Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2013.846552

53 (2015) 91–98
January

Taylor & Francis
Taylor & Francis Group

Application of fly ash for adsorptive removal of malachite green from aqueous solutions

Shikha Dubey[a], Uma[a], Lavanchawee Sujarittanonta[b], Yogesh Chandra Sharma[a,*]

[a]*Department of Chemistry, Indian Institute of Technology, Banaras Hindu University, Varanasi 221 005, India*
Tel. +91 542 6701865; Fax: +91 542 2368428; email: ysharma.apc@itbhu.ac.in
[b]*Silpakorn University International College, Bangkok, Thailand*

Received 29 June 2013; Accepted 12 August 2013

ABSTRACT

Present study investigates the adsorption of malachite green (MG) on fly ash. Batch adsorption experiments were performed to evaluate the influence of various experimental parameters like initial concentration and contact time, adsorbent dose, and pH of solution on the removal of MG. Adsorption of MG followed pseudo-second-order kinetics. Intra-particle diffusion seems to control the removal of MG. Isotherms for the adsorption of MG onto fly ash is also investigated. Adsorption of MG on fly ash is favorably influenced by an increase in the temperature. Values of the change in enthalpy ($\Delta H^\circ = 2.87\,\text{kcal mol}^{-1}$), and change in entropy ($\Delta S^\circ = 4.99\,\text{kcal mol}^{-1}\,\text{K}^{-1}$) for MG adsorption on fly ash were positive. The high negative value of change in Gibbs free energy ($\Delta G^\circ = 1.76\,\text{kcal mol}^{-1}$) indicates the feasible and spontaneous adsorption of MG on fly ash. The surface physico-chemical characteristic of adsorbent fly ash was studied in an effort to establish a quantitative understanding of removal of the selected dye MG by adsorption. Results showed that the fly ash has a pH_{zpc} value of 7.96.

Keywords: Adsorption; Fly ash; Isotherm; Kinetics; Malachite green

1. Introduction

Rapid industrialization and increasing indifference of human society has led to increased contamination of water with different classes of pollutants day-by-day. Among various pollutant species, dyes comprise a large group of chemicals discharged almost daily in natural waters. Synthetic dyes are extensively used in various industries viz. textile, paper, cosmetics, pharmaceutical, rubber, plastics, fabrics, leather, etc. Malachite green (MG) is most commonly and frequently used for the dyeing of cotton, silk, paper, leather, and also in manufacturing of paints and printing inks. MG is widely used in distilleries for coloring purpose [1]. Direct contact with MG can cause injuries to humans and animals by inhalation and ingestion [2,3], effects such as carcinogenesis, mutagenesis, teratogenesis, respiratory toxicity, and reduced fertility in humans have been reported [4]. Therefore, the treatment of water containing such dye effluents is of interest due to its harmful impacts on receiving water.

There are many treatment technologies viz. precipitation, coagulation, flocculation, chemical oxidation, filtration, adsorption, electro-dialysis, membrane processes,

---

*Corresponding author.

1944-3994/1944-3986

etc. [5,6] which are used for the treatment of colored effluents, but most of these methods pose some problems of introduction of metallic impurities, incomplete dye removal, and production of large amount of sludge which requires further disposal [7–9].

Among all these treatment technologies, adsorption offer flexibility in design and operation, and in many cases generates high quality treated effluents. In addition, owing to reversible nature of most adsorption processes, adsorbents can be regenerated with desorption processes which are of low-maintenance cost, high efficiency, and easy to operate [10,11]. Therefore, adsorption process has come to the forefront as one of major technique for dye removal from discharged effluents.

Of various adsorbents being commercially available, activated carbon is the most promising, popular, and efficient material for dye removal, but its high cost and regeneration limits its wide application [12]. To reduce the cost, the cost of treatment, various non-conventional adsorbents viz. bagasse pith, coconut coir, orange peel, fly ash, rice husk, saw dust, banana pith, and maize cob [13,14] have been used.

Fly ash, a solid waste material of thermal power plants is produced in large amounts from high-temperature combustion of coal and wood. At present, a number of thermal power plants fueled with coal are in operation in many countries. In modern coal-firing power stations, pulverized coal is used and fly ash is obtained as a waste product in large quantities.

India alone produces 100 million tons of fly ash annually, and approximately 400 acres of land is utilized in its disposal. Therefore, an inexpensive by-product management technology is needed for fly ash reuse. Besides being a waste material, it exhibits good sorption capacity, nontoxicity, hydrophilicity, biocompatibility, and susceptibility to biodegradation.

