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Assessment on thermodynamics and kinetics parameters on reduction of methylene blue dye using flyash

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ABSTRACT

Flyash has been explored in the laboratory scale experiment as a low cost adsorbent for the removal of methylene blue dye from aqueous solution. The influence of dye concentration, weight of adsorbent, stirring rates, influence of temperature, pH on adsorption capacity was studied in batch experimental method. From experimental results it was observed that almost 95–99% of dye colour could be removed from the solution using flyash at different initial conditions. Langmuir, Freundlich and Tempkin isotherm models were used to describe the distribution of dye between the liquid and solid phases in batch studies and it has observed that Langmuir isotherm better represents the phenomenon than Freundlich and Tempkin isotherms. From the experimental results the adsorption rate constant, activation energy, Gibbs free energy, enthalpy and entropy of the reaction were calculated in order to determine the mechanism of the sorption process.

Keywords: Adsorption; Methylene blue; Adsorption isotherm; Adsorption kinetics; Thermodynamic parameters

1. Introduction

The adsorption is defined as the process where solute is removed from the liquid phase through contact with a solid adsorbent which has a special affinity for that particular solute [1]. The adsorbents are highly porous materials, and primarily adsorption takes place on the walls of the pores or at specific sites inside the particles. The use of porous material provides a very high surface area or high micropore volume and for this volume high adsorptive capacity can be achieved. This porous volume is associated with small pores, and so adsorbate molecules have to find their way to the micropore volume and as a result diffusional resistance will occur.

Dyes and their intermediates are used in different industries to colour the products. It is found that nearly 100,000 commercial available dyes are produced, and release of these dye creates serious environmental problem. Many of synthetic dyes are carcinogenic, highly toxic in nature and create problems in life system and cause allergic dermatitis, skin irritation and mutation to humans. These dyes interfere with the growth of bacteria and hinder photosynthesis in aquatic plants and environment.

Methylene blue is a heterocyclic aromatic compound [$C_{16}H_{18}ClN_3S$]. It is solid, odourless powder which appears as blue solution when dissolved in water. This dye is used in printing, cotton dyeing, leather dyeing, etc. It is also used in dairy industry to determine the microbial load present in milk [2]. Excess use of the dye causes various health problems like hypertension, pre-cordial

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pain, dizziness, headache, fever, faecal discoloration, haemolytic anaemia, etc [3].

The reduction of dye can be achieved using different methods like coagulation, floatation, chemical oxidation, membrane separation, biological treatment, enzymatic decomposition, photooxidation, adsorption using activated carbon or activated charcoal, etc. [4–12]. But these treatment methods (except biological treatment and adsorption) are costly and also suffer from incomplete removal besides being based on labour-intensive operation and high energy requirement. Biological treatment is disadvantageous as it requires a large surface area and in some cases toxic chemicals can be found from the experiments. Disposal of the treated sludge is also a problem. The search for new and cost effective technologies involving the removal of dye has been oriented to adsorption based on dye binding capacities of different biological, agricultural materials or industrial wastes [13–17]. The main advantages of adsorption are low operating cost, easily available sources, minimization of volume of sludge to be disposed from the adsorbents. A number of natural and synthetic adsorbents have been studied by various researchers for the removal of different anionic and cationic dye.

Flyash is a pozzolanic material where main components are silicon dioxide, alumina, iron oxide. Use of flyash as the base material in sorption is an attractive alternative for both economical and environmental points of view as it is the by-product of coal-fired power plants [18]. The adsorbent is prepared by hydrating the flyash with lime so that the product has a large specific surface area and good pore structure [19]. It is observed that due to the increase of alkalinity of flyash, greater amounts of SO_2 and CO_2 removal can be possible [20–22].

The objective of the present study is to investigate adsorption properties of the dye using flyash as adsorbent. For this, batch experiments were conducted. Attempt was also made to understand the kinetic rate constant of the reaction and thermodynamic parameters of the adsorption of methylene blue on flyash.

2. Materials and methods

2.1. Preparation of raw adsorbents

Flyash was obtained from a coal based power plant Industry of Durgapur, West Bengal, India. The solid flyash was dried at 373 K in an oven drier and used for further study.

2.2. Preparation of methylene blue solutions

Stock solution of methylene blue (1000 mg L^{-1}) was prepared by dissolving A.R grade methylene blue powder in distilled water (Hi-Media). Experimental methylene blue solution of different concentration was prepared by diluting the stock solution using required amount of distilled water.

2.3. Characterization of the adsorbent

Surface morphology of flyash was studied using scanning electron microscope (Hitachi S-3000N). The particles were coated with gold using a Sputter Coater to give the conductivity of the samples. The scanning electron micrographs were then taken.

2.4. Determination of methylene blue contents in the solutions

Calibration curve was prepared by recording the absorbance values of various concentrations of methylene blue dye at maximum absorbance of wavelength (664 nm). The free dye content of the solution after adsorption in the effluent before and after treatment was determined spectrophotometrically (UV/VIS spectrophotometer, Model Hitachi-2800).

2.5. Influence of agitation speed

Influences of agitation during adsorption were studied. The adsorption capacity was determined at different agitation speeds ranging from 100 rpm to 400 rpm using a fixed amount (1 g) of flyash and fixed amount of methylene blue solution of concentration 20 mg L^{-1} at 310 K (Incubator shaker, Model Innova 42, New Brunswick Scientific, Canada). The initial and final concentrations of the solution were measured using UV/VIS spectrophotometer (UV/VIS spectrophotometer, Model U-2800, Hitachi) and adsorption capacities of the adsorbent were calculated.

