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Application of potato (*Solanum tuberosum*) plant wastes for the removal of methylene blue and malachite green dye from aqueous solution



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Abstract Dye pollutants from the textile, paper, and leather industries are important sources of environmental contamination. In the present study an agricultural waste from potato plant (potato stem powder, PSP and potato leaves powder, PLP) was used as an adsorbent for removal of the methylene blue (MB) and malachite green (MG) dyes from aqueous solution. The adsorbent materials were characterized by scanning electron microscope (SEM) and Fourier transform infrared (FTIR) spectroscopy. Batch experiments were performed to investigate the effect of physico-chemical parameters, such as pH_{pzc}, ionic strength, adsorbent dose, contact time, initial dyes concentration and temperature. The kinetics of adsorption was studied by applying the pseudo-first order, pseudo-second order and intraparticle diffusion models. The pseudo-second order model better represented the adsorption kinetics and the mechanism was controlled by surface adsorption and intraparticle diffusion. Equilibrium data were analyzed using Langmuir and Freundlich isotherm models. The thermodynamic parameters such as change in enthalpy (ΔH°), entropy (ΔS°) and Gibbs' free energy (ΔG°) of adsorption systems were also determined and evaluated.

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1. Introduction

Methylene blue (MB) and malachite green (MG) are cationic dyes, used in several industries such as paper, leather, cotton, pulp, wool etc., for coloring their final products. The effluents of these industries containing huge amount of dyes, discharged into waters bodies, cause severe damage to the environment (Gad and El-Sayed, 2009). Acute exposure to MB will cause increased heart rate, vomiting, shock, Heinz body formation, cyanosis, jaundice, quadriplegia, and tissue necrosis in humans (Hameed and Ahmad, 2009). MG dye is extensively used all over the world in the fish farming industry as fungicide, ectoparasiticide and disinfectant (Gong et al., 2006). Scientific evi-

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dence indicated that malachite green (MG) and especially its reduced form, leucomalachite green (LMG) (a metabolite), might persist in edible aquatic organisms, consumption of these organisms leads to toxicity of human beings for extended periods of time (Sudova et al., 2007). Various conventional methods such as physical, chemical and biological processes have been tried for the removal of dyes from aquatic media (Barka et al., 2010; Bielska and Szymanowski, 2006; Elahmadi et al., 2009; Karim et al., 2009; Khadhraoui et al., 2009; Lodha and Chaudhari, 2007). Adsorption is one of the physico-chemical methods, which is found to be most simple and economical to remove the dyes from effluents. Several adsorbents have been reported in the literatures such as clay (Tehrani-Bagha et al., 2011), zeolite (Han et al., 2009), fly ash (Rastogi et al., 2008), silica gel (Kushwaha et al., 2010), chitosan (Mahmoodi et al., 2011) and algae (Ncibi et al., 2009) regarding the adsorption of basic dyes from aqueous solution.

The efficiency of the adsorption process mainly depends on the cost and removal capacity of adsorbents used. Now days, agricultural waste materials are receiving much more attention as adsorbents for the removal of dyes from waste water due to its low cost and good availability. *Solanum tuberosum* (potato) plant is a herbaceous perennial of the Solanaceae family. Tuber is the only edible part of the entire plant, the rest of the parts remain as an agricultural waste after the harvesting. The objective of this study was to explore the potential of potato leaves and stem as an adsorbent to remove MB and MG dyes from the aqueous solution.

2. Materials and methods

2.1. Preparation of adsorbents

The potato leaves and stems were washed thoroughly by double distilled water to remove the dust and other impurities. Leaves were firstly dried at room temperature and then in a hot air oven at 60 °C. The washed stems were boiled in double distilled water for 45 min to separate the fibers and dried in a hot air oven at 60 °C (Mas-Haris and Sathasivam, 2009). The dried leaves and stem were ground in a domestic grinder and screened to separate the particles of 100–150 µm. Resulting potato leaves powder (PLP) and potato stem powder (PSP) were kept in a glass bottle for use in adsorption studies. Characteristics of the PSP and PLP were determined and the results are summarized in Table 1.

2.2. Adsorption experiments

A stock solution (1000 mg/L) of MB and MG (obtained from Merck) was prepared by dissolving an appropriate amount of each dye in double distilled water, which was diluted to desired

concentrations of 10, 20, 30, 40 and 50 mg/L. Batch adsorption experiments were carried out to investigate the effect of pH, ionic strength, adsorbent dose, initial dye concentration, contact time and temperature on the adsorption of MB and MG on PLP and PSP by varying the parameters under study and keeping other parameters constant. In each experiment pre-weighed amount of adsorbent was added to 50 mL of dye solution taken in a 150 mL of conical flask and the pH was adjusted by using 0.1 M NaOH or 0.1 M HCl. The resulting solution was agitated at 200 rpm on a stirrer at constant temperature and centrifuged (Remi Research centrifuge). The dye concentration in supernatant solution were determined at characteristic wavelength (MB $\lambda_{\max} = 665$ nm; MG $\lambda_{\max} = 617$ nm) by double beam UV–visible spectrophotometer (Systronics 2202).

The percentage removal of dye and amount of dye adsorbed on PSP and PLP (q_e) was calculated by Eqs (1) and (2), respectively:

$$\% \text{removal} = 100(C_0 - C_e)/C_0 \quad (1)$$

$$q_e = (C_0 - C_e)V/M \quad (2)$$

where q_e is the quantity of dye adsorbed on the adsorbent at the time of equilibrium (mg/g), C_0 and C_e are the initial and equilibrium concentrations (mg L⁻¹) of the dye in solution, respectively, V is the volume (L) of solution and M is the mass of adsorbent (g). All adsorption experiments were performed in triplicate and the mean values were used in data analysis.

