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Kinetics and thermodynamics of malachite green adsorption on banana pseudo-stem fibers

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ABSTRACT

In present work, the banana pseudo-stem fiber was used as an adsorbent for the removal of harmful malachite green dye. Functional groups, morphology and crystallinity of the adsorbent have been determined using Fourier transform infrared (FT-IR) spectroscopy, scanning electron microscope (SEM) and X ray diffractometer (XRD). Batch experiments were performed to observe the effect of pH, contact time, initial dye concentration, adsorbent dose and temperature on the adsorption. The adsorption process followed pseudo-second order kinetics and intra-particle diffusion rate model. Equilibrium data were fitted to Langmuir and Freundlich isotherm models. Gibb's free energy change ($\Delta G°$), enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) indicate the nature of process. The negative values of $\Delta G°$ and $\Delta H°$ show that the process is spontaneous and exothermic, respectively. The negative values of $\Delta S°$ show that the dye molecules are organized on the adsorbent surface in less randomly fashion than in solution.

Keywords: Adsorption; Banana pseudo-stem fibers; Malachite green; Isotherm; Kinetics.

INTRODUCTION

The synthetic dyes are largely used in the process industries like textiles, paints, pulp and paper, carpet and printing. The release of effluents from these industries into water bodies causes serious environmental problems due to persistent and recalcitrant nature of some of these dyes. A number of physical and chemical treatment processes exist for removal of dyes from wastewater, viz. precipitation, coagulation/flocculation, electroplating, ion-exchange, solvent extraction, irradiation, photo-degradation and membrane separation. Some of these techniques have shown to be effective, although they have limitations such as high reagent and energy requirement, incomplete colour removal and generation of toxic waste products that require disposal and further treatment. Adsorption is an efficient and economical process used for the removal of dyes from industrial wastewater. Dyes are broadly classified as anionic, cationic, non-ionic and zwitterionic, depending upon the presence of ionic charge on the dye [1].

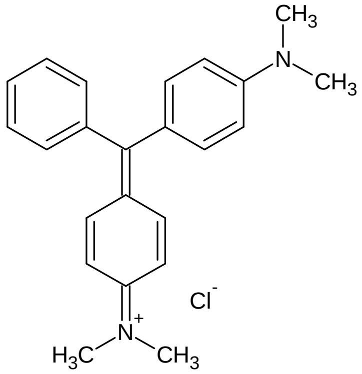

Fig. 1. Molecular structure of Malachite Green dye

Malachite green (MG) is a cationic dye of triphenylmethane type that exists as a cation in aqueous medium (Fig. 1). This dye is traditionally used for the dyeing of cotton, jute, silk, wool, leather and as an antifungal, antibacterial and anti-parasitical therapeutic agent. Scientific evidences indicate that malachite green (MG) and especially its reduced form, leucomalachite green (LMG), may persist in edible fish tissues for extended periods of time and the general public may become exposed to malachite green through the consumption of treated fish [2]. LMG has been reported to have mutagenic and carcinogenic effects. Inexpensive and more easily available adsorbent would make the removal of pollutants an economically viable alternative. Various agricultural products and by-products have been investigated to remove malachite green dye from the aqueous solution such as wheat bran [3], coffee bean [4], sawdust [5], deoiled soya [6], ginger waste [7], rice husk [8], lemon peel [9], durian peel [10] and wood fiber [11].

Banana pseudo-stem which is clustered, cylindrical aggregation of leaf stalk bases [12], richer in fibers, at present is a waste product of banana cultivation because each plant produce only one bunch of bananas, after its harvesting the bare pseudo-stems are cut and usually left in the soil plantation to be used as organic materials [13]. Banana fiber obtained from the pseudo-stem of banana plant, is a bast fiber with relatively good mechanical properties [14, 15]. This could be a new source of ligno-cellulosic fibers rich in lignin, hemicelluloses and cellulose; and are used for various applications, depending on their composition and physical properties such as for paper making and composite materials [16-19].

The aim of present study is to use fiber from outer bark of banana pseudo-stem as an adsorbent material for the removal of malachite green dye from aqueous solution.

EXPERIMENTAL SECTION

Adsorbent

Rolled banana leaves of pseudo-stem were chopped into cubes of average size of 2×2 cm. The cubes were boiled in double distilled water for 45 minutes and then dried in an oven at 80 °C until a constant weight was obtained. The resulted material was ground with commercial grinder and sieved to isolate fibers of size 200-300µ. The powder was preserved as an adsorbent in glass bottle.

