Utilization of Fly ash as Low-Cost Adsorbent for the Removal of Methylene Blue, Malachite Green and Rhodamine B Dyes from Textile Wastewater

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Abstract

Fly ash was utilized as a potential low-cost adsorbent for the removal of methylene blue, malachite green and rhodamine B from artificial textile wastewater. The adsorbent was characterized by its physico-chemical analyses, porosity, surface area, ignition loss measurements and scanning electron micrograph. Adsorption studies were carried out in a batch process with different concentrations of dyestuffs, pH, temperature and contact time. The removal of methylene blue, malachite green and rhodamine B varied from 0.228 to 0.814, 0.219 to 0.644, and 0.184 to 0.618 mgg^{-1} respectively when the initial dye concentration was raised from 5 to 20 mgL^{-1}. The amount of dye adsorbed (mgg^{-1}) was found to increase with increase in the contact time; with 80 minutes for malachite green and rhodamine B and 100 minutes for methylene blue. The equilibrium data closely followed both Langmuir and Freundlich isotherms, but the latter isotherm fitted the data better. The changes in standard free energy ($\Delta G°$), standard entropy ($\Delta S°$) and standard enthalpy ($\Delta H°$) were calculated. The adsorption of all the dyes onto fly ash was found to be physical and exothermic in nature.

Keywords: Methylene Blue; Malachite Green; Rhodamine B; Fly ash; Adsorption, Langmuir and Freundlich Isotherms.

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1. Introduction

The discharge of colored wastewater from paper and pulp, textile and dyeing, leather, printing industries and food process industries is posing a serious environmental concern due to their poor biodegradability, carcinogenicity and toxicity [1-4]. Similarly, the disposal of fly ash, which is a voluminous by-product of coal burning power plants, is posing a major problem as per its storage space and the cost involved. The fly ash is abundantly available in India and according to one estimate about 125 million tons of fly ash is generated per annum and it is expected to increase to about 200 million tons in the near future [5] At present about 2 % of the total fly ash is gainfully utilized [5]. Adsorption [6,7] has emerged as an effective method for the removal of many aqueous contaminants. Activated carbon, due to its large surface area and the presence of many different types of surface functional groups, is a very effective adsorbent. However, the high cost of activated carbon has led to the development of new cost-effective adsorbents with similar adsorption characteristics.

A number of low-cost adsorbents such as activated carbon prepared from various wastes [8-15], diatomaceous earth [16], industrial waste products [17-19], bagasse fly ash [20], clay mineral [21], biodegradable waste [22], hydrotalcite [23], coffee grounds [24], dusts [25-27], kudzu [28], 'waste' metal hydroxide sludge [29], agricultural waste [30], dolomitic sorbents [31], charcoal from extracted residue of coffee beans [32], bentonite and polyaluminum hydroxide [33] have been studied for adsorption of different dyes from solutions. Fly ash, containing about 2-5 % un-burn carbon, has been reported to adsorb metals [34-37] and dyes [38-41] from aqueous solutions. In the present paper, reports are presented on the removal of the most commonly used coloring dyes (i.e. three basic dyestuffs methylene blue, malachite green and rhodamine B, Fig. 1) from artificial textile wastewater using fly ash as low-cost adsorbent. These dyes are chosen for the present study because they are the brightest class of soluble dyes used in the textile industry [42].

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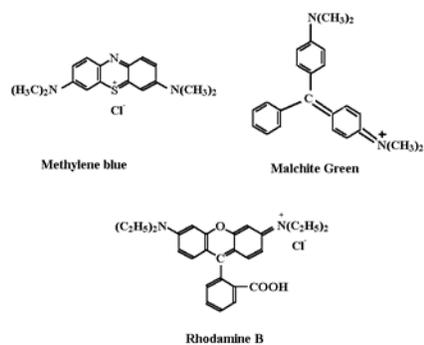
Figure 1. Chemical structure of methylene blue, malachite green and rhodamine B.

2. Experiments

2.1 Materials and Methods

Fly ash, obtained from Indraprastha Thermal Power Station, New Delhi, India. 10.0 g of fly ash was washed with distilled water (50 mL) five times, dried in an oven at 110 °C for 24 h, sieved to desired particle sizes (75, 150 and 300 µm) and finally stored in vacuum desiccators. Stock solutions of the dyes were prepared in double distilled water. The chemical analysis of fly ash was done following standard methods [43,44]. Surface area was determined by N_2-BET method [45] employing a Quantasorb surface analyzer, QS/7. Porosity was measured by mercury intrusion porosimeter, Micrometric model 9310 [46] while the mean particle diameter was determined [46] with the Laser particle size analyzer, Malvern 36000. Absorbance measurements were made with a Jasco-7800 UV-VIS spectrophotometer at corresponding wavelength for maximum absorbance (λ_{max}) 665 nm for methylene blue, 615 nm for malachite green and 555 nm for rhodamine B. The pH measurements were made using a pH-meter. The scanning electron micrograph was obtained with a scanning electron microscope (Model JEOL JSM 840).

