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Dye removal using carbonized biomass, isotherm and kinetic studies

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ABSTRACT

Effect of thermal treatment on green tea dredge, an abundant waste, for dye removal was investigated in the present study. Variable temperature (800 and 900°C) and residence time in furnace (10 min, 1 and 2 h) were used to prepare six adsorbents which were characterized for surface morphology. The adsorption study was carried out using methylene blue as a model molecule and the effect of shaking time, pH and concentration was determined. Adsorbents prepared at 900°C were found to be more effective than those prepared at 800°C while longer residence time in furnace yielded adsorbents with higher adsorption capacity. The maximum adsorption capacity achieved in this case study was 71.4 ± 4.6 mg/g which is better than many activated carbons derived from other materials. Langmuir model was a better fit in isotherm studies while the sorption process followed pseudo-second-order kinetics.

Keywords: Pyrolysis; Methylene blue; Tea dredge; Lagergren model; Intraparticle diffusion

1. Introduction

Large volumes of wastewater contaminated with various toxic dyes are discharged into water bodies every year from various industries and pose a threat to aquatic organisms and water quality. Treatment of dye wastewater from textile and dyestuff industries is not easy due to complex molecular structures and low biodegradability of the dyes. As many organic and inorganic chemical reagents are also used in the textile sector, dyes can have both direct and indirect toxic effects on humans in the form of tumours, cancers and allergies. They can inhibit growth at different trophic levels including bacteria, protozoa, algae, plants and animals [1–4].

Treatment methods such as photocatalytic degradation, biodegradation, electrochemical degradation, membrane process, adsorption and several others are in practice to treat such wastewater [5–10]. Adsorption is a promising and well-studied method for pollutant removal from aqueous solutions. It is highly effective

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in the treatment of wastewater containing stable pollutants which are difficult to remove using common conventional methods [11].

Activated carbon from coal is an effective adsorbent but due to its inhibitive cost alternative materials are being produced and tested for the same purpose. Biomass-derived low-cost activated carbons are emerging as efficient adsorbents for dyes containing wastewater treatment. Carbonized biomass materials are reported to have better removal efficiencies than unmodified cellulosic materials but are less effective than activated carbons. Different materials like guava seed, almond shell, fly ash, walnut shell, apricot stones, hazelnut shell, bamboo dust, coir pith, rejected tea, peach stone, walnut straw, activated carbon fibres, diatomite-templated carbons, oil palm shell and rice hull ash were pyrolysed and investigated as materials for methylene blue (MB) removal from aqueous solutions (Table 1) [12–17].

Green tea dredge is a renewable and abundant waste with the green tea market predicted to approach 1.2 million ton per annum by 2015 with China as the largest producer and leading exporter [18]. Tea industry waste activated carbon [19,20], tea waste activated carbon using microwave energy [21], potassium acetate activated carbon from tea waste [22] and other forms of black tea [23,24] were studied to remove various pollutants but thermally activated carbonized green tea dredge for MB removal, to best of our knowledge, has not yet been reported.

Table 1
Various activated carbons used for MB removal

Adsorbent used	Adsorption capacity (mg/g)	Reference
Peach stone activated carbon	412	[28]
Almond shell activated carbon	1.33	[13]
Fly ash	2.75–3.07	[29]
Walnut shell activated carbon	3.53	[13]
Apricot stones activated carbon	4.11	[13]
Hazelnut shell activated carbon	8.82	[13]
Bamboo dust based activated carbon	143	[30]
Coir pith activated carbon	5.87	[31]
Rejected tea (unmodified)	147	[24]
Wheat straw biochar	12.0	[32]
Rice hull ash	45	[33]
Vegetable fiber activated carbon	33.74	[34]
Corn husk activated carbon	662	[35]
Carbon monolith powder	127	[36]
Pyrolysed green tea dredge	71.42	Present study

The aim of the present study was therefore to explore possible utilization of carbonized green tea dredge for the removal of organic molecules and colourants from aqueous solutions. MB dye was chosen to serve as a model compound to investigate the adsorptive behaviour and efficacy of carbonized green tea dredge. MB is commonly used in the medical, textile and printing industry [25], and although not acutely toxic, various health effects, such as eye burns, rapid or difficult breathing, burning sensation, nausea, vomiting, profuse sweating, mental confusion and methemoglobinemia, are associated with it [26,27].