2.6. Influence of pH

Adsorption of dye on flyash was carried out through batch method. After loading the adsorbent 0.1 N hydrochloric acid and 0.1 N sodium hydroxide were added to adjust the initial pH of the solution. The pH of the resulting mixture was determined by using pH meter (Model EUTECH make digital microprocessor). 1 g of flyash was added to 100 ml of 20 mg L^{-1} dye solution in each of the 0.25 L Erlenmeyer flasks, and pH was maintained using hydrochloric acid and sodium hydroxide. pH of the solution ranged from 2 to 10.0. These 0.25 L flasks were stirred in a digital incubator shaker at 200 rpm at a constant temperature (310 K), and samples were collected from the flasks at a particular time interval, and solution concentrations were analyzed using UV/VIS spectrophotometer to determine the dye concentration.

2.7. Adsorption experiment

The adsorption capacity was determined at different dye concentrations ranging from 5 to 35 mg L^{-1}. 100 ml of different concentrations of dye solution ranging from 5 to 35 mg L^{-1} were used and flyash (1 g) was added to

Erlenmeyer flasks and agitated at 310 K and 200 rpm for 2 h. The initial and final concentrations of the solutions were measured using UV/VIS spectrophotometer, and adsorption capacities of the adsorbent were calculated. After the equilibrium was attained by each system, the dye uptake capacity for each sample was calculated according to mass balance on the dye using:

$$q_e = \frac{(C_i - C_e)V}{m} \tag{1}$$

The extent of sorption in percentage was calculated using the following equation [25]:

$$\text{Sorption (\%)} = \frac{C_i - C_e}{C_i} \times 100 \tag{2}$$

Langmuir, Freundlich and Tempkin adsorption isotherm models were used to analyse the experimental data.

For the Langmuir model the following equation was used:

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^o} \tag{3}$$

For the Freundlich isotherm constants were calculated using the following equation:

$$\ln q_e = \ln K_F + (1/n)\ln C_e \tag{4}$$

For the Tempkin isotherm model the following equation was used [23,25]:

$$q_e = B_T \ln K_T + B_T \ln C_e \tag{5}$$

2.9. Error analysis

In order to compare the applicability of different models, a normalized standard deviation was calculated [25].

$$\Delta q(\%) = 100 \times \sqrt{\frac{\Sigma\left[\left(q_{\exp} - q_{cal}\right)/q_{\exp}\right]^2}{N-1}} \tag{6}$$

Another error analysis method is chi-square (χ^2) analysis method. This analysis in turn evaluates the optimum adsorption isotherm model for dye and the system.

$$\chi^2 = \Sigma \frac{\left(q_{\exp} - q_{cal}\right)^2}{q_{cal}} \tag{7}$$

Smaller values of chi-square indicate a smaller deviation between models derived data and experimental values and vice versa.

2.10. Influence of different amount of adsorbent on adsorption

To achieve the optimized amount of adsorbent different amount of adsorbent (from 1 to 20 g L^{-1} of flyash) were used with 100 ml of 20 mg L^{-1} dye solution for 1 h at 200 rpm speed and at 310 K.

2.11. Influence of temperature and kinetic study

To achieve the optimized temperature and to determine the reaction rate constant and activation energy, the sorption process was carried out at different temperatures ranging from 303 K to 315 K. 100 ml of dye solution was taken in a Erlenmeyer flask, a known fixed amount of flyash was added and the mixture was agitated at 200 rpm for 1 h. Kinetic rate constant was calculated at different temperatures. From the rate constant activation energy the adsorption of dye was determined using Arrhenius equation [24,25].

$$\ln k_2 = \ln A_0 - \frac{E_a}{RT} \tag{8}$$

2.12. Thermodynamic parameter

The thermodynamic parameters of the adsorption of dye were determined using the following basic equations:

$$K_C = \frac{C_a}{C_e} \tag{9}$$

$$\Delta G^0 = -RT \ln K_C \tag{10}$$

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{11}$$

3. Results and discussion

3.1. Effect of agitation speed

Adsorption capacity of flyash calculated at different agitation speed is shown in Fig. 1. It shows that as the agitation speed increases from 100 to 300 rpm, the adsorption capacity of flyash increases from 1.954 to 1.972 mg g^{-1} and % sorption increases from 97.7 to 98.33%. With further increase in the agitation speed beyond 300 rpm, the adsorption capacity was observed to decrease (1.948 mg g^{-1}, % removal 97.44). The reason behind the phenomenon is that at a higher agitation speed (>300 rpm) the adsorbed dye experiences a strong centrifugal force and as a result loosely bound dye material is desorbed from the flyash surface.

