

Assessment of hydrothermally modified fly ash for the treatment of methylene blue dye in the textile industry wastewater

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Abstract Dyes and pigments are one of the major water pollutants and if not discharged properly cause ecological disturbance. Considering this, the current study investigates the application of thermal power plant by-product, i.e., fly ash for the elimination of a hazardous methylene blue dye from its synthetic aqueous solution. Experiments were conducted in batch mode to study the effect of pH, temperature, adsorbent dose and contact time. Highest dye removal (94.3%) was achieved at pH 10 using adsorbent dose of 10 g/L in 90 min of contact time at 40 °C. However, for cost-effective operation at neutral pH and room temperature (30 °C), it yields 89.3% dye removal having similar dose and contact time. Equilibrium isotherms for adsorption were analyzed by Langmuir and Freundlich, Temkin and Dubinin–Radushkevich isotherm equations. The results revealed that the best fit model of adsorption closely followed Langmuir adsorption. Based on adsorption

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isotherm models, thermodynamics parameters ΔG , ΔH and ΔS were calculated. The negative value of ΔG and ΔH revealed that adsorption process was exothermic, spontaneous and physical. The present work suggests that through simple process hydrothermally modified fly ash has the potential to be used as cost-effective and efficient adsorbent for the treatment of wastewater from textile industries.

Keywords Hydrothermal activation · Waste material · Fly ash · Methylene blue · Textile industry · Radushkevich isotherm model

1 Introduction

The widespread use of synthetic dyes in various industries such as textile, leather, food processing, dyeing, cosmetics, paper and dye manufacturing industries results in enormous amount of wastewater, which is of serious environment concern (Banerjee et al. 2014; Hor et al. 2016; Khodam et al. 2015). Wastewater generated from textile industries contains high amount of suspended organic compounds, inorganic salts, azo dyes, non-azo dyes and heavy metals such as chromium, nickel and lead and volatile and nonvolatile recalcitrant organic compounds (Visa and Chelaru 2014). Synthetic dyes used for coloration are highly visible, may be toxic and mutagenic and are sometimes also resistant to biological breakdown (Doğan et al. 2007; Salleh et al. 2011). Most of the synthetic dyes reduce sunlight penetration and photosynthetic activity, therefore imparting adverse threat to aquatic life (Pengthamkeerati et al. 2010). Potential toxicity and high color index of dyes are the major concerns for textile effluents, as even a trace amount of dye degrades esthetic value (Tavlieva et al. 2013). As reviewed by Rafatullah et al. 2010 and other studies, methylene blue is one of the most commonly used basic azo dyes in textile industry and printing industry (Hor et al. 2016). The dye exhibits toxic effects on inhalation shortness of breath, and if ingested it may cause burning sensation, nausea, vomiting, dizziness, headache, discoloration of urine and methemoglobinemia (Rafatullah et al. 2010). Therefore, these harmful effects of the dye make its removal from the effluents imperative.

There are many techniques proposed for wastewater treatment such as electrocoagulation, chemical oxidation, ozonation, photo-degradation and membrane filtration (Arelano-Cárdenas et al. 2013; Chowdhury et al. 2011). However, adsorption is most preferred method due to simple and easy operation, low cost and efficient removal of target compounds (Matheswaran and Karunanithi 2007; Mittal 2006; Vargas et al. 2012). Rani et al. (2016) highlight that activated carbon has high dye removal capacity; however, relatively high cost and regeneration limit its application in adsorption studies. Hence, most of the studies focus on locally availability of raw material as adsorbents for the treatment of textile industry wastewater.

Various low-cost adsorbents such as canola residues (Balarak et al. 2015), cocoa pod husk (Pua et al. 2013), mango seed kernel powder (Kumar and Kumaran 2005), sludge ash (Weng and Pan 2006), potato waste (Gupta et al. 2011), cashew nut shell (Ahmad and Kumar 2010; Subramaniam and Kumar Ponnusamy 2015), natural zeolites (Hor et al. 2016), fly ash and red mud (Wang et al. 2005), fly ash (Wang and Zhu 2005) have been used for the removal of methylene blue dye from wastewater. The use of fly ash for dye removal has been reported in number of investigations, but due to (Balarak et al. 2015) versatility of the fly ash, it still needs to be explored (Pengthamkeerati et al. 2008).