2. Materials and methods

2.1. Preparation of the adsorbent materials

Spent green tea dredge was washed with deionized water to remove dirt and dried at 105˚C until it attained constant weight and subsequently pyrolysed at 800 or 900˚C for 10 min, 1 or 2 h to get six adsorbents classified as given in Table 2. For this purpose, pre-weighed amounts of the dried green tea dredge

Table 2
Process conditions to prepare adsorbents

Adsorbent	Abbreviation used	Pyrolysis temperature (˚C)	Residence time (min)
Pyrolysed green tea dredge-1	PGT-1	800	10
Pyrolysed green tea dredge-2	PGT-2	800	60
Pyrolysed green tea dredge-3	PGT-3	800	120
Pyrolysed green tea dredge-4	PGT-4	900	10
Pyrolysed green tea dredge-5	PGT-5	900	60
Pyrolysed green tea dredge-6	PGT-6	900	120

were put in containers, covered with lids and carefully placed inside a Gallenkamp Eurotherm Sheffield furnace, with temperature control as required for the process. The containers were removed from the furnace after the pre-allocated time and allowed to cool. The carbonized material thus obtained were weighed, washed and dried to constant weight at 110˚C and stored in airtight containers. These carbonized materials were used for experimental purposes without any further chemical or physical activation.

2.2. Surface area analysis

A Quantachrome Autosorb automated gas sorption system was used for textural characterization of pyrolysed green tea (PGT) adsorbents by N_2 adsorption at 77 K. The Brunauer–Emmett–Teller (BET) surface area, total pore volume and average pore diameter are given in Table 3.

2.3. Adsorbate preparation

An MB stock solution of 1,000 mg/L was prepared by dissolving 1 g of MB (BDH) in one litre of distilled water. Working solutions of various concentrations were prepared using this stock solution and adjusted to the desired pH using 0.01 M NaOH or HCl solutions.

2.4. Batch mode adsorption studies

Dye removal studies using the above-prepared adsorbents were carried out in batch mode to investigate the effect of contact time, dye concentration and pH on adsorption of MB from aqueous solution. 50 mL solutions containing varying concentrations of MB dye and 200 mg of adsorbent were added to 250 mL Erlenmeyer flasks covered with aluminium foil and agitated at 180 rpm on a mechanical orbital shaker at 25˚C. Solutions were frequently purged with N_2 to avoid the effects of atmospheric CO_2 on solution pH.

Samples were collected at suitable time intervals, centrifuged and supernatants analysed for residual dye absorbance at 665 nm using spectrophotometer (Camlab, DR 2800). The initial and residual concentrations of MB dye were calculated using linear equation derived from the calibration curve. All experiments were performed in triplicates with negative controls.

2.5. Isotherms

Irving Langmuir, in 1916, developed an equation to study the monolayer adsorption on a solid surface at constant temperature [37]. The basic assumption is that the forces exerted by chemically unsaturated surface atoms do not extend further than the diameter of one adsorbed molecule (monolayer coverage). The linear form is given in Eq. (1).

$$C_e/q_e = 1/K_d q_m + (1/q_m)C_e \tag{1}$$

where q_e (mg/g) is the amount of adsorbate bound to absorbent at equilibrium; C_e is the concentration of adsorbate in solution at equilibrium; K_d is constant and q_m is the maximum amount of adsorbate that can be adsorbed to adsorbent (monolayer capacity). C_e/q_e against C_e plot is used to determine q_m and K from slope and intercept of straight line, respectively.

