Asian Journal of Chemistry; Vol. 28, No. 10 (2016), 2139-2145

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2016.19886

Paper Industry Waste Sludge: A Low-Cost Adsorbent for Removal of Malachite green Dye

ANITA THAKUR and HARPREET KAUR*

Department of Chemistry, Punjabi University, Patiala-147 002, India

*Corresponding author: E-mail: preetjudge@yahoo.co.in

Received: 3 February 2016; *Accepted*: 13 May 2016; *Published online*: 30 June 2016; AJC-17956

In the present work, paper industry waste sludge has been used as a low-cost adsorbent for the investigation of adsorption isotherms, kinetics and thermodynamic parameters of Malachite green dye adsorption from aqueous solution. Three kinetic models, pseudo-first-order, pseudo-second-order and intra-particle-diffusion model have been used to predict the adsorption rate constants. The kinetics of adsorption has been best described by pseudo-second-order model and is supported by intra-particle-diffusion model. The equilibrium adsorption capacity has been determined by subjecting the experimental data to Langmuir, Freundlich and Temkin isotherms. The thermodynamic parameters such as; change in free energy, enthalpy and entropy have been calculated.

Keywords: Malachite green, Adsorption, Kinetics, Thermodynamics.

INTRODUCTION

Environmental pollution is one of the major and most critical problems of the modern world, because every day synthetic and toxic chemicals are released into the environment which affects our water, air and soil. Now-a-days, water pollution caused by the industrial effluents containing synthetic dyes is of major serious concern due to carcinogenic nature of most of the dyes [1]. Synthetic dyes are the coloured aromatic compounds that can be applied on a substrate by the various processes like dyeing, printing, surface coating, *etc*. and widely used in the different industries [2]. The effluents of these industries are directly discharged into water bodies, which is aesthetically displeasing, due to the presence of organic compounds [3].

Various conventional waste treatment methods such as coagulation/flocculation, electrochemical oxidation, membrane filtration, reverse osmosis, solvent extraction, photodegradation, *etc*. have been used for the removal of dyes [4-9] but these methods have not been very successful for the removal of dyes due to various disadvantages like expensive processes, sludge disposal problems, *etc*., [10,11]. The adsorption process is widely acknowledged as the most promising and efficient methods because of its simplicity of design, low capital investment, ease of operation, *etc*., [12,13]. The paper industries produce a large amount of sludge every year. If this sludge is used as an adsorbent for the removal of dyes then it is an effective and positive step to remove the waste of one industry by using waste of another industry.

Malachite green (MG) dye has been widely used for dyeing of silk, leather, wool, jute, paper, as a food colourant and as a fungicide and antiseptic in aquaculture industry to control fish parasites and disease [14]. Malachite green is environmentally persistent and extremely toxic to humans and animals because on inhalation, it causes toxicity to respiratory system [15]. It affects the cells of mammals and a major cause of tumour in liver [16]. Thus keeping in view the hazardous nature of dye, the present study is undertaken to investigate the efficiency of paper industry waste sludge (chemically modified) as a low cost adsorbent for the removal of malachite green dye from aqueous solution.

EXPERIMENTAL

The adsorbate, Malachite green (MG) dye has been purchased from S.D. Fine Chemical Limited, Mumbai, India having molecular formula $C_{23}H_{25}N_2Cl$ and molecular weight 365 g/mol. The adsorbent, paper industry waste sludge has been obtained from paper industry. The reagents used in the work were concentrated H_2SO_4 and diluted NaCl and HCl. Deionized water has been used throughout the experiment. Instruments employed for the work include UV-visible spectrophotometer (Shimadzu-1800), Mechanical Shaker (Remi Motor), FT-IR (Perkin-Elmer spectrophotometer-RXI) and pH meter (ELICO PRIVATE LIMITED, Hyderabad (India).

Preparation of adsorbent: The waste material (sludge) from paper industry has been used as an adsorbent for the removal of dye. The sludge has been washed with deionized

water and dried (under sunlight) and then kept in oven at 100 °C for 3 days. The dried material has been grounded into fine powder. The finely powdered sludge has been mixed with concentrated sulphuric acid and kept overnight and then washed with deionized water to remove residue acid. The material has been dried at 100 °C for 24 h and then grounded, sieved and kept in air tight container for further uses.

Preparation of adsorbate: The dye stock solution has been prepared by dissolving 1 g of dye in 1 L of deionized water (1000 mg/L) and the other concentration, *i.e.*, 75, 100, 125, 150 and 175 mg/L has been prepared by diluting the stock solution.

