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Adsorption studies on treatment of textile dyeing industrial effluent by flyash

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Abstract

Textile effluents are highly toxic as they contain a large number of metal complex dyes. The high concentration of such dyes causes many water borne diseases and increases the BOD of the receiving waters. On the other hand, flyash is a major pollutant generated in coal-based thermal power plants and has potentiality for use as an adsorbent. In the present work, adsorption studies were made in treating the dye solutions of methylene blue (M-B) and Congo red (CR) textile dyes by using flyash. Effects of quantity of adsorbent, time of contact, initial effluent concentration, pH and temperature have been investigated experimentally and the results were compared with those obtained by using activated carbon. The first-order adsorption rate constants were determined and found decreasing with temperature. The results obtained were fitted by Langmuir model since monolayer formation observed. Also, Langmuir adsorption isotherm parameters were estimated from the experimental data obtained for both methylene blue and Congo red dyes using both the adsorbents.

Keywords: Dyeing industrial effluent; Methylene blue dye; Cong red dye; Flyash; Activated carbon; Adsorption; Percentage of colour removal; Equilibrium concentration; First-order rate constants; Langmuir isotherm parameters

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1. Introduction

Industrial development is directly related to quantity of power generation and utilization in any country. Therefore, industrial development and environmental pollution go hand in hand. In India, where a projected quantity of about 250 million tonnes of coal and lignite are to be used in power generation by the year 2010, an estimated 80–100 million tonnes of flyash will be generated. The concentration and effective utilization of flyash generated from burning fuels in thermal power plants have attracted worldwide attention in view of the large disposal problems without detriment to environment. The potentiality of flyash as catalyst in destructive decolourization of various aqueous dye solutions using hydrogen peroxide was reported [1,2]. Also, it is widely reported that flyash generated from coal/lignite fired thermal power stations is a very good adsorbent for colour removal [3].

On the other hand, India is facing another type of environmental problem. Thousands of small-scale dyeing units, employing millions of people, generate enormous amount of polluted water. Mostly, the areas situated around industrial belts are under stress due to the continuous disposal of the untreated water. The quality of water is continuously deteriorating due to addition of toxic dyeing effluents. Dyeing effluents from textile industries are highly toxic as they contain a large number of metal complex dyes [4,5] (e.g. Cr and Co complexes). The high concentration of such dyes causes many water borne diseases and increases the BOD of receiving waters [6]. Hundreds of small-scale dyeing industries are facing closure since they are not treating their effluents. It is not economical for them to treat the effluent. Hence, it is imperative that a suitable treatment method should be devised.

Also, though activated carbon is an ideal adsorbent for organic matter due to its organophilic character, it is not economical for wastewater treatment owing to its high production and regeneration costs, and about 10–25% loss during regeneration by chemical or thermal treatment. High cost of activated carbon and synthetic resins in India has promoted seconds for cheaper substitutes such as flyash [1]. The equilibrium adsorption of dyes onto several low-cost adsorbents such as peat, wood, chitin, chitosan, palm-fruit bunch, biogas residual slurry etc., was studied previously [9–13]. The suitability of flyash to remove dye colours and factors governing the adsorption phenomena is to be

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Nomenclature

b	Langmuir constant related to energy of adsorption (l/mg)
C_{Ae}	equilibrium concentration of dye on adsorbent (mg/l)
C_{Be}	equilibrium concentration of dye in solution (mg/l)
C_e	equilibrium concentration of dye (mg/l)
K_C	equilibrium constant
K_T	overall rate constant (min^{-1})
k_1	rate constant of adsorption (min^{-1})
k_2	rate constant of desorption (min^{-1})
q_e	amount of dye adsorbed at equilibrium (mg/g)
Q^0	Langmuir constant related to capacity of adsorption (mg/g)
t	time (min)
$u(t)$	fractional attainment of equilibrium

fully understood. In the present work, adsorption studies are carried out for treatment of dyeing effluents by using flyash and activated carbon as adsorbents. Flyash obtained from Vijayawada Thermal Power Plant (VTPS), Vijayawada & National Thermal Power Corporation (NTPC), Ramagundam and activated carbon from M/S R.K. Carbons, Hyderabad in Andhra Pradesh, India were used for studies.