3.2. Effect of different amount of adsorbent

From Fig. 2 it is observed that as the amount of the adsorbent increases from 1 to 20 g.L^{-1} the adsorption capacity of dye using flyash increases from 72% to about 99%. It was observed from the experimental results that

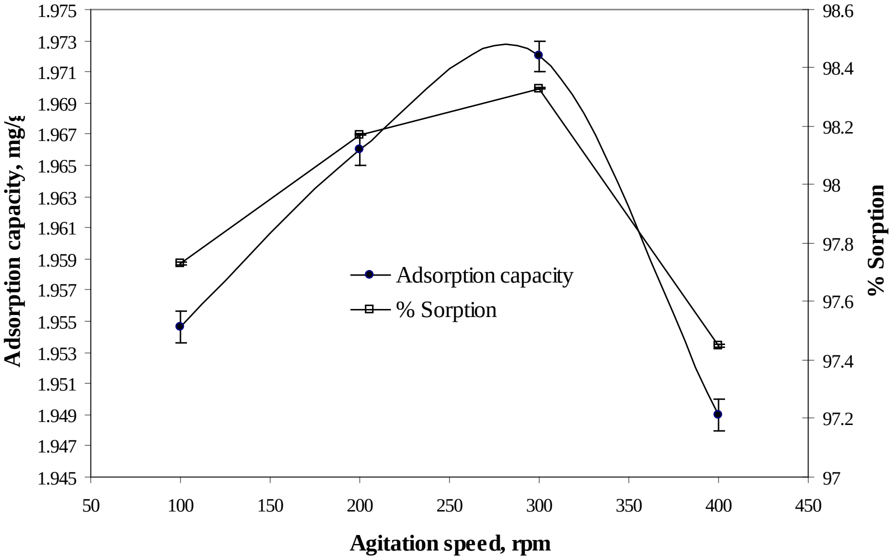

Fig. 1. Adsorption capacity and % sorption of dye using flyash as adsorbent at different agitation speeds (initial dye concentration 20 mg L^{-1}, weight of adsorbent 10 g L^{-1}, pH 7).

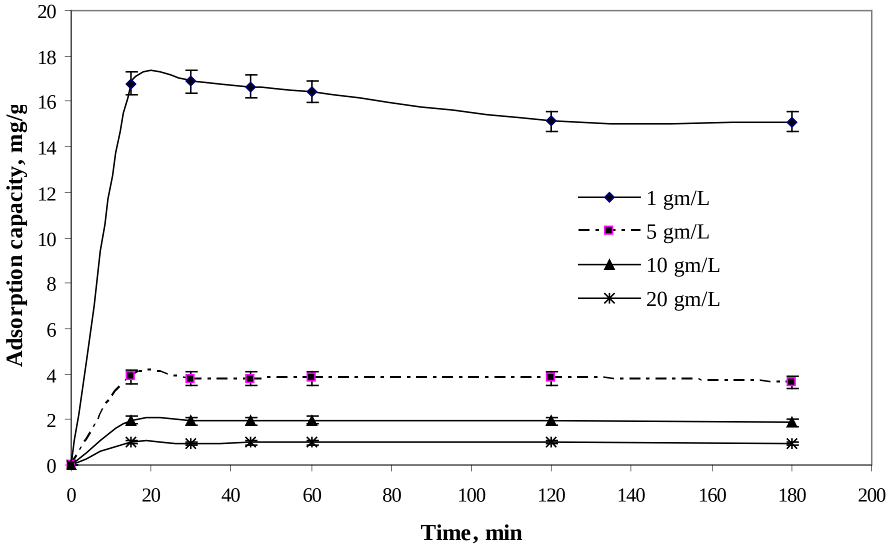

Fig. 2. Adsorption capacity of dye using different amounts of flyash (initial metal concentration 20 mg L^{-1}, pH 7, agitation speed 200 rpm).

within 20–30 min the equilibrium was attained for all the experiments using different amount of adsorbents.

3.3. *Effect of pH*

Adsorption of dye was measured at given contact times for 5 different pH solutions (pH 2, pH 3, pH 5, pH 7, pH 10) (Fig. 3). At higher pH values (higher than 10), dye particles precipitated because of the high concentrations of $(OH)^{-1}$ in the medium. As methylene blue is a cationic dye, it is adsorbed onto the adsorbent surface at higher pH values. As a result, adsorption of dye achieved better removal of dye on increasing the solution pH. From the experimental results it is observed that at pH 7–10, maximum sorption capacity (1.966 mg g^{-1}) was obtained for 20 mg L^{-1} 100 ml dye solution and at pH 7, % removal of dye was 98.8%. Dye binding capacity by flyash is reduced at low pH values due to increasing competition of protons for the same binding sites that dye can also use.

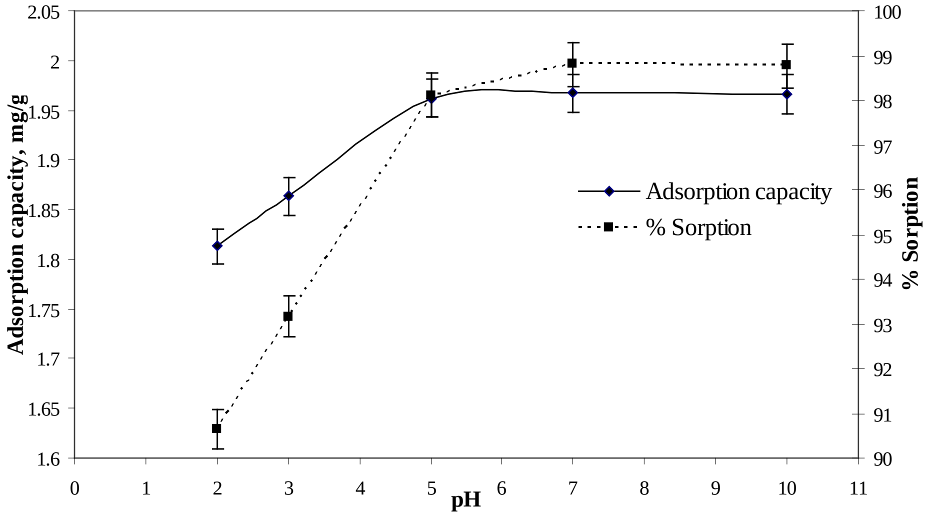

Fig. 3. Adsorption capacity and % sorption of dye using flyash (initial dye pH 2–10, initial dye concentration 20 mg L^{-1}, adsorbent amount 10 g L^{-1}, agitation speed 200 rpm).