Other quite often used isotherm is Freundlich isotherm which is related to the heterogeneity of the surface and assumes that adsorption occurs at heterogeneous surfaces at non-identical sites with different energies [38]. This empirical model is used for non-ideal adsorption and linearized form is expressed in Eq. (2).

$$\log q_e = \log K_F + 1/n(\log C_e) \tag{2}$$

where K_F and n are indicators of relative adsorption capacity and intensity, respectively, and their values

Table 3
Textural characteristics of PGT adsorbents

Adsorbent	BET surface area (m^2/g)	Total pore volume (cc/g)	Average pore diameter (A˚)	Micro-pore surface area (m^2/g)	Micro-pore surface area (%)	External surface area (%)
PGT-1	76.2	0.101	53.0	3.13	4.1	95.9
PGT-2	434	0.246	22.7	377	86.9	13.1
PGT-3	600	0.318	21.2	536.5	89.41	10.59
PGT-4	67	0.087	52.0	8.23	12.28	87.72
PGT-5	628	0.362	23.1	564	89.8	10.2
PGT-6	563	0.330	23.5	504	89.5	10.5

can be obtained from the intercept and the slope of linear plot of log q_e vs. log C_e.

Temkin isotherm is based on the assumption that the heat of adsorption of all the molecules in the layer decreases linearly due to sorbate/sorbent interactions; hence, a linear fall of heat of adsorption is proposed rather than logarithmic as in Freundlich equation [39]. The linear form of isotherm is given as (Eq. (3)).

$$q_e = B \ln A + B \ln C_e \tag{3}$$

where $B = RT/b$ and b is the Temkin isotherm constant; A (L/g) is the Temkin isotherm constant; R is the gas constant and T is the absolute temperature (K). The q_e vs. ln C_e plot can be used to determine Constant A and B.

2.6. Kinetics

2.6.1. Lagergren kinetic models

Lagergren, in 1898, introduced his kinetic model for adsorption of oxalic acid and malonic acid onto charcoal [40]. It is most widely used kinetic model for adsorption of pollutants like metals, dyes and organic moieties from aqueous phase using activated carbon, biological organic compounds, agricultural biomasses in chemically and thermally modified forms and inorganic adsorbents [41–48]. Mathematical form of Lagergren pseudo-first-order model is described in Eq. (4).

$$\log(q_e - q_t) = (\log q_e - K_1 t)/2.303 \tag{4}$$

A linear plot of log (q_e − q_t) vs. t can be used to determine rate constant.

The pseudo-second-order equation can be expressed as linear form as given in Eq. (5).

$$t/q_t = 1/K_2 q_e^2 + 1/q_e t \tag{5}$$

A linear plot of t/q_t vs. t can give the values of K_2 and q_e along with correlation coefficients.

2.6.2. Diffusion models

Diffusion models are based on a stepwise process of adsorption: (1) diffusion across the liquid film surrounding the adsorbent particles (film diffusion); (2) diffusion in liquid contained in the pores and/or along the pore walls, which is the so-called internal diffusion or intraparticle diffusion; and (3) adsorption and desorption between the adsorbate and active sites, i.e. mass action [49].

In film diffusion, the boundary plays the most significant role in adsorption during the transport of the solute molecules from the liquid phase up to the solid phase. The liquid film diffusion model may be applied as given in Eq. (6).

$$\ln(1 - F) = -K_{fd}\, t \tag{6}$$

where $F = q_t/q_e$ and is the fractional attainment of equilibrium. A linear plot of –ln (1 – F) vs. t with zero intercept would suggest that the kinetics of the sorption process is controlled by diffusion through the liquid film surrounding the solid sorbent.

Most commonly used model is Weber Morris model (see Eq. 7). Weber Morris found that in many adsorption cases, solute uptake varies almost proportionally with $t^{1/2}$ rather than with the contact time t [50].

$$q_t = K_{int}\, t^{1/2} \tag{7}$$

where K_{int} is the intraparticle diffusion rate constant. A plot of q_t vs. $t^{1/2}$ should be a straight line with a slope of K_{int} when intraparticle diffusion is the rate limiting step. The straight line should pass through the origin if only intraparticle diffusion is the sole mechanism for adsorption.