Additionally, fly ash has been discovered to be an effective adsorbent for water treatment in the removal of dissolved organic carbons. Its alkalinity makes it functional in water treatment to hasten metallic particles. Moreover, fly ash is also used in the cement industry due to its cementation property. Undoubtedly, it has been demonstrated that fly ash possesses interesting properties for the removal of metal particles and organics; the residual sludge handled is utilized within cement industries and in landfill sites. Requisition of fly ash powder as adsorbent in treating wastewater solves the issue of color removal as well as dispenses with waste disposal. All the more significantly, fly ash is promptly accessible at practically zero cost and subsequently does not require any complicated recovery methodology, unlike activated carbon. It has been contemplated on some sorts of dyes, for example omega chrome red, basic violet 10, congo red, methylene blue, and rhodamine blue. To the best of our knowledge, no report has been recorded on the treatment of MG dye utilizing fly ash [15,16].

2. Materials and methods

2.1. Adsorbent

The adsorbent, fly ash was obtained from a nearby thermal power plant, Patratu Thermal Power Station (PTPS), Jharkhand, India. Fly ash is a cheap, abundant, and well-known waste material of thermal power plants. It contains mixtures of different metal oxides with silica and alumina; some details are given in Table 1. Fly ash was washed several times with normal water and then with distilled water prior to its use in the experiments to remove impurities.

2.2. Adsorbate

MG was obtained from E. Merck (Mumbai, India Limited) having 99.0% purity was used for the preparation dye solution without any prior purification. Dye stock solution (1,000 mg L^{-1}) was prepared by dissolving accurately weighed quantity of the dye in double-distilled water. Experimental dye solution of different concentrations was prepared by diluting the stock solution with suitable volume of double-distilled water. Molecular structure of MG is shown in Fig. 1.

Table 1
Physio-chemical analysis PTPS fly ash

Components	% by weight
Silica	53.80
Alumina	28.24
Calcium oxide	2.42
Others	14.81
pH_{zpc}	7.96

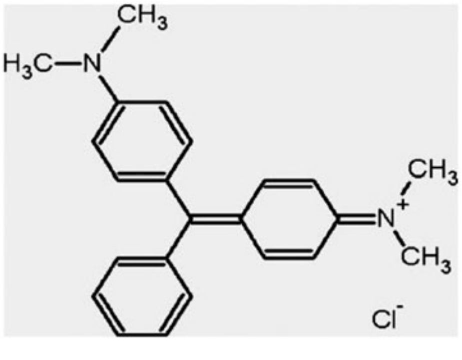

Fig. 1. Molecular structure of MG.

3. Methods

3.1. Physiochemical characterization of fly ash

The selected adsorbent was sieved mechanically through sieves to maintain an uniform particle size of 150 µm. The point of zero charge (pH_{zpc}) of fly ash was determined by a titration method [17]. The pH_{zpc} value is the point where the plots of pH final and pH initial intersect each other, and subsequently that point was recorded as pH_{zpc} of the surface of fly ash and was found to be 7.96.

3.2. Batch adsorption experiment

To estimate the applicability of fly ash as an adsorbent for dye wastewater treatment, adsorption experiments were performed using MG as the adsorbate. Stock solution of MG was prepared by dissolving approximately 1.0 g of MG in 1 L of double-distilled water. A range of dilutions (4.0–8.0 mg/L) from the stock solution was done to obtain the desired MG concentrations used in the study. Equilibrium experiments were carried out by contacting 1.0 g of fly ash and 50 mL of MG solution at different concentrations. Batch adsorption experiments, for optimization of experimental conditions like temperature, adsorbent dose, contact time, and pH were carried out by adding a fixed amount of adsorbent (1.0 g) to a series of 250-mL conical flasks filled with 50 mL diluted solutions (4.0–8.0 mg/L). The conical flasks were then sealed and placed in a water bath shaker and shaken at 100 rpm with a required adsorbent time. The flasks were then taken from the shaker at regular time intervals. At the adsorption period, the supernatant was centrifuged for 10 min at 10,000 rpm. To examine the effect of temperature on the adsorption process, the temperature of the adsorbate solution was controlled between 298 and 308 K. Observations on pH effects were measured by a pH meter, which was calibrated using 0.1 M HCl and 0.1 M NaOH solutions to maintain pH at pH values ranging from pH 4 to 8. Blank experiments were also carried out with dye solution and without adsorbent to ensure that no dye was adsorbed onto the walls of the conical flasks. After centrifugation, the concentration of supernatant solutions was determined at their λ_{max} using a UV-visible spectrometer (Spectronic 20) at 618 nm.