2.3. Characterization of PLP and PSP

FTIR study was carried out on FTLA 2000 spectrophotometer to analyze functional groups, using potassium bromide (KBr) disk method and the morphology of adsorbents was investigated by FEI Quanta 200 scanning electron microscope operated at 20 kV accelerated voltage.

3. Results and discussion

3.1. Characterization

The FTIR technique is an important tool to identify functional groups, which are capable of adsorbing dyes. FTIR spectra of PSP and PLP, before and after adsorption of MB and MG dye, were shown in Fig. 1a and b. It was observed that spectra of PSP and PLP having similar bands confirm the presence of same functional groups in both the adsorbents. The broad absorption peaks around 3400 cm⁻¹ was due to vibration of the hydroxyl group linked in cellulose and lignin and adsorbed water (Mas-Haris and Sathasivam, 2009). The peak observed at 2930 cm⁻¹ was assigned to the stretching vibration of C–H bond in methyl group. The peaks located at 1630 cm⁻¹ were characteristics of carbonyl group stretching. The peak at 1609 cm⁻¹ was due to bending vibration of O–H groups. The peak around 1365 cm⁻¹ was due to bending vibration of C–H of methyl group. The C–O stretching band at 1246 cm⁻¹ also confirms the lignin structure of the adsorbents and corresponding bending peak present around 600 cm⁻¹. The peak around 1050 cm⁻¹ was due to C–O–C stretching of cellulose present in PSP and PLP. Characteristic changes were observed in the FTIR spectrum of PSP and PLP after adsorption of MB

Table 1 Physical and chemical properties of adsorbents.

Physical and chemical properties	PSP	PLP
Moisture content (%)	8.175	8.19
Volatile matter (%)	68.75	72.07
Ash (%)	21.35	17.59
Fixed carbon (%)	1.725	2.15

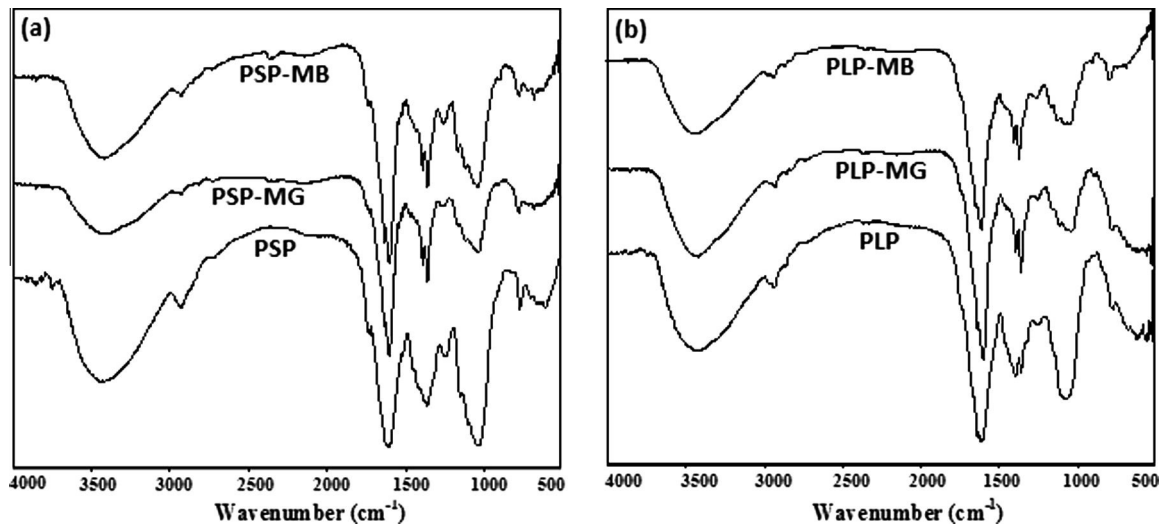


Figure 1 FTIR spectra of PSP (a) and PLP (b) before and after the adsorption of MB and MG.

and MG dye on its surface. The results indicated that some peaks were shifted or disappeared, and new peaks were also detected. These changes observed in the spectrum indicated the possible involvement of those functional groups on the surface of the PSP and PLP in the adsorption process. The SEM micrograph of a typical PLP and PSP sample at 1000 \times magnification depicted in Fig. 2a and b shows the uneven and rough surface in PSP and PLP which provides suitable binding sites for MB and MG dye molecule.

3.2. Determination of pH_{PZC} of PSP and PLP

The point of zero charge (pH_{PZC}) of an adsorbent is a very important characteristic that determines the pH at which the adsorbent surface has net electrical neutrality (El-Qada et al., 2006). To find out pH_{PZC} , the experiments were conducted at different pH ranges from 3 to 11, by adding 0.1 g of adsorbent to 50 mL of 0.1 M KNO_3 solution and agitated on a magnetic stirrer. The pH of the solution was measured after 25 min. As shown in Fig. 3, the pH_{PZC} of PSP and PLP was determined to be 6.1 and 5.9, respectively. At the solution pH > pH_{PZC} , the adsorbent surface negatively charged and favors uptake of cationic dyes due to increased electrostatic force of attraction. At pH < pH_{PZC} , the surface becomes positively charged, concentrations of H^+ were high and they compete with positively