2.2 Adsorption Studies

Batch experiments were carried out using a series of Erlenmeyer flask of 50 mL capacity covered with aluminum foil to prevent the introduction of any foreign particle contamination. The effect of pH, concentration, dose, temperature and shaking time was studied. Isotherms were run by taking selected different concentrations of methylene blue, malachite green and rhodamine B at desired temperatures (20, 30 and 40 ℃) and pH. After the required experimentation, the solutions were filtered and the concentrations of methylene blue, malachite green and rhodamine B were determined in filtrate using a UV-visible spectrometer. For kinetic studies the batch technique was used due to its simplicity. A series of Erlenmeyer flasks of 50 mL capacity containing a defined

volume of solutions of methylene blue, malachite green and rhodamine B of known concentrations were kept in a thermostatic shaking water bath. After attaining the desired temperature (30 ℃), a known amount of the adsorbent was added to each flask and the flasks were allowed to agitate mechanically. At given time intervals, the solutions were filtered and the supernatants were analyzed for methylene blue, malachite green and rhodamine B as mentioned above.

One gram of fly ash was maintained in contact with 50 mL dye solution (initial concentration; 5, 10, 15, 20, 25 mg L^{-1}) in an Erlenmeyer flask and was shaken in a thermostatic water bath (120 cycle/min). After the different contact times, the solution was filtered on a Whatman filter paper No. 42. The residual dye concentration in each solution was measured spectrophotometrically at the corresponding λ_{max} (665, 615 and 555 nm for methylene blue, malachite green and rhodamine B, respectively). The original pH of the dye solution was adjusted to the desired value by adding required quantities of decimolar solutions of sulphuric acid or sodium hydroxide. Effects of initial dye concentration, particle size, and pH at different agitation time were also studied following the same experimental procedures. In order to eliminate error due to adsorption of dyes on filter paper; a parallel control set (without fly ash) was run in an identical manner. The percentage removal of dye was calculated on the basis of color of wastewater in the control set.
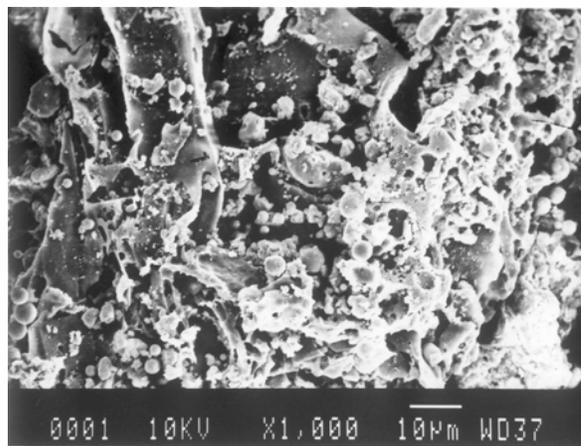
Figure 2. Scanning Electron Micrograph of the fly ash sample

2.2.1 Adsorption Isotherms

The adsorption equilibrium models often provide insight into the sorption mechanism, surface properties and affinity of adsorbent. The most commonly used equilibrium models are Langmuir and Freundlich isotherms [47]. The fractional coverage, θ, on an adsorbent surface at constant temperature is given by Langmuir isotherm. Langmuir isotherm is based on the assumption of

uniform energy of adsorption on the surface of the adsorbent. The total monolayer capacity of the adsorbent is equal to $Q_\circ$, a Langmuir constant. The rearranged Langmuir isotherm is represented by following equation:

$$C_e/q_e \ = \ 1/Q_\circ \, b \ + \ C_e/Q_\circ \qquad (1)$$

where, C_e is the equilibrium concentration of dye (mg L^{-1}), q_e is the amount of dye adsorbed at equilibrium (mgg^{-1}), $Q_\circ$ is the monolayer adsorption capacity (mgg^{-1}), and b is the constant related to the free energy of adsorption. Hence, a plot of C_e/q_e versus C_e yields a straight line with $Q_\circ$ calculated from the slope and the value of b as its intercept.

Freundlich isotherm is an exponential equation and can be written as:

$$q_e \ = \ K_F \ C_e^{\,1/n}$$
$$\log q_e \ = \ \log K_F + \ 1/n \log \ C_e \qquad (2)$$

where, K_F is the constant indicative of the relative adsorption capacity of the adsorbent (mg g^{-1}), and $1/n$ is the constant indicative of the intensity of the adsorption. The Freundlich equation possesses two constant, K_F and $1/n$. High and low values of K_F and $1/n$ indicate high adsorption throughout the concentration range studied whereas high values of $1/n$ and low values of K_F show low adsorption. When $1/n \ = \ 1$, the adsorption is favorable.

2.2.2 Adsorption Thermodynamics

The adsorption at any interface between two phases can be regarded as an equilibrium process, the point of equilibrium being dictated by the relative energies of the adsorbate in the two phases. These energy values can be defined in terms of thermodynamic parameters such as change in free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$). The feasibility of the removal process is often evaluated by determining these thermodynamic parameters using the following equations:

$$\Delta G° \ = \ \ -RT \ \ln b \qquad (3)$$
$$\Delta H° \ = \ \ R(T_2 \, T_1) \, / \, (T_2 - T_1) \ln (b_1 \, / \, b_2), \qquad (4)$$
$$\Delta S° \ = \ \ (\Delta H° \ - \ \Delta G°) \, / \, T \qquad (5)$$

where b, b_1, and b_2 are the Langmuir constants at temperature T, T_1 and T_2, respectively.