The percentage removal of MG at equilibrium on solid phase, q_e (mg/g), was calculated using the following relationship:

$$\text{Percentage dye removal} = \frac{C_o - C_t}{C_o} \times 100 \tag{1}$$

Amount of adsorbed dye per g of adsorbent

$$q_e = (C_o - C_e)\frac{V}{W} \tag{2}$$

where C_o (mg/L) is the initial concentration of MG, C_e (mg/L) is equilibrium residual concentration of dye in solution, V is volume of solution (l), and W (g) is mass of the fly ash.

4. Results and discussion

4.1. Adsorption studies

4.1.1. Effect of contact time and initial concentration

Contact time and initial concentration have pronounced effect on the removal of dye from aqueous solutions. The variation in percentage removal of dye with contact time at different initial concentrations ranging from 4.0 to 8.0 mg/L was carried out. It was observed that the removal of MG acquires maximum at the time of equilibrium, viz. 50 min and becomes steady thereafter. The removal is very fast in initial stages and after equilibrium, no significant change in the extent of adsorption is observed.

Initial concentration of MG (4.0 mg/L) has significant effect on removal of dye which has been shown in Fig. 2. This figure shows that the removal increases from 37.5 to 47.98% by decreasing the initial concentration of MG from 4.0 to 8.0 mg/L. Further, the removal is rapid in the initial stages, decreases slowly, and acquires a maximum at the time of equilibrium. Removal of selected dye (MG) was found maximum, 47.98%, at 4 mg/L MG [18].

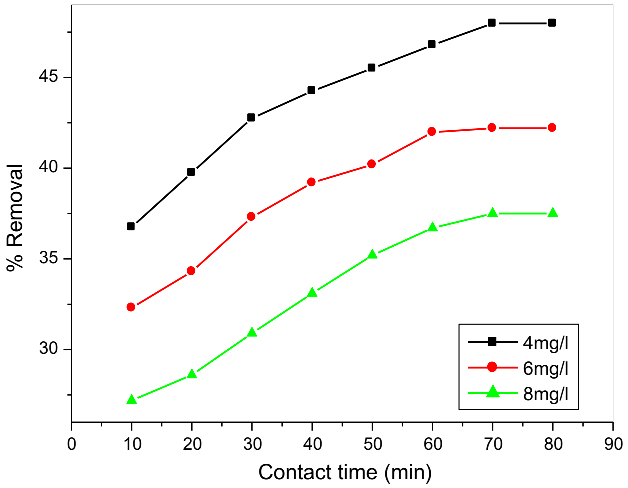

Fig. 2. Effect of initial concentration on removal of MG by adsorption onto fly ash.

4.1.2. Effect of adsorbent dose

The amount of adsorbent dose was varied from 0.5 to 1.5 g in 50 mL dye solution keeping all the variables such as pH, agitation speed, contact time, and temperature constant. The removal increased from 38.2 to 73.5% by increasing adsorbent dose which may be attributed to larger availability of active sites and seems to be the obvious reason [19].

4.1.3. Effect of pH

The pH of the dye solution plays a vital role in removal of pollutants from water and wastewater by adsorption processes and it particularly affects the adsorption capacity. The pH also controls the degree of ionization and speciation of the adsorbate. In the present study, the removal of MG by fly ash was studied at pH values of 4.0, 6.0, and 8.0. Maximum removal was 76.71% at pH 8, and it decreased with decrease in the pH value. With an increase in the pH from 4.0 to 8.0, the uptake of MG increased from 60.86 to 76.71% at 298 K, agitation speed 100 rpm, and initial dye concentration of 1.0 mg/L as shown in Fig. 3.

This behavior can be explained on the basis of change in the surface charge of the fly ash. In this case, as the MG is a basic dye, at lower pH the H^+ ions will compete with dye cations causing a decrease in q_e value. This can be observed from the higher and lower sorption capacity of MG at higher and lower pH, respectively [20].

4.1.4. Effect of temperature

Temperature is an important parameter for adsorption processes, and generally has significant impact on the extent of removal. It has significant influence on the removal of MG by fly ash also. Fig. 4 depicts the effect of temperature investigated in the temperature range of 298–308 K. The experimental result shows that the removal of MG increased from 50 to 73.5% by increasing the temperature, indicating the endothermic nature of the adsorption process. The decrease in the removal of MG with increase in temperature could be due to weakening of the physical bonds between the dye molecules and the active site of the fly ash molecules. Also, with the increase of temperature, the solubility of MG should have increased. As a result, the solute was more difficult to adsorb. The enhancement in the adsorption capacity might be due to the chemical interaction between adsorbate and adsorbent [21].