3. Results and discussion

3.1. Pyrolysis conditions on adsorption capacity of PGT adsorbents

The conditions under which PGT adsorbents were prepared had a significant effect on the morphology and adsorption capacity of these materials. BET surface area, pore volume, micro-, meso- and macro-pore size distributions and surface chemistry of adsorbents were affected by pyrolysis temperature and residence time. Short residence time in furnace (PGT-1 and PGT-4) resulted in mesoporous adsorbents having low surface area and pore volume (Table 3), and hence exhibited lowest adsorption capacities (Fig. 4) irrespective of high pyrolysis temperature. Adsorbents prepared at 900°C for 1 or 2 h residence time (PGT-5 and PGT-6) exhibited higher adsorption capacity owing to their larger surface areas with high proportion of micropores (89%) as compared to others (Table 3). PGT adsorbents appeared to have low surface area than many activated carbons already reported due to the fact that these PGT adsorbents were prepared in a single-step carbonization method and were not activated using further chemical or physical treatment.

3.2. *Effect of contact time and concentration of dye*

Contact time and dye concentration are important factors to determine rate of dye uptake, time required for adsorbent-adsorbate system to reach an equilibrium and adsorption capacity of adsorbent. These factors also play significant role in isotherm studies related to adsorption processes.

For PGT adsorbents, MB uptake rate was high at initial stages as compared to later stages where rate gradually decreased till equilibrium (Fig. 1). For example, the dye uptake rate for PGT-6 adsorbent (250 mg/L) was 0.73 mg/(g min) for first 30 min, 0.53 mg/(g min) for the 30–60 min time interval and 0.0705 mg/(g min) for 60–350 min. It was also noticed that 84% of maximum MB removal was achieved within the first 100 min, followed by another 5% in the next 100 min. As most PGT adsorbents have porous structure with high percentage of internal surface area (except PGT-1 and PGT-4) and initially more active sites for adsorption were available to dye molecules, this resulted in fast adsorption and afterwards the sites were gradually reduced till system acquired equilibrium. Similar trend was observed for most PGT adsorbents with variable uptake values, which was due to variation in physical structure and surface properties.

The adsorption capacity of adsorbents was a function of MB concentration as all the six tested adsorbents showed increased uptake capacities for increase in MB initial concentration (Fig. 2). Adsorption capacity (q_e) of PGT-6 increased from 5.67 to 61.7 mg/g when initial concentration of MB increased from 20 to 288 mg/L. This trend appeared to be least significant in PGT-1 and 4 (Fig. 2) adsorbents which can be related to their least internal surface area (Table 3), whereas it was much prominent in the case of PGT-5 and 6 adsorbents. Similar trend was reported in another study where bamboo-based carbon was utilized for MB removal [9]. It also shows that at lower concentrations of dye, adsorbent surface was still unsaturated at equilibrium and more sites were occupied by dye molecules at higher concentrations due to the concentration gradient.

A decrease in percent removal of dye was observed at higher concentrations of dye for all PGT adsorbents (Fig. 3). At higher initial concentrations of dye, the amount of dye taken up by the adsorbent (mg of dye per g of adsorbent) was high (Fig. 2) but the fraction of dye removed from initial high concentration was relatively less.

3.3. *Effect of pH*

The pH appeared to have very little effect on the removal of MB from aqueous solution by these adsorbents. Only a slight increase (3% ± 1) in removal of MB was observed in basic medium at pH 8 and 9, which is not very significant (Fig. 5). A similar observation was reported by Bhattacharyya [51] for MB removal using neem leaf powder. Change in adsorbent surface properties and adsorbate molecules over a pH range are important factors that contribute to the extent of variation of adsorption. MB can exist in molecular and cationic form and the latter seems to be more dominant in basic medium. As adsorbent surface