2. Materials and methods

2.1. Characteristics of flyash

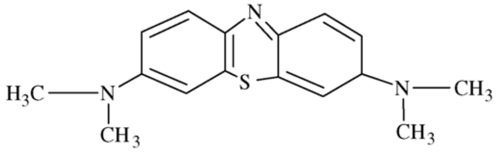
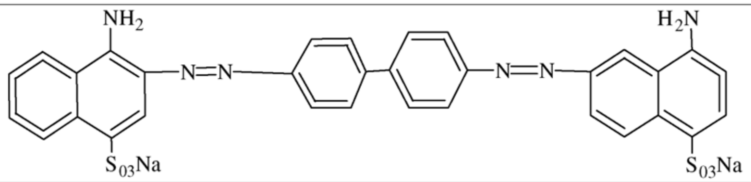
Flyash is a finely divided residue resulting in from the combustion of powdered coal or lignite and collected from flue gas of pulverized fuel fired boilers with the help of electrostatic precipitators. It is generally gray in colour, abrasive, refractory, acidic in nature. It has a specific surface area, which varies between 2500 and 7000 cm^2/g. Particle size of flyash ranges from as high as 120–960 μm to less than 5 μm. The specific gravity is found to vary between 2.3 and 2.5 and bulk density is in the range of 600–900 kg/m^3. Flyash possesses an adsorbent capacity, which depends mainly on the amount of unburnt substances within its surface, usually ranging from 12 to 30% by weight [7]. Chemical composition of flyash is given in Table 1. This adsorbent capacity allows the removal from wastewaters of either the colour or the soluble and suspended organic pollutants. Flyash is found to have also good settling capacity, which enables it to remove suspended solids by behaving as a “settling aid”. The quick flyash settling also provokes the formation of an impermeable layer on the bed of the receiving body which prevents the pollutants from going up to the surface water. It has been noticed that the increase of water hardness induced by flyash addition is not remarkable [7]. Further more, calcium salts contained in flyash (mainly $CaSO_4$ and CaO) lead to the neutralization of acid waters and alkaline dephosphorisation up to such low concentrations as to permit the reduction of the eutrophications phenomena [8]. By such adsorptive treatment of effluents from chemical industries and textile dying industries with different amounts of flyash, significant reductions induced in COD and adsorbance was clearly observed.

Table 1
Chemical composition of flyash

Content	Flyash from VTPS (%)	Flyash from NTPC (%)
SiO_2	63.14	54.02
Al_2O_3	24.63	28.10
Fe_2O_3	3.00	5.15
CaO	2.15	3.85
MgO	1.65	2.25
SO_3	2.25	3.75
Alkalies	2.11	1.16
Combustibles	1.07	1.72

2.2. Experimental aspects

Flyash and activated carbon are used for experimental purpose as adsorbents and methylene blue (MB) liquor dye and Congo red (CR) basic dye as synthetic effluents. Chemical structures of dyes used for experiments are shown in Scheme 1. Initially, the flyash has been washed several times with hot (60 °C) distilled water, filtered and dried. The sample has been then treated with dilute sulfuric acid and washed with distilled water to remove the excess sulfuric acid. Then it is heated at

Dye	Structure	λ_{max}(nm)
Methylene Blue (MB) CI 51015		661
Congo Red (CR) CI 22120		497

Scheme 1. Chemical structure of dyes used for experiment.

Table 2
Screen analysis of flyash

Mesh size	Percentage
+250	0.08
−250 + 150	1.12
−150 + 75	5.35
−75	93.45

120 °C in an oven for 12 h to activate and, cooled to room temperature and finally sieved. Screen analysis of the flyash is given in Table 2.

The dyes used in the present study are obtained from Qualigens Fine Chemicals Glaxo India Limited. To prepare dye solution samples of having 0.1 g/l initial concentration, to 1 g of the dye a few drops of soap solution is added in a beaker and diluted using hot water that is at a temperature of 60 °C. The dye is stirred well to form a homogeneous solution and is made to a solution of 100 ml. The mixture is poured into a 100 ml standard flask and shaken well to form a homogeneous solution. Similarly, the solution samples of different concentrations are prepared. Since the dye solution gets hydrolyzed if stored, they are prepared in small quantities up to requirements.

Batch adsorption experiments have been carried out by taking various doses of adsorbents with 50 ml of dye solution of known initial concentrations in different conical glass flasks in a shaking thermostat with a constant speed of 120 rpm. At different intervals of time, samples have been drawn out for estimation of colour removed. Percentage of colour removed has been measured colorimetrically using a spectrophotometer (Shimadzu 160A) in the visible range. The experiments have been conducted at three different temperatures of 30, 40, and 50 °C, for two adsorbents flyash and activated carbon by using various initial concentrations of dye samples. The effect of pH is also found by adjusting system pH by using H_2SO_4 and NaOH.