4.2. Kinetic studies

4.2.1. Pseudo-first-order kinetic model

The kinetics of MG adsorption on fly ash were studied with respect to its different initial concentrations of MG. For evaluating the adsorption kinetics of MG, the pseudo-first-order kinetic model, Lagergren's equation has been used and found fit to the experimental data. For evaluating the adsorption kinetics of MG, the pseudo-first-order kinetic models (Lagergren's equation) has been used and found fit to the experimental data. The Lagergren's model can be represented as follows [22]:

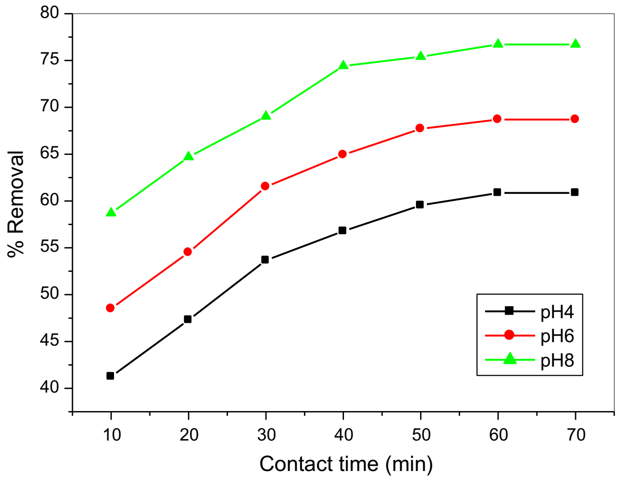

Fig. 3. Effect of pH on % removal of MG by adsorption onto fly ash.

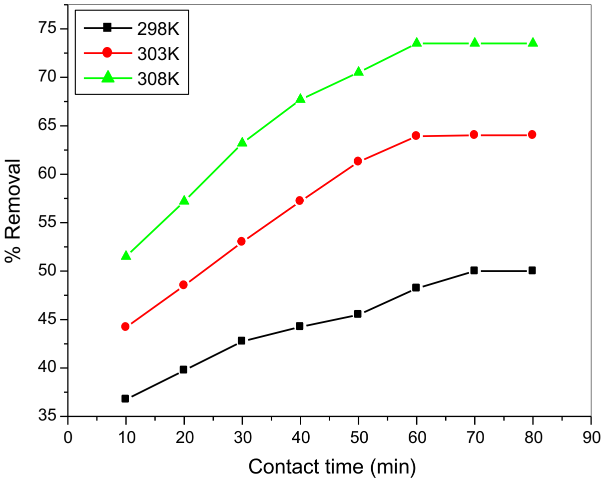

Fig. 4. Effect of temperature on % removal of MG by adsorption onto fly ash.

$$\frac{dq_t}{dt} = k_{ad}(q_e - q_t) \tag{3}$$

The integrated linear form of the model is

$$\log(q_e - q) = \log q_e - \left(\frac{K_{ad}}{2.303}\right)t \tag{4}$$

where q_e and q (both in mg/g) are amounts of MG adsorbed at any time and at equilibrium, respectively, and K_{ad} (min^{-1}) is the rate constant of adsorption.

The value of pseudo-first-order constant K_{ad} increases by increasing temperature for MG adsorption on fly ash (Table 2). It reveals that higher temperature favor the adsorption of MG on fly ash and confirms the MG adsorption on fly ash is endothermic in nature.

4.2.2. Pseudo-second-order kinetic model

The plot of t/q_t against t at different temperatures is shown in Fig. 5. In comparison of the pseudo-first-order equation. The expression for fitting of the kinetic data in the pseudo-second-order equation first-order showed excellent linearity with high correlation coefficient ($R^2 > 0.997$) over the temperature range of 298–308 K. The data obtained for the pseudo-second-order kinetic model at three different temperatures are tabulated in Table 2. The initial adsorption rate, h, as well as the rate constant, k_2 increased with increase in temperature [23].

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{5}$$

$$h = k_2 q_e^2 \tag{6}$$

4.2.3. Intra-particle diffusion

Adsorption onto fly ash for MG removal results through intra-particle diffusion and pore diffusion because of their porous nature. The nature of the rate-limiting step in a batch system can be determined from the properties of the adsorbate and adsorbent. In adsorption systems where there is the possibility of intra-particle diffusion being the rate-limiting step, the intra-particle diffusion approach described by Weber and Morris [24] was used. To elucidate the mechanism of diffusion, the kinetic results were analyzed by the intra-particle diffusion model [24]:

$$q_t = K_{id}\, t^{1/2} + C \tag{7}$$

where q_t = amount adsorbed at time t (mg/g), $t^{1/2}$ = the time of half adsorption ($\text{min}^{1/2}$). The values of K_{id} were calculated from the slopes of curves of the plots of "amount adsorbed per unit mass of adsorbent vs.