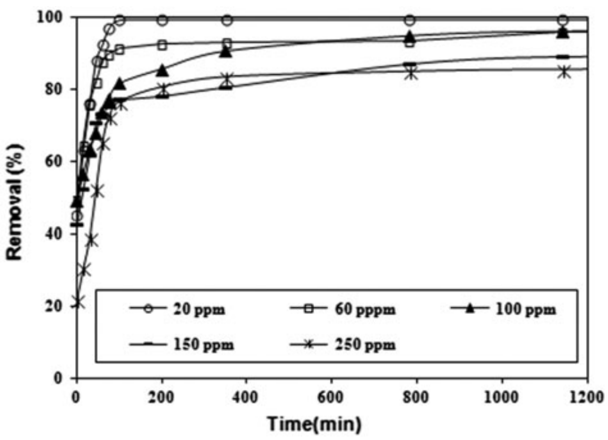

Fig. 1. Effect of contact time on percentage removal of MB by PGT-6 at various initial concentrations.

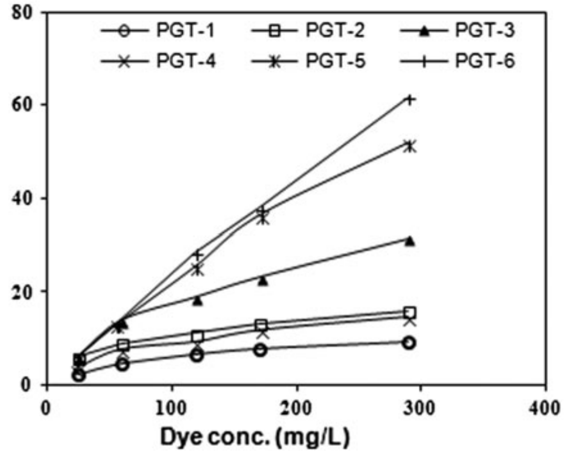

Fig. 2. Uptake capacity of adsorbents as function of concentration of MB dye for various PGTs.

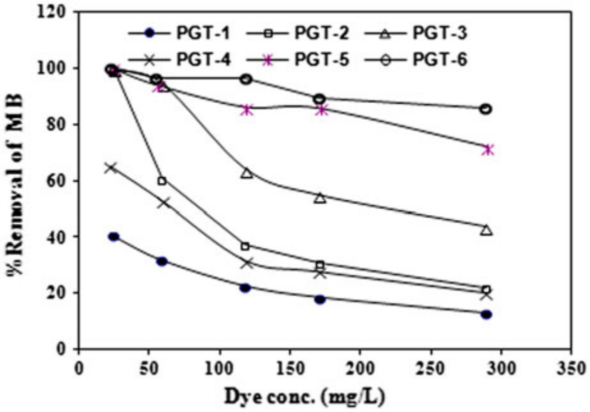

Fig. 3. percentage removal of MB as function of dye concentration for all adsorbents.

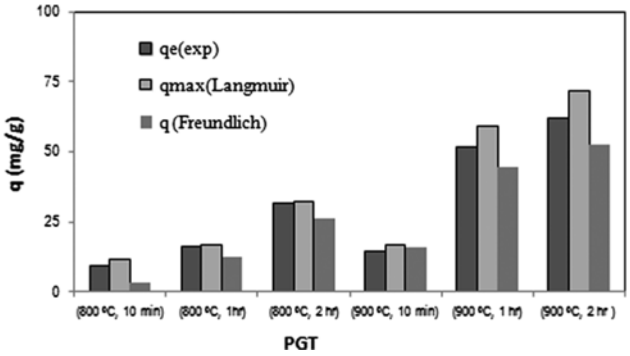

Fig. 4. Comparison of experimental, Langmuir and Freundlich adsorption capacities for six PGT adsorbents for MB removal.