Different classes of fly ash show different adsorption behaviors for several categories of dyes (acidic, basic, azo and non-azo, direct and non-direct dyes). Further various treatments like sonochemical (Wang and Zhu 2005), microwave and ultrasound (Bukhari et al. 2015), hydrothermal treatment (Abdalqader et al. 2015; Pengthamkeerati et al. 2010; Wang et al. 2006) and chemical acid treatment of fly ash (Bai et al. 2011) change the porous structure and surface area of the adsorbent on which adsorption capacity is highly dependent (Lin et al. 2008).

Fly ash is a by-product obtained from combustion of coal in coal-powered thermal power plants. It is estimated that around 160 million tons of fly ash is generated every year in India. Disposal of fly ash has become increasing economic and environmental burdens, which demand its effective utilization. Hence, this current study explores the application of hydrothermally treated fly ash for the treatment of methylene blue dye using synthetic wastewater.

2 Materials and methods

2.1 Batch sorption experiments and characterization

Fly ash was procured from a coal-fired thermal power plant situated in Panipat, Haryana, India. It was sieved through BSS –40-mesh particle size and washed several times with distilled water to remove dust and other impurities. After washing, fly ash was dried in oven at 100 °C for 24 h and stored in vacuum desiccators. The activation of fly ash was done by immersing it in 3 N NaOH solution. The ratio of sodium hydroxide to fly ash was kept 1.2 by weight. The solution was heated at 90 °C and stirred mechanically for 3–4 h. The slurry prepared was aged for 3–4 days before washing and filtering it and drying at 100 °C for 24 h to have the activated fly ash. Methylene blue dye (Fig. 1) was procured from Merck chemicals. Stock solution of dye was prepared by dissolving 1 g of dye in 1000 ml of double-distilled water as reported by (Sadaf et al. 2015). The further working dye solutions of standard were prepared from serial dilution of the stock solution.

The X-ray diffraction of the raw fly ash and processed fly ash was analyzed on Panalytical D/Max-2500 X-ray diffractometer equipped with Cu-k radiation (1.5406 Å) operating at 40 kV, 50 mA with scanning rate of 0.02 s⁻¹ to examine the crystalline phases of the fly ash. The chemical composition of raw and activated fly ash was analyzed using WD-XRF (wavelength-dispersive X-ray fluorescence), Model: S8 TIGER, Make-Bruker, Germany. Pellet was prepared using homogenized fly ash (8 gm) powder of particle size of up to 5 micron. For spectrophotometric analysis, samples were centrifuged at 10,000 rpm for 10 min at room temperature, and supernatant was analyzed using UV spectrophotometer (SHIMADZU, Germany) at 665 nm for determination of residual dye

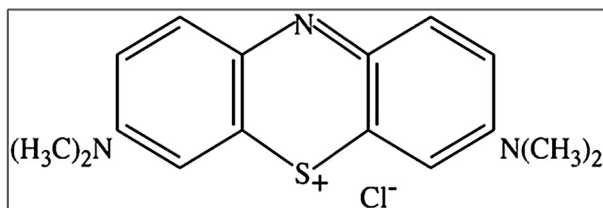


Fig. 1 Chemical structure of the methylene blue

concentration. The study was conducted using batch method and by varying pH, temperature, dose, and adsorbent contact time using 250-ml flask and maintaining shaking speed of 200 rpm. The removal efficiency was calculated using the following equation:

$$\text{Percentage Removal}(\%) = \frac{C_i - C_o}{C_i} \times 100 \quad (1)$$

where C_i is the initial concentration of methylene blue in solution and C_o is the final concentration of methylene blue in solution.