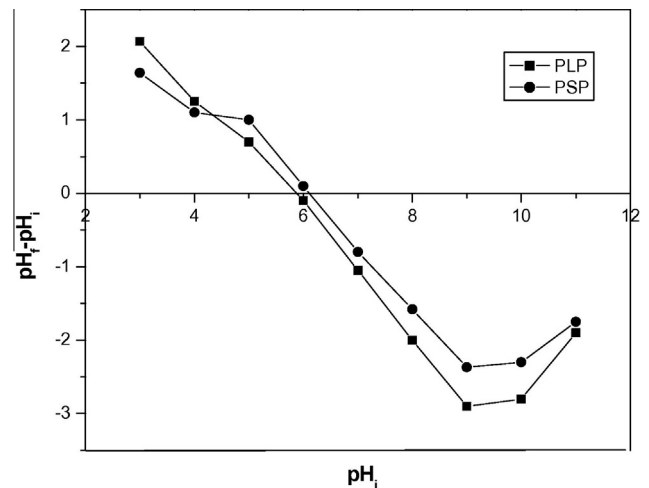


Figure 3 The plots of $pH_f - pH_i$ vs. pH (adsorbent dose: 2 g/L; temperature: 303 K; contact time: 25 min).

charged MB and MG cations for vacant adsorption sites causing a decrease in dye uptake. Thus, MB and MG adsorption onto PSP and PLP is favoured at pH higher than pH_{PZC} . It

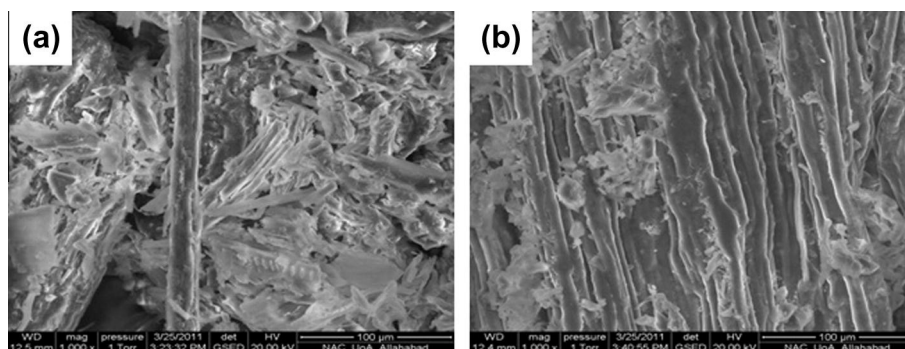


Figure 2 SEM images of PSP (a) and PLP (b).

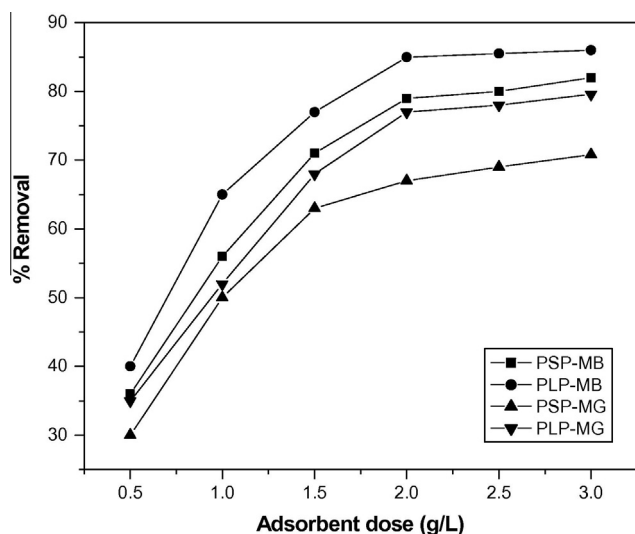


Figure 4 Effect of adsorbent dose on adsorption of MB/MG onto PSP/PLP (initial dye concentration: 10 mg/L; pH 7; temperature: 303 K; contact time: 25 min).

was found that the percentage color removal was less at low pH and maximum at the pH 7. Therefore, all the experiments were carried out at the pH 7.

3.3. Effect of adsorbent dose

The effect of adsorbent dose on removal of the dye from aqueous solution was studied using adsorbent dose of PSP and PLP ranging from 0.5 to 3.0 g/L and plots between percentage removal against adsorbent dose (g/L) shown in Fig. 4. It can be seen that the %dye removal increased as the dose increased from 0.5 to 2 g/L. The uptake of dye that (MB/MG) increased with increase in the adsorbent (PSP/PLP) dose can be attributed to increased surface area and the adsorption sites (Liu et al., 2011). Further increase in adsorbent dose, did not show significant increase in %removal of dye, this was due to the concentration of MB/MG reached at equilibrium status between solid and solution phase. Therefore, 2 g/L adsorbent dose was chosen for further experiments.