3. Results and discussion

3.1. Effect of quantity of adsorbent

It has been observed from Fig. 1(A) for flyash, the removal of dye from solution increases with the lapse of the time and attains equilibrium. It can also be observed that the amount of adsorbent used effects the maximum percentage of colour removed. In case of methylene blue, the equilibrium contact times are 40 min for 4 g and 60 min for 8 g of adsorbent. Whereas the percentage of colour removed are 30 and 89.5%, respectively. In case of Congo red dye also similar trend has been observed (Fig. 1(B)). It indicates that the maximum colour removed is depending on contact time and quantity of adsorbent used. Fig. 2 gives the variation of percentage of adsorption versus time. These curves are

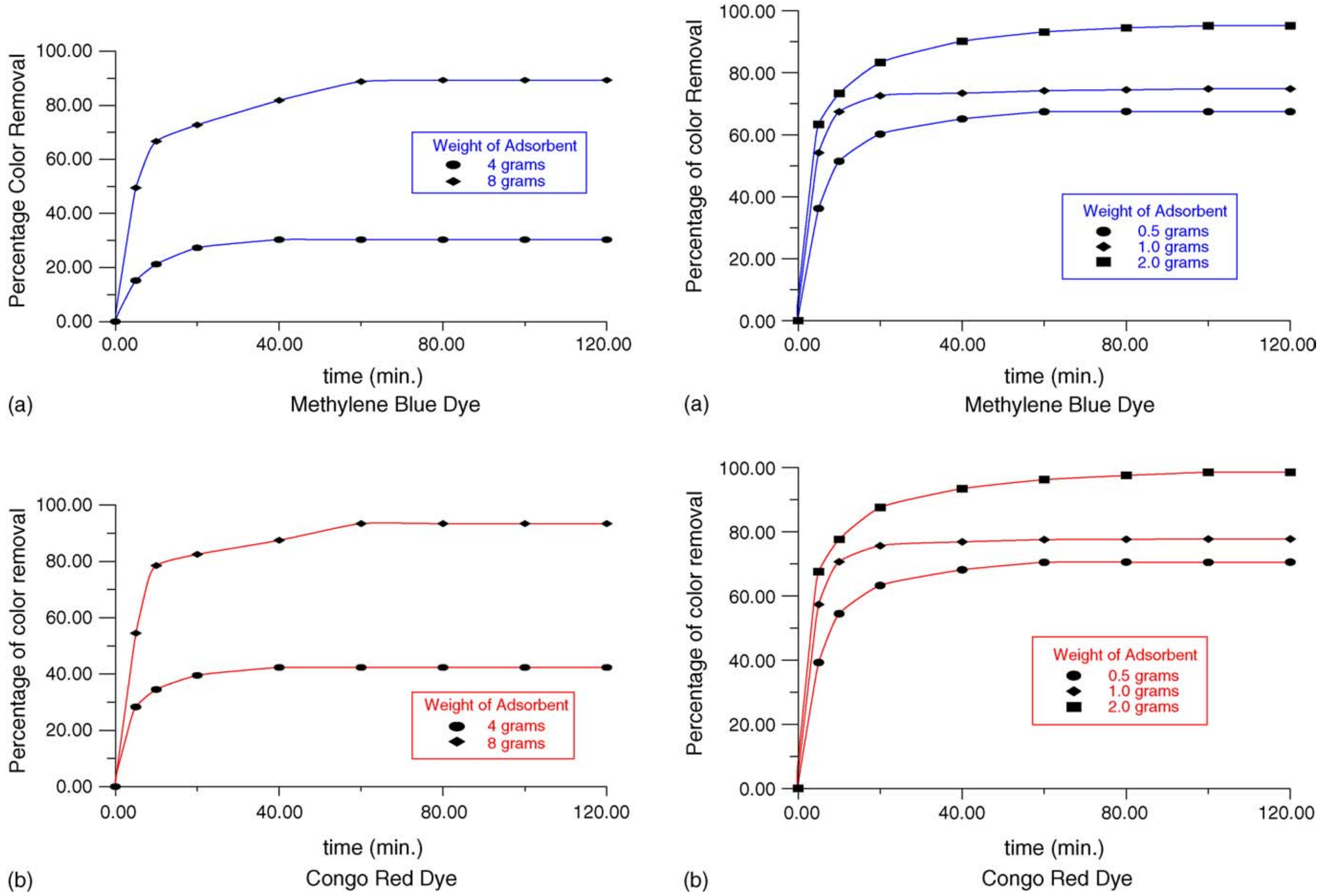


Fig. 1. (A) Effect of quantity of adsorbent flyash on colour removal (temperature 30 °C, pH 7.5 and initial dye concentration in the solution 0.2 g/l). (B) Effect of quantity of adsorbent activated carbon on colour removal (temperature 30 °C, pH 7.5 and initial dye concentration in the solution 0.2 g/l).