Characterization of adsorbent

FT-IR spectra were recorded on FTLA 2000 spectrophotometer to analyze functional groups, using potassium bromide (KBr) disc method and the morphology of BPF was investigated by FEI Quanta 200 scanning electron microscope operated at 20 KV accelerating voltage. XRD was performed on Rigaku D/max-2200 PC diffractometer operated at 40 KV/40 mA, to determine crystallinity of material using $CuK_{\alpha 1}$ radiation with wavelength of 1.54 Å in the wide angle region from 10° to 80° on 2θ scale.

Adsorbate

MG dye (C.I.: 42000, Basic Green 4, FW: 927.02) was obtained from the Merck and used without further purification. A stock dye solution of 1000 mg/L was prepared by dissolving required amount of dye in double distilled water. The experimental solution of desired concentration was obtained by successive dilution of stock solution. A number of standards were also prepared from the stock solution and calibration curve was drawn by measuring the absorbance at λ_{max} 617 nm of the solution.

Adsorption experiments

To study the effect of important parameters like pH, adsorbent dose, agitation speed, initial dye concentration, contact time and temperature on the adsorptive removal of MG, batch experiments were conducted at 25 °C. The batch adsorption was carried out in 150 ml of conical flasks by mixing a pre-weighed amount of the BPF with 50 ml of the aqueous dye solution of particular concentration. The mixture was agitated on stirrer at constant speed, pH, contact time and temperature. The effect of pH was studied over the pH range of 3 to 7 which was adjusted by adding 0.1 M HCl or 0.1 M NaOH. For the optimum amount of adsorbent per unit mass of adsorbate, a 50 mL of dye solution was contacted with different amounts of BPF (0.05 to 3.5 g/L) till equilibrium was attained. The kinetics of adsorption was determined by analyzing the removal of dye by adsorbent from the aqueous solution at different time intervals. Adsorption isotherm was studied by agitation of different initial concentration of dye with known amount of adsorbent till equilibrium was attained. The effect of temperature on the adsorption process was investigated at 298, 308 and 318 K for different initial dye concentrations.

After adsorption was over, the mixture was centrifuged in laboratory centrifuge (Remi Research Centrifuge). The dye remaining unadsorbed was determined spectrophotometrically (Systronics 2203) at λ_{max} 617 nm. The amount of MG adsorbed on BPF was calculated by the mass balance relationship:

$$q_e = (C_0 - C_e) V/W \qquad (1)$$

where C_0 is the initial dye concentration (mgL^{-1}), C_e is the concentration of dye at equilibrium (mgL^{-1}), V is the volume of solution (L) and W is the mass of fibers (g).

RESULTS AND DISCUSSION

Characterization of adsorbent

Infrared spectra of BPF give the information about the functional groups present in the fibers. Identification of characteristic peaks is based on previous studies of fibers. Fig. 2 shows the adsorption at 3427 cm^{-1} is due to stretching of hydroxyl groups of cellulose, hemicelluloses and lignin that are present in BPF [20]. The band at 2924 cm^{-1} is due to the C-H stretching of saturated carbon. The band at 1613 cm^{-1} is due to C=C stretching of fibers containing lignin [21]. The bands at 1363 and 1247 are assigned to C-O stretching and O-H bending, respectively. The bands at 1318 and 1156 are due to O-H bending and C-O vibration, respectively [20]. The bands at 1105 and 1024 are assigned to C-O-H and C-O-C stretching, respectively [22].