General procedure: Batch adsorption studies have been conducted to study the influence of important parameters such as initial dye concentration, contact time, adsorbent dose, pH and temperature on the removal of malachite green dye onto paper industry waste sludge by varying the parameter under study and keeping the others constant. For each adsorption experiment, 100 mL of dye solution of different concentrations (75-175 mg/L) with known amount of adsorbent dose (1 g) has been agitated on Remi stirrer at room temperature (308 K) with known pH (4.15). Then, 5 mL of suspension has been withdrawn at different intervals of time and adsorbent has been removed by centrifugation for 15 min. The concentration of dye at particular time intervals has been determined spectrophotometrically at wavelength λ_{max} = 616 nm. The amount of dye adsorbed per gram of adsorbent, *i.e.*, q_t and percentage removal of dye at time t has been calculated by the following formula:

$$q_e = \frac{(C_0 - C_e)V}{W}$$

$$\text{Removal } (\%) = \frac{(C_0 - C_e)}{C_0} \times 100$$

where, C_0 and C_e represent initial and final equilibrium concentration (mg/L), V is the volume of solution and W is weight of adsorbent. q_e is the amount of dye adsorbed at equilibrium.

RESULTS AND DISCUSSION

Effect of initial dye concentration and contact time: The percentage of dye removal is highly dependent on the contact time and initial concentration of dye. In order to study the effect of contact time on adsorption capacity of dye, 100 mL solution of different initial dye concentrations, *i.e.*, 75, 100, 125, 150 and 175 mg/L has been agitated along with fixed amount of adsorbent dose (1 g) for different intervals of time (10, 20, 30, 45, 60, 75, 90 and 120 min). The experiments have been conducted at constant temperature and pH. Fig. 1(a) and (b) indicates that the both percentage removal of dye and adsorption capacity of dye are fastly increases initially and then become slower and finally attained equilibrium at 60 min. But in case of initial dye concentration, percentage of dye removed decreased with increase in concentration and adsorption capacity increased and the results shown in Fig. 1(a) and (b). The percentage of removal of dye decreases with increase in initial dye concentration, which may be due to the saturation of adsorption sites on adsorbent surface. But the

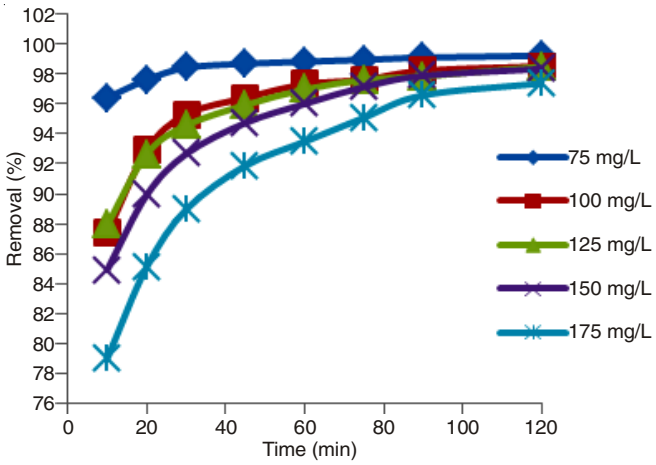

Fig. 1(a). Effect of contact time and initial dye concentration on percentage removal of dye

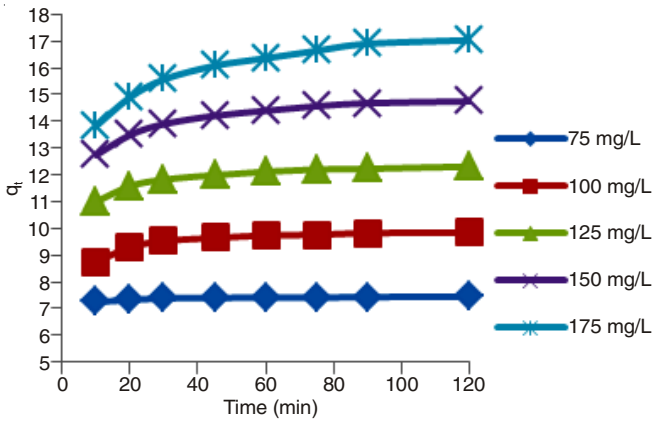

Fig. 1(b). Effect of contact time and initial dye concentration on adsorption capacity of dye

adsorption capacity increases with increase in initial concentration of dye solution because the increased initial dye concentration enhances the interaction between dye and adsorbent [17].

Effect of adsorbent dose: The effect of adsorbent dose on the amount of dye adsorbed has been investigated by agitating 100 mL of dye solution of fixed initial dye concentration (100 mg/L) with varying amount of adsorbent dose (0.5, 0.7, 1.0, 1.3 and 1.5 g). Fig. 2(a) indicates that percentage of dye increases with an increase in adsorbent dose. This may be attributed to the fact that with increase in adsorbent dose, there is increase in adsorption surface, so there is availability of more adsorption sites [18]. But the adsorption capacity decreases (Fig. 2(b)) because with increase in adsorbent dose there is overlapping or aggregation of adsorbent sites, which results in decrease in total adsorption surface area [19].