3.4. Adsorption isotherms

Experimental data were fitted to Langmuir, Freundlich and Tempkin models (Figs. 4a–c). It is observed that Langmuir isotherm better represents the experimental data than Freundlich and Tempkin isotherm models. From Fig. 4 it is observed that the Langmuir constants Q^0 is 1.91 mg g^{-1} and b is 48.94 L mg^{-1} with a regression coefficient of 0.999 whereas in the Freundlich model K_F is 1.903 (mg g^{-1})(L mg^{-1})^n and n is 34.01 and the regression coefficient is 0.931. For Tempkin model it is observed that B_T is 0.029, K_T is 1.073 L.mg^{-1} and regression coefficient is 0.935. The experimental results indicate that dye ions adsorb on flyash as a monolayer. As the temperature increases the adsorption capacity increases indicating that the process is endothermic in nature (Tables 1,2). The separation factor (R_L) can be calculated by using this equation:

$$R_L = \frac{1}{1+bC_0} \tag{12}$$

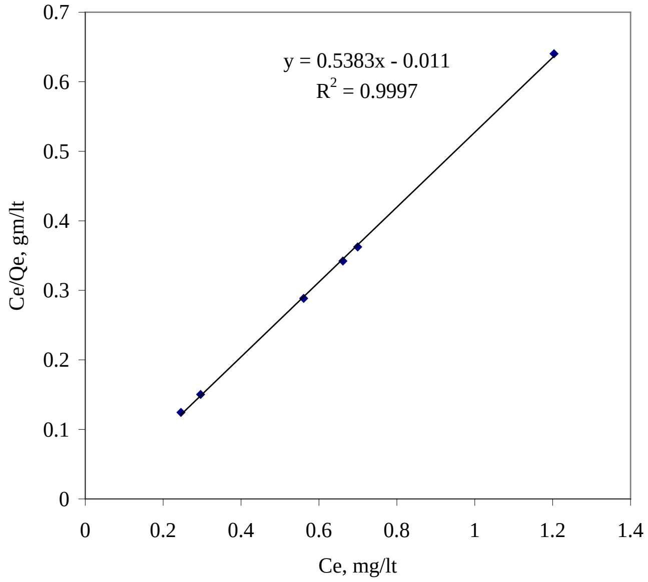

Fig. 4a. Langmuir adsorption isotherm of dye using flyash (initial pH 7, dye concentration 20 mg L^{-1}, adsorbent amount 10 gL^{-1}, agitation speed 200 rpm).

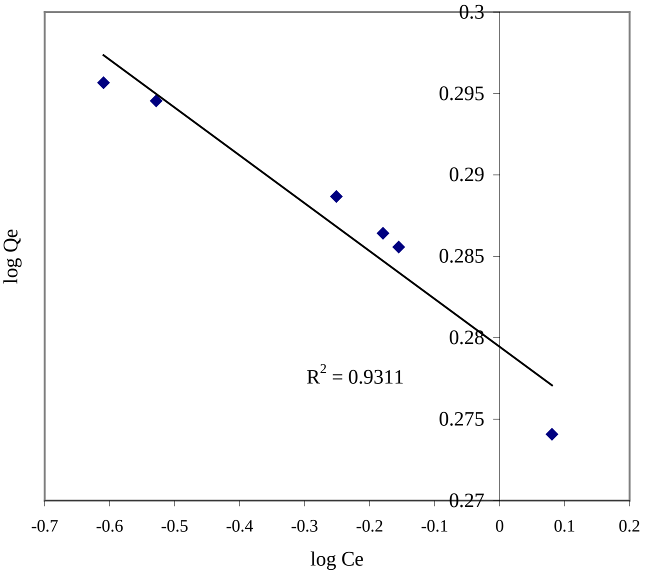

Fig. 4b. Freundlich isotherm model on adsorption of dye using flyash (initial pH 7, dye concentration 20 mg L^{-1}, adsorbent amount 10 g L^{-1}, agitation speed 200 rpm).

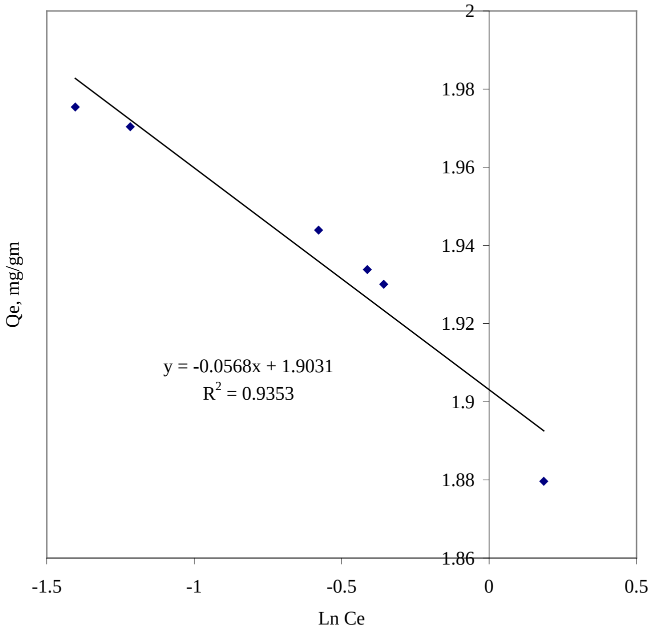

Fig. 4c. Tempkin isotherm model on adsorption of dye using flyash (initial pH 7, dye concentration 20 mg L^{-1}, adsorbent amount 10 g L^{-1}, agitation speed 20 rpm).