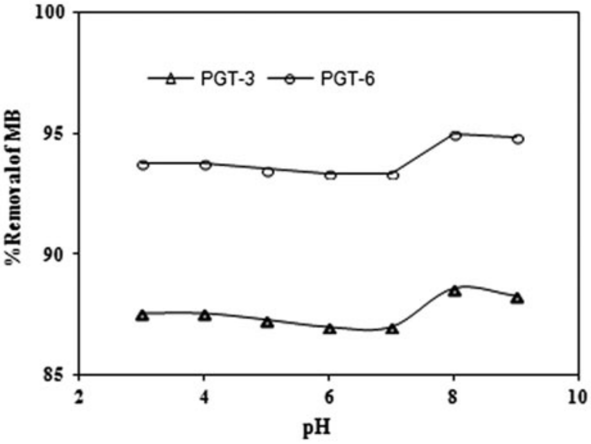

Fig. 5. Effect of pH on MB removal by PGT-3 & PGT-6 adsorbents (dye concentration = 20 mg/L).

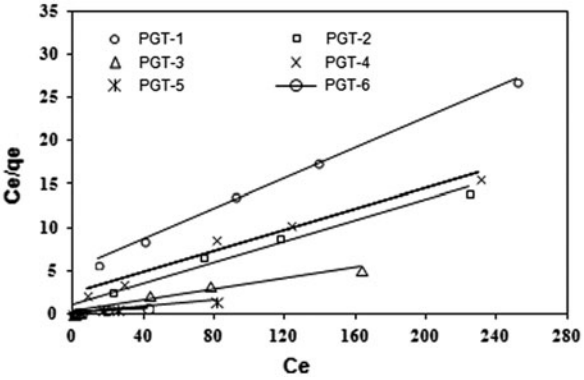

Fig. 6. Langmuir isotherm plot for removal of MB by all adsorbents.

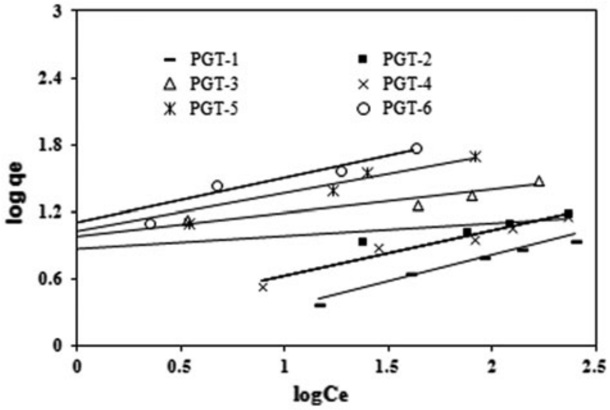

Fig. 7. Freundlich isotherm plot for the removal of MB by PGT adsorbents.

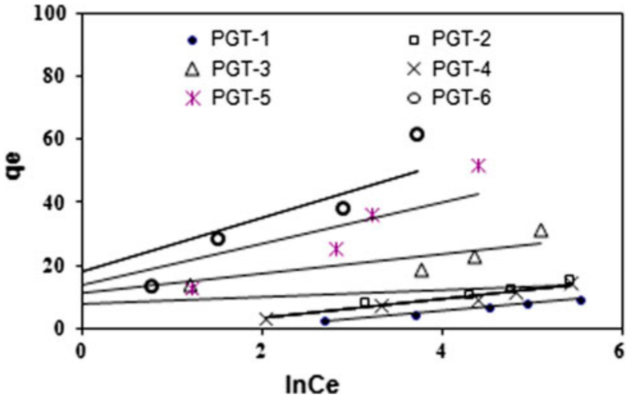

Fig. 8. Temkin isotherms of removal of MB by PGT adsorbents.

Table 4
Values of different isotherm parameters for removal of MB by PGT adsorbents

	Freundlich isotherm				Langmuir isotherm				Temkin isotherm		
	R^2	K_F ($mg^{1-N}L^N/g$)*	n	q_e (mg/g)	q_{max} (mg/g)	K_L (L/mg)	R^2	R_L	B (J/mol)	A_T (L/g)	R^2
PGT-1	0.977	0.765	2.14	3.47	11.36	0.017	0.997	0.1658	2.419	0.1823	0.998
PGT-2	0.918	7.398	10.2	12.68	16.67	0.0543	0.972	0.0600	1.082	1294.3	0.776
PGT-3	0.977	9.731	5.10	26.41	32.26	0.0759	0.947	0.0436	3.092	37.909	0.875
PGT-4	0.947	1.652	2.42	15.86	16.67	0.0249	0.972	0.1219	3.091	0.3863	0.965
PGT-5	0.953	10.81	3.11	44.75	58.82	0.0876	0.953	0.0380	6.558	8.5200	0.814
PGT-6	0.944	12.82	2.65	52.38	71.42	0.14	0.925	0.0241	8.576	8.1856	0.819