Effect of pH: The effect of pH on malachite green adsorption onto paper industry waste has been studied while the other parameters such as initial dye concentration, contact time, adsorbent dose have been fixed at 100 mg/L, 60 min and 1 g. The adsorption experiments have been conducted at different pH (2.15, 4.15, 8.15 and 10.15). The pH of solution has been adjusted with 0.1 N HCl and 0.1 N NaOH solutions. It is evident from Fig. 3 that the removal efficiency of dye is reasonably high in pH range 2-4. The high adsorption in acidic medium could be due to the interaction between the positively charged

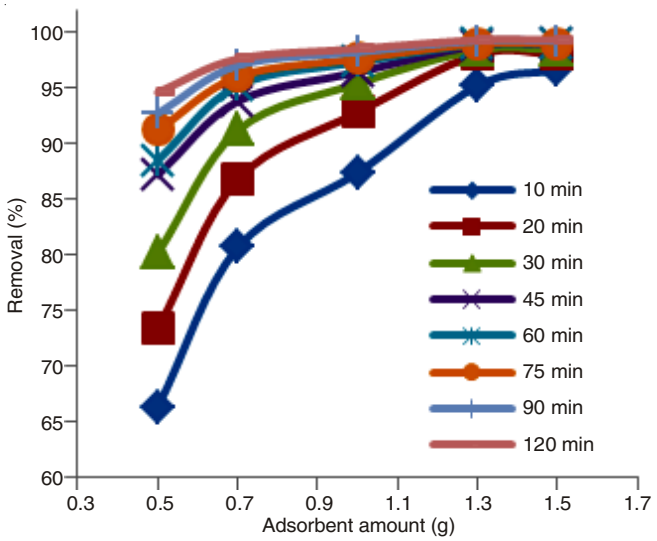

Fig. 2(a). Effect of adsorbent dose on % removal of malachite green dye

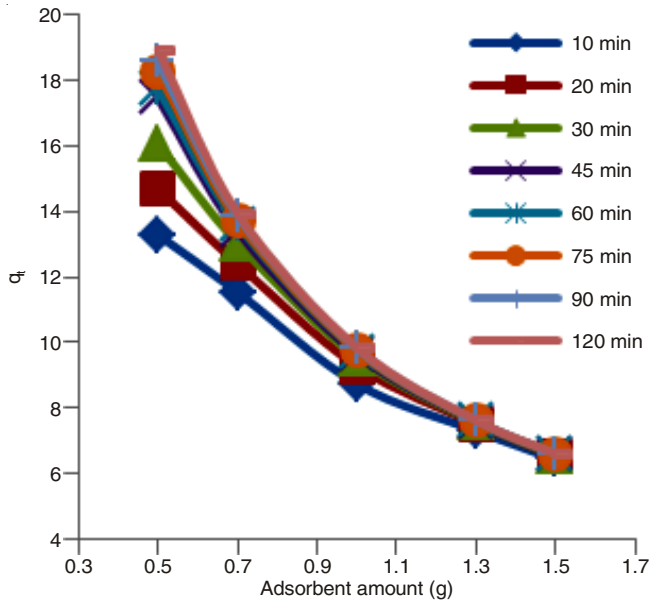

Fig. 2(b). Effect of adsorbent dose on adsorption capacity of malachite green dye

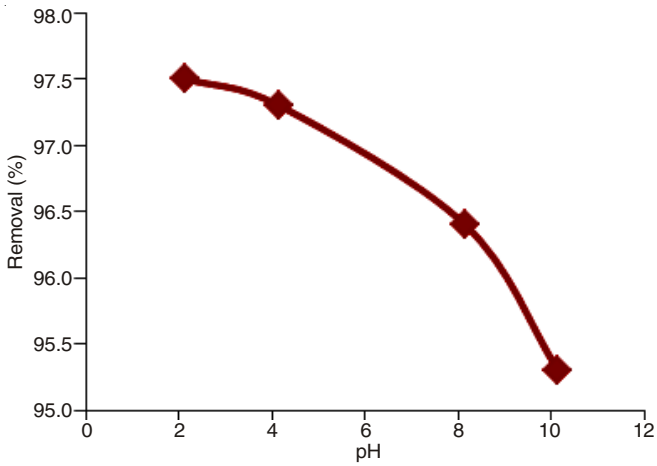

Fig. 3. Effect of pH on % removal of malachite green dye adsorption

dye cations with the surface functional group present in the adsorbent. There is a small decrease in percentage removal of dye at higher pH, which may be due to the formation of soluble hydroxyl complexes.

Effect of surfactant: The adsorption of Malachite green dye has also been studied in the presence of sodium dodecyl sulfate (SDS), an anionic surfactant along with paper industry waste sludge. In order to study the effect of surfactant, 100 mL of dye solution has been agitated with 1 g of adsorbent and 10 mg of sodium dodecyl sulfate for 60 min (equilibrium time). The result indicates that 98.40 % of dye has been removed by using sodium dodecyl sulfate along with the adsorbent. This can be explained on the fact that malachite green is cationic dye and sodium dodecyl sulfate is anionic surfactant, so there is more adsorption of ionic solute in the presence of oppositely charged surfactant.