From Fig. 4, R_L was calculated as 0.00041 which was found to be less than 1 and greater than 0.

3.5. Influence of initial dye concentration

The effect of initial concentration of dye can be inferred from Fig. 5. As initial concentration of dye increases from 5 to 20 mg L^{-1}, the adsorption capacity increases and the percentage removal of dye from solution increases. But as the initial solution concentration increases beyond 20 mg L^{-1}, the percentage removal of dye decreases. The reason behind the phenomenon may be due to the interference between binding sites at higher concentration.

3.6. Influence of temperature and kinetic study

As temperature of the solution changes from 303 to 319 K, the amount of dye adsorbed increases from 1.89 to 1.97 mg g^{-1} for 100 ml 20 mg L^{-1} dye solution. This may be due to the increase in the mobility of dye ions with temperature. Experimental results shows that the pseudo second order kinetic model better represents the process than first order model. The pseudo second order kinetic model equation is:

$$\frac{t}{q_t}=\frac{1}{k_2 q^2_e}+\frac{t}{q_e} \tag{13}$$

The initial adsorption rate, h (mg. g^{-1} min^{-1}) as $t \to 0$ can be calculated as

$$h = k_2 q_e^2 \tag{14}$$

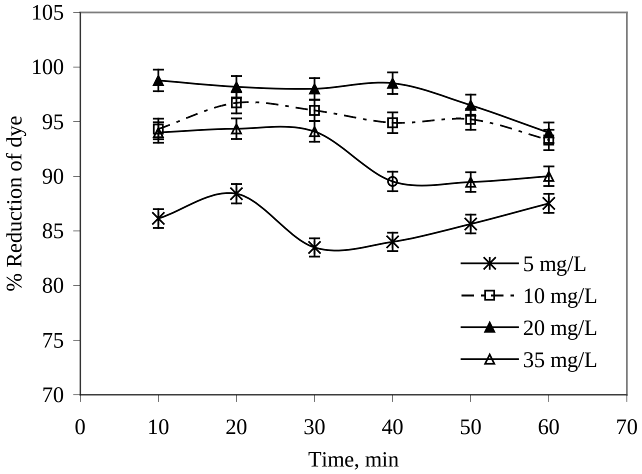

Fig. 5. % reduction of methylene blue at different initial dye conditions using flyash as adsorbent (pH 7, adsorbent amount 10 g L^{-1}, agitation speed 200 rpm).

The linear plots of t/q_t vs. t at different temperatures and different initial concentrations are shown in Figs. 6a and 6b.

It is observed from Table 1 that the rate constant increases as the temperature increases indicating that the adsorption of dye is endothermic process. At temperature of 310 K, the rate constant is 0.92 g. mg^{-1} min^{-1} and initial adsorption rate is 3.39 mg. g^{-1} min^{-1}. It is observed from Fig. 6a that at different temperatures, t/q_t vs. t plots are straight lines in nature and regression coefficient is 0.999. Chi-square value and normalized standard deviation values are also very low. So the adsorption of dye using fly ash follows pseudo second order kinetics.

It is observed from Table 2 and Fig. 6b that the rate constant decreases as the initial dye concentration increases. From Fig. 6b it is observed that at different initial dye concentrations, t/q_t vs. t plots are straight lines in nature and regression coefficient is >0.92. Chi-square value and normalized standard deviation values are also very low. So it can be inferred from these results that the adsorption of dye using flyash follows pseudo second order rate equation.

From the pseudo second order rate constant k_2 (at different temperature), the activation energy E_a is calculated using Arrhenius equation. By plotting log k_2 vs. $1/T$ (Fig. 7) activation energy for dye adsorption is calculated as 45.27 kJ.$mole^{-1}$. Since the activation energy value is higher than 40 kJ $mole^{-1}$, it follows that the process is chemical adsorption [24].

Surface morphology of flyash was studied using scanning electron microscope (Fig. 8). This figure revealed the surface texture and porosity of original flyash.