2.2 Adsorption isotherms

The following adsorption isotherms were plotted to evaluate the adsorption process of dye on the adsorbent.

2.2.1 Langmuir adsorption isotherm

The Langmuir adsorption isotherm model works on the principle that adsorption takes place at specific homogenous sites within the adsorbent (Anirudhan and Ramachandran 2015). The equation can be represented as follows:

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \quad (2)$$

where C_e denotes the equilibrium concentration of the dye molecules in mg/L, whereas q_e is the amount dye uptake in mg/g at equilibrium). Further, Q_o represent maximum adsorbent dose capacity, whereas b is known as constants related to the energy of adsorption as mentioned by Matheswaran and Karunanithi (2007). The graphs of C_e/q_e versus C_e were plotted for best fit model of Langmuir adsorption isotherm.

2.2.2 Freundlich adsorption isotherm

This model explains adsorption process working on heterogeneous system. The equation can be represented as follows:

$$q = K * C_e^{1/n} \quad (3)$$

In this equation, K and n are the constants where k indicates adsorbent capacity and n is representative of degree of affinity between adsorption and adsorbent density (Liu et al. 2015). The equation in the linear form can be depicted as follows (Ahmaruzzaman 2009)

$$\text{Log } q = \log K + 1/n \log C_e \quad (4)$$

For Freundlich isotherm, graphs of $\log Q_e$ versus $\log C_e$ were plotted. The value of $1/n$ between 0 and 1 indicates favorable adsorption (Tan et al. 2015). The model that shows R -square values closest to unity is selected.

2.2.3 Temkin isotherm

It is based on the assumption that heat of adsorption of the molecules decreases linearly with coverage of adsorbent surface (Mall et al. 2005). It can be represented by the following linear equation.

$$q_e = B \ln k_2 + B \ln C_e \quad (5)$$

where q_e is the amount of the dye adsorbed at equilibrium (mg/g) and B is Temkin isotherm energy constant. The isotherm constants were obtained from linear graph of q_e and $\ln C_e$.

2.2.4 Dubinin–Radushkevich isotherm model

The equation of Dubinin–Radushkevich isotherm in liner form is defined as below:

$$\ln C_{\text{ads}} = \ln X_m - \beta \varepsilon^2 \quad (6)$$

where C_{ads} is the dye adsorbed at equilibrium (mg/g) and X_m and β values are obtained from intercept and slope of linear plot of $\ln C_{\text{ads}}$ versus ε^2 (Mittal et al. 2009a, b). Polanyi potential is given as follows:

$$\varepsilon = RT \ln + \frac{1}{C_e} \quad (7)$$

Dubinin–Radushkevich constant gives an account of mean free energy of adsorption by the following relation:

$$E = \frac{1}{2\beta^{\frac{1}{2}}} \quad (8)$$

The mean free energy value gives an idea about the controlling mechanism that is physical or chemical process (Chaudhary et al. 2014). The values of mean energy ranging between 1 and 8 kJ/mol signify physisorption, and values ranging from 8 to 16 kJ/mol indicate chemisorption process (Mittal et al. 2010a, b)

2.3 Adsorption kinetics

As detailed below, pseudo-first-order and pseudo-second-order rate models were fitted to adsorption data for better understanding the controlling factors that govern the adsorption and dynamics of the adsorption process.

2.3.1 Pseudo-first-order model

Pseudo-first-order kinetics equation is given below:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (9)$$

where q_e is the amount of dye adsorbed at equilibrium, whereas q_t is the dye adsorbed at time t . The pseudo-first-order rate constant is marked as K_1 (Lin et al. 2013)

2.3.2 Pseudo-second-order model

The current work also evaluated the adsorption kinetics using the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (10)$$

where q_e is the equilibrium adsorption amount, q_t is the adsorption amount at time t , K_1 and K_2 are pseudo-first-order and pseudo-second-order rate constants, respectively (Chaudhary et al. 2013a, b)