Desorption studies: Desorption is a very important process because it will provide the beneficial features such as reusability of adsorbent, recovery of pollutants, reducing the process cost, reducing the generation of secondary wastes and identifying the adsorption mechanism. In order to evaluate the possibility of regeneration and reuse of the adsorbent, first of all the adsorbent collected after adsorption has been dried and divided into three parts. One part is dissolved in distilled water, other in 1 N acetic acid and remaining in 1 N hydrochloric acid for 24 h and then washed gently with water to remove any unadsorbed dye.

In order to study the recycling efficiency, 100 mL solution of fixed initial dye concentration (100 mg/L) has been agitated along with 1 g of each adsorbent that is collected after desorption with water, acetic acid and hydrochloric acid for 60 min separately. The solutions after adsorption were subjected to UV-visible spectrophotometer to determine the amount of dye adsorbed. The effect of various reagents used for desorption studies shows that hydrochloric acid is better reagent because maximum amount of dye, *i.e.*, 82.20 % has been removed by using the adsorbent desorbed with hydrochloric acid.

Adsorption isotherms: The adsorption isotherm indicates the relation between amounts of dye adsorbed at constant temperatures per unit mass of the adsorbent. The adsorption equilibrium data has been analyzed for three well known isotherm models; Freundlich, Langmuir and Temkin adsorption isotherm.

Freundlich adsorption isotherm: Freundlich adsorption isotherm is well known empirical equation assuming that adsorption takes place on a heterogeneous surface or surface supporting sites of varied affinities through multilayer adsorption mechanism.

The linear form of Freundlich adsorption isotherm is represented by the equation [20]:

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

where, q_e is the amount of dye adsorbed at equilibrium concentration C_e (mg/L), K_f and 1/n are Freundlich constant associated with adsorption capacity and adsorption intensity respectively. The linear plot between log q_e *versus* log C_e shows that adsorption of malachite green dye follows Freundlich adsorption. The value of 1/n and K_f has been calculated from the slope and intercept of plot (Fig. 4). The magnitude of the exponent 1/n gives an indication of the favourability of adsorption. The value of n > 1 represents favourable adsorption condition.

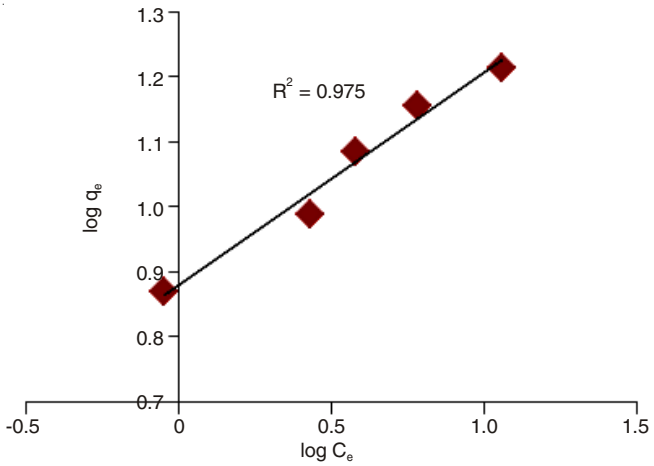

Fig. 4. Freundlich adsorption isotherm for malachite green dye adsorption at 308 K

Langmuir adsorption isotherm: Langmuir adsorption isotherm is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute on homogeneous adsorbent surface. *i.e.*, once a dye molecule occupies a site, no further transmigration can be takes place at the same site.

The Langmuir isotherm is represented by the following equation [21]:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m \cdot b_L}$$

where q_m and b_L are Langmuir constants related to adsorption efficiency and energy of adsorption respectively. The linear plot of specific adsorption capacity C_e/q_e against the equilibrium concentration C_e shows that the adsorption obeys Langmuir model. The Langmuir constant q_m and b_L have been determined from the slope and intercept of the plot (Fig. 5, Table-1).