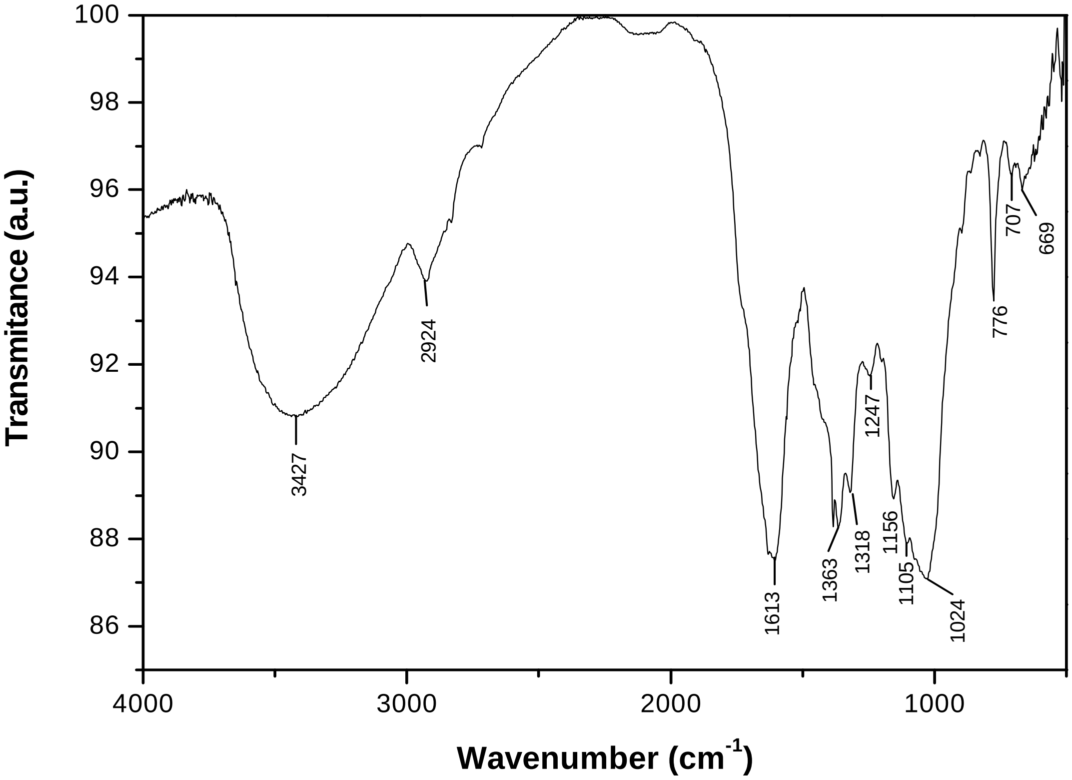

Fig. 2. Infrared spectra of banana pseudo-stem fibers

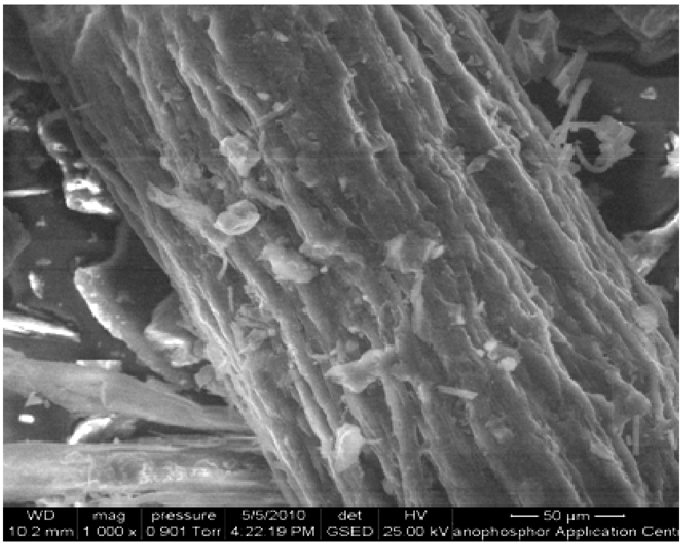

Fig. 3. SEM micrograph of banana pseudo-stem fibers

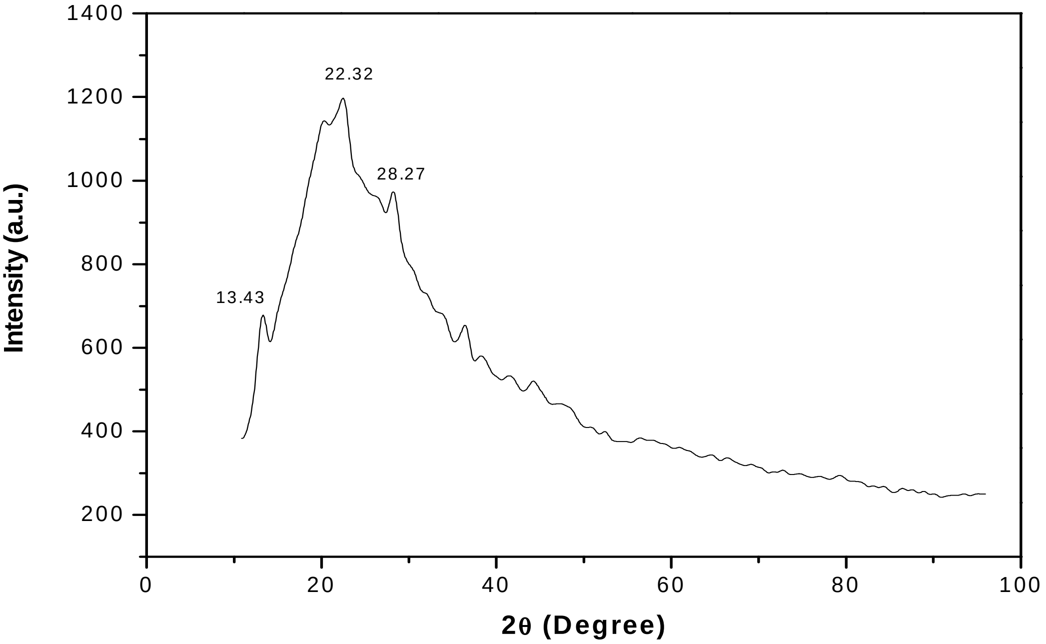

Fig. 4. XRD spectra of banana pseudo-stem fibers

The morphology of fibers could provide vital information on the adsorption between the adsorbent and adsorbate. The SEM micrograph (Fig. 3) shows rough texture of fibers which indicate that surface is ideal for adsorption [20].

The XRD spectrum of BPF shows (Fig. 4) that the fibers are partially crystalline as seen by three diffraction peaks at 13°, 22° and 28° on 2θ scale [23].

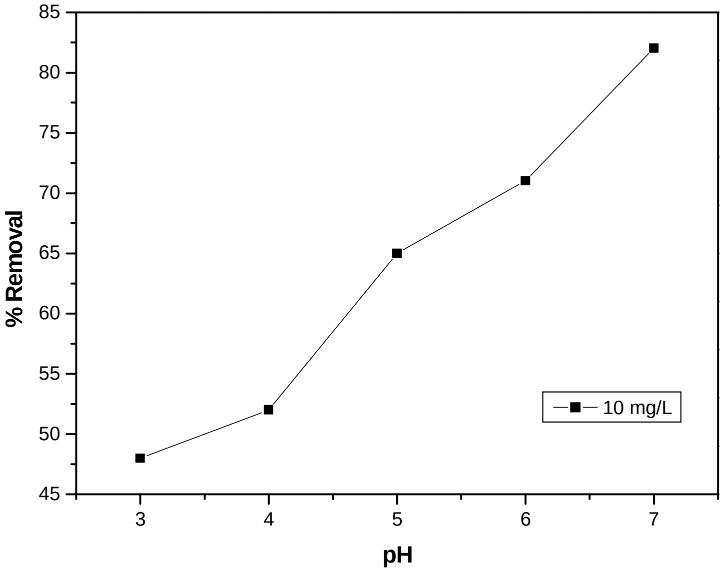

Fig. 5. Effect of pH on adsorption of MG on BPF (Adsorbent dose: 2g/L; Contact time: 60 min; Temperature: 298 K).

Effect of pH

The efficiency of adsorption depends on pH of the solution because variation in pH leads to change in degree of ionization and surface charge of the adsorbent. The effect of pH on adsorption is shown in Fig. 5.

It is observed that the percentage removal of dye increases from 48 to 82.6 % as the pH increases from 3 to 7 for 10 mgL^{-1} of dye solution. Further increase in pH causes degradation of dye due to formation of soluble hydroxyl complexes [24]. Therefore, all subsequent studies were carried out at pH 7.

Effect of adsorbent dose

Fig. 6 shows that the adsorption increases as dose increases. Initially, the rate of adsorption was very rapid from 0.5 to 2 g/L. This is because at higher dose of the adsorbent, due to increased surface area, more adsorption sites are available causing higher removal of MG. Above 2g/L of adsorbent dose, removal of MG becomes very slow, as the surface MG concentration and the solution MG concentration come to equilibrium with each other.