*$1/n = N$

is more negatively charged in basic pH, more effective adsorbent–adsorbate interactions are likely to happen. The slight variation in dye uptake indicates that adsorption is dominated by physio-sorption where adsorbent–adsorbate interactions take place due to weak electrostatic attractions which are least affected by a change in pH over a wide range.

3.4. Isotherm studies

Langmuir, Freundlich and Temkin isotherms were used to analyse the adsorbent–adsorbate interaction phenomenon (Figs. 6–8 and Table 4).

The data obtained in the present investigation showed a better fit with the Langmuir model with experimental adsorption capacities close to q_{max} (Langmuir) (Fig. 4), which indicates more extent of homogenous surface on adsorbents. R^2 values less than unity for Langmuir model also indicate certain degree of heterogenity [52]. R_L values for the six adsorbents varied from 0.017 to 0.14 which also indicates favourable monolayer adsorption ($0 < R_L < 1$). In case of PGT-3 and PGT-6, Freundlich regression coefficients were slightly greater for Langmuir (Table 4); however, the calculated $q_{e,calc}$ from the Freundlich model were lower as compared to experimental ($q_{e,exp}$) values. For example, for PGT-6,

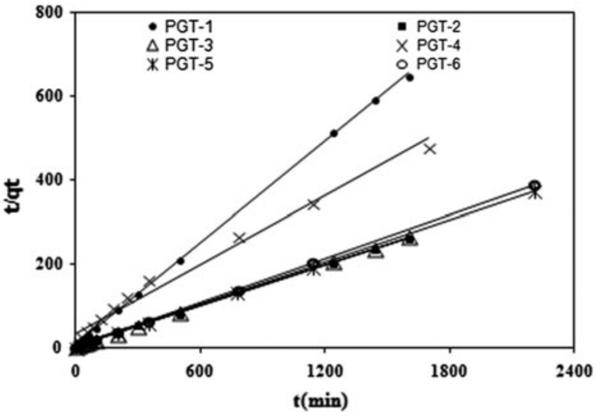

Fig. 9. Pseudo-second-order plot for removal of MB by PGT adsorbents.

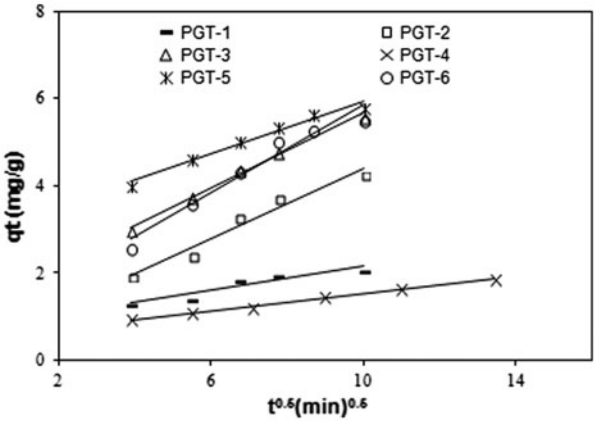

Fig. 10. Intraparticle diffusion model plot for removal of MB by PGT adsorbents.

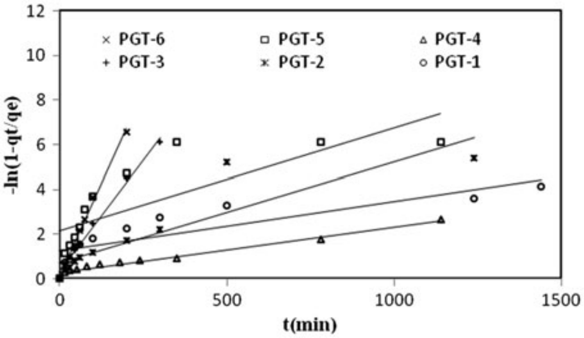

Fig. 11. Liquid film diffusion model for removal of MB by PGT adsorbents.