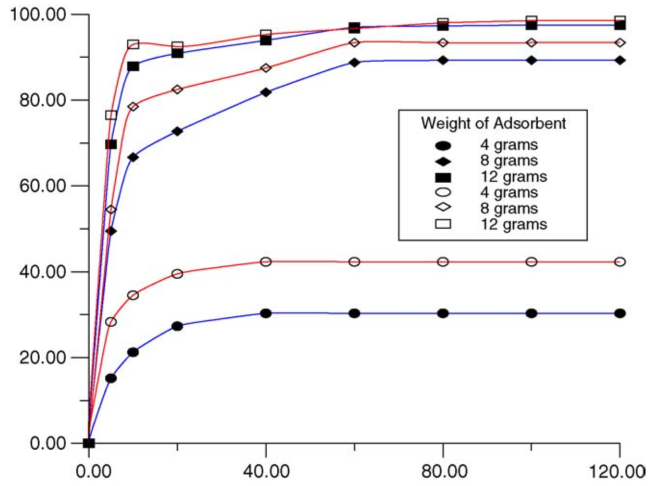


Fig. 2. Effect of quantity of adsorbent on colour removal for flyash (temperature 30 °C, pH 7.5 and initial dye concentration in the solution 0.2 g/l).

smooth and continuous, indicating the formation of monolayer coverage on the surface of adsorbents. The maximum colour removed is obtained as increasing with quantity of adsorbent used can be observed from Fig. 3. The maximum percentage of colour removed in case of activated carbon is noted as 98.5% by using 2 g. Further addition of activated carbon does not affect the adsorption process. Similarly, in case of flyash the maximum possible reduction in the colour is found to be 96% obtained for 12 g of total adsorbent. Therefore, it can be said that flyash consumption is more whereas activated carbon is consumed less for equal percentage of removal. Since cost of activated carbon is considerably higher than the flyash and which may also be available free of cost, it can be a better substitute.

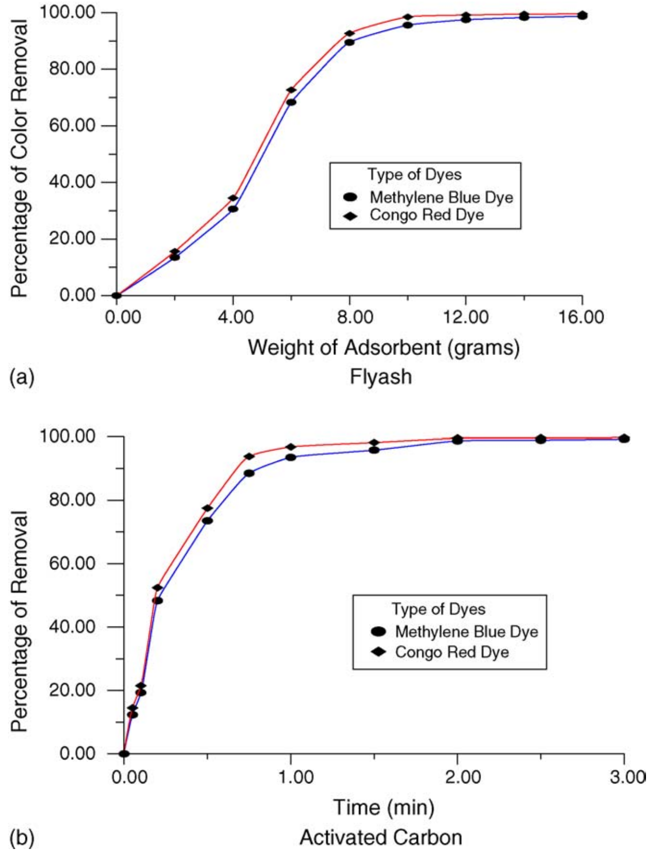


Fig. 3. Variation of percentage of colour removed with weight of adsorbent (temperature 30 °C, pH 7.5 and initial dye concentration 0.2 g/l).