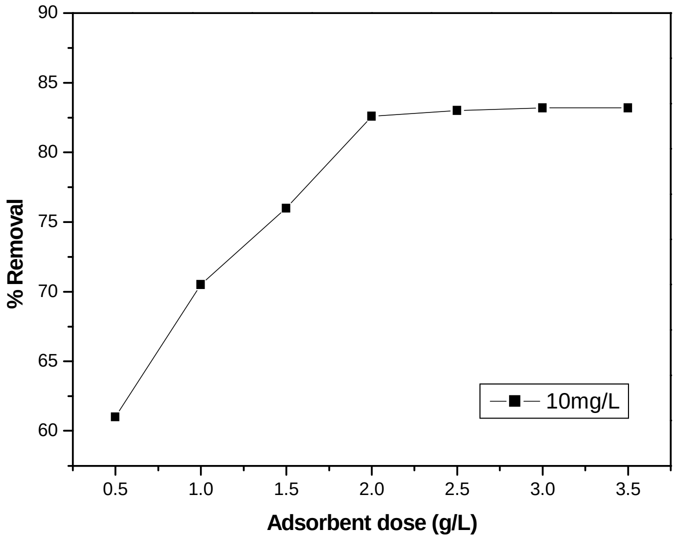

Fig. 6. Effect of adsorbent dose on adsorption of MG on BPF (pH: 7; Contact time: 60 min; Temperature: 298 K).

Effect of contact time and initial dye concentration

The effect of contact time and initial dye concentration on the adsorption of dye was investigated and is shown in Fig. 7. It depicts that maximum removal of MG occurs within 10 min, thereafter removal rate becomes slow and after 60 min of contact time no change was observed which established that the system has reached the equilibrium point. On increasing the initial concentration of dye from 10 to 40 mg/L, adsorption of MG on BPF decreases from 82.6 to 70 %. This shows that at higher concentration there will be an increased competition for the active adsorption sites which results in slowing down of adsorption. This explains the lower adsorption rate for higher concentration.

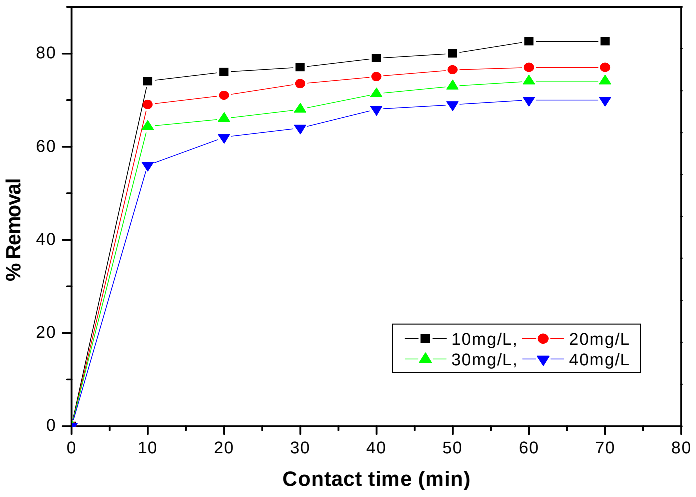

Fig. 7. Effect of contact time and initial MG concentration on the extent of adsorption (Adsorbent dose: 2g/L; pH: 7; Temperature: 298 K).

Kinetics of adsorption

The rate constants for the adsorption of MG on BPF were obtained using the pseudo-first order (Lagergren) and pseudo-second order (Ho) kinetic models. The intra-particle diffusion model was also considered.

Pseudo-first order kinetic model

When the adsorption is preceded by diffusion through a boundary, the kinetics in most cases follows the pseudo-first order rate equation. The differential rate equation is of the form:

$$dq_t / dt = k_1 (q_e - q_t) \qquad (2)$$

where q_t and q_e are the amounts of dye adsorbed at time t (mg/g) and at equilibrium (mg/g), respectively and k_1 is the pseudo-first order rate constant (min^{-1}). Integrating the above equation using the boundary condition, $q_t = 0$ at $t = 0$ leads to [25]:

$$\log (q_e - q_t) = \log q_e - (k_1/2.303)\, t \qquad (3)$$

The values of k_1 and q_e were calculated from the slopes and intercepts of the linear plots of log ($q_e - q_t$) vs. t, respectively and presented in Table 1. There is a great disagreement between experimental and calculated values of q_e as shown in Table 1. Therefore, it may be concluded that the adsorption of MG on BPF is not followed the pseudo-first order kinetic model.