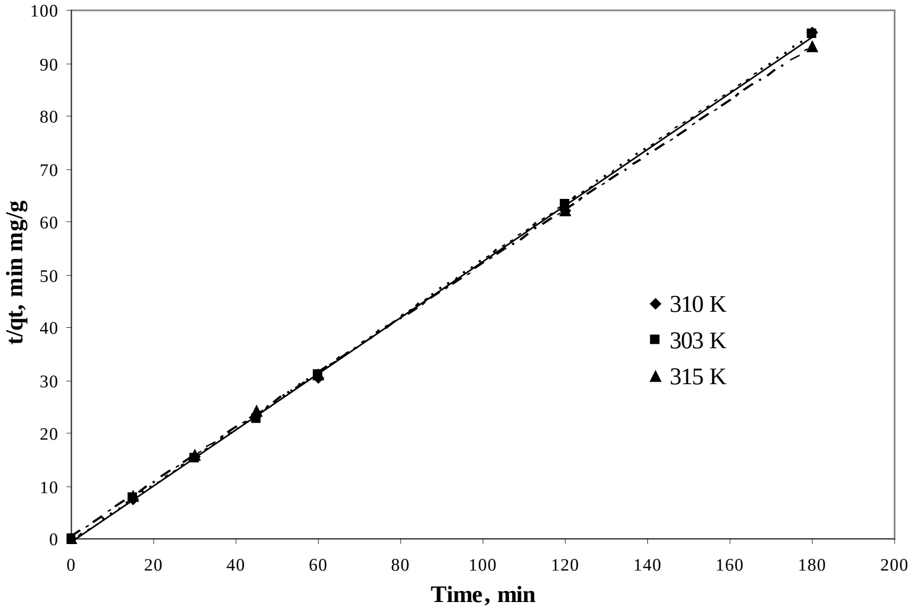

Fig. 6a. Pseudo second order kinetics on the adsorption of methylene blue at different temperatures using flyash (initial dye concentration 20 mg L^{-1}, pH 7, agitation speed 200 rpm).

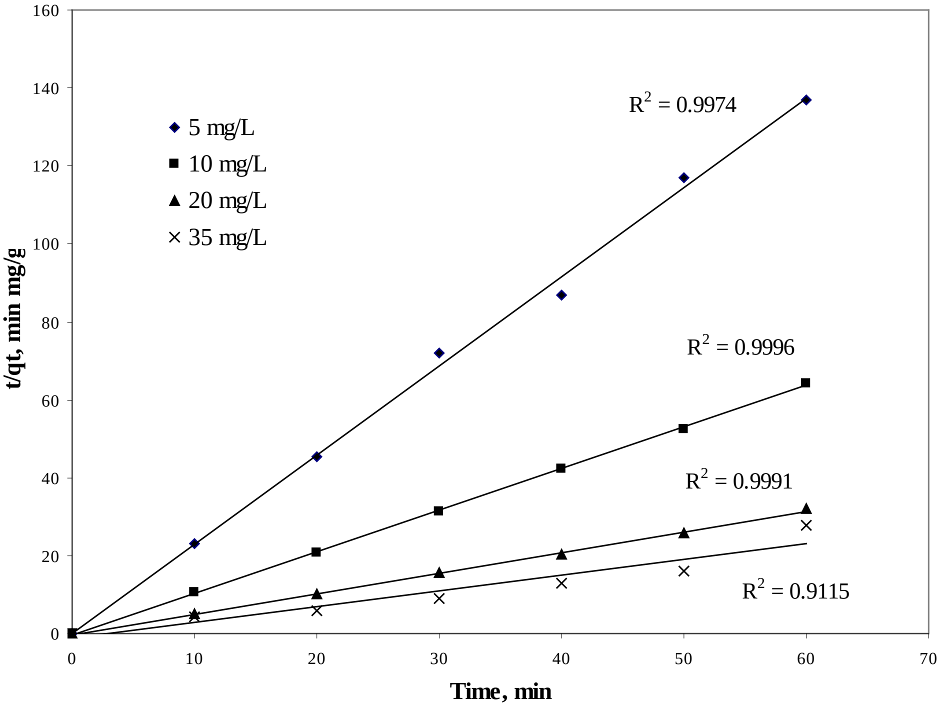

Fig. 6b. Pseudo second order kinetics on the adsorption of methylene blue at different initial concentrations using flyash (pH 7, agitation speed 200 rpm).

Table 1
Adsorption capacity and rate constant at different temperature using Langmuir isotherm model equation

Temperature (K)	Q_{exp} (mg/g)	Q_{cal} (mg/g)	χ^2	Δq (%)	R^2	Rate constant (g. mg^{-1}min)	h (mg g^{-1} min^{-1})
303	1.898	1.881	0.0015	3.60	0.999	0.485	1.723
310	1.966	1.91	0.0011	2.07	0.999	0.92	3.39
315	1.97	1.936	0.002	2.14	0.999	0.93	3.485

Table 2
Adsorption capacity and rate constant at different initial dye concentrations using pseudo second order rate expression

Initial dye concentration (mg L^{-1})	Q_{exp} (mg g^{-1})	Q_{cal} (mg g^{-1})	χ^2	Δq (%)	R^2	Rate constant (g. mg^{-1}min)
5	0.436	0.439	0.0026	3.46	0.997	11.9
10	0.95	0.931	0.0033	2.59	0.999	8.46
20	1.966	1.92	0.023	4.75	0.999	0.925
35	3.04	3.027	0.055	5.61	0.921	0.198