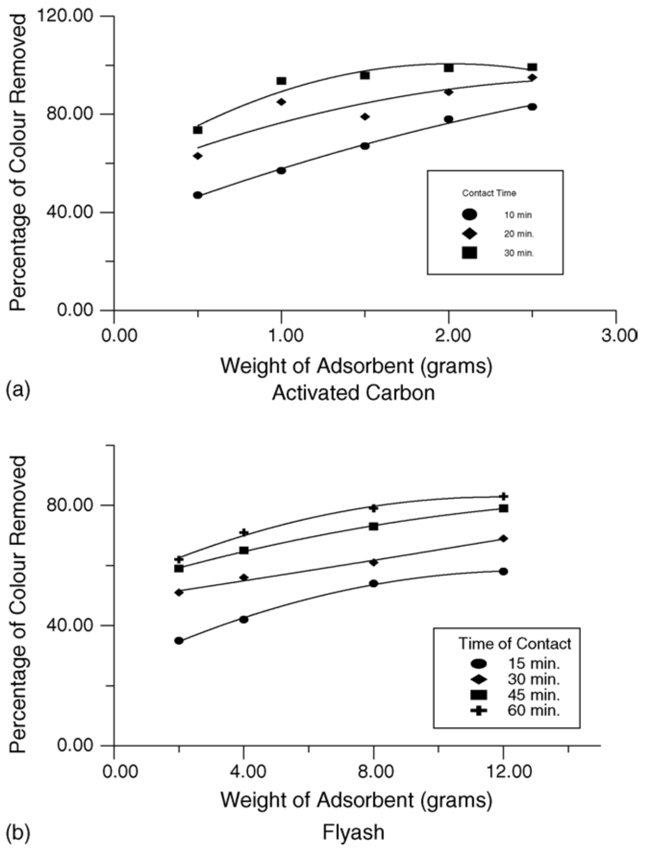


Fig. 4. Effect of contact time on percentage of colour removed for methylene blue dye (temperature 40 °C, pH 7.5 and initial concentration 0.1 g/l).

3.2. *Effect of contact time on colour removal*

Fig. 4 indicates the effect of contact time on percentage of colour removed. The percentage of colour removed is observed to increase with increasing contact time. For 10 min contact time, 2 g of flyash removed the colour to 34% for initial dye concentration of 0.1 g/l solution and at 40 °C, whereas for same solution activated carbon removed as high as 64% of colour. Further contact time (i.e. 40 min) could only reduce up to 50% removal in case of flyash but incase of activated carbon it is 98%. Therefore, it can be said that flyash requires not only more quantity but also greater contact time than the conventional adsorbent of activated carbon to remove the maximum percentage of colour.

3.3. *Effects of dye initial concentration on colour removal*

The methylene blue dye and Congo red dye solutions having initial concentrations of 0.1, 0.2 and 0.4 g/l have been tested to observe effect of initial dye concentration on percentage of colour removed. Fig. 5 shows that for dilute solution (0.1 g/l) the percentage of colour removed is almost 93% for 6 g of adsor-

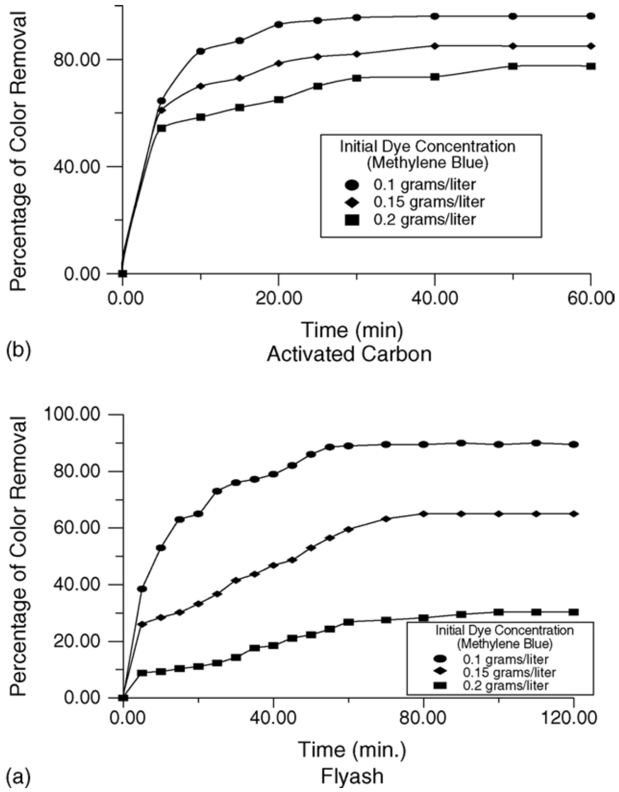


Fig. 5. Effect of initial effluent concentration on percentage of colour removed for methylene blue dye [temperature 40 °C, pH 7.5 and flyash (6 g) and activated carbon (3 g)].

bent and for long contact time. But, in case of concentrated solution used in the experimentation (0.4 g/l), interestingly it is observed to decrease to 34%. Similar observation is made for activated carbon also (Fig. 4(b)) It means that the adsorption process is highly dependent on initial concentration of effluent. It is because of that at lower concentration, the ratio of the initial number of dye molecules to the available surface area is low and subsequently the fractional adsorption becomes independent of initial concentration. However, at higher concentration the available sites of adsorption becomes fewer and hence the percentage removal of dye is dependent upon initial concentration Further, it can also be said that the curves in Fig. 5 are single, smooth and continuous indicating the formation of monolayer coverage on the outer interface of the adsorbent.