3.4. Effect of ionic strength

The wastewater has commonly higher salt concentration which makes it necessary to study the effects of ionic strength on the adsorption of dye. The effect of ionic strength on the adsorption capacities of MB/MG on PSP/PLP was studied at 0–0.1 mol/L NaCl concentrations at 303 K and solution pH. From Fig. 5, increasing ionic strength has significantly decreased the adsorption capacity of MB/MG on PSP/PLP. The values of q_e decreased from 3.95 to 2.6 mg/g, 4.25 to 3.2 mg/g, 3.35 to 2.2 mg/g and 3.85 to 2.55 mg/g for the PSP-MB, PLP-MB, PSP-MG and PLP-MG systems, respectively, as the concentration of NaCl increased from 0 to 0.1 mol/L. This trend indicated that the adsorbing efficiency decreased when NaCl concentration increased in the dye solution, which could be attributed to the competitive effect be-

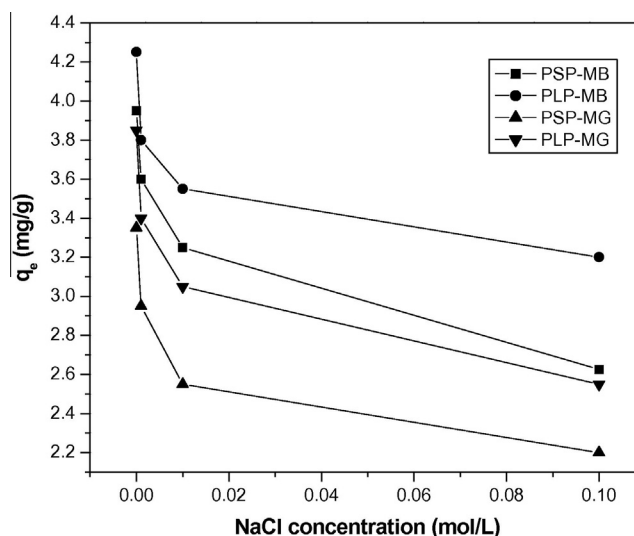


Figure 5 The effect of NaCl concentration on adsorption of MB/MG on PSP/PLP (adsorbent dose: 2 g/L; initial dye concentration: 10 mg/L; pH: 7; temperature: 303 K; contact time: 25 min).

tween dye ions and Na^+ from the salt for the sites available for the sorption process (Hamdaouia et al., 2008). As the ionic strength increased the effective concentration of MB and MG decreased, therefore, the adsorptive capacity of dyes onto adsorbents decreased.

3.5. Adsorption kinetic studies

Kinetic adsorption experiments were carried out to investigate the contact time necessary for each adsorption system to come to equilibrium. The experiments were carried out by agitating 10 mg/L of dye solution with 2 g/L of adsorbent at different periods of contact time ranging from 0 to 33 min. From

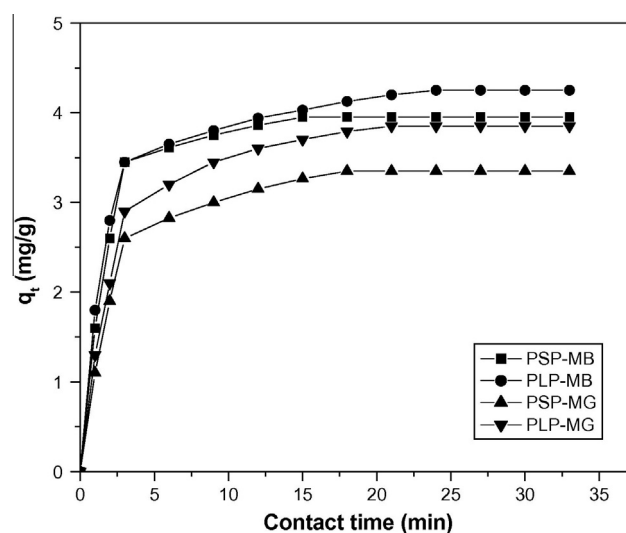


Figure 6 Adsorption kinetics of the adsorption of MB/MG on PSP/PLP (adsorbent dose: 2 g/L; initial dye concentration: 10 mg/L; pH: 7; temperature: 303 K).

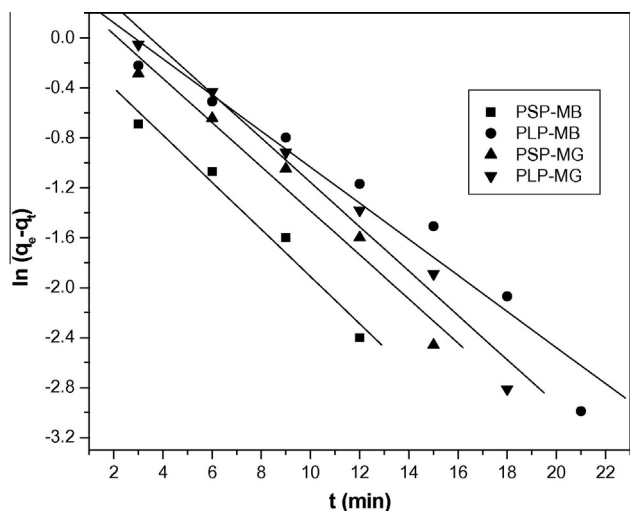


Figure 7 Pseudo-first order kinetics plots for the adsorption of MB/MG on PSP/PLP (adsorbent dose: 2 g/L; initial dye concentration: 10 mg/L; pH: 7; temperature: 303 K).

Fig. 6, it can be seen that the adsorption of dye molecules was rapid in the initial stages and was gradually decreased with the progress of adsorption until the equilibrium was reached. The equilibrium time for PSP-MB, PLP-MB, PSP-MG and PLP-MG systems were found to be 15, 24, 18 and 21 min, respectively. It revealed that systems based on PLP need more time to reach equilibrium point than that of PSP based systems.

The principle behind the adsorption kinetics involves the search for a best model that well represents the experimental data. Two classical kinetics models (i) a pseudo-first order kinetic model of Lagergren (ii) a pseudo-second order kinetic model of Ho were employed to simulate the experimental data of PSP-MB, PLP-MB, PSP-MG and PLP-MG systems.