2.2.3 Adsorption Kinetics

The study of kinetics of adsorption describes the solute uptake rate at the solid-solution interface. The rate constant of adsorption of dyes on to fly ash, K_{ad}, has been studied using the Lagergren first order rate equation:

$$\log (q_e - q_t) \ = \ \log q_e \, - \, K_{ad} \, t \, / \ 2.303 \qquad (6)$$

where, q_e is the amount of dye adsorbed at equilibrium, and q_t is the amount of dye adsorbed at time t (both in mgg^{-1}).

3. Results and Discussion

3.1 Characterization of the Adsorbent

The chemical analyses indicated that the major constituent of the fly ash was SiO_2, (60.10 %) followed by Al_2O_3 (18.60 %) and Fe_2O_3 (6.40 %). Other constituents included CaO (6.30 %) and MgO (3.60 %). The adsorbent had surface area of 40.16 m^2 g^{-1}; porosity, 0.43 cm^3 g^{-1}; bulk density, 3.51 g cm^{-3}; and showed an ignition loss of 4.90 %. The scanning electron micrograph at 1000 x magnification (Fig. 2) of fly ash (75 µm) shows typical fly ash morphology and surface texture. The adsorbent consisted mainly of solid spheres of a wide range of sizes with the zero charge of the fly ash being 5.8. Some adsorbents such as fly ash and bottom ash contain 2-15 % un-burnt carbon, which may attach organic functional groups containing oxygen. On contact with the aqueous medium, these oxides form surface hydroxyl compounds and are amphoteric in nature. The overall interaction of metal oxides with water may be described according to Ahmed [48]. The charged interface thus formed interacts with the charged aqueous pollutant species of the wastewater. Electrical charge on the interface is also determined by zero point charge (pH$_{zpc}$), of the adsorbent species. It is understood that below pH$_{zpc}$, the adsorbent acquires positive charge and, above it, the surface of the adsorbent remains negatively charged. Weber and Morris [49] correlated molecular weight of substances with capacity of adsorption and concluded that by increasing the molecular weight the capacity was significantly increased. It is noteworthy that the rate dependence on molecular size can be generalized only within a particular chemical class of molecules. For example, large molecules of one chemical class of compounds may adsorb more rapidly than smaller ones of another class. Further, this rate dependence on size is applicable for rapidly agitated batch reactors.

3.2. Effect of Initial Concentrations

To study the effect of different concentrations of dyes on adsorption behavior three concentrations (5, 10 and 20 mg L^{-1}) were used and the amounts adsorbed were calculated and given in Table 1 and plotted in Fig. 3. Table 1 and Fig. 3 indicate that the amount of dye adsorbed is increased from 0.228 to 0.814 mgg^{-1}, 0.219 to 0.644 mgg^{-1} and 0.184 to 0.618 mgg^{-1} when the initial concentration was increased from 5 to 20 mg L^{-1}, for methylene blue, malachite green and rhodamine B, respectively. The observed increase in the adsorption of dyestuffs with increasing concentration may be due to sufficient adsorption sites at adsorbent [50].

Table 1. Amount (mg g⁻¹) and percentage of dyes adsorbed at 30±1 °C

Concn. of dyes	Methylene blue		Malachite green		Rhodamine B	
(mgL⁻¹)	(mg g⁻¹)	(%)	(mg g⁻¹)	(%)	(mgg⁻¹)	(%)
5.0	0.228	91.20	0.219	87.60	0.184	73.64
10.0	0.434	86.80	0.387	77.38	0.334	66.80
20.0	0.814	81.38	0.644	64.42	0.618	6178

3.3 Effect of Contact Time

The adsorption experiments were also carried out at different time intervals (from 15-200 minutes) and the results of these findings are plotted in Fig. 4. The effect of contact time was also studied at different values of pH (pH 3, 5, 7 and 9). The uptake of adsorbate species was rapid in the initial stages of the contact period and became slow near the equilibrium. In between these two stages of the uptake, the rate of adsorption was found to be nearly constant. This result is expected because a large number of surface sites are available for adsorption at the initial stages and after a lapse of time, the remaining surface sites are difficult to occupy because of repulsion between the solute molecules of the solid and bulk phases [50]. The structure of dyes indicates the presence of secondary and tertiary amines, carboxylic group, and oxygen and sulphur atoms and adsorbents contains silica, iron and calcium oxides. Therefore, adsorption may be due to hydrogen bonding, van der Waal forces, and others. Examination of dye structure indicates that malachite green should absorb strongly but methylene blue adsorbed the most. This behavior may be explained on the basis of steric effect in malachite green and rhodamine B dyes versus methylene blue that has no steric effect