3 Results and discussion

3.1 Characterization of the adsorbent

X-ray diffraction study was conducted to understand about the crystalline phases of fly ash. The main crystalline phases identified in fly ash and activated fly ash are quartz and mullite as shown in Fig. 2 and Visa and Chelaru (2014) also report similar findings. The various peaks in Fig. 2 also confirm the presence of various minerals like hematite and magnetite. The prominent peaks of quartz were identified at 2 theta value of 20.8776 and 26.6370, and mullite was identified at 16.4747 and 25.905 (Banerjee et al. 2014). Interestingly, there was no major change or shift of peaks was observed after hydrothermal modification of raw fly ash. Elemental composition of raw and activated fly ash was studied using X-ray fluorescence technique. Important elements and their percentage values in raw and activated fly ash are listed in Table 1. The major elements in fly ash are silicon and aluminum, and their percentage varies depending on the type of coal and combustion method used in a thermal power plants. Table 1 suggests that activation of fly ash with base decreases the silica content and makes the residual ash more aluminum enriched (Mor et al. 2016); however, percentage values of other elements remain more or less similar. Scanning electron microscopy was done to understand the internal morphology of the processed fly ash. SEM images (Fig. 3) show several hollow and compact spheres adhered to small particles, which is similar to (Sun et al. 2010) and Pengthamkeerati et al. (2010). Plate b in Fig. 3 depicts magnified view of a big microsphere and smaller particles adhered to it. Hydrothermal activation of fly ash affected the ball-shaped surfaces into rough surfaces

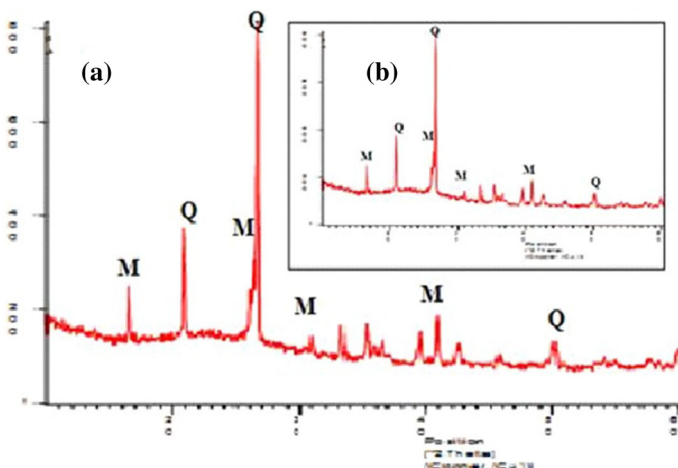
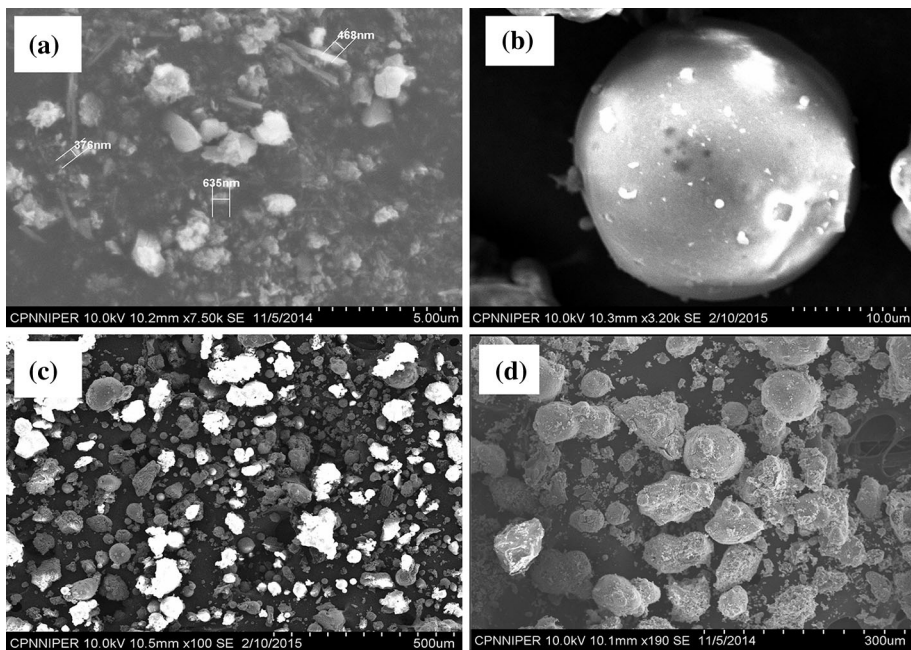


