as the larger the intercept, the greater the boundary layer effect [24].

Effect of Adsorbent Concentration: The removal of dyes on Bottom ash was studied by changing the quantity of adsorbent while keeping constant initial dye concentration, temperature and pH at equilibrium time. Fig. 8 shows the effect of adsorbent concentration on the removal of dyes with different adsorbent doses for single and tertiary systems respectively. From the Fig. 8(a), it can be observed that the removal efficiency increases up to a certain level and beyond that it is more or less constant. The decrease in qe may be due to the solute transfer rate on to the adsorbent surface, that is, the amount of solute adsorbed onto unit weight of adsorbent get splitted with increasing adsorbent dosage [25]. The maximum MG removal of 92.5% was observed at 1g/L, MB removal of 95% and 99% for CV was observed at 1.6 g/L. From the Fig.8 (b), it was found that MG removal of 89% was achieved at 1.8 g/L, 92% of MB removal at 1.6 g/L and 91% for CV at 1.6 g/L. By comparing the adsorbent dosage (corresponding to maximum removal efficiency) of the individual system with tertiary system, the dosage requirement was more or less equal in case of tertiary system when compared to the single system.
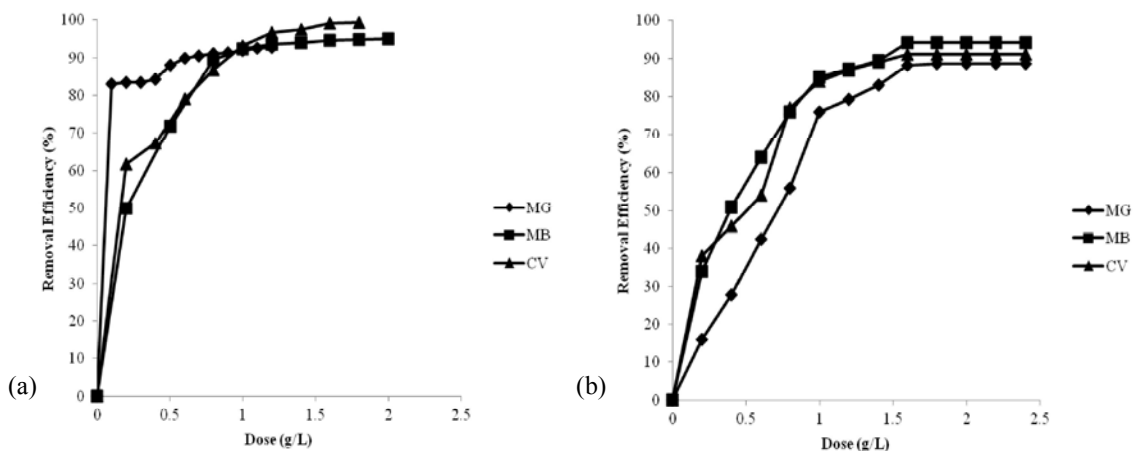
Fig. 8: Effect of Dose (a) Single System (b) Tertiary System

Isotherm Modelling: The equilibrium isotherm is of fundamental importance in the design of adsorption. The isotherm expresses the relation between the mass of dye adsorbed at constant temperature per unit mass of the adsorbent and liquid phase concentration [25]. Equilibrium data should accurately fit into different isotherm models to find a suitable model that can be used for the design process [26]. The parameters obtained from the different models provide important information on the sorption mechanisms, the surface properties and affinities of the sorbent [27]. The adsorption isotherm study was carried out on two well-known isotherms, the Langmuir [28] and the Freundlich [29] adsorption isotherm models. The Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane of surface [30]. While, the Freundlich isotherm model assumes heterogeneous surface energies, in which the energy term in the Langmuir equation varies as a function of the surface coverage [31].

The linear form of Langmuir isotherm is expressed as [28]:

$$\frac{1}{X/M} = \frac{1}{q_{max}} + \frac{1}{q_{max}b}\frac{1}{C_e} \qquad (4)$$

Where

b = Constant that increases with increasing molecular size

q_{max} = Amount adsorbed to form a complete monolayer on the surface

The Freundlich isotherm in linear form is expressed as [29]:

$$\log q_e = \log K + \frac{1}{n} * \log C \qquad (5)$$

Where,

X = weight of substance adsorbed

M = Weight of adsorbent

C = Concentration remaining in solution

k, n = constants depending on temperature, the adsorbent and the substance to be adsorbed. The coefficients k and n can be estimated from slopes and by substituting values from a line fitted to a graph of log (X/M) versus log C.