3.4 Effect of pH

The effect of pH and contact time on removal of dyestuffs is shown in Fig. 5 and it is evident from this figure that maximum adsorption of malachite green is at pH value of 7.0 while the adsorption of methylene blue and rhodamine B was maximum at high pHs (7-9). But due to pH of natural water being in the range of 7 to 8, 7.5 was considered as the optimum pH for maximum adsorption of these dyes. The effect of variation of pH can be seen in Fig. 4 and it is clear from this figure that adsorption of dyes increases from 0.426 to 0.467, 0.232 to 0.394 and 0.286 to 0.367 mg g⁻¹ for methylene blue, malachite green and rhodamine B, respectively as the pH is increased from 3 to 9. It appears that silica and alumina, which are chief constituents of fly ash, form metal-hydroxide complexes in solution and the subsequent acidic or basic dissociation of these complexes at the solid-solution interface leads to either positive or negative surface charge [51]. At acidic pH, the dissociation of the metal-hydroxide complexes

causes the surface to become positively charged. However, with increasing pH, the surface becomes negatively charged as in the alkaline medium the silica and alumina get converted into SiO_2^- and $Al_2O_3^-$ type of functional sites and, therefore, the binding of positively charged dyes onto these surfaces become much favorable resulting in enhanced adsorption of dyes [38,52].The variation of adsorption with pH can be explained by considering the difference in the structure of the dyes, as well as the point of zero charge of the fly ash (which is 5.8). The main constituents of fly ash are silica and alumina. The ZPC (a concept; related to the adsorption process; describes the condition when the electrical charge density on a surface is zero) of silica is 2.3, while that of alumina is 8.2, and as such the surface of fly ash would have high positive charge density below pH value of 5.8, i.e. ZPC of the fly ash [48]. Under these conditions the uptake of positively charged dyes would be low; with increasing pH, the negative-charge density on the surface increases resulting in enhanced removal.

3.5 Effect of Particle Size

The relationship between the amounts of dye adsorbed at 75, 150 and 300 µm particle sizes is shown in Fig. 6, which shows that the adsorption capacity increases with decreasing particle size of the adsorbent. This could be due to substantial increase in the surface area for small particle [53,54]. Adsorption capacity at 300 µm is very low and for particle sizes between 75 and 150 µm, adsorption capacity is 12.4, 15.8 and 12.6 percent higher than that at 75 µm for methylene blue, malachite green and rhodamine B respectively. Therefore, 75 µm is considered as optimum particle size.

3.6 Adsorption Dynamics

The adsorption of dyes onto the fly ash at different time intervals is depicted in Fig. 4. The adsorption of dye increased with lapse of time and gradually attained equilibrium at 80 minutes. The adsorption rate constant, K_{ad} at 20, 30 and 40 °C, is calculated from the slope of the linear plots of log $(q_e - q)$ vs. t (Fig. 7), based on Lagergren first order rate equation 6 [55] The adsorption rate constants were determined from the slopes of the plots and were found to be 6.45, 5.01 and 4.51 $\times 10^2$ min⁻¹ for methylene blue, 4.70, 4.42 and 4.23 $\times 10^2$ min⁻¹ for malachite green and 4.79, 4.65 and 4.61 $\times 10^2$ min⁻¹ for rhodamine B at 20, 30 and 40 °C respectively (Table 2). The plots were found to be linear with significant regression coefficients in the range 0.923-0.975, indicating that Lagergren's equation is applicable to the dye adsorption process with first order process.

3.6.1 Adsorption Isotherms

Both Langmuir and Freundlich isotherm models have been employed to evaluate the adsorption data for methylene
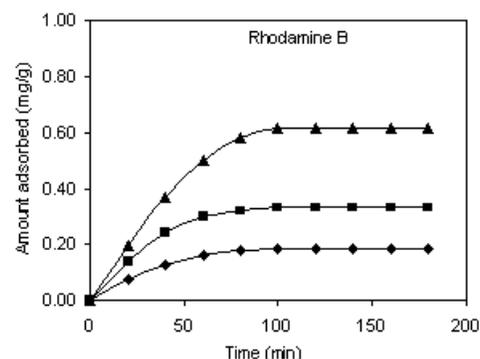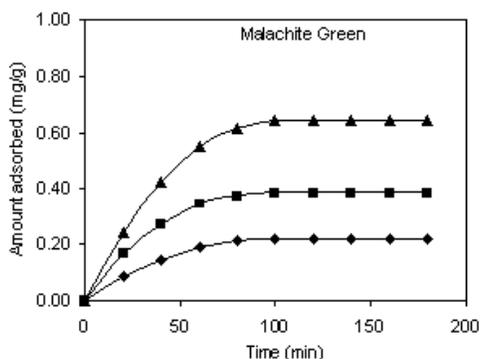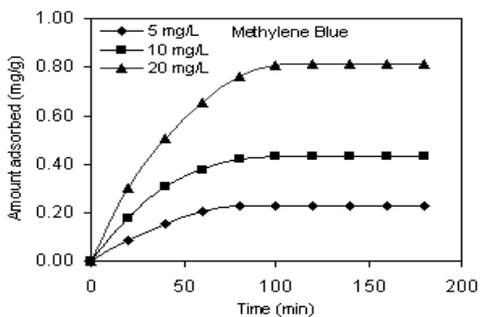
Figure 3. Effect of concentration on the adsorption of dyes, (Temp. 30ºC, Particle size 75 µm)

Figure 4. Effect of contact time at different pHs (Temp. 30ºC, Particle size 75 µm, Conc. 10 mgL^{-1})