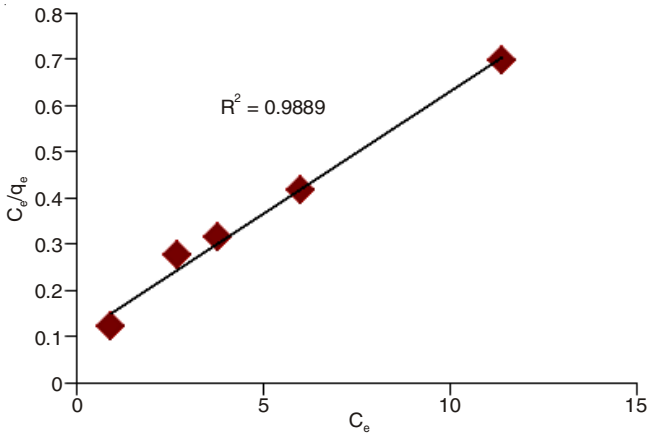

Fig. 5. Langmuir adsorption isotherm for malachite green dye adsorption at 308 K

In order to find out the feasibility of the isotherm, the essential characteristics of Langmuir isotherm can be expressed in terms of dimensionless constant separation factor R_L by the equation:

$$R_L = \frac{1}{(1 + b_L \cdot C_0)}$$

The R_L values lies between 0 to 1, indicate the process is a favourable adsorption.

Temkin adsorption isotherm: Temkin adsorption isotherm proposed that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbate-adsorbent interactions.

The linear Temkin equation is [22]:

$$q_e = B \ln K_T + B \ln C_e$$

where, K_T is the equilibrium binding constant corresponds to the maximum binding energy, B is the constant related to the heat of adsorption. K_T and B have been calculated from the slope and intercept of q_e *versus* ln C_e linear plot (Fig. 6).

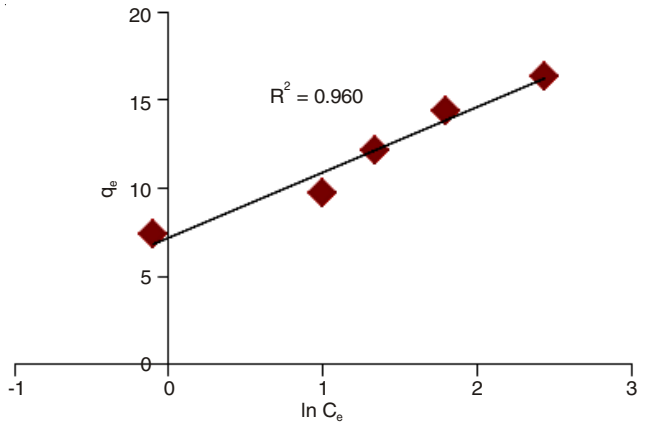

Fig. 6. Temkin adsorption isotherm for malachite green dye adsorption at 308 K

Adsorption kinetics: The kinetics of malachite green adsorption onto paper industry waste has been analyzed by pseudo-first-order, pseudo-second-order and intra-particle diffusion model.

Pseudo-first-order-kinetic model: Pseudo-first-order Lagergren model is described by the equation given below [23]:

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

K_1 is the pseudo-first order rate constant (min^{-1}).

The plot between log $(q_e - q_t)$ *versus* time t should be a straight line plot if the data follow pseudo-first order kinetic model. It has been found that it does not fit to straight line.

TABLE-1
ADSORPTION ISOTHERM PARAMETERS FOR MALACHITE GREEN ADSORPTION ONTO PAPER INDUSTRY WASTE SLUDGE

Temp. (K)	Langmuir constants				Freundlich constants			Temkin constants		
	q_m (mg/g)	b_L (L/mg)	R^2	R_L	N	K_f	R^2	B	K_T	R^2
308	19.23	0.500	0.988	0.019	3.058	7.551	0.975	3.690	91.833	0.960
313	20.83	0.572	0.961	0.017	2.695	8.185	0.983	4.182	89.950	0.939
318	21.28	0.734	0.989	0.013	2.525	9.683	0.986	4.580	105.68	0.978

TABLE-2
KINETIC PARAMETER FOR THE ADSORPTION OF MALACHITE GREEN BY PAPER INDUSTRY WASTE SLUDGE

C_0 (mg/L)	Pseudo-second-order calculated			Intra-particle diffusion parameters		
	K_2 (g mg^{-1} min^{-1})	q_e (mg/g)	R^2	K_{ipd} (mg g^{-1} min^{-1})	C (mg/g)	R^2
75	0.390	7.463	1.000	0.022	7.222	0.831
100	0.069	10.000	1.000	0.125	8.653	0.791
125	0.052	12.500	1.000	0.154	10.810	0.850
150	0.029	15.150	1.000	0.248	12.330	0.894
175	0.016	17.540	0.999	0.400	13.070	0.924

Pseudo-second-order kinetic model: The linearized equation for pseudo-second-order kinetic model [24] is represented as:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$$

where, K_2 (g mg^{-1} min^{-1}) is the rate constant of pseudo-second-order adsorption. The plot of t/q_t *versus* t should give a linear relationship from which the value of q_e and K_2 have been determined from the slope and intercept respectively. Pseudo-second-order rate constant K_2 and R^2 have been summarized in Table-2.