Table 2
Values of rate constants of pseudo-first-order ($\times 10^{-2}\,\text{min}^{-1}$), pseudo-second-order ($\times 10^{-3}\,\text{g}\,\text{mg}^{-1}\,\text{min}^{-1}$) reaction, intra-particle diffusion, and Elovich at different temperatures for the removal of MG by adsorption on fly ash

Pseudo-first-order		K_{ad} ($\times 10^{-2}\,\text{min}^{-1}$)	R^2
	298	2.0	0.997
	303	2.07	0.877
	308	2.16	0.975
Pseudo-second-order		k_2 ($\times 10^{-3}\,\text{g}\,\text{mg}^{-1}\,\text{min}^{-1}$)	R^2
	298	1.69	0.988
	303	3.36	0.993
	308	5.78	0.998
Intra-particle diffusion		K_{id} ($10^{-6}\,\text{mg}\,\text{g}^{-1}\,\text{min}^{-1/2}$)	R^2
	298	1.09	0.941
	303	1.18	0.995
	308	1.7	0.978
Elovich		α ($\times 10^{-3}\,\text{mg}\,\text{g}^{-1}\,\text{min}^{-1}$)	R^2
	298	2.41	0.931
	303	2.07	0.858
	308	1.02	0.980

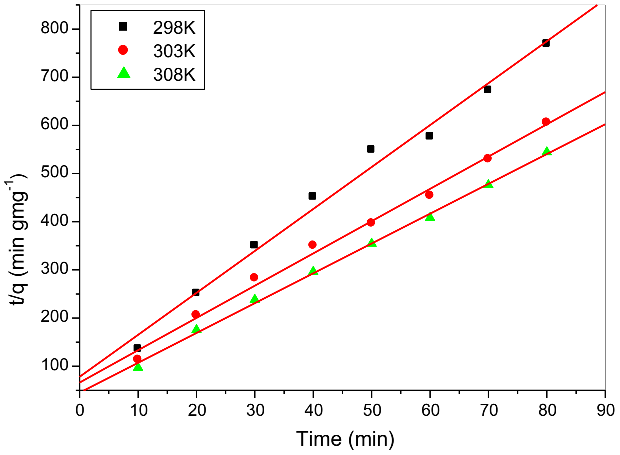

Fig. 5. Plot of pseudo-second-order kinetic plot for the removal of MG by adsorption onto fly ash at different temperatures.

square root of time” (Fig. 6). The values are shown in Table 2.

4.2.4. Elovich models

The kinetics of adsorption can also be described by The Elovich model [25]. The mathematical form of this model can be represented as:

$$q = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \tag{8}$$

where α is the initial adsorption rate (mg g^{-1} min^{-1}) and β is the desorption constant (g g^{-1}) during any one experiment. A plot of q_t vs. ln t (Fig. 7) should yield a linear relationship with a slope of $(1/\beta)$ and an intercept of $1/\beta$ ln $(\alpha\beta)$. The calculated parameters are listed in Table 2.

4.3. Equilibrium isotherm study

To analyze the experimental data, different equilibrium isotherm models like Langmuir, Freundlich, and Tempkin isotherm models have been used. On the basis of R^2 values, it was found that Freundlich adsorption isotherm is the best-fit model for the adsorption of MG for this system.

4.3.1. Freundlich adsorption isotherm

Freundlich adsorption isotherm is based on the assumption of a heterogeneous surface with a non-uniform distribution of heat of adsorption. The linear form of the isotherm can be represented as follows [26]:

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \tag{9}$$

where q_e is the equilibrium dye concentration on adsorbent (mg g^{-1}), C_e is the equilibrium dye concentration in solution (mg L^{-1}), K_f (mg g^{-1}), and $1/n$ (L g^{-1}) is the Freundlich constant related to sorption capacity, and heterogeneity factor respectively. K_f and $1/n$ are calculated from the intercept and slope of the straight line of the plot log q_e vs. log C_e (Fig. 8). The values of K_f 1.0 (mg/g), and that of $1/n$ are found to be 1.29 l/g at 298 K with higher correlation coefficient (R^2) values (0.994) of the straight lines obtained at each temperature confirm the validity of Freundlich adsorption isotherm for fly ash.