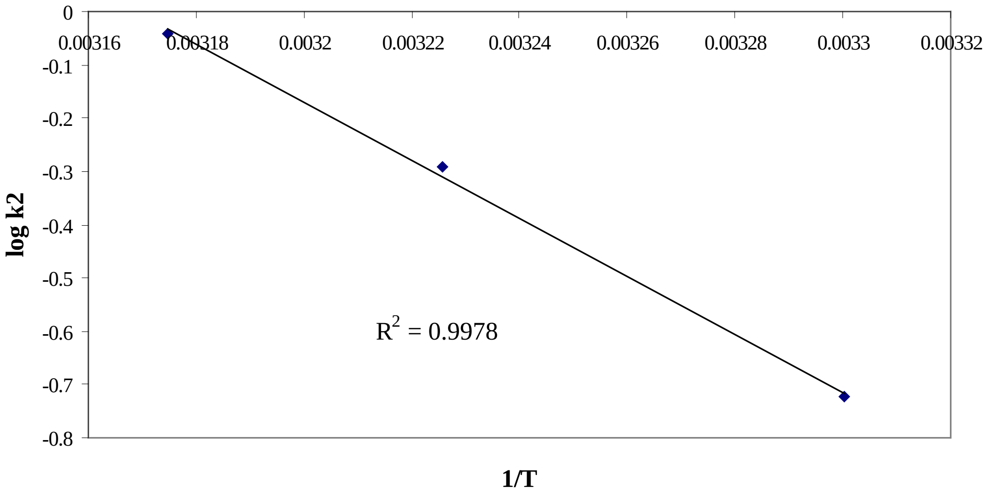

Fig. 7. Plot of rate constant vs. temperature using Arrhenius equation.

3.7. Thermodynamic parameters

The values of ΔH^0 and ΔS^0 are determined from the slopes and intercept of plot of ln K_c vs. $1/T$ (figure not shown). It was observed that ΔG^0 at all temperatures is negative indicating the spontaneous nature of the adsorption process. ΔG^0 ranges from –7.49 to –8.574 kJ mole^{-1} depending on the temperature ranging from 303 to 315 K suggesting that adsorption at high temperature is thermodynamically favourable. The positive value of enthalpy (Table 3) infers that the reaction is an endothermic process and so the reaction consumes energy. For dye adsorption using flyash in an aqueous system, initially dye has to displace more than one water molecule previously adsorbed on flyash. This phenomenon reflects that the process is endothermic in nature and so the enthalpy of the reaction is positive. Entropy of the reaction is positive as the displaced water molecules gain more translational entropy than is lost by the dye and as a result there will be increased randomness at the solid/solution interface.

4. Conclusion

The experimental results show 95–99% methylene blue dye can be removed from the wastewater using

Table 3
Thermodynamic parameters for the adsorption of dye onto flyash

No.	Temperature (K)	ΔG (kJ mole^{-1})	ΔH (kJ mole^{-1})	ΔS (kJ mole^{-1}.K)
1	303 K	–7.49	67.78	286
2	310 k	–8.55		
3	315 K	–8.574		

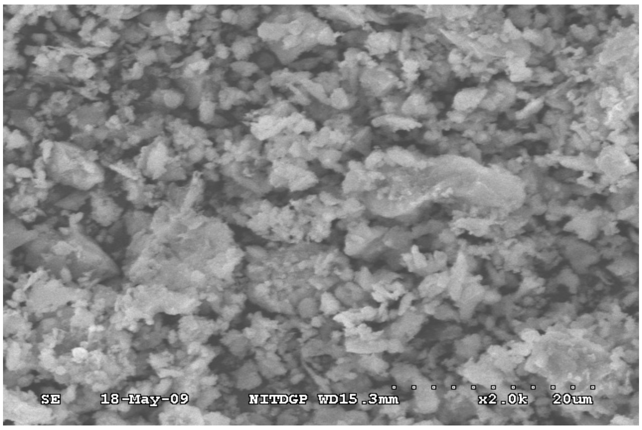

Fig. 8. Scanning electromicrograph of flyash.

flyash. Flyash has the potential adsorption capacity to remove dye from concentrated dye solution. As the amount of flyash increases, the % removal of dye also increases as contact time and agitation speed increases. The equilibrium time for the adsorption is within 20–30 min. Furthermore the results show that the adsorption equilibrium data fitted very well with the Langmuir adsorption isotherm at different temperatures, and the pseudo second order kinetic model provides the best correlation of the experimental data. From ΔG^0 calculation it is observed that the reaction is spontaneous in nature. As flyash is waste material of the power plant, this flyash can be used as an effective adsorbent to treat the wastewater. The process of the treatment of wastewater using this wasted flyash will be economically viable as the flyash is low-cost waste material. So, it can be concluded that flyash can be used as an efficient adsorbent to remove dye.

Symbols

A_0 — Arrhenius constant, mg L^{-1}
b — Langmuir constant, L mg^{-1}
B_T — Tempkin adsorption isotherm constant
C_a — Dye adsorbed per unit mass of the adsorbent, mg L^{-1}
C_i — Initial dye concentration, mg L^{-1}
C_e — Equilibrium dye concentration, mg L^{-1}
E_a — Activation energy, kJ mole^{-1}
ΔG^0 — Change of Gibb's free energy, kJ mole^{-1}
ΔH^0 — Change of enthalpy, kJ mole^{-1}
k_2 — Pseudo second order rate constant of adsorption, g. mg^{-1} min^{-1}
K_c — Distribution coefficient for the adsorption
K_F — Freundlich constant, (mg g^{-1}) (L mg^{-1})^n
K_T — Tempkin equilibrium constant, L mg^{-1}
m — Weight of the flyash, g
n — Feundlich adsorption isotherm constant
N — Number of data points
q_{cal} — Calculated values of the equilibrium adsorbate solid concentration in solid phase, mg g^{-1}
q_e — Amount of dye adsorbed at equilibrium, mg L^{-1}
q_{exp} — Experimental values of the equilibrium adsorbate solid concentration in solid phase, mg g^{-1}
q_t — Amounts of dye adsorbed at time t, mg g^{-1}
Q^0 — Langmuir constant, mg g^{-1}
R — Gas constant, mol^{-1} K^{-1}
ΔS^0 — Change of entropy, J mole^{-1}.K
T — Absolute temperature, K
V — Volume of the solution, L