Table 2. The values of Langmuir constants

Adsorbate (Dyes)	Temp. (ºC)	Q_o	B	r^2	R_L	K_{ad} x 10^2/min^{-1}
Methylene blue	20	4.2793	0.0123	0.9758	0.0242	6.45
	30	2.9434	0.0183	0.9230	0.0770	5.01
	40	2.6868	0.0197	0.9251	0.0749	4.51
Malachite green	20	1.5805	0.0358	0.9661	0.0339	4.70
	30	1.3717	0.0407	0.9694	0.0306	4.42
	40	1.2290	0.0455	0.9669	0.0334	4.23
Rhodamine B	20	2.3257	0.0190	0.9230	0.0770	4.79
	30	1.8706	0.0231	0.9492	0.0508	4.65
	40	1.3045	0.0317	0.9461	0.0539	4.61

blue, malachite green and rhodamine B. Langmuir isotherm is based on the assumption of uniform adsorption energy throughout the surface of the adsorbents. When

adsorption is in accordance with the Langmuir equation, the total monolayer capacity of the adsorbent is equal to Q^o, a Langmuir constant. When the amount adsorbed at equilibrium is quite small, the equilibrium concentration shows a linear relationship with the amount of adsorption at equilibrium. The experimental data on the uptake of dyestuffs at 20, 30 and 40º C have been fitted in the rearranged Langmuir equation (equation no. 1). Adsorption is in accordance with the Langmuir equation, the total monolayer capacity of the adsorbent is equal to the plot of Ce/q versus Ce at different temperature is linear (Fig. 8). This suggests the applicability of the Langmuir adsorption model, and is indicative of monolayer coverage of the adsorbate at the outer surface of the adsorbent. The values of Q_o and b, at different temperatures, determined

from the slopes and intercepts of the respective plots, and the

Table 3. The values of Freundlich constants

Adsorbate (Dyes)	Temperature, (°C)	K_F	1/n	r^2
Methylene blue	20	0.0619	0.8703	0.9969
	30	0.0655	0.8277	0.9894
	40	0.0650	0.8183	0.9873
Malachite green	20	0.0777	0.7103	0.9812
	30	0.0797	0.6777	0.9824
	40	0.0796	0.6626	0.9720
Rhodamine B	20	0.0552	0.8150	0.9906
	30	0.0556	0.7856	0.9892
	40	0.0575	0.7214	0.9855

regression coefficients, r^2 are summarized in Table 2. The values of Q_o (i.e. maximum uptake) decrease with increase in temperature, thereby confirming that the process is exothermic. The dimensionless separation factor or equilibrium parameter [38], R_L ($R_L = 1/1+bC_i$) at different temperature is calculated from the Langmuir isotherms. The values of R_L lie between zero and one, suggesting that the adsorption process is favorable [56,57]. Freundlich, isotherm has been widely used for determining the adsorption capacity of different unconventional adsorbents The equilibrium adsorption data at different dye concentrations are fitted in the linear form of Freundlich isotherm model (equation no. 2). The plots of log q_e against log C_e, shown in Fig. 9 are linear and the values of K_F and 1/n, calculated from intercept and slope of the plot (Figure 9), respectively, are given in Table 3. The calculated values of 1/n are less than 1, which suggest the favorable adsorption of dyestuffs onto the fly ash [58]. The values of the regression coefficients at different temperatures indicate that the data satisfactorily follow both Langmuir and Freundlich models but the Freundlich isotherm fits the experimental data better. The values of Q_o and K_F are observed to be higher for methylene blue and malachite green dyes, respectively.

3.6.2 Thermodynamic Parameters
The amount of dye adsorbed decreased from 0.234 to 0.221 mg g^{-1} (methylene blue), 0.223 to 0.209 mg g^{-1} (malachite green) and 0.193 to 0.173 mg g^{-1} (rhodamine B) with rise in temperature from 20 to 40 °C and at 5.0 mg L^{-1} concentration, suggesting the exothermic nature of the adsorption process. It has been reported by several authors [38, 59, 60] that the chemical potential of the adsorbates are the main controlling factor in the adsorption process. If the solubility of adsorbates increases with an increase in temperature, the chemical potential is decreased, thereby causing a decrease in adsorption. The steady decrease in

Q_o values with increase in temperature indicates that the adsorption is governed by the same factor. Thermodynamic data for the adsorption of methylene blue, malachite green and rhodamine B onto fly ash are summarized in Table 4. The change in standard free energy ($\Delta G°$), standard enthalpy (ΔH^o) and standard entropy ($\Delta S°$) are calculated using equations 3, 4 and 5. The negative values of $\Delta G°$ show the spontaneous nature of the adsorption process while the small negative values of ΔH^o indicate adsorption process physical in nature. The positive values of $\Delta S°$ suggest favorable affinity of the adsorbent for the dyes.

Table 4. The values of thermodynamic parameters

Adsorbate (Dyes)	Temperature, (°C)	$-\Delta G^o$ (kJmol^{-1})	$-\Delta H^o$ (kJmol^{-1})	ΔS^o (kJmol^{-1})
Methylene blue	20	10.719	29.354	63.57
	30	10.083	5.818	14.07
	40	10.224	59.778	18.76
Malachite green	20	8.115	9.478	4.65
	30	8.069	8.799	2.41
	40	8.045	5.273	16.58
Rhodamine B	20	9.65	14.43	16.30
	30	9.49	24.97	51.05
	40	8.98	55.775	17.52

3.7 Mechanism of Adsorption
The variation in the adsorption of cations may be explained on the basis of the surface hydroxylation of oxides at the solid-solution interface. It is established that hydroxylated oxides surfaces are influenced by minute concentrations of potential determination ions, H^+ and OH^- and develops positive and negative charges at the surface. The acid-base dissociation of solid surface may be represented in the following manner [59,61].