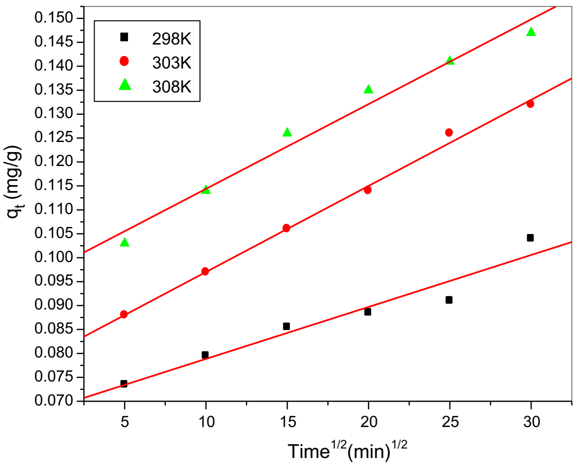

Fig. 6. Plot of intra-particle diffusion for removal of MG by adsorption onto fly ash at different temperatures.

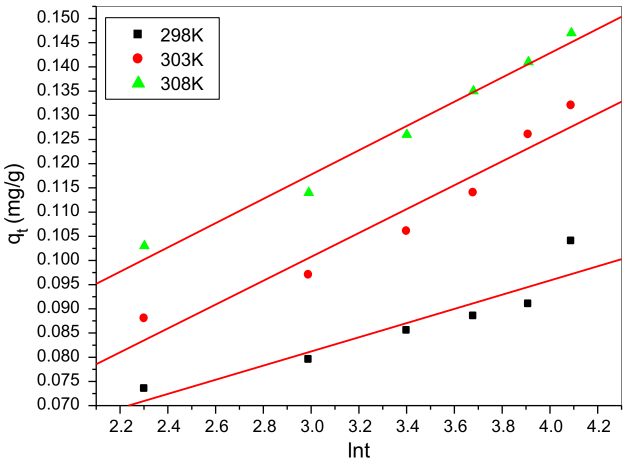

Fig. 7. Plot of Elovich kinetic model for removal of MG onto fly ash at different temperatures.

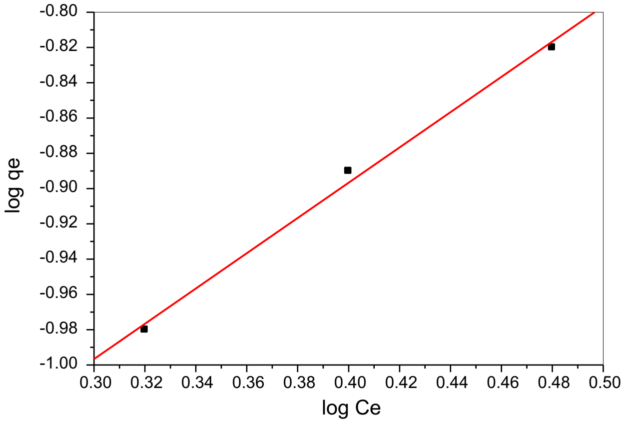

Fig. 8. Plot of Freundlich adsorption isotherm for removal of MG onto fly ash at 298 K.

Fly ash is a solid waste material used as an adsorbent for the removal of MG a cationic dye and its adsorption capacity for this study was evaluated (1.09 mg/g). Further, there are a large number of non-conventional adsorbents which have been used for the removal of MG from their aqueous solutions. Some of such adsorbents with their respective adsorption capacities for the removal of selected dyes have been discussed. Degreased coffee bean (55.3 mg/g) [27], neem sawdust (2.82 mg/g) [28], and Arundo donax root carbon (8.69 mg/g) [29] have been reported. The data of equilibrium modeling shows the feasibility of application of this solid waste (fly ash) for the removal of MG in particular and other dyes from aqueous solutions in general.

4.4. Thermodynamic study

The thermodynamic parameters, such as change in standard free energy (ΔG°), enthalpy (ΔH°), and entropy(ΔS°) were undertaken to understand the process of removal of MG by adsorption onto fly ash. Their values were calculated at different temperatures viz. 298, 303, and 308 K using the following equations [30]:

$$\Delta G^{\circ} = -RT\ln K \tag{10}$$

$$K = C_{ac}/C_e \tag{11}$$

where K_c is equilibrium constant, C_{ac} and C_e is equilibrium concentration of malachite green on the adsorbent and equilibrium concentration of dye in the solution, respectively (mol/L), T is absolute temperature (K), and R is gas constant (1.987 cal/mol/K).

