Adsorptions of high concentration malachite green by two activated carbons having different porous structures

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Abstract

The adsorption of malachite green (MG) from aqueous solution by two different adsorbents (CZn5, PETNa8) were studied. Adsorbents were prepared from pine sawdust and polyethyleneterephatalate (PET) by chemical activation with ZnCl$_2$ and NaOH, respectively. The adsorption was carried out in a batch system as a function of dye concentration, pH and contact time. Both adsorbents were found to be very effective in removing the dye at high concentration with adsorption percentage in the order of CZn5 > PETNa8. The pH of dye solution in the range of 6–10, was found favorable for the removal of malachite green by using the two adsorbents at high concentrations. Equilibrium times were 120 and 90 min for CZN5 and PETNa8, respectively. Kinetics of removal MG was studied using Lagergren equation and diffusion phenomena was analyzed using Weber and Morris intraparticle diffusion plots. It was also showed that the adsorption isotherm followed Langmuir model.
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Keywords: Adsorption; Activated carbon; Chemical activation; Malachite green; Kinetics

1. Introduction

Water pollution is a very persistent problem; the intensive disposal of different toxic substance without control constitutes a real danger. Waste waters from the textile, cosmetics, printing, dying, food coloring, and papermaking, etc., are polluted by dyes [1,2]. These colored effluents pollute surface water and ground water system. Many dyes and pigments are toxic and have carcinogenic and mutagenic effects that affect aquatic biota and also humans [3–6]. Malachite green selected in this study has been extensively used all over the world as a fungicide and ectoparasiticide in aquaculture and fisheries since 1936. The dye is an organic dye, popular for dyeing materials such as leather, acrylic fibers, wool and paper [7,8].

Industries use biological treatment, coagulation, floatation, oxidation, hyper filtration and adsorption for removing

dye from the aqueous medium. Every process has its own limitations and advantages. Biological treatment is not found to be advantageous but it requires large land area and is constrained by sensitivity toward diurnal variation as well as toxicity of some chemicals, and less flexibility in design and operation. Adsorption onto granulated activated carbon (GAC) or powdered activated carbon (PAC) is widely practiced particularly for the removal of the persistent organics [9–11]. Low cost adsorbents have found use at least in laboratory scale for treatment of colored effluents with different degrees of success [12–17,2]. A large number of low cost adsorbents have been treated for dye removal. For example, Garg et al. have studied the adsorption of methylene blue on Indian rosewood sawdust, the adsorption of MG onto treated sawdust and agro-industry waste [18,19]. Kadirvelu et al. [20] have studied the dyes and metal ions from aqueous solution onto activated carbon prepared various precursor. Annadurai et al. [21] have studied the adsorption of various dyes onto cellulose based wastes. Gupta et al. [22] have studied the adsorption of MG from using bottom ash. Guo et al. [23] have investigated the removal of MG on micro- and meso-

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pores rice husk based activated carbon. Malik [24] has studied the adsorption of acid yellow 36 using activated carbon based sawdust and rice-husk. Moreover, Mittal et al. [25] have also studied the removal and recovery of MG using an agricultural waste material, de-oiled soya. In another work, the removal of Congo red from aqueous solution has been studied by coir pith an agricultural solid waste by Namasivayam and Kavitha [26]. In Addition, Jain et al. have studied the removal of basic dyes using activated carbons having $380\,m^2/g$ surface area. In this study, adsorbent dosage and dye concentration have been selected $0.01\,g/10\,ml$ and $4\text{–}6 \times 10^{-4}\,M$, respectively [27]. Adsorption of Quinoline yellow using bottom ash and de-oiled soya [28]; of anionic dyes and basic dye using activated carbons prepared from steel and fertilizer industries waste [29,30]; of Rhodamine B, fast green, methylene blue from waste water using red mud [31]; of alizarin yellow, fast green, methyl violet using bottom ash [32] have been studied by Gupta et al.

The objective of this work is to investigate the feasibility of using activated carbon prepared from pine sawdust and PET for removing malachite green (MG) from aqueous solution. The effects of contact time, initial dye concentration and pH of dye solution on the adsorption percentage are investigated.