Intra-particle diffusion model: The limiting step in dye adsorption may be either by the boundary film formation or intra-particle (pore) diffusion of the dye on the solid surface from bulk of solution. Weber and Morris explain the diffusion mechanism through the following equation [25]:

$$q_t = K_{ipd}\, t^{1/2} + C$$

where, C is the intercept (mg/g) and its value provides information about the thickness of boundary layer, K_{ipd} is intra-particle diffusion rate constant (mg/g/min) which have been calculated from the intercept and slope of the plot between q_t *versus* $t^{1/2}$ (Table-2).

Thermodynamic parameters: Energy and entropy are the two important parameters, which are used to determine spontaneity of process. The adsorption process has been carried out at three different temperatures (308, 313 and 318 K) in order to calculate the thermodynamic parameters such as free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) by using equilibrium constant K_0. Gibbs free energy change (ΔG) is the fundamental criterion of spontaneity. Reaction occurs spontaneously at a given temperature if ΔG is negative. ΔG has been calculated by using the given equation and given in Table-3.

TABLE-3
THERMODYNAMIC PARAMETERS OF MALACHITE GREEN ADSORPTION BY PAPER INDUSTRY WASTE SLUDGE

C_0 (mg/L)	ΔG (KJ/mol)			ΔH (KJ/mol)	ΔS (KJ mol^{-1} K^{-1})
	308 K	313 K	318 K		
75	11.2945	12.1391	12.7442	31.09	0.1378
100	9.1791	10.4073	11.2485	50.86	0.1952
125	8.8659	9.3883	11.0280	52.48	0.1987
150	8.1382	8.9869	10.1154	48.61	0.1841
175	6.8209	8.5987	9.2691	64.48	0.2321

$$\Delta G = -RT \ln K_o$$

where, T is temperature in Kelvin, R is the universal gas constant (8.314 J mol/k)

van't Hoffs equation has been used to calculate enthalpy and entropy change.

$$\ln K_o = \Delta S/R \;\; \Delta H/RT$$

From the slope and intercept of van't Hoffs plot between $\ln K_0$ *versus* 1/T, the value of enthalpy and entropy change has been calculated. The negative value of ΔG indicates that adsorption is spontaneous; also the value of free energy became more negative with rise in temperature suggesting that the adsorption became more favourable at higher temperatures (Table-3). The positive value of ΔH confirms the endothermic nature of adsorption process and the positive ΔS showed increased randomness at the solid-solution interface during the adsorption of malachite green adsorption onto paper industry waste sludge.

SEM and FT-IR analysis: The surface morphology of paper industry waste sludge before and after adsorption has been visualized by using scanning electron microscope (SEM) and has been shown in Fig. 7(a) and (b). The SEM image of adsorbent before adsorption shows that the material surface is rough and porous, which allowed the binding of dye particles easily on the surface. Fig. 7(b) indicates that after adsorption the surface becomes smooth, which indicates that all the dye molecules, gets coated over the surface of adsorbent.

FT-IR spectra of unloaded and loaded adsorbent have been shown in Fig. 8(a) and (b), which indicated that there is slight shifting of peaks of adsorbent after adsorption but no new peak has been observed, which indicates that no chemical bond is formed between adsorbate and adsorbent after adsorption. Thus, the FT-IR data supports that adsorption of dye on adsorbent is due to physical forces.