Table 5
Values of different kinetic parameters of various models for removal of MB by PGT adsorbents

	Pseudo-first-order model			Pseudo-second-order model			Intraparticle diffusion model			Liquid film diffusion model		
	K	q_e	R^2	K	Q_e	R^2	K	C	R^2	K	C	R^2
PGT-1	0.009	1.361	0.781	1.098	2.47	0.999	0.14	0.7674	0.8822	0.0002	1.25	0.742
PGT-2	0.007	4.60895	0.908	0.147	6.25	0.999	0.4	0.3947	0.9602	0.004	0.7	0.801
PGT-3	0.021	4.8260	0.993	0.046	6.14	0.999	0.429	1.3771	0.9925	0.029	0.61	0.948
PGT-4	0.003	2.92	0.828	2.513	3.65	0.981	0.099	0.5479	0.9931	0.002	0.277	0.977
PGT-5	0.035	4.3012	0.972	0.022	5.95	1	0.30	2.9363	0.9731	0.0046	2.158	0.617
PGT-6	0.036	5.865	0.995	0.041	5.71	0.999	0.50	0.8313	0.9591	0.0331	0.086	0.996

the $q_{e,calc}$ value determined by Freundlich model was 52.38 mg/g which was even lower than the experimental value (61.7 mg/g) which suggests that the Langmuir model was a better fit to explain the adsorption model. This finding is in agreement with literature for the removal of MB by various sorbents [9,51,53–57].

3.5. Kinetics

The mechanisms of dye uptake and sorption rate are vital elements in adsorption process. Dye uptake rate is useful in determining suitable time required for completion of the process. In order to investigate the dynamics in liquid–solid adsorption processes, the Lagergren pseudo-first-order, pseudo-second-order, intraparticle diffusion and liquid film diffusion models were explored (Figs. 9–11 and Table 5).

The MB adsorption process followed pseudo-second-order kinetics as in the experimental and the calculated q_e values are in close agreement at given MB concentrations with high regression coefficients. Similar kinetic behaviour was observed for wood sawdust, rattan sawdust and bamboo-based activated carbon, natural clay mineral and coconut bunch waste for MB removal form aqueous solutions [9,57–60].

As surface diffusion, intraparticle diffusion and adsorption are three stages in such systems, intraparticle and liquid film diffusion models were also applied for identification of diffusion mechanics. It is assumed that either liquid film or intraparticle or both can be rate limiting mechanisms. Intraparticle plot was obtained after neglecting initial time interval which represents rapid external diffusion and surface adsorption stage (sharper linear stage) and considering gradual linear stage to identify intraparticle diffusion as rate limiting step. As intraparticle diffusion model plots have intercepts not equal to zero which diminish the possibility of intraparticle diffusion as sole rate limiting step; so, it can be concluded that kinetics was controlled by both liquid film and intraparticle diffusions simultaneously.

4. Conclusions

Green tea dredge in pyrolysed form was proven to be a good adsorbent to remove MB dye from aqueous solutions. PGT prepared at higher temperature and longer residence had the greatest uptake capacity for MB due to improved surface. Short residence time of 10 min was insufficient to produce micro-porous adsorbent with high surface area. The pH appeared to have no significant effect on MB removal and it can be recommended to treat water containing basic dyes without adjustment of pH. The dye uptake rate in the first 100 min was high while lower ppm concentrations of MB were almost completely removed.

Adsorption capacities of investigated materials were of significant magnitude when compared with other materials which are physically or chemically activated, indicating the potential of pyrolysed tea dredge as a cost-effective alternative for the removal of basic dyes. The adsorption of MB on PGT adsorbents followed pseudo-second-order kinetics.

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