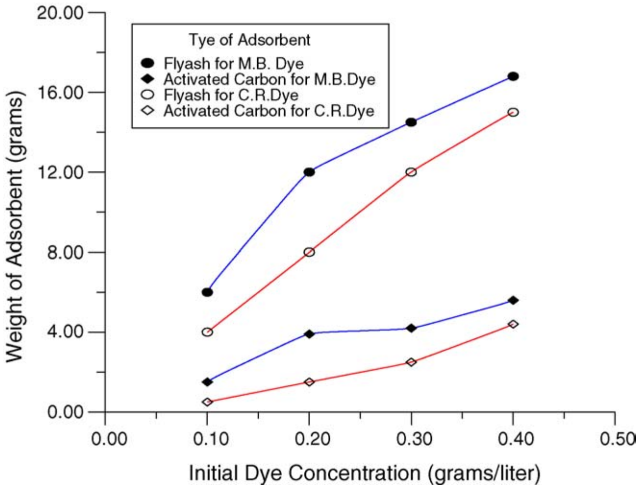


Fig. 6. Amount of adsorbent requirement for various types of adsorbents (temperature 40 °C, pH 7.5 and for 60 min equilibrium time).

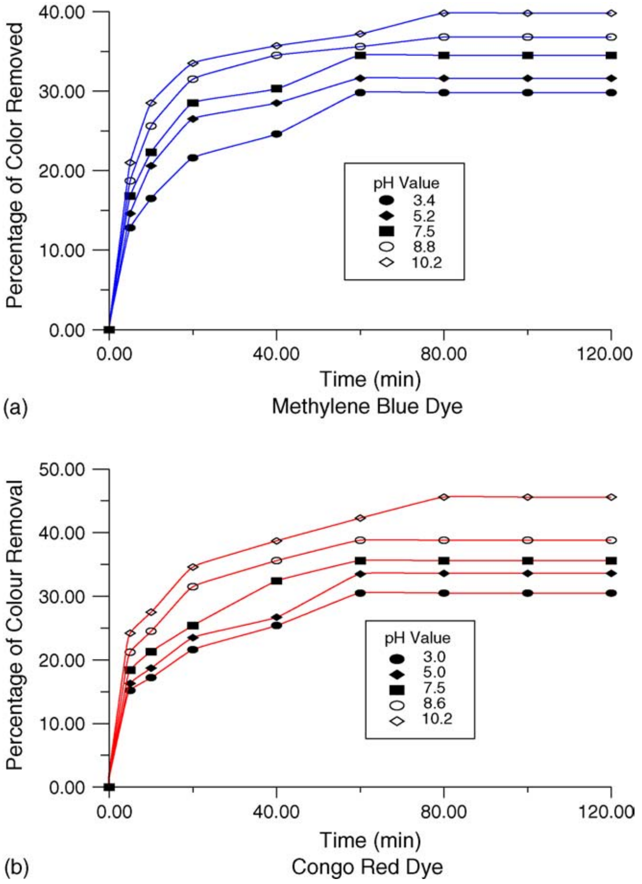


Fig. 7. Effect of dye solution pH on colour removal by flyash (temperature 40 °C, 4 g of adsorbent and 0.15 g/l of initial concentration).

3.4. Effect of temperature on colour removal

The temperature of solution is also observed to affect the percentage of colour removed. In the case of flyash when 4 g was used the percentage of colour (MB dye) removal for a 0.1 g/l dye solution at a temperature of 30 °C is found to be 85.7%. At 40 °C, the colour removal fell to 78.4% and at a temperature of 50 °C it further reduced to 74.2%. A similar trend has been observed in the case of activated carbon too. The reason for the fall in the percentage of colour removal at elevated temperatures may be that at higher temperatures a part of the dye leaves the solid phase and re-enters the liquid phase.

3.5. Effect of type of the adsorbent

From Fig. 6, it has been observed that different substances adsorb differently. Adsorption mainly depends on the surface area available for adsorption and the composition of the adsorbent like the amount of alumina present, the amount of unburnt carbon and also on the silica content. It has been observed that