The pseudo-first order rate expression can be given as (Lagergren, 1898):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

where q_e and q_t are the amount of dye adsorbed at equilibrium and at time t (mg/g), respectively, and k_1 (min^{-1}) is rate constant of adsorption. The values of k_1 and q_e^{cal} were calculated from the slopes ($-k_1$) and intercepts ($\ln q_e$) of the plots of $\ln(q_e - q_t)$ vs. t (Fig. 7), respectively, and are presented in Table 2. Although the correlation coefficient values are reasonably high, the calculated q_e values obtained from this kinetic model did not show good agreement with the experimental one. This finding suggested that the adsorption process does not follow the pseudo-first order adsorption rate expression of Lagergren.

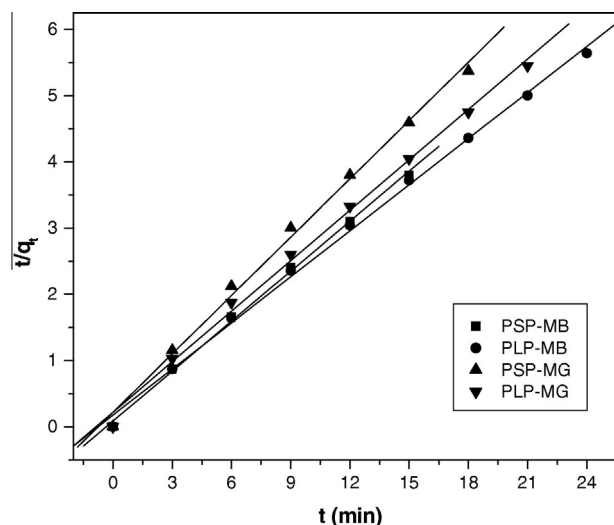


Figure 8 Pseudo-second order kinetics plots for the adsorption of MB/MG on PSP/PLP (adsorbent dose: 2 g/L; initial dye concentration: 10 mg/L; pH: 7; temperature: 303 K).

The adsorption kinetics may be described by a pseudo-second order model can be expressed as (Ho and McKay, 1999):

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (4)$$

where k_2 is the rate constant of adsorption (g/mg min), q_e and q_t are the amount of dye adsorbed (mg/g) at equilibrium and time t (min), respectively. The values of k_2 and q_e^{cal} were calculated from the intercepts ($1/k_2 q_e^2$) and slopes ($1/q_e$) of the plots of t/q_t vs. t (Fig. 8), respectively, and are presented in Table 2. Results showed high correlation coefficient values (> 0.99) for all the four systems and a good agreement between calculated and experimental q_e values indicating the applicability of the pseudo-second order kinetic model for PSP-MB, PLP-MB, PSP-MG and PLP-MG systems. Adsorption of MB and MG dyes onto PSP showed higher k_2 values than onto PLP, suggested the rate of adsorption on PSP was high and required less time to reach equilibrium point.

Adsorption kinetics is usually controlled by different mechanisms of which the most general are the diffusion mechanisms which can be explained by intraparticle diffusion model proposed by Weber and Morris. Intraparticle diffusion model can be expressed as (Weber and Morris, 1963):

$$q_t = k_i t^{0.5} + C \quad (5)$$

where k_i is the intraparticle diffusion constant ($\text{mg/g min}^{0.5}$) and the intercept (C) reflects the boundary layer effect. The values of k_i were calculated from slopes (k_i) of the plots of q_t vs. $t^{0.5}$ (Fig. 9) and are presented in Table 2. Fig. 9 showed that

Table 2 Kinetic parameters for adsorption of MB/MG on PSP/PLP.

Adsorption system	q_e^{exp}	Pseudo-first order			Pseudo-second order			Intraparticle diffusion		
		q_e^{cal}	k_1	R^2	q_e^{cal}	k_2	R^2	k_i	C	R^2
PSP-MB	3.95	0.97	0.18	0.972	3.98	0.75	0.998	0.235	3.04	0.999
PLP-MB	4.25	1.50	0.14	0.948	4.31	0.31	0.997	0.256	3.02	0.995
PSP-MG	3.35	1.46	0.17	0.965	3.41	0.39	0.994	0.303	2.08	0.997
PLP-MG	3.85	1.85	0.17	0.976	3.93	0.29	0.996	0.335	2.38	0.977

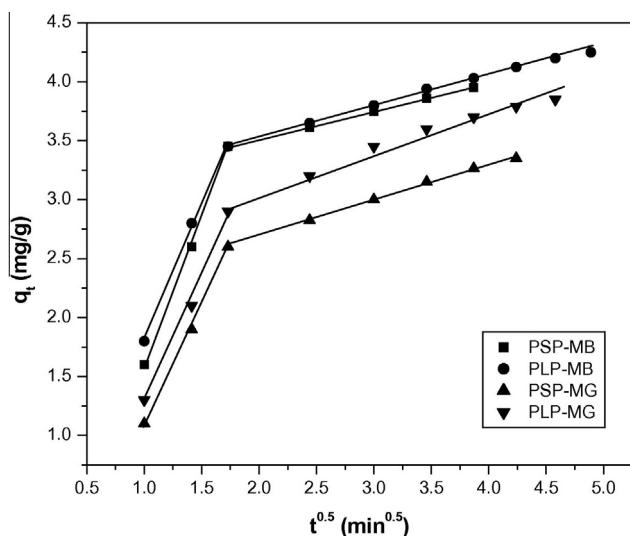


Figure 9 Intraparticle diffusion plots for the adsorption of MB/MG on PSP/PLP (adsorbent dose: 2 g/L; initial dye concentration: 10 mg/L; pH: 7; temperature: 303 K).

the involvement of two steps in adsorption process, first one representing adsorption of dyes on the surface of adsorbent and second one described diffusion of dyes to adsorption site. Surface adsorption mechanism was dominant in first 3 min of contact time, thereafter diffusion became rate-limiting process. Values of C were higher for MB than MG indicating more surface adsorption of MB on both the adsorbents. Diffusion rate of MG was higher than MB due to its higher concentration, remained in solution phase after surface adsorption, results in an increase of the driving force, which increases the diffusion rate. Results confirmed that the surface adsorption was more dominant in the initial stage of contact time, thereafter diffusion became a rate-limiting process.