K_1 and K_2 are the equilibrium concentrations at T_1 and T_2, respectively:

$$\Delta H^{\circ} = R\left(\frac{T_2T_1}{T_2 - T_1}\right)\ln\frac{K_2}{K_1} \tag{12}$$

$$\Delta S^{\circ} = \frac{(\Delta H^{\circ} - \Delta G^{\circ})}{T} \tag{13}$$

The values of the thermodynamic parameters were determined for the present system. Gibbs free energy change ΔG° was -1.76 (kcal mol^{-1}), enthalpy change, 2.87 (kcal mol^{-1}), and the value of change in entropy was 4.99 (kcal mol^{-1} K^{-1}). For this sytem, the adsorption of MG on fly ash, the values of ΔG° were found to be negative which indicate that the process of removal of MG is feasible at all the temperatures. The value of enthalpy change, ΔH°, was positive for this system which further confirms endothermic nature of the process of adsorption. Positive values of ΔS° show the increased randomness at the solid/solution interface during the adsorption of dye molecules on surface of fly ash. With rise of temperature ΔS° decreased which depicts that the disorderness decreases with a rise in temperature. Hence, mobility of dye ions to escape from the adsorbent surface to the aqueous solution decreases with increase of temperature, which is authenticated by the rise of adsorption at higher temperature than at lower temperature. It also indicates some structural changes in the adsorbate and adsorbent and an affinity of the adsorbent toward MG and also confirm the possibility of favorable adsorption. This can also be expected because of the mass transfer of dye molecules from solution phase to the adsorbent which consequently might have resulted in increase of relative disorderness in the system and at the solid-liquid interface. It can be understood that spontaneity of the process might have also resulted due to a rise in the value of ΔS° as the system moves to more stable and uniform state. The values of ΔG° also suggest that the adsorption is physical in nature [31–34].

5. Conclusions

Fly ash is a solid waste and is abandoned to the environment. Fly ash has been successfully used for removal of MG from aqueous solutions. Removal was increased by increasing pH and maximum removal was obtained at pH 8.0. Adsorption of MG was very rapid and equilibrium was achieved in less than 60 min. The removal of MG was governed by pseudo-first-order kinetics. The adsorption isotherms were also determined and were appropriately described by different isotherm models like Langmuir, Freundlich, Temkin, etc. with a better fitting to the Freundlich model. Process of MG removal is endothermic in nature with maximum removal at 308 K. Thermodynamic parameters have been calculated and indicate that the process of removal is spontaneous.

References

[1] S.D. Khatri, M.K. Singh, Color removal from dye wastewater using sugarcane dust as an adsorbent, Adsorpt. Sci. Technol. 17(4) (1999) 262–282.

[2] M.M. Nassar, Y.H. Magdy, Removal of different basic dyes from aqueous solutions by adsorption on palm-fruit bunch particles, Chem. Eng. J. 66 (1997) 223–226.

[3] S.J. Culp, F.A. Beland, Malachite green: A toxicological review, J. Am. Colloid Toxicol. 15 (1996) 219–238.

[4] S. Srivastava, S. Rangana, D. Roy, Toxicological effects of malachite green: A review, Aquat. Toxicol. 66 (2004) 319–329.

[5] M. Valix, W.H. Cheung, G. McKay, Preparation of activated carbon using low temperature carbonization and physical activation of high ash raw bagasse for dye adsorption, Chemosphere 56 (2004) 493–501.

[6] P. Basakaralingam, M. Pulikesi, V. Ramamurthi, S. Sivanesan, Equilibrium studies for the adsorption of acid dye onto modified hectorite, J. Hazard. Mater. 136 (2006) 1.

[7] A.A. Adriana, A.S. Nunes, L.S. Oliviera, Activated carbons from waste biomass: An alternative use for biodiesel production solid residues, Bioresour. Technol. 100 (2009) 1786–1792.

[8] N.K. Amin, Removal of reactive dyes from aqueous solutions onto activated carbons prepared from sugarcane bagasse pith, Desalination 223 (2008) 152–161.

[9] E.N. El Qada, S.J. Allen, G.A. Walker, Adsorption of basic dyes from aqueous solution onto activated carbons, Chem. Eng. J. 135 (2008) 174–184.

[10] A. Dabrowski, Adsorption—from theory to practice, Adv. Colloid Interface 93 (2001) 135–224.

[11] N. Hoda, E. Bayram, E. Ayranci, Kinetic and equilibrium studies on the removal of acid dyes from aqueous solutions by adsorption onto activated carbon cloth, J. Hazard. Mater. B137 (2006) 344–351.

[12] Y.C. Sharma, S. Uma, Optimization of parameters for adsorption of methylene blue on a low-cost activated carbon, J. Chem. Eng. Data 55 (2010) 435–439.

[13] C. Namasivayam, D. Kavitha, IR, XRD and SEM studies on the mechanism of adsorption of dyes and phenols by coir-pith carbon from aqueous phase, Microchem. J. 82 (2006) 43–48.

[14] Y.C. Sharma, S. Uma, S.N. Upadhyay, Removal of a cationic dye from wastewaters by adsorption on activated carbon developed from coconut coir, Energy Fuels 23 (2009) 2983–2988.