Fig. 2 X-ray diffraction images of raw fly ash (a) and (b) hydrothermally modified fly ash

Table 1 Elemental composition of raw and hydrothermally modified fly ash

Elements	Hydrothermally modified fly ash	Raw fly ash
SiO ₂	47.04	62.28
Al ₂ O ₃	30.34	25.32
Na ₂ O	10.62	0.10
Fe ₂ O ₃	7.42	6.44
TiO ₂	1.90	1.52
CaO	0.94	0.69
MgO	0.085	0.62
K ₂ O	0.33	2.02
BaO	0.09	0.08
MnO	0.09	0.08

**Fig. 3** Scanning electron micrograph of raw **a, b** and **c, d** hydrothermally modified fly ash

and agglomeration of small particles as shown in micrograph. Further SEM micrographs also indicates change in internal surface and increase in roughness of surface area.

3.2 Effect of adsorbent dosage

The effect of various doses of activated fly ash ranging from 1 to 20 g/L was studied using synthetic wastewater of known dye solution (5 mg/L). The maximum dye removal (89.3%) was observed after a contact time of 90 min using adsorbent dose of 1 g/L. Similar to Mor et al. (2016a, b), adsorbent dose and contact time were optimized on the basis of maximum percentage removal in minimum time. Initially, the percentage removal of the dye

increased with increase in adsorbent dose and for particular period of contact time and started declining after attaining equilibrium (Fig. 4). This trend is attributed to the fact that with increase in the amount of adsorbent, the availability of active sites for the adsorption also increases, leading to higher percentage removal of dye until equilibrium is achieved and then decline is observed (Chaudhary et al. 2013a, b). Further decline in adsorption capacity could be due to the formation of monolayer of the adsorbate molecules on adsorbent surface (Mor et al. 2007) including the diffusion through pores to inner surface of the adsorbent (Yadav et al. 2006). Similar trend was also reported for chrysoidine dye using fly ash in batch process (Matheswaran and Karunanithi 2007) and hazelnut shell for the removal of methylene blue by Doğan et al. (2009).

3.3 Effect of pH

As highlighted by Kaur et al. (2016), pH is very crucial factor to understand the mechanism of adsorption of dye on adsorbent surface. The pH influences chemistry of dye solution and charge on the surface of the adsorbent (Chaudhary et al. 2013a, b; Doğan et al. 2007). In the current study, pH of the synthetic wastewater was varied from pH 2 to pH 12, and it shows that there is gradual increase in percentage removal of the dye as pH of the medium increases (Fig. 5). This could be due to the fact that methylene blue is basic dye which releases positively charged ions in the solution. The shift from acidic medium to basic medium affects the charge on the surface of the adsorbent; thus, electrostatic forces of attraction between negatively charged adsorbent and positively charged dye molecules favor the adsorption process (Lin et al. 2008; Singh et al. 2016; Tolba et al. 2015).