3.6. Equilibrium studies

The analysis of the adsorption process requires the relevant adsorption equilibrium for better understanding of the adsorption process. Adsorption equilibrium describes the nature of adsorbate-adsorbent interaction. The equilibrium experiments were conducted for different initial dye concentrations and it was observed that the amount of dye adsorbed of PSP-MB, PLP-MB, PSP-MG and PLP-MG systems increased from 3.95 to 17.4 mg/g, 4.25 to 19.9 mg/g, 3.35 to 13.25 mg/g and 3.85 to 16.4 mg/g, respectively, as the initial dye concentration was increased from 10 to 50 mg/L, indicating that the initial concentration provided a powerful driving force to overcome

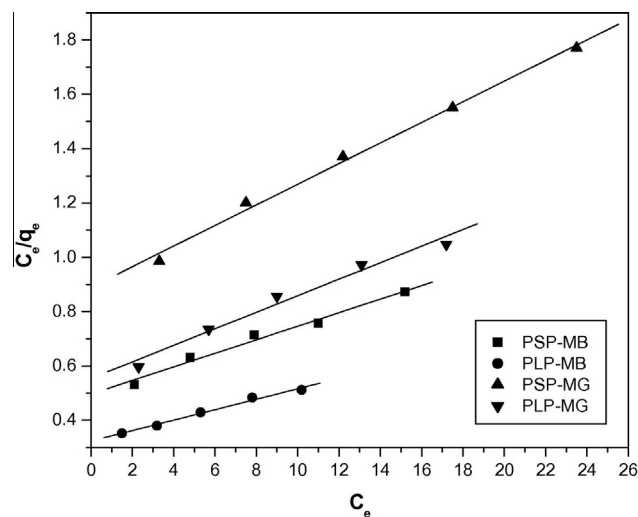


Figure 10 The Langmuir plots for the adsorption of MB/MG on PSP/PLP (adsorbent dose: 2 g/L; initial dye concentration: 10 mg/L; pH: 7; temperature: 303 K).

the mass transfer resistance between the aqueous and solid phases. Whereas the percent dye removal decreased from 82% to 76%, 87% to 83%, 67% to 58.8% and 75% to 68.2% for PSP-MB, PLP-MB, PSP-MG and PLP-MG systems, respectively, for an increase in initial dye concentration from 10 to 50 mg/L. These equilibrium data were analyzed using the Langmuir and Freundlich isotherm models.

3.6.1. Langmuir isotherm model

The Langmuir isotherm is valid for monolayer adsorption onto a surface with a finite number of identical sites. It can be expressed as:

$$q_e = Q_m b C_e / (1 + b C_e) \quad (6)$$

The linearized forms of Eq. (6) (Ghoul et al., 2003) can be written as follows:

$$C_e/q_e = 1/bQ_m + C_e/Q_m \quad (7)$$

where q_e is the amount of dye adsorbed on adsorbent (mg/g) at equilibrium, C_e is the equilibrium concentration (mg/L) of the dye in solution, Q_m is the monolayer adsorption capacity (mg/g) and b is the Langmuir constant (L/mg) related to the free energy of adsorption. The values of Q_m and b were calculated from the slopes ($1/Q_m$) and intercepts ($1/bQ_m$) of the linear plots of C_e/q_e vs. C_e (Fig. 10) and are given in Table 3. Values for the correlation coefficients strongly supported the assumption that the adsorption data follows the Langmuir

Table 3 Isotherm parameters for adsorption of MB/MG on PSP/PLP.

Adsorption system	Langmuir isotherm parameters				Freundlich isotherm parameters			
	Q_{max}	b	R^2	ARE (%)	K_F	n	R^2	ARE (%)
PSP-MB	41.6	0.048	0.983	0.44	2.27	1.3	0.997	0.636
PLP-MB	52.6	0.058	0.988	1.161	3.15	1.2	0.996	3.322
PSP-MG	27.0	0.041	0.994	0.0307	1.45	1.4	0.997	2.862
PLP-MG	33.3	0.054	0.977	1.765	2.06	1.3	0.998	0.792

Table 4 Previously reported adsorption capacities of various agricultural and plant wastes for MB and MG.