(Basic Dissociation)   (Acidic Dissociation)
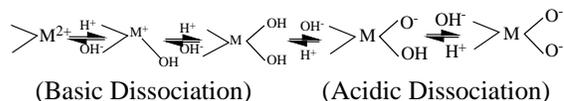
where M denotes Si, Ca, Fe etc. It is evident from the above equilibrium that with a decrease in the pH of the solution, the positive charge density on the surface increases and, hence, the adsorption of cations decreases. A decrease in pH lowers the dissociation of acid and a high pH produces negatively charged surfaces which would favor the removal of cations from the bulk. The increase in adsorption with pH is attributed due to the development of negative charges on the surface of different adsorbents. Thus, it is obvious that the adsorption of the cationic dyes

would be maximal at high (alkaline) pH ranges; due to coulomb attraction [38]. The surface charge of the major constituents of the adsorbents used plays an important role in the removal of methylene blue, malachite green and rhodamine B. The polar functional groups of the adsorbents are involved in the formation of bonds with cationic dyes. The observed decrease in the removal of dyes at lower pH is apparently due to the higher concentration of H^+ ions present in the reaction mixture, which compete with dye cations for the adsorption sites [62,63]. The determining ions are H^+ and OH^-. Generally, the solid surfaces adsorb anions favorably at low pH due to association of H^+ ions, whereas cations are adsorbed at high pH due to deposition of OH^- ions on the adsorbent surface. The mechanism of adsorption may be described as:

$$S + H^+ + A^- \rightleftharpoons S \diagup_A^H$$

and

$$S + OH^- + A^+ \rightleftharpoons S \diagup_A^{OH}$$
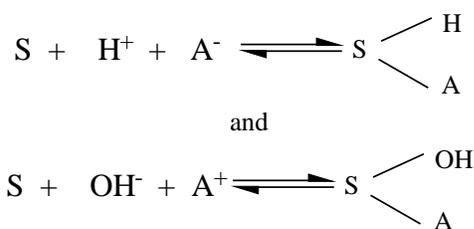
where S and A denote the surface of the adsorbent and adsorbate, respectively [64,65]. Oxides of metal and non-metals are the main constituents of many unconventional adsorbents like clays, minerals, soils, fly ash, furnace slag, etc. Such oxides are first hydroxylated in contact with water and then develop either positive or negative charges on the interface, according to pH of the solution as follows:

$$M\diagup_{OH}^{O^-} \xrightleftharpoons[-H_2O]{OH^-} M\diagup_{OH}^{OH} \xrightleftharpoons[-H_2O]{H^+} M^+\diagdown_{OH}$$
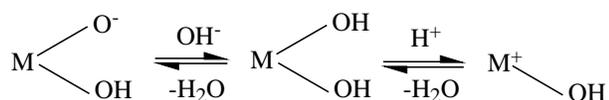
In such systems, charged species of the aqueous phase are withheld on the surface of the adsorbent by columbic forces.