3.4 Effect of temperature

To understand the application and efficiency of fly ash as an adsorbent in practical sense, the study also evaluates the effect of temperature on dye removal. As shown in Fig. 5, dye removal increases significantly when the temperature was raised from 20 to 40 °C having 10 °C temperature grading. However, further increase in temperature removal efficiency

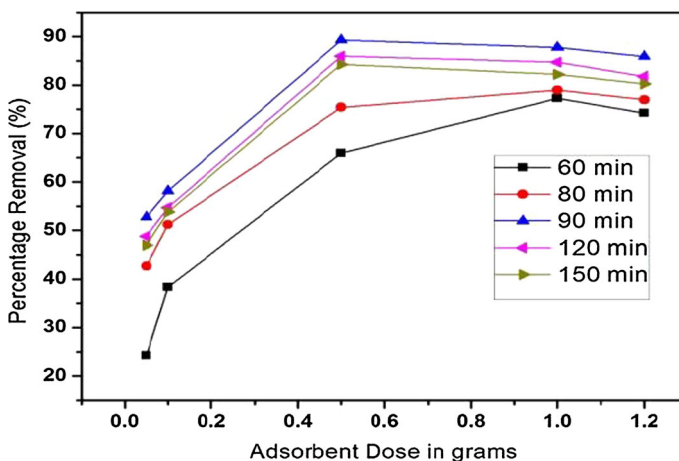


Fig. 4 Effect of adsorbent dose and contact time on dye removal using hydrothermally modified fly ash as an adsorbent

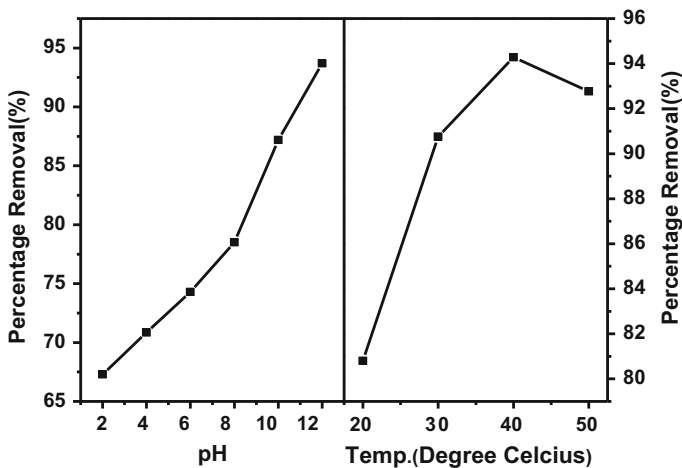


Fig. 5 Effect of pH (*left*) and temperature (*right*) on dye removal using hydrothermally modified fly ash as an adsorbent

starts declining. It can be explained by the fact that with increase in temperature there may be swelling effect in the internal structure of the adsorbent leading to greater adsorption of large size dye molecules into the active sites of the adsorbent. The kinetic energy of the adsorbate molecules is low at lower temperature, which may decrease the adsorption. Further, at high temperature the mobility of dye ions increases and due to high kinetic energy of the dye ions than attractive potential of active sites of the adsorbent, resulting in decline in dye removal as reported by Mor et al. (2007). The maximum dye removal (94.3%) was observed at 40 °C, but looking at field and practical consideration it is suggested to use at room temperature (30 °C), which yield 89.3% removal from the synthetic wastewater.

3.5 Adsorption isotherms

The adsorption data obtained were appraised using standard isotherms models, e.g., Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (Figs. 6 and 7). Both figures show that all the models in general were in good agreement with the experimental data and showed good R^2 values. However, Langmuir model was found to be best fit adsorption model at temperature 40 °C. The energy constant calculated from Dubinin–Radushkevich isotherm model also supports physical adsorption model. The calculated energy constant from the graph of Dubinin–Radushkevich is 1.49 kJ/mol, which indicates physisorption as if value of constant E lies between 1 and 8 kJ/mol (Mor et al. 2016a, b). The value of $E > 8$ kJ/mol suggests chemisorption (Mittal et al. 2010a, b). The values of correlation coefficients R^2 and constants of all the isotherm models studied are listed in Table 2.