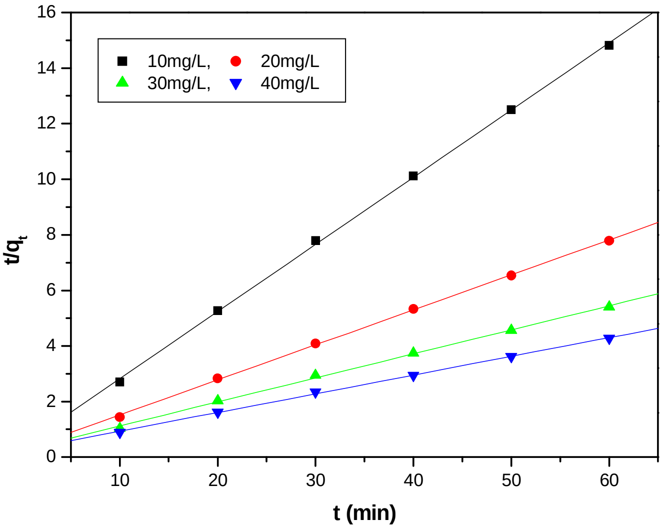

Fig. 8. Pseudo-second order kinetic model for the adsorption of MG on BPF (Adsorbent dose: 2g/L; pH: 7; Temperature: 298 K).

Pseudo-second order kinetic model

The pseudo-second order kinetic model [26] is presented as:

$$dq_t /dt = k_2 (q_e - q_t)^2 \quad (4)$$

where q_t and q_e are the amount of dye adsorbed at time t (mg/g) and at equilibrium (mg/g), respectively and k_2 is the pseudo-second order rate constant (g/mgmin). Integrating the above equation using the boundary condition, $q_t = 0$ at $t = 0$ leads to:

$$t/q_t = 1/k_2 q_e^2 + t/ q_e \quad (5)$$

The values of k_2 and q_e were calculated from intercepts and slopes of the linear plots of t/q_t vs. t (Fig. 8), respectively and presented in Table 1. Table 1 shows that the calculated q_e values are very close to that of experimentally obtained q_e and the values of correlation coefficients (R^2) are closer to unity confirms that adsorption of MG on BPF follows pseudo-second order kinetics.

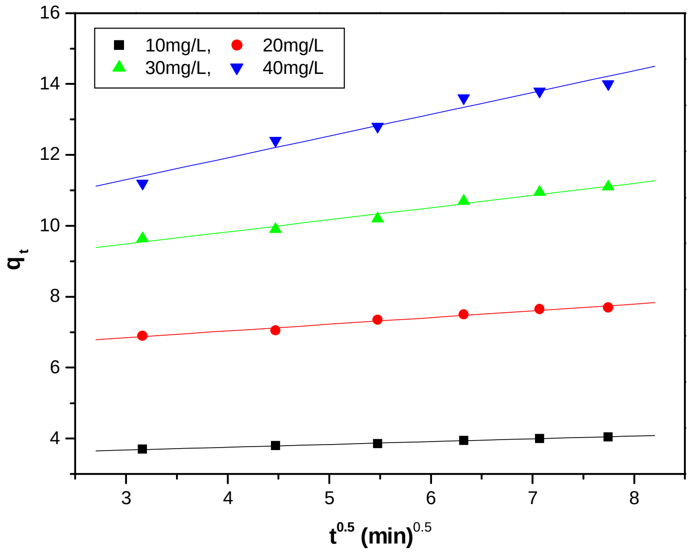

Fig. 9. Intra-particle diffusion model for the adsorption of MG on BPF (Adsorbent dose: 2g/L; pH: 7; Temperature: 298 K).

Intra-particle diffusion model

Adsorption is multistep process involving the transfer of solute from bulk of solution to surface of adsorbent. Intra-particle diffusion plays an important role in the extent of adsorption with time at different initial concentrations. The intra-particle diffusion model [27] is given as:

$$q_t = k_i t^{0.5} + I \quad (6)$$

where k_i is intra-particle diffusion rate constant (mg/gmin$^{0.5}$) and I gives an idea about the thickness of the layer. The values of k_i and I were obtained from the slopes and intercepts of the plots of q_t vs. $t^{0.5}$ (Fig. 9), respectively and listed in Table 1.

Fig. 9 shows that all the lines are not passing through the origin and thus it can be concluded that the surface adsorption and intra-particle diffusion, both occur simultaneously. It seems that as the concentration of solution increases, linearity of the plot is lost because intra-particle diffusion occurs at a faster rate than surface adsorption.