3.8 Validation of the Method
The developed adsorption method was validated by carrying out seven sets (n = 7) of the experiments. The regression analysis was carried out using Microsoft Excel program. The values of standard deviation (SD) and correlation coefficients (R^2) ranged from ±0.10 to ±0.50 and 0.9997 to 0.9999 respectively. In addition, the confidence levels ranged from 99.5 to 99.8 for all the experiments.
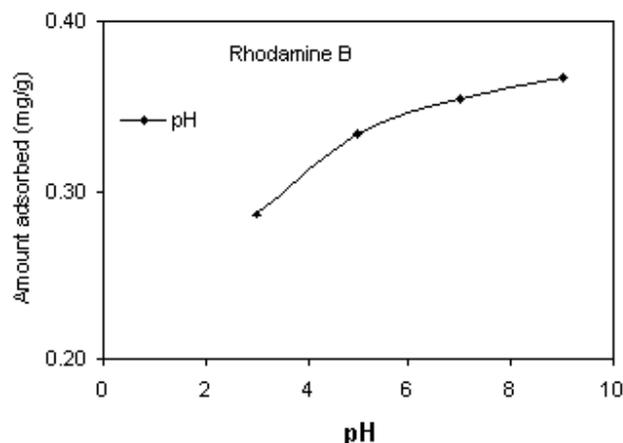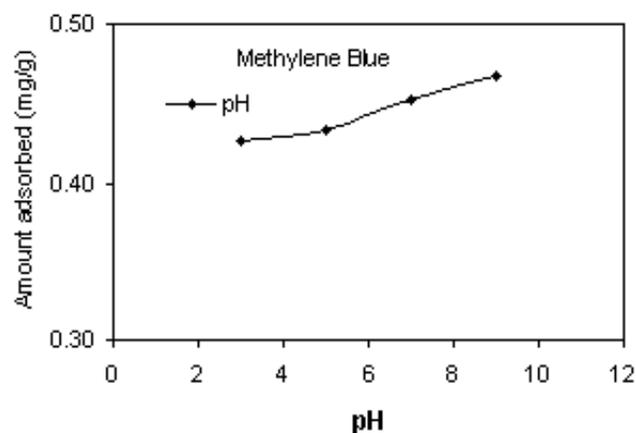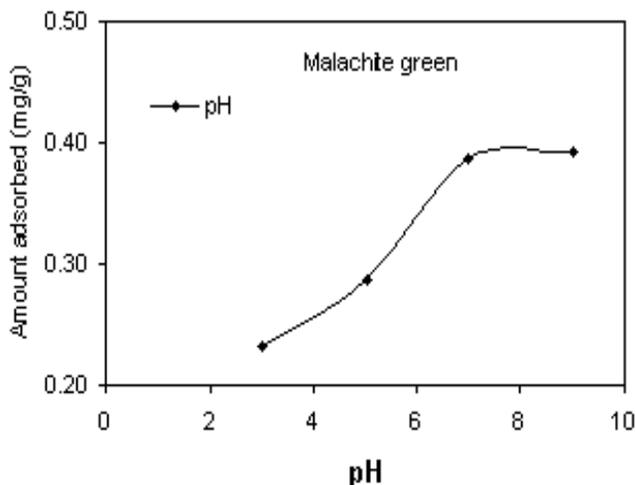
Figure 5. Adsorption versus pH (Temp. 30 °C, Particle size 75 µm, Conc. 10 mgL^{-1}).
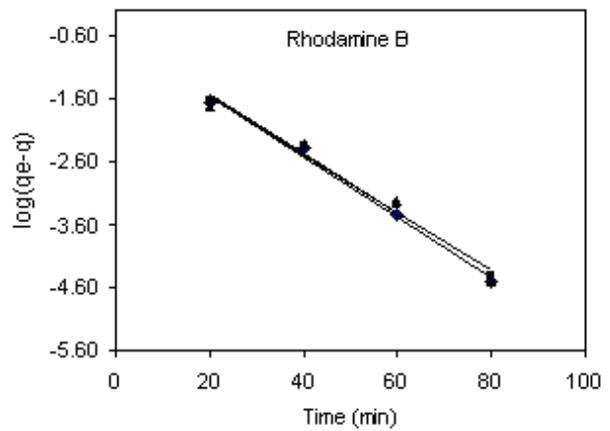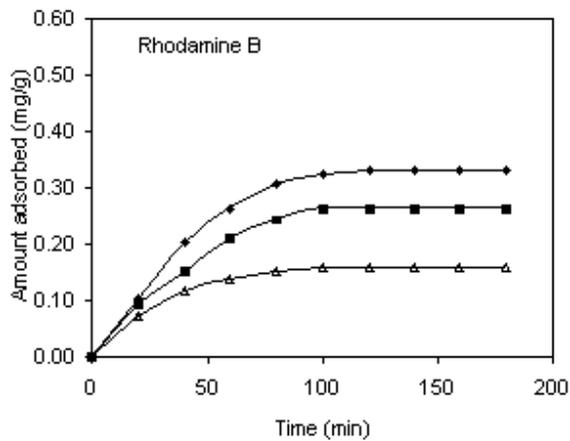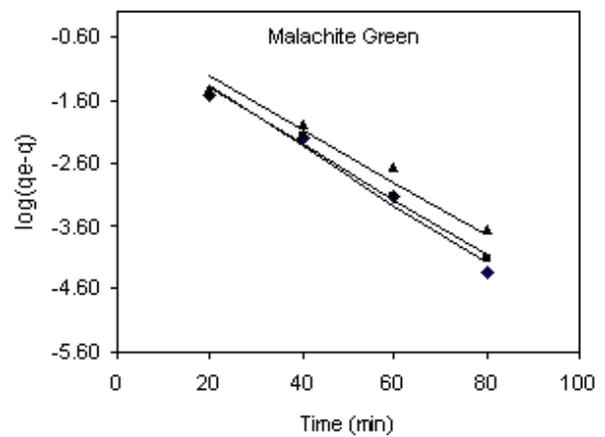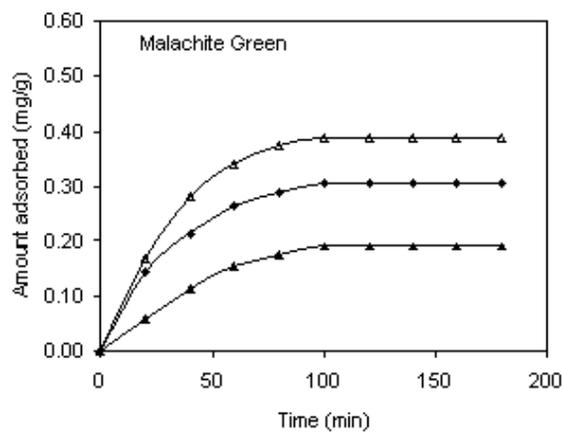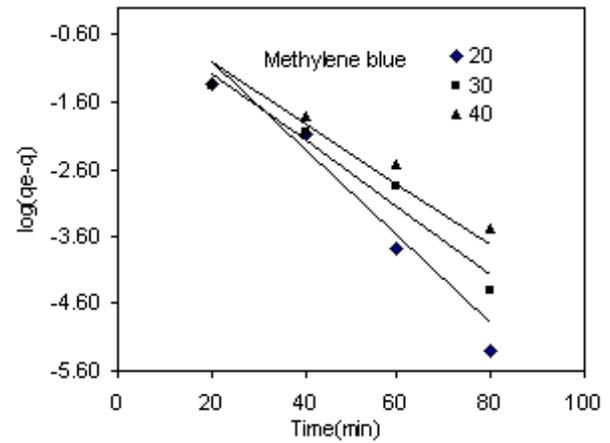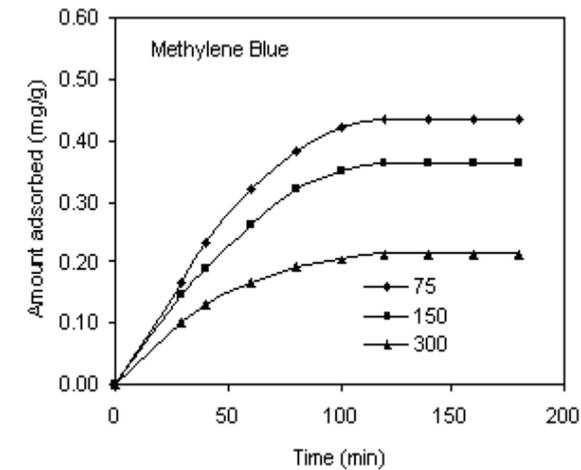
Figure 6. Effect of particle size on adsorption of dyes (Temp. 30ºC, Particle size 75 µm, Conc. 10 mgL^{-1})