[15] M. Özacar, I.A. Şengil, Adsorption of metal complex dyes from aqueous solutions by pine sawdust, Bioresour. Technol. 96 (2005) 791–795.

[16] D. Kavak, N. Ozturk, Adsorption of boron from aqueous solutions using fly ash: Batch and column studies, J. Hazard. Mater. 127 (2005) 81–88.

[17] S. Nethaji, A. Sivasamy, G. Thennarasu, S. Saravanan, Adsorption of malachite green dye onto activated carbon derived from *Borassus aethiopum* flower biomass, J. Hazard. Mater. 181 (2010) 271–280.

[18] V.K. Garg, R. Kumar, R. Gupta, Removal of malachite green dye from aqueous solution by adsorption using agro-industry waste: A case study of *Prosopis cineraria*, Dyes Pigm. 62(1) (2004) 1–10.

[19] A.A. Jalil, S. Triwahyono, M.R. Yaakob, Z.Z.A. Azmi, N. Sapawe, N.H.N. Kamarudin, H.D. Setiabudi, N.F. Jaafar, S.M. Sidik, S.H. Adam, B.H. Hameed, Utilization of bivalve shell-treated *Zea mays* L. (maize) husk leaf as a low-cost biosorbent for enhanced adsorption of malachite green, Bioresour. Technol. 120 (2012) 218–224.

[20] L. Wang, Application of activated carbon derived from "waste" bamboo culms for the adsorption of azo disperse dye: Kinetic, equilibrium and thermodynamic studies, J. Environ. Manage. 102 (2012) 79–87.

[21] G. Annadurai, J. Ruey-shin, L. Duu-Jong, Use of cellulose based wastes for adsorption of dyes from aqueous solutions, J. Hazard. Mater. B92 (2002) 263–274.

[22] S. Lagergren, Zur theorie dersogenannten adsorption geloster stoffe [Theory for adsorption of dissolved substances dersogenannten], Kung Sven. Veten. Hand. 24 (1898) 1–39.

[23] Y.S. Ho, G. McKay, Sorption of dye from aqueous solution by peat, Chem. Eng. J. 70 (1998) 115–124.

[24] W.J. Weber, J.C. Morris, Advances in water pollution research: Removal of biologically resistant pollutant from wastewater by adsorption, International Conference on Water Pollution Symposium, Pergamon, Oxford 2 (1962) 231–266.

[25] F. Deniz, S.D. Saygideger, Equilibrium, kinetic and thermodynamic studies of Acid Orange 52 dye biosorption by *Paulownia tomentosa* Steud. leaf powder as a low-cost natural biosorbent, Bioresour. Technol. 101 (2010) 5137–5514.

[26] G.S. Gupta, G. Prasad, V.N. Singh, Removal of color from wastewater by sorption from water reuse, J. Environ. Sci. Health 23 (1988) 205–217.

[27] S.-A. Ong, K. Uchiyama, D. Inadama, Y. Ishida, K. Yamagiwa, Treatment of azo dye Acid Orange 7 containing wastewater using up-flow constructed wetland with and without supplementary aeration, Bioresour. Technol. 101 (2010) 9049–9057.

[28] S.D. Khattri, M.K. Singh, Removal of malachite green from dye wastewater using neem sawdust by adsorption, J. Hazard. Mater. 167 (2009) 1089–1094.

[29] B.H. Hameed, M.I. El-Khaiary, Batch removal of malachite green from aqueous solutions by adsorption on oil palm trunk fibre: Equilibrium isotherms and kinetic studies, J. Hazard. Mater. 154 (2008) 237–244.

[30] Y.C. Sharma, S. Uma, S.N. Upadhyay, An economically viable removal of methylene blue by adsorption on activated carbon prepared from rice husk, Can. J. Chem. Eng. 89 (2011) 377–383.

[31] A. Mittal, V. Thakur, J. Mittal, H. Vardhan, Process development for the removal of hazardous anionic azo dye Congo red from wastewater by using hen feather as potential adsorbent, Desalin. Water Treat. (2013) 1–11, doi: 10.1080/19443994.2013.785030.

[32] A.A. Ahmad, A. Idris, B.H. Hameed, Organic dye adsorption on activated carbon derived from solid waste, Desalin. Water Treat. 51 (2013) 2554–2563.

[33] H. Freundlich, Uber dye adsorption on lunsungen, J. Phys. Chem. 57 (1985) 387–470.

[34] B. Pan, P. Huang, M. Wu, Z. Wang, P. Wang, X. Jiao, B. Xing, Physico-chemical and sorption properties of thermally-treated sediments with high organic matter content, Bioresour. Technol. 103 (2012) 367–373.