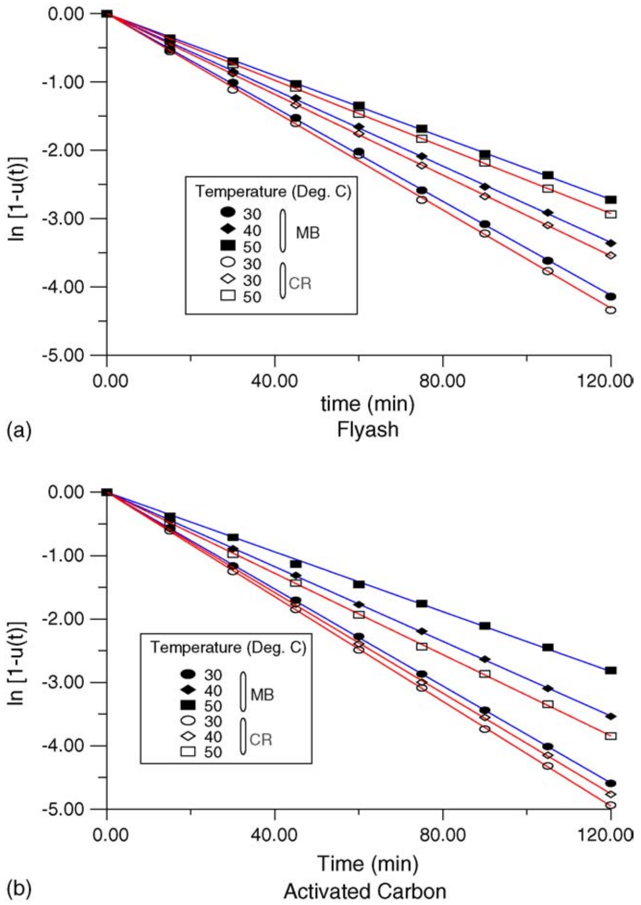


Fig. 8. First-order kinetics of adsorption process for methylene blue dye.

activated alumina is the best among the three tested for, followed by activated carbon, which inturn is followed by flyash. It took just 0.5 g of activated alumina for maximum removal of colour in a 0.1 g/l dye solution while in the case of activated carbon it is 1.5 and 6.5 g in the case of flyash.

3.6. *Effect of dye solution pH*

With the increase of dye solution pH from 3 to 10.2, in case of flyash, the adsorption of dye increases for both the dyes used (Fig. 7). Further, it is observed that the percentage of colour removed is 25.5% when the Congo red dye solution pH is 3.0 and it attains maximum to 43.8% when dye solution pH increases to 10.2. Above this pH no further adsorption has been observed. Similar trends are obtained for methylene blue dye solution. Therefore, it indicates that the flyash is good adsorbent for the removal of dye colours from aqueous solutions at higher pH values. Flyash contain various oxides on the adsorbent surface in alkaline medium. At higher pH the association of dye cations occurs with negatively charge oxide surfaces. Therefore, with decrease in pH of solution the positive charge densities on the surface increase and adsorption decreases.

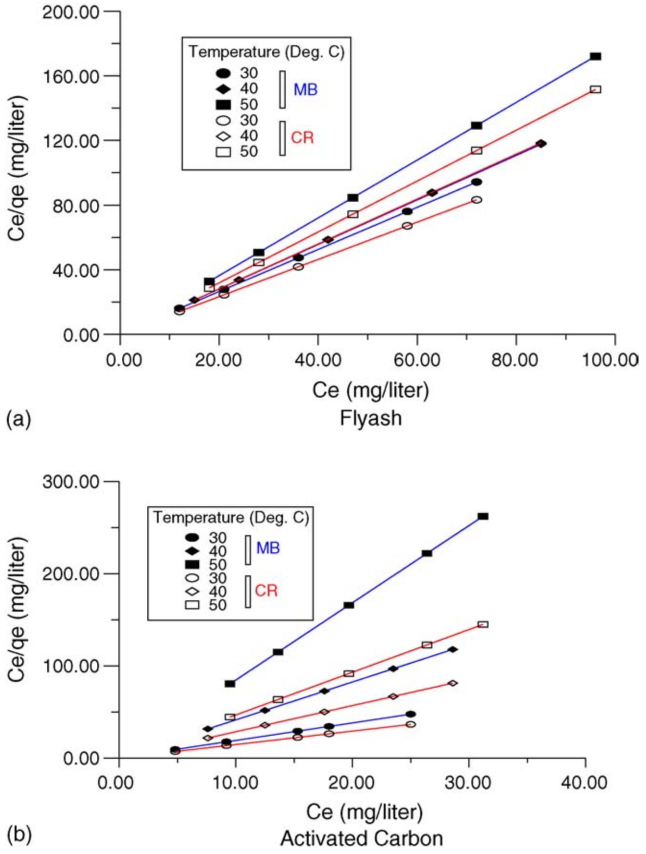


Fig. 9. Parameters of Langmuir adsorption isotherm.