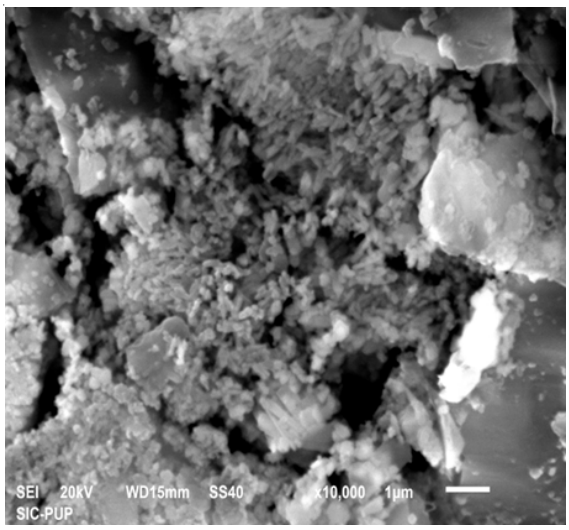

Fig. 7(a). SEM image of adsorbent before adsorption

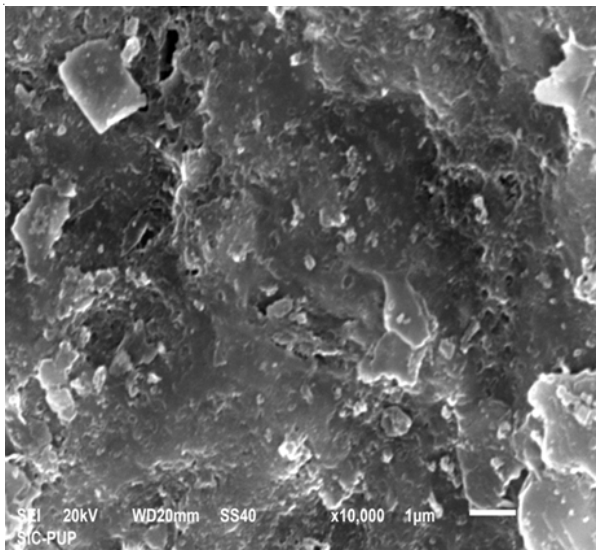

Fig. 7(b). SEM image of adsorbent after adsorption

Conclusion

In the present study, a novel low-cost adsorbent has been prepared from waste sludge of paper industry and has been used for the removal of malachite green dye. The prepared adsorbent has proved to be good adsorbent because 97.30 % of dye has been removed within 60 min by using only 1.0 g of adsorbent for 100 mg/L dye concentration. The adsorption data has been correlated with Langmuir, Freundlich and Temkin isotherm models and all the three models were well fitted for the present study. The kinetics of adsorption of Malachite green dye has been well described by pseudo-second order model. The thermodynamic parameters ΔG, ΔH and ΔS have been calculated and the adsorption process has been found to spontaneous and endothermic. Thus the present method has been used for waste water treatment plant for the removal of toxic dyes as the raw material coming from paper industry is available in large quantity.

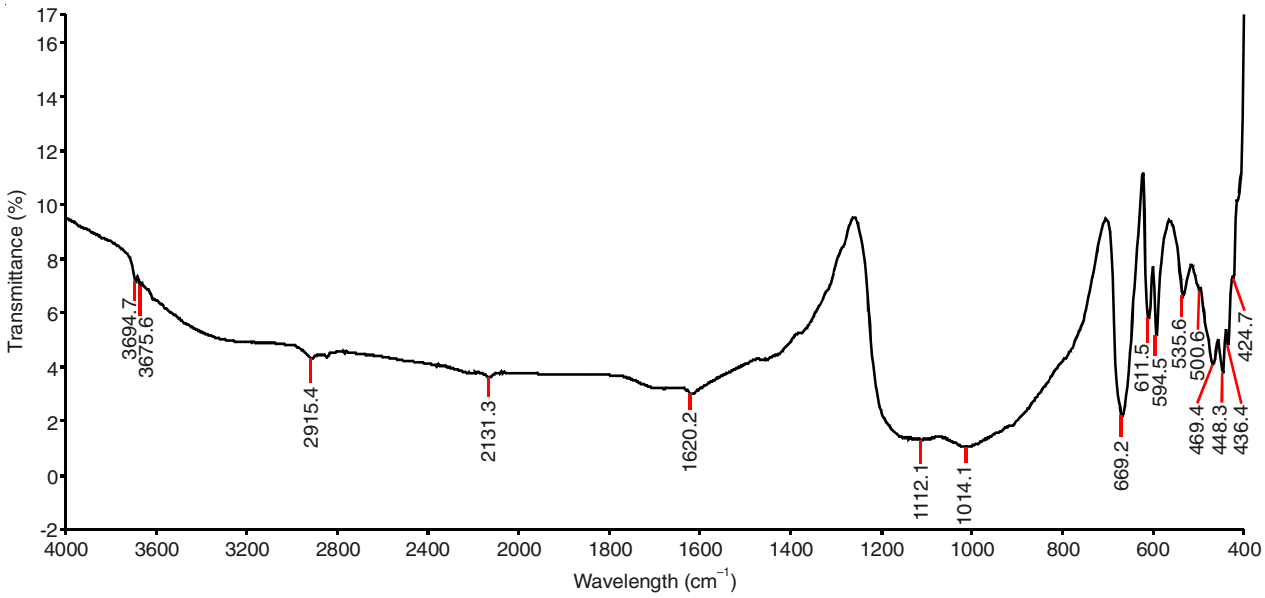

Fig. 8(a). FT-IR spectra of paper industry waste sludge before adsorption.