Table 1: Kinetic parameters for MG adsorption on BPF

Initial dye concentration (mg/L)	$q_{e,\ exp}$	Pseudo-first order			Pseudo-second order			Intra-particle diffusion		
		$q_{e,\ cal}$	k_1	R^2	$q_{e,\ cal}$	k_2	R^2	K_i	I	R^2
10	4.05	0.65	0.048	0.975	4.13	0.144	0.999	0.077	3.450	0.995
20	7.70	2.13	0.067	0.956	7.93	0.061	0.999	0.188	6.279	0.989
30	11.10	3.38	0.056	0.951	11.56	0.029	0.999	0.342	8.456	0.986
40	14.0	6.22	0.06	0.982	14.84	0.017	0.999	0.613	9.463	0.982

Adsorption isotherms

Equilibrium data commonly known as adsorption isotherms, describes how adsorbates interact with adsorbents. The most common types of isotherms are Langmuir (Eq. 7) and Freundlich (Eq. 8) models. The Langmuir isotherm model is applicable to monolayer adsorption while Freundlich isotherm model is used to describe adsorption on surface having heterogeneous energy distribution.

Langmuir isotherm: $C_e / q_e = (1/bq_{max}) + (1/q_{max})\ C_e$ (7)
Freundlich isotherm: $\ln q_e = \ln K_F + (1/n) \ln C_e$ (8)

where C_e is concentration of dye solution at equilibrium (mgL^{-1}), q_e is the amount of dye at equilibrium in unit mass of adsorbent ($mg\ g^{-1}$), q_{max} and b are the Langmuir coefficient related to adsorption capacity ($mg\ g^{-1}$) and adsorption energy ($L\ mg^{-1}$), respectively. K_F and n are the Freundlich coefficient related to adsorption capacity [$mg\ g^{-1}\ (mg\ L^{-1})^{-1/n}$] and adsorption intensity of adsorbent, respectively.

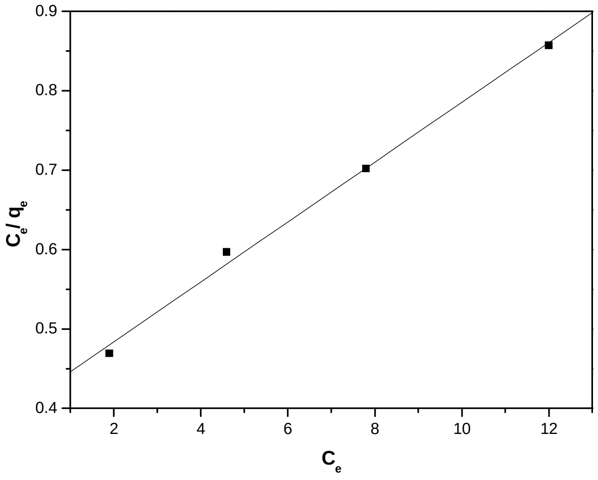

Fig. 10. Langmuir isotherm model for adsorption of MG on BPF (Adsorbent dose: 2g/L; pH: 7; Temperature: 298 K; Contact time: 60 min).

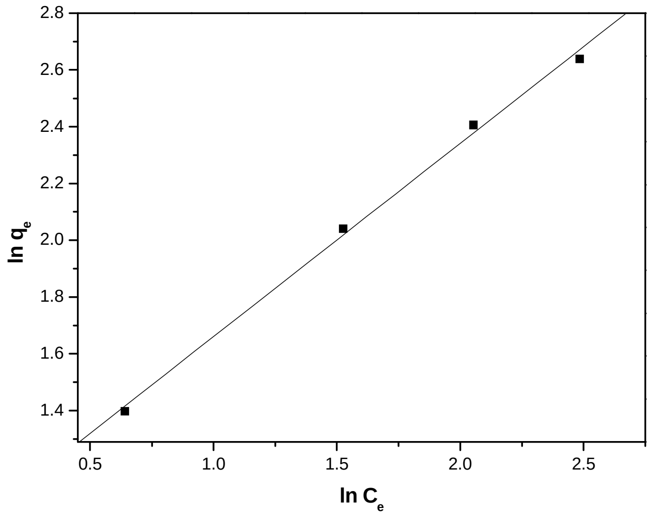

Fig. 11. Freundlich isotherm model for adsorption of MG on BPF (Adsorbent dose: 2g/L; pH: 7; Temperature: 298 K; Contact time: 60 min).