Table 3
Values of first-order rate constants and equilibrium constants

Dye solution	Adsorbent	Temp (°C)	$k_1 \times 10^2$ (min^{-1})	$k_2 \times 10^2$ (min^{-1})	$K_T \times 10^2$ (min^{-1})	K_C
Methylene blue dye	Flyash	30	3.025	0.411	3.436	7.36
		40	2.346	0.447	2.793	5.25
		50	1.731	0.531	2.262	3.26
	Activated carbon	30	3.506	0.305	3.811	11.5
		40	2.567	0.371	2.938	6.92
		50	1.874	0.468	2.342	4.00
Congo red dye	Flyash	30	3.262	0.378	3.61	8.64
		40	2.543	0.407	2.95	6.25
		50	1.978	0.452	2.43	4.38
	Activated carbon	30	3.882	0.249	4.131	15.6
		40	3.563	0.407	3.97	8.76
		50	2.780	0.465	3.245	5.98

Table 4
Langmuir's adsorption isotherm parameters

Type dye	Adsorption	Temperature (°C)	Q^0 (mg/g)	b (l/mg)
Methylene blue dye	Flyash	30	3.074	0.7674
		40	2.926	0.7254
		50	2.755	0.5599
	Activated carbon	30	9.813	0.5270
		40	11.40	0.2436
		50	13.35	0.1194
Congo red dye	Flyash	30	4.125	0.8678
		40	4.063	0.7197
		50	3.982	0.6353
	Activated carbon	30	15.80	0.6870
		40	13.60	0.3530
		50	10.70	0.2160

3.7. Adsorption process

The adsorption of dye on the adsorbent can be considered as a first-order reversible reaction.

$$\mathrm{A} + \mathrm{dye} \Leftrightarrow \mathrm{A-dye} \qquad (1)$$

The rate constants of adsorption, desorption and overall reaction are determined using the equation

$$\ln[1-u(t)] = -K_\mathrm{T}t \qquad (2)$$

$$K_\mathrm{C} = k_1/k_2 = C_\mathrm{Ae}/C_\mathrm{Be} \qquad (3)$$

$$K_\mathrm{T} = k_1 + k_2 \qquad (4)$$

where $u(t)$ is the fractional attainment of equilibrium, K_T the overall rate constant, K_C the equilibrium constant, k_1 the rate constant of adsorption, k_2 the rate constant of desorption and C_Ae and C_Be (both in mg/l) are the equilibrium concentrations of dye on adsorbent and in solution respectively.

Fig. 8, $\ln[1-u(t)]$ versus time, plots at different temperatures are found to be linear for different adsorbents. It indicates that the process involves a first-order kinetics. The value of K_T calculated from slopes and tabulated in Table 3. The values of the constants k_1, k_2 and K_C at different temperatures are calculated using Eqs. (2)–(4) and are given in Table 3. It has been observed that k_1 decreases with temperature whereas k_2 increases. It may be due to a relative increase in escaping tendency of molecules from the solid phase to bulk liquid phase with increase in temperature of the solution. It indicates the process is to be exothermic in nature.

3.8. Adsorption isotherm

The experimental data for the adsorption of the colour from Procian Blue by flyash and activated carbon at 30, 40 and 50 °C have been correlated with modified Langmuir's model

$$C_\mathrm{e}/q_\mathrm{e} = (1/Q^0b) + C_\mathrm{e}/Q^0 \qquad (5)$$

where C_e is the equilibrium concentration (mg/l) of the dye, q_e the amount (mg/g) of dye adsorbed at equilibrium, Q^0 and b are Langmuir parameters related to the capacity and energy of adsorption respectively.

The linear plots of $C_\mathrm{e}/q_\mathrm{e}$ versus C_e at different temperatures (Fig. 9) suggest the applicability of Langmuir isotherm for present systems, showing the formation of monolayer coverage of the adsorbate at the outer surface of adsorbent. The values of Q^0 and b at different temperatures have been determined from the slopes and intercepts of respective plots and are tabulated in Table 4.

4. Conclusions

Removal of dyes, methylene blue and Congo red, from aqueous solutions by adsorption with flyash has been experimentally determined and the following observations are made:

1. The percentage of colour removed increase with increasing adsorbent dosage, increase with increasing contact time, decrease with increasing initial dye concentration and increase with dye solution pH.
2. The adsorption rates decrease with increasing temperatures.
3. The monolayer formation on the adsorbent surface and exothermic nature. Therefore, the first-order adsorption rate constants have been obtained. They are found to decrease with temperature.

The equilibrium contact times and equilibrium concentrations have been obtained from the kinetic data and using them Langmuir isotherms parameters have been estimated.

It is observed from the experiments that about 90–100% removal is possible at lower concentration ranges. Eventhough the contact times and dosages required for flyash are more than the conventional adsorbents, taking high costs of conventional adsorbents into consideration flyash can be used for colour removal for effluents. Therefore, the present study shows that the flyash from power generation units can be effectively used as adsorbent for the removal colour from dyeing industrial effluents.

Further, it may be noted that after wastewater treatment, the used up flyash should be replaced. Since flyash is cheap and the availability is not restricted, regeneration is not necessary. The major problem with this method of treatment is that the treated flyash is itself a waste and disposal of it will be a major problem. Also flyash contains elements such as chromium and titanium in trace amounts. During the use of flyash for water treatment, these can be leached into the water. Hence flyash treatment may have to be followed by the usual ion exchange methods.

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