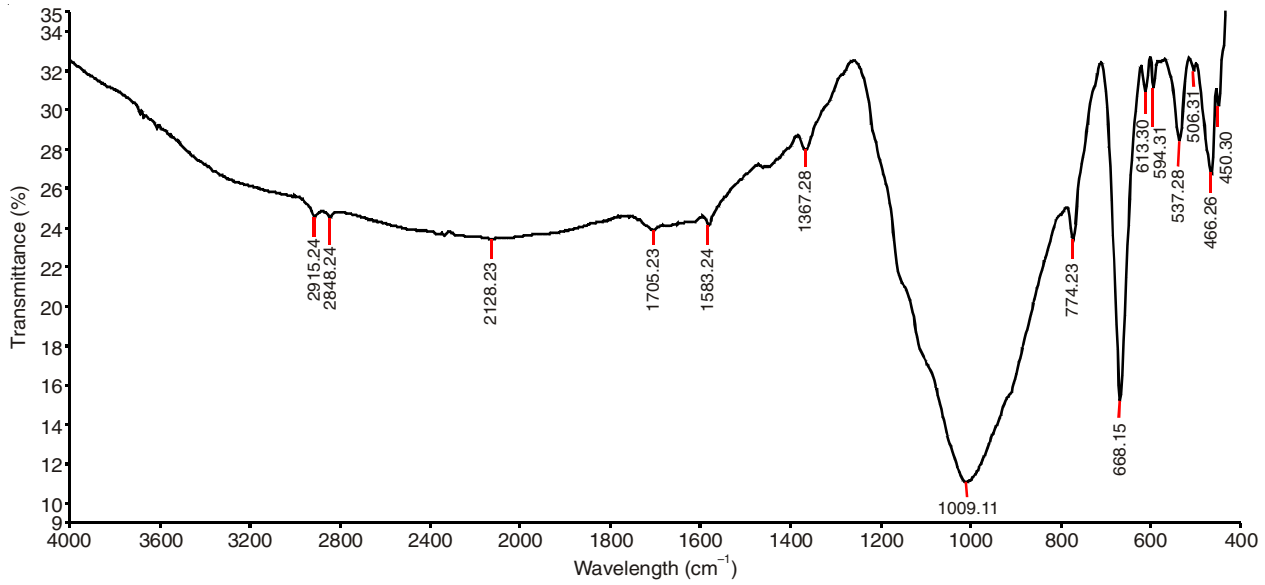

Fig. 8(b). FT-IR spectra of paper industry waste sludge after adsorption

REFERENCES

1. Z.N. Garba, Z.U. Zango, A.A. Babando and G. Galadima, *J. Chem. Pharm. Res.*, **7**, 710 (2015).
2. M. Santhi, P.E. Kumar and B. Murlidharan, *J. Appl. Chem.*, **8**, 33 (2015).
3. S.A. Ahmed, A.A.A. Gaber and A.M.A. Rahim, *Int. J. Adv. Res.*, **3**, 621 (2015).
4. E.S. Dragan and I.A. Dinu, *Res. J. Chem. Environ.*, **12**, 5 (2008).
5. N. Nordin and S.F.M. Amir, *Int. J. Electrochem. Soc.*, **8**, 11403 (2013).
6. J. Wu, M. Eiteman and S. Law, *J. Environ. Eng.*, **124**, 272 (1998).
7. M.K. Asl and F. Bahramin, *Bull. Georg. Natl. Acad. Sci.*, **8**, 260 (2014).
8. P. Pandit and S. Basu, *Ind. Eng. Chem. Res.*, **43**, 7861 (2004).
9. R. Katwal, H. Kaur, G. Sharma, M. Naushad and D. Pathania, *J. Ind. Eng. Chem.*, **31**, 173 (2015).
10. H. Kaur and A. Thakur, *Chem. Sci. Rev. Lett.*, **3**, 159 (2014).
11. T.A. Khan, V.V. Singh and D. Kumar, *J. Sci. Ind. Res. (India)*, **63**, 355 (2004).
12. H. Kaur and R. Kaur, *J. Mater. Environ. Sci.*, **5**, 1830 (2014).
13. H.A. Al-Aoh, I.A.M. Mihaina, F.M. Alzuaibr, A.D. Althaqafy, M.J. Maah, R. Yahya, M.R.B. Abas, I. Tyagi, S. Agarwal and V.K. Gupta, *Asian J. Chem.*, **28**, 714 (2016).
14. J. Zhang, Y. Li, C. Zhang and Y. Jing, *J. Hazard. Mater.*, **150**, 774 (2008).
15. M. Makeswari and T. Santhi, *J. Water Resource Prot.*, **5**, 222 (2013).
16. Z.M. Abou-Gamra and M.A. Ahmed, *Adv. Chem. Eng. Sci.*, **5**, 373 (2015).
17. S.K. Ponnusamy and R. Subramaniam, *Int. J. Ind. Chem*, **4**, 17 (2013).
18. C.H. Supriya, *J. Pharm. Res.*, **4**, 307 (2015).
19. H. Kaur, Swati and R. Kaur, *Chem. Sci. Trans.*, **3**, 1300 (2014).
20. H. Freundlich and W. Heller, *J. Am. Chem. Soc.*, **61**, 2228 (1939).
21. I. Langmuir, *J. Am. Chem. Soc.*, **40**, 1361 (1918).
22. M.J. Temkin and V. Pyzhev, *Acta Physiochim. U.R.S.S.*, **12**, 217 (1940).
23. S. Lagergren, *Handlingar*, **24**, 01 (1898).
24. Y.S. Ho and G. McKay, *Process Biochem.*, **34**, 451 (1999).
25. W.H. Weber and J.C. Morris, *J. Sanit. Eng. Div.*, **89**, 31 (1963).