References

[1] W.L. McCabe, J.C. Smith and P.Harriott, Unit Operations of Chemical Engineering. McGraw Hill, 7th ed., 2005, pp. 836–860.
[2] P. Bapat, S.K. Nandy, P. Wangikar and K.V. Venkatesh, Quantification of metabolically active biomass using methylene blue dye reduction test (MBRT): Measurement of CFU in about 200 s, J. Microbiol. Meth., 65 (2006) 107–116.
[3] G. McKay, S.M. Otterburn and A.D. Aga, Fullers earth and fires clay as adsorbent for dye stuffs. Equilibrium and rate constants. Wat. Air Soil Pollut., 24 (1985) 307–322.
[4] M.J. Brown, Metal recovery and processing, In: V. Moses and R.E. Cape, eds., Biotechnoology: The Science and the Business, Harvard Academic Publishers, Switzerland, 1991, p. 567.
[5] B. Volesky, Biosorption for the next century, Hydrometal., 59 (2001) 203–216.
[6] S. Schiewer and B. Volesky, Modelling multi-metal ion exchange in biosorption, Environ. Sci. Technol., 30 (1996) 2921–2927.
[7] R. Gong, Y. Ding, M. Li, C. Yang, H. Liu and Y. Sun, Utilization of powdered peanut hull as biosorbent for removal of anionic dyes from aqueous solution, Dyes Pigments, 64 (2005) 187–192.
[8] R. Gong, Y. Sun, C. Jian, H. Liu and C. Yang, Effect of chemical modification on dye adsorption capacity of peanut hull, Dyes Pigments, 67 (2005) 175–181.
[9] K. Marungrueng and P. Pavasant, High performance biosorbent (*Caulerpa lentillifera*) for basic dye removal, Biores. Technol., 98 (2007) 1567–1572.
[10] Z. Bekci, Y. Seki and L. Cavas, Removal of malachite green by using an invasive marine alga *Caulerpa racemosa* var. *cylindracea*, J. Hazard. Mater., 61 (2009) 1454–1460.
[11] G. Crini and P.-M. Badot, Application of chitosan, a natural inopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: A review of recent literature, Progr. Polymer Sci., 33 (2008) 399–447.
[12] E. Sayan, Optimization and modeling of decolorization and COD reduction of reactive dye solutions by ultrasound-assisted adsorption, Chem. Eng. J., 119 (2006) 175–181.
[13] M. Dogan, H. Abak and M. Alkan, Biosorption of methylene blue from aquesous solutions by hazelnut shells: Equilibrium, parameters and isotherms, Wat. Air Soil Pollut., 192 (2008) 141–153.

[14] R. Han, Removal of methylene blue from aqueous solution by chaff in batch mode, J. Hazard. Mater., 137 (2006) 550–557.

[15] R. Han, Biosorption of methylene blue from aqueous solution by fallen phoenix tree leaves, J. Hazard. Mater., 141 (2007) 156–162.

[16] O. Hamdaoui and M. Chiha, Removal of methylene blue from aqueous solutions by wheat bran, Acta Chim. Sloven., 54 (2007) 407–418.

[17] S. Chandrasekhar and N.P. Pramada, Rice husk ash as an adsorbent for methylene blue — effect of ashing temeparature, Adsorption, 12 (2006) 27–43.

[18] A. Arenillas, K.M. Smith, T.C. Drage and C.E. Snape, CO_2 capture using some fly ash-derived carbon materials, Fuel, 84 (2005) 2204–2210.

[19] K. Wasewar, B. Prasad and S. Gulipalli, Adsorption of selenium using bagasse fly ash, Clean Soil Air Wat., 37(2009) 534–543.

[20] L. Shi and X. Xu, Study of the effect of flyash on desulfurization by lime, Fuel, 80 (2001) 1969–1973.

[21] K. Lee, K.C. Tan, I. Dahlan and A.R. Mohamed, Development of kinetic model for the reaction between SO_2/NO and coal fly ash/CaO/$CaSO_4$ sorbent, Fuel, 87 (2008) 2223–2228.

[22] B. Gorkem and H. Oguz, Development of an active sorbent from fly ash for dry desulphurization of simulated flue gas in a fluidized-bed reactor, Chem. Eng. J., 119 (2006) 147–152.

[23] A.K. Bhattacharya, T.K. Naiya, S.N. Mandal and S.K. Das, Adsorption, kinetics and equilibrium studies on removal of Cr(VI) from aqueous solutions using different low-cost adsorbents, Chem. Eng. J., 137 (2008) 529–541.

[24] T.S. Anirudhan and P.G. Radhakrishnan, Thermodynamics and kinetics of adsorption of Cu(II) from aqueous solutions onto a new cation exchanger derived from tamarind fruit shell, J. Chem. Thermodyn., 40 (2008) 702–709.

[25] H. Jaman, D. Chakraborty and P. Saha, A study of the thermodynamics and kinetics of copper adsorption using chemically modified rice husk. Clean-Soil Air Wat., 37 (2009) 704–711.