Figure 7. Lagergren plots for the adsorption of dyes at different temperatures (Temp. 30ºC, Particle size 75 µm, Conc. 10 mgL^{-1})
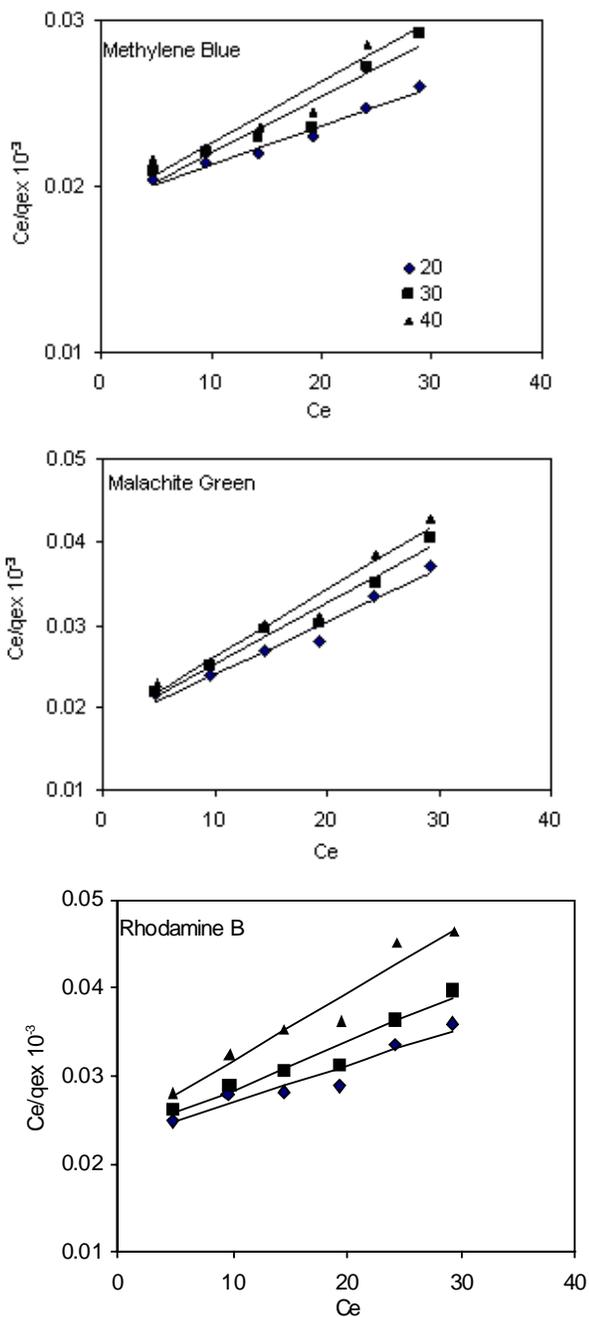
Figure 8. Langmuir plots for the adsorption of dyes at different temperatures (Temp. 30° C, Particle size 75 µm)

Figure 9. Freundlich plots for the adsorption of dyes at different temperatures (Temp. 30° C, Particle size 75 µm)

4. Conclusions

The results of the present sorption studies indicate that the maximum adsorption of malachite green and rhodamine B was obtained at 5.0 mg L^{-1}, 80 minutes, 1.0 g L^{-1}, 7.5, 75 µm and 30 ºC initial concentration, contact time, dose, pH, particle size and temperature respectively. On the other hand, the maximum adsorption of methylene blue was

observed at 100 minutes contact times with other similar conditions as in case of malachite green and rhodamine B dyes. The adsorption process was of first order; physical and exothermic in nature. The adsorption data was analyzed by Langmuir and Freundlich models and fitted well; slightly better fitted with Freundlich adsorption isotherms; indicating the appropriateness of the experiments. The fitness of Langmuir's model indicated the formation of monolayer coverage of the adsorbate on

the outer surface of the adsorbent. The fly ash adsorbent was capable of adsorbing basic dyes with high affinity and capacity indicating its potential as a low cost alternative adsorbent. The negative values of ΔG^o and ΔH^o indicated that adsorption was a spontaneous and exothermic process. The developed adsorption system is useful and can be used for the removal of the reported dyes from contaminated water.

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