Adsorbents	Dye	Q_{max}	References
Oil palm trunk fiber	MG	149	Hameed and El-Khaiary (2008a)
Dead leaves of <i>Platanus vulgaris</i>	MG	85.47	Hamdaouia et al. (2008)
Banana pseudo-stem fiber	MG	26.5	Gupta et al. (2011)
Neem sawdust (<i>Azadirachta indica</i>)	MG	4.3	Khattria and Singhb (2009)
Treated ginger waste	MG	84	Ahmad and Kumar (2010)
<i>Arundo donax</i> root carbon	MG	8.6	Zhang et al. (2008)
Leaves of <i>Solanum tuberosum</i>	MG	33.3	This study
Stem of <i>Solanum tuberosum</i>	MG	27	This study
Pineapple stem	MB	119	Hameed et al. (2009)
Tea waste	MB	85	Uddin et al. (2009)
Date stones and palm-trees waste	MB	40 and 35	Belala et al. (2011)
Yellow passion fruit waste	MB	44.7	Pavan et al. (2008)
Sulfuric acid treated Parthenium and phosphoric acid treated Parthenium	MB	39 and 88	Lata et al. (2007)
Pumpkin seed hull	MB	141	Hameed and El-Khaiary (2008b)
Garlic peel	MB	82.6	Hameed and Ahmad (2009)
Neem (<i>Azadirachta indica</i>) leaf powder	MB	19.6	Bhattacharyya and Sharma (2005)
Leaves of <i>Solanum tuberosum</i>	MB	52.6	This study
Stem of <i>Solanum tuberosum</i>	MB	41.6	This study

model of adsorption. Values of Q_m for different systems were found to be in the order PLP-MB > PSP-MB > PLP-MG > PSP-MG suggested that the adsorption capacity of PLP was greater than PSP for both the dyes and adsorption capacity of both the adsorbents were greater for MB than MG dye. The Langmuir parameter, Q_{max} values obtained in this work were compared with other results reported in the literature (Table 4).

3.6.2. Freundlich isotherm model

The Freundlich isotherm is an empirical equation assuming that the adsorption process takes place on heterogeneous surfaces. This isotherm can be expressed by the following equation (Kumar et al., 2006):

$$q_e = K_f C_e^{1/n} \quad (8)$$

The logarithmic forms of Eq. (8) can be written as follows:

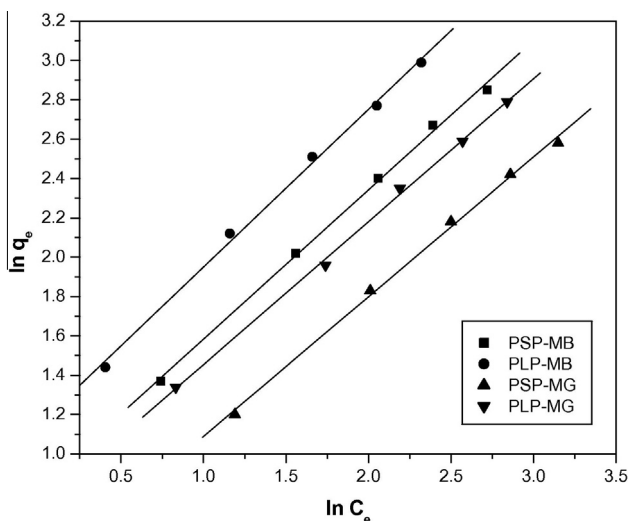


Figure 11 The Freundlich plots for the adsorption of MB/MG on PSP/PLP (adsorbent dose: 2 g/L; pH: 7; temperature: 303 K).

$$\ln q_e = \ln K_f + (1/n) \ln C_e \quad (9)$$

where K_f and n are Freundlich constants related to adsorption capacity [$\text{mg g}^{-1} (\text{mg L}^{-1})^{-1/n}$] and adsorption intensity of adsorbents. The values of the K_f and n were calculated from the intercepts ($\ln K_f$) and slopes ($1/n$) of the plots $\ln q_e$ vs. $\ln C_e$ (Fig. 11) and are presented in Table 3. The high values of the correlation coefficient indicate that the experimental data were also fitted well in Freundlich model. The order of adsorption capacity was similar as to that observed in the Langmuir isotherm. Values of $n > 1$ represented favorable adsorption condition for all the four adsorption systems (Hameed, 2009).

3.6.3. Error analysis

In the single-component isotherm studies, the optimization procedure requires an error function to be defined in order to evaluate the fit of the isotherm to the experimental equilibrium data. The error analysis was done by evaluating average

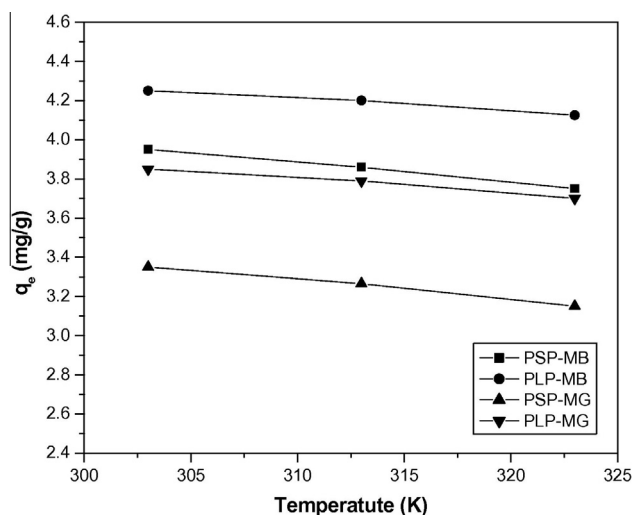


Figure 12 Effect of temperature on adsorption of MB/MG on PSP/PLP (adsorbent dose: 2 g/L; initial dye concentration: 10 mg/L; pH 7).

Table 5 Thermodynamic parameters for adsorption of MB/MG on PSP/PLP.