The Langmuir and Freundlich adsorption isotherm plot for single and tertiary systems of dyes are shown in Fig. 9 and 10. The Langmuir and Freundlich adsorption constants evaluated from the isotherms together with the correlation coefficients are presented in Table 6. In point of the numerical values of correlation coefficients the comparison it appeared that the equilibrium data were well described to a lesser extent by Langmuir model but Freundlich model seemed to be more appropriate for MG, MB and CV in all three system. The value of Freundlich constant *n* (Table 6) is greater than unity for all the dye system, indicating that both basic dyes were favorably adsorbed by Bottom ash [32] where as n is less than unity for MG in single system. As expected with the kinetic studies, the maximum fixation capacity, q_{max} was obtained at 30°C for MG to be 13.87 mg/g, for MB to be 151.51 mg/g and 12.1 mg/ g for CV in single system.

A comparison of adsorption capacity for single system (in the absence of other dyes) and multi-component adsorption (in the presence of other dyes) of MG, MB and CV is given in Table 7.
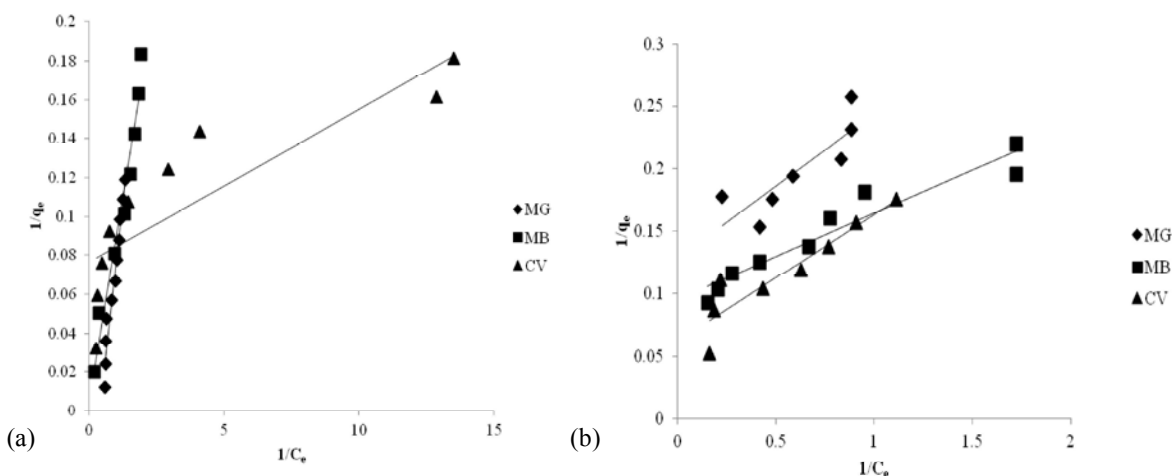
(a)

(b)

Fig. 9: Langmuir Isotherm (a) Single System (b) Tertiary System
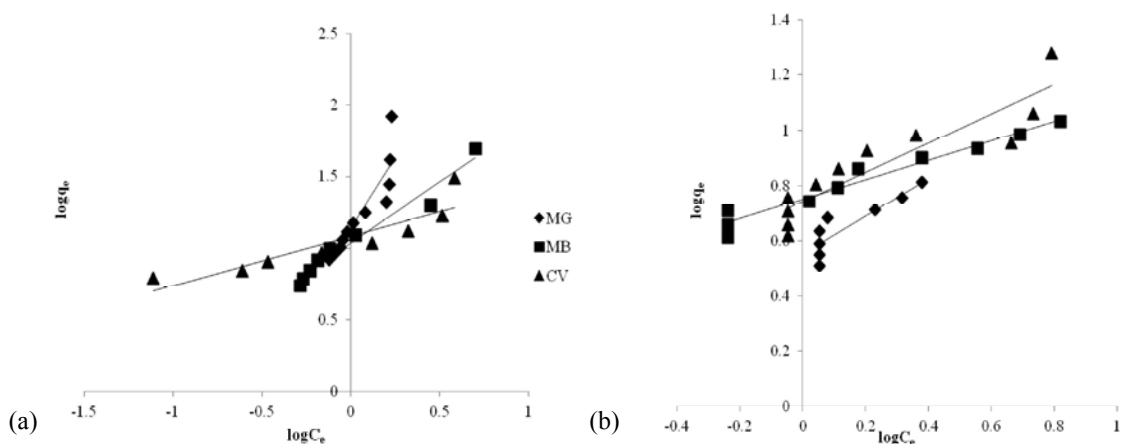