3.6 Adsorption kinetics

The adsorption data were also analyzed using pseudo-first-order and pseudo-second-order kinetic model to understand the mechanism of adsorption. As shown in Fig. 8, pseudo-

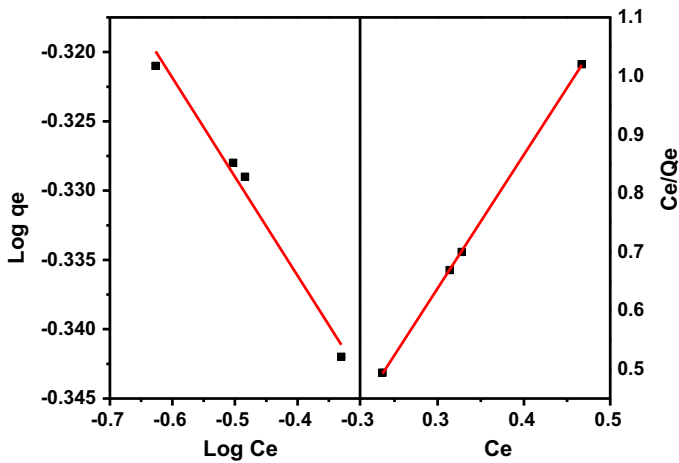


Fig. 6 Freundlich (*left*) and Langmuir isotherm (*right*) curve for the removal of dye using hydrothermally modified fly ash as an adsorbent

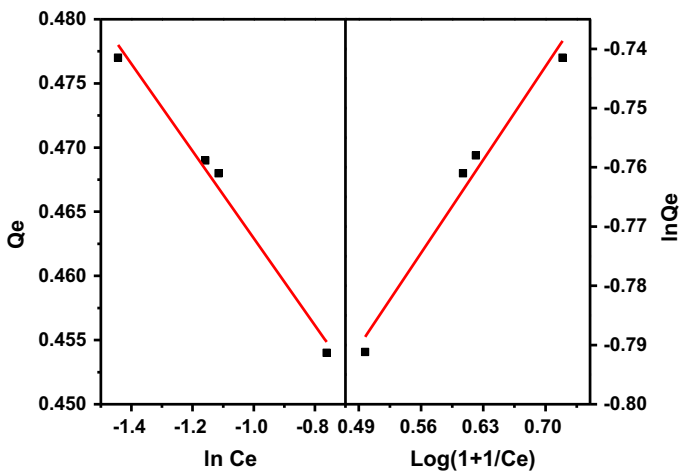


Fig. 7 Temkin (*left*) and Dubinin–Radushkevich (*right*) isotherm model for the removal of dye using hydrothermally modified fly ash as an adsorbent

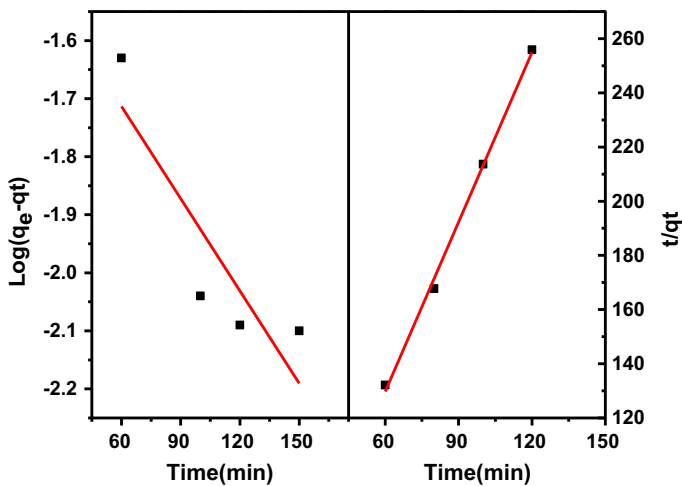
second-order kinetic model shows the best fit to the experimental data. The value of various constants of pseudo-first order and pseudo-second order is also listed in Table 2.