Adsorption system	ΔH° (kJ/mol)	ΔS° (J/mol/K)	ΔG° (kJ/mol)		
			303 K	313 K	323 K
PSP-MB	-9.087	-18.9	-3.361	-3.172	-2.983
PLP-MB	-7.497	-10.3	-4.377	-4.274	-4.171
PSP-MG	-7.026	-17.2	-1.815	-1.643	-1.471
PLP-MG	-6.304	-10.7	-3.062	-2.955	-2.848

relative error (*ARE*) function, which measures the differences of the amount of dye adsorbed on the adsorbent (q_e), measured experimentally and predicted by the models.

$$ARE (\%) = 100/n \sum_{i=1}^n (q_{e,exp} - q_{e,cal}/q_{e,exp}) \quad (10)$$

where $q_{e,exp}$ is each value of q_e measured experimentally and $q_{e,cal}$ is each value of q_e predicted by the fitted model and n is the number of experiments performed. The values of *ARE* (%) for Langmuir and Freundlich isotherm models are presented in Table 3.

3.7. Thermodynamic studies

The effect of temperature on the adsorption of MB and MG on PSP and PLP adsorbents were investigated at 303, 313, and 323 K. Fig. 12 showed that the adsorption capacity decreased from 3.95 to 3.75 mg/g, 4.25 to 4.12 mg/g, 3.35 to 3.15 mg/g and 3.85 to 3.7 mg/g of PSP-MB, PLP-MB, PSP-MG and PLP-MG systems, respectively, as the temperature increased from 303 to 323 K. These findings indicated that the decrease in feasibility of adsorption at higher temperature due to increase in kinetic energy of dye molecule may cause escape of dye from solid surface to solution phase. A similar observation was also reported in the study on the adsorption of MB onto *Scolymus hispanicus* L. (Baraka et al., 2011).

Thermodynamic parameters, such as change in enthalpy (ΔH°), entropy (ΔS°) and Gibb's free energy (ΔG°) were determined for the PSP-MB, PLP-MB, PSP-MG and PLP-MG systems, using Eq. (11) (Nandi et al., 2009) and (12).

$$\ln(q_e m/C_e) = \Delta S^\circ/R - \Delta H^\circ/RT \quad (11)$$

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

where m is the adsorbent dose (mg/L), C_e is the equilibrium concentration (mg/L) of the dye in solution and $q_e m$ is the solid-phase concentration (mg/L) at equilibrium. R is the gas constant (8.314 J/mol/K) and T is the temperature (K). ΔH° , ΔS° and ΔG° are changes in enthalpy (kJ/mol), entropy (J/mol/K) and Gibb's free energy (kJ/mol), respectively.

The values of ΔH° and ΔS° were determined from the slope ($-\Delta H^\circ/R$) and the intercept ($\Delta S^\circ/R$) of the plots of $\ln(q_e m/C_e)$ vs. $1/T$. The ΔG° values were calculated by using Eq. (12). The values of thermodynamic parameters are presented in Table 5. Negative values of ΔG° indicated that the adsorption process was feasible and spontaneous in nature. The values of ΔG° increased in the order PSP-MG < PLP-MG < PSP-MB < PLP-MB indicate the adsorption was more spontaneous for PLP-MB system. It also revealed that adsorption of MB/MG

on PLP was more spontaneous than on PSP and adsorption of MB dye was more spontaneous than MG dye. Negative value of ΔS° described the decrease in randomness at the adsorbent-solution interface during the adsorption. Negative values of ΔH° confirm the overall adsorption of MB/MG on PSP/PLP is an exothermic process and are < -10 kJ/mol, which indicates that physical adsorption was the predominant mechanism in the adsorption process (Bhatnagar et al., 2010; Kumar and Gayathri, 2009).

3.8. Recovery of adsorbents and dyes

In order to assess the practical utility of the PSP and PLP adsorbents, desorption experiments were conducted to regenerate the adsorbents and to recover the dyes. For desorption experiment, dye loaded adsorbents were treated by 1% (v/v) of HCl/ethanol solution for a predetermined time. Treated solution were collected and analyzed for dye content in solution after desorption. The regeneration efficiency (%*RE*) of the adsorbents was calculated using Eq. (13).

$$\%RE = 100 \times q_r/q_0 \quad (13)$$

where q_0 and q_r are the adsorption capacities of adsorbents before and after regeneration, respectively. Three consecutive cycles of adsorption-desorption experiments were performed for all the four systems. After the three cycle of regeneration, 3.8%, 4.5%, 4% and 4.9% reduction in the adsorption capacities was observed for PSP-MB, PLP-MB, PSP-MG and PLP-MG systems, respectively. The solution containing desorbed dye was distilled off and the dye was recovered and solvent was reused for the next cycle.

4. Conclusion

The results of the present investigation showed that potato plant wastes can be a promising adsorbent for the removal of cationic (MB and MG) dyes from water. The characterization of PSP and PLP revealed that the rough surface and functional groups made PSP and PLP beneficial to adsorb dyes from aqueous solution. The optimum pH and temperature for removal was found to be 7 and 303 K, respectively. The presence of salt in solution reduced the adsorption of dyes on adsorbents by competitive inhibition. Pseudo-second order and intraparticle diffusion model were found to better fit in kinetic data of adsorption. Equilibrium data were fitted well in both Langmuir and Freundlich isotherm models and the adsorption capacities of different systems were in the order PLP-MB (52.6 mg/g) > PSP-MB (41.6 mg/g) > PLP-MG (33.3 mg/g) > PSP-MG (27 mg/g). Thermodynamic study re-

vealed that the adsorption was exothermic, spontaneous and physical in nature.

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