Table 2: Isotherm parameters for MG adsorption on BPF

Langmuir Constants			Freundlich Constants		
q_{max}	b	R^2	K_F	n	R^2
26.518	0.092	0.997	2.663	1.468	0.998

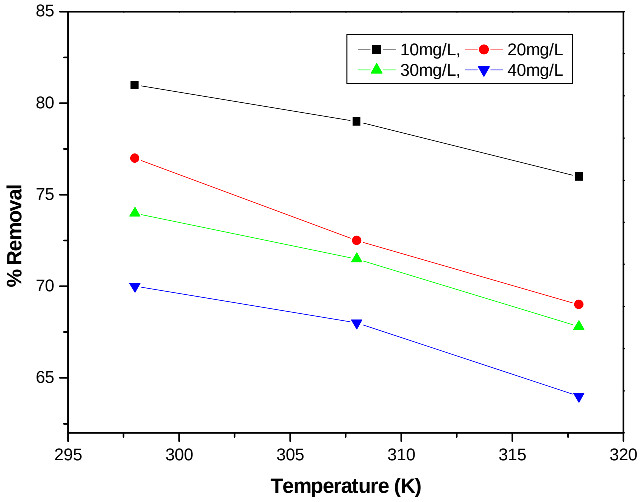

Fig. 12. Effect of temperature on the adsorption of MG on BPF (Adsorbent dose: 2g/L; pH: 7; Contact time: 60 min).

The Langmuir isotherm parameters q_{max} and b were determined from slope ($1/q_{max}$) and intercept ($1/bq_{max}$) of the plot of C_e/q_e vs. C_e (Fig. 10), respectively. The plot gives a straight line, indicating that adsorption of MG on BPF follows the Langmuir isotherm. The values of Freundlich constants n and K_F were obtained from the slope (1/n) and intercept ($\ln K_F$) of the plot of ln q_e vs. ln C_e (Fig. 11), respectively. The plot gives a straight line and this shows that adsorption of MG on BPF also follows the Freundlich isotherm. The Langmuir and Freundlich isotherms constants and regression coefficients are listed in Table 2.

Effect of temperature and thermodynamic parameters

The effect of temperature on the adsorption of MG on BPF was investigated by conducting experiments for different initial dye concentrations at 298, 308, and 318 K. Fig. 12 indicates that on increasing the temperature percentage removal of dye decreases. This shows that the process is exothermic in nature.

The thermodynamic parameters Gibb's free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were calculated using the following equations:

$$\text{Log}\,(q_e m/C_e) = \Delta S°/2.303R + -\Delta H°/2.303RT \quad (9)$$

$$\Delta G° = \Delta H° - T\Delta S° \quad (10)$$

where m is the adsorbent dose (g L^{-1}), C_e is concentration of dye solution at equilibrium (mgL^{-1}), q_e is the amount of dye at equilibrium in unit mass of adsorbent (mg/g), q_e/C_e is called the adsorption affinity. ΔH°, ΔS° and ΔG° are change in enthalpy (KJ mol^{-1}), entropy (J mol^{-1} K^{-1}) and free energy (KJ mol^{-1}), respectively, R is the gas constant (8.314 J/mol/K) and T is the temperature (K). The values of ΔH° and ΔS° were obtained from the slopes and intercepts of the Van't Hoff plots of log ($q_e m/C_e$) vs. 1/T, respectively, thereafter ΔG° values were determined from Eq. 10. The values of thermodynamic parameters are presented in Table 3. The negative values of ΔG° and ΔH° indicate that adsorption process is spontaneous and exothermic in nature. The negative values of ΔS° suggest decreased randomness during adsorption.

Table 3: Thermodynamic parameters for MG adsorption on BPF

Initial Dye concentration (mg/L)	-ΔH° (kJ mol^{-1})	-ΔS° (J $mol^{-1}K^{-1}$)	-ΔG° (kJ mol^{-1})		
			298 K	308 K	318 K
10	11.7	27.14	3.63	3.36	3.09
20	16.16	44.19	2.99	2.55	2.11
30	11.90	31.10	2.63	2.32	2.01
40	10.69	28.67	2.15	1.86	1.57

CONCLUSION

This study shows that the BPF is an effective adsorbent for the removal of MG dye from aqueous solution. The small dose of adsorbent (2 gL^{-1}) was able to remove about 80 % of MG dye within 60 min at 298 K. The rate of adsorption decreases on increasing the initial concentration of dye. It has been found that maximum removal of dye occurred at around pH 7. The adsorption kinetics followed pseudo-second order kinetics and intra-particle diffusion model. The adsorption of MG dye onto the BPF followed both, Langmuir and Freundlich isotherm models. The temperature effect is used to calculate the thermodynamic parameters ΔG°, ΔH° and ΔS°. The negative values of ΔG° and ΔH° suggest the adsorption is spontaneous and exothermic in nature, respectively. The negative values of ΔS° indicate decreased randomness at adsorbent-solution interface during adsorption.

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