3.7 Adsorption thermodynamics

Using the data results of the adsorption kinetics, thermodynamic analysis was conducted to understand the adsorption mechanism. The value of various thermodynamic coefficients, i.e., ΔG (free energy), ΔS (measure of entropy) and ΔH (enthalpy), was also estimated using the following equations as defined in detail by Mor et al. (2016a, b)

Table 2 Adsorption isotherms and kinetics models for the adsorption of methylene blue

Equations	Parameters	Hydrothermally modified fly ash
Langmuir	$Q_{\max}$ (mg/g)	0.045
	B (l/mg)	49.61
	R^2	0.9999
Freundlich	K (mg/g)	0.43196
	$1/n$	0.0713
	R^2	0.97518
Temkin	B (J/mol)	0.03392
	K_T	4.455
	R^2	0.98055
Dubinin–Radushkevich	q_{DR}	0.900
	E (KJ/mol)	1.49
	R^2	0.9658
Pseudo-first order	Q_e (mg/g)	1.235
	K_t	0.016
	R^2	0.868
Pseudo-second order	K_2 (g/mg)	0.850
	Q_e (mg/g)	0.482
	R^2	0.998

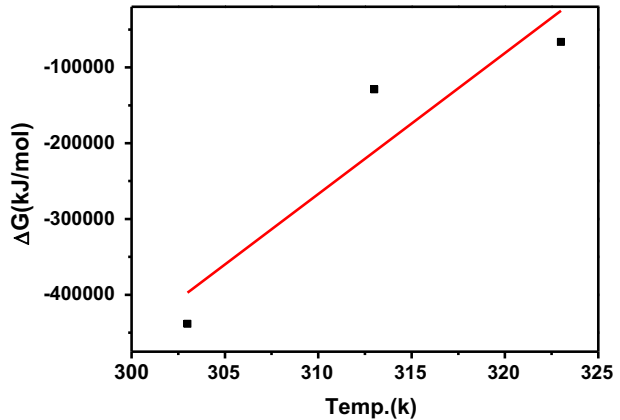
**Fig. 8** Pseudo-first-order (*left*) and pseudo-second-order (*right*) kinetics for the removal of dye using hydrothermally modified fly ash as an adsorbent

$$(\Delta G = -RT \ln b) \quad (11)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S \quad (12)$$

Table 3 Thermodynamic parameters for the removal of dye using hydrothermally modified fly ash as an adsorbent

Temperature (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol)
303	−438,271.66	−6.0314	18,594.8
313	−129,105.68		
323	−66,372		

Fig. 9 Thermodynamic plot for the removal of dye using hydrothermally modified fly ash at different temperature

The value of thermodynamic constants is listed in Table 3, whereas Fig. 9 shows the trend of ΔG versus temperature. The negative value of ΔG indicates that adsorption process is spontaneous and favorable, whereas negative value of ΔH shows that process is exothermic in nature. Further, the positive value of ΔS suggests increase in randomness with increase in temperature (Mittal et al. 2009a, b).

4 Conclusions

The present study assesses the feasibility of hydrothermally processed fly ash for the removal of hazardous methylene blue dye from its synthetic aqueous solution of textile industry. Scanning electron micrographs revealed change in surface of the adsorbent which enhanced its adsorption capacity for the removal of cationic dye. Dye removal efficiency increased with increase in adsorbent dose and contact time and pH of the synthetic wastewater. Various isotherm models including Temkin and Dubinin–Radushkevich were fitted at different temperatures, and it was noticed that Langmuir isotherm best fitted to the experimental data, which depicts monolayer physical adsorption process. Maximum percentage removal of (94.3%) was achieved in 90-min time duration by using adsorbent dose of 10 g/L at pH 10. The negative value of ΔG indicates that adsorption is spontaneous, whereas negative value of ΔH depicts exothermic adsorption. Hence, it could be suggested that hydrothermally modified fly ash, a thermal industry by-product, offers easy and economical option for the treatment of textile industry wastewater.

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Compliance with ethical standards

Conflict of interest Authors declare that they have no conflict of interest.

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