(a)

(b)

Fig. 10: Freundlich Isotherm (a) Single System (b) Tertiary System

Table 6: Isotherm Constants for Single System

System	Dyes	Langmuir Coefficients			Freundlich Co-efficients		
		q_{max} (mg/g)	b (1/min)	R^2	n	k_f (mg/g)	R^2
Single	MG	-	-0.373	0.949	0.501	13.87	0.8167
	MB	151.52	0.080	0.9582	1.175	10.86	0.9597
	CV	13.06	9.696	0.7332	2.897	12.10	0.81
Tertiary	MG	7.81	1.102	0.7156	1.468	3.57	0.7911
	MB	10.54	1.364	0.924	2.825	5.63	0.956
	CV	16.05	0.616	0.8614	1.889	5.51	0.9351

Table 7: Adsorption Capacities for Single and Tertiary System

Adsorbents	Dyes	Adsorption Capacity (mg/g)		
		Single System (Q_0)	Tertiary System (Q_{mix})	Q_{mix}/Q_0
	MG	13.82	3.57	0.258
Bottom ash	MB	10.86	5.63	0.537
	CV	12.10	5.51	0.456

Table 8: Comparison of adsorption capacities of various low cost adsorbents for MB removal

Adsorbent	Adsorption Capacity (mg/g)	Reference
Wheat Shells	16.56	[34]
Natural Jordanian Tripoli	16.60	[35]
Sawdust	19.41	[36]
Polypyrrole coated sawdust	34.36	[36]
Fly ash clay sand	3.88	[37]
Walnut Shell	6.70	[38]
Peanut hull	123.50	[39]
Yellow Passion fruit waste	44.70	[40]
Bottom ash	10.86	Present study

From the Table 7, it was found that the sorption capacity of single system have higher values than the multi component adsorption. Adsorption in multi-component systems is much complicated because of the solute-surface interactions and competition of dyes with each other. The effect of dye interaction [33] on the sorption process may be represented by the ratio of the sorption capacity of one dye in the presence of the other dyes, Q_{mix}, to the sorption capacity of same dyes when it is presented alone in the solution, Q_0, such that for:

- $(Q_{mix}/Q_0) > 1$ the sorption is promoted by the presence of other dyes,
- $(Q_{mix}/Q_0) = 1$ there appears no observable net interaction,
- $(Q_{mix}/Q_0) < 1$ the sorption is suppressed by the presence of other dyes.

The values of Q_{mix}/Q_0 are found to be <1 for all dyes (Table 7). These results indicated that the sorption of individual dye is suppressed by the presence of other dyes. Q_{mix} increased in the order (MB < CV< MG) for the adsorption of MG, MB and CV in multi-component system. Overall, it may be concluded that the adsorption capacity of Bottom ash decreases in tertiary system as compared to the single system [33]. Comparisons of adsorption capacities of various low cost adsorbents for MB removal are listed in Table 8. From Table 8, it was found that the adsorption capacity of Bottom ash is comparable.

CONCLUSIONS

Bottom ash, a thermal power plant waste has the ability to remove basic dyes (MG, MB and CV) from single and tertiary (MG+MB+CV) dye solution. In the single system, the optimum contact time, the optimum dose for MG was found to be 15 min, 1g/L with the removal efficiency of 92%, for MB 210 min, 1.6g/L with 95% removal and for CV 180 min, 1.6 g/L with 99% removal. In the tertiary system, the optimum contact time, the optimum dose for MG was found to be 45 min, 1.8g/L with the removal efficiency 89%, for MB 60 min, 1.6g/L with 94.2% removal and for CV, 60 min, 1.6 g/L with 91% removal. Removal efficiency of Bottom ash increases with increasing the adsorbent dosage up to an optimum dosage. In the kinetic study, Pseudo 1st and 2nd order models were fitted for all dye systems. Based on the experimental sorption capacity values compared with model values it may be concluded that pseudo second order model fitted better than Pseudo First order model for all system of MG, MB and CV. From the isotherm study, the adsorption capacity increased in the order of MB< MG<CV for single and MB<CV<MG for tertiary system. It may be concluded that the adsorption capacity of Bottom ash decreases in tertiary system as compared to single system. Langmuir and Freundlich isotherm models were fitted for all system of dyes, Freundlich isotherm model found to be the best fit for all systems.

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