2. Experimental

2.1. Preparation of activated carbon

First adsorbent (CZn5), was prepared from pine sawdust by chemical activation with $ZnCl_2$, activation temperature and $ZnCl_2$/pine sawdust ratio (Impregnation ratio) was selected as $500\,°C$ and 1:1, respectively. Second adsorbent (PETNa8), were prepared from polyethyleneterephatalate (PET supplied by SASA Dupont in Turkey) by chemical activation with NaOH at $800\,°C$. Impregnation ratio was 1:1. The impregnated sample was raised to the activation temperature under N_2 (100 ml/min) atmosphere with $10\,°C/min$ flow rate and hold at impregnation temperature for 1h [33,34]. After the activation, the sample was cooled down under N_2 flow and washed several times successively with hot distilled water until filtrate was neutral. The washed sample was dried at $110\,°C$. The pore structures of activated carbon were investigated by using the standard Micromeritics DFT plus software. Nitrogen adsorption was recorded at 77 K by means of a TriStar 3000 (three port) surface analyzer (Micromeritics USA). BET equation was used to calculate the specific surface area. All samples were degassed at $300\,°C$ for 3 h.

2.2. Dye solution preparation

The dye, Malachite Green, CI = 42,000, chemical formula = $C_{50}H_{52}N_4O_8$, MW = 927.03, $\lambda_{max} = 617\,nm$ was supplied by Merck (101398). A 2000 mg/l stock solution was prepared by dissolving the required amount of dye in double distilled water. Working solutions of the desired concentra-

tions were obtained by successive dilution. Dye concentration was analyzed using absorbance values with a Shimadzu UV–vis spectrophotometer (Model UV-2100S).

2.3. Adsorption experiments

In the each experiment, 25 ml dye solution of known concentration (50–2000 mg/l) and natural pH was added 0.1 g of CZn5 or PETNa8 in a 250 ml round bottom flask at room temperature ($26\,°C$). The mixture was stirred on a IKA 15 position electromagnetic stirrers. Reaction period was selected 3 h to establish the equilibrium. After this period, the supernatant liquid was filtered off using Whatman filter paper and uptake of the dye was monitored spectrophotometrically at 617 nm. Experiments were carried out at initial pH values ranging from 2 to 10; initial pH was adjusted by addition of dilute HCl or NaOH solutions. The pH values were measured by using microprocessor based pH meter (Hanna Instruments pH 211).

Contact time studies were carried out at different time (15–150 min) for CZn5 in 1000 mg/l and PETNa8 in 450 mg/l.

3. Results and discussion

3.1. Characteristics of adsorbents

Nitrogen adsorption isotherms of CZn5 and PETNa8 are shown in Fig. 1. Nitrogen adsorption isotherm of CZn5 and PETNa8 shows a Types I and II isotherm in BDDT classification [35,36]. The main adsorption characteristics of the carbon were summarized in Table 1. Pore size distributions of activated carbons are displayed in Fig. 2. It can be seen that two activated carbons have different porous structure. The total surface area of CZn8 is $1390\,m^2/g$, of which 39% is contained in micropores. Thus, the amount of mesopores
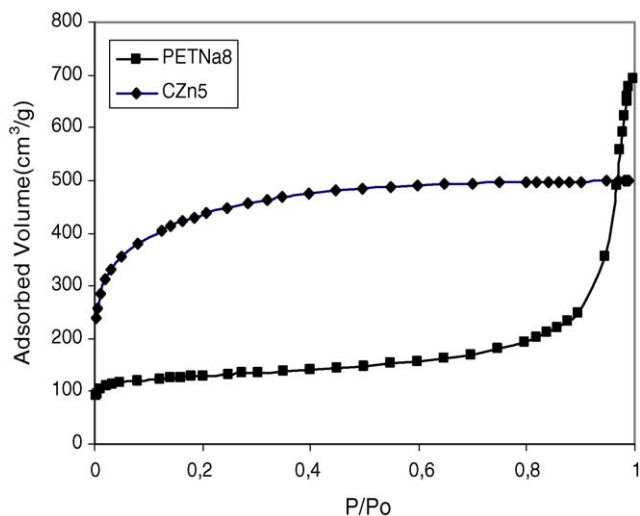

Fig. 1. Adsorption isotherms of CZn8 and PETNa8.

Table 1
Results of surface area of activated carbons

Parameter	CZn5	PETNa8
BET surface area (m^2/g)	1390	410
Micropore area (m^2/g)	544	241
Meso + macro area (m^2/g)	846[a]	169
Total volume (cm^3/g)	0.77	0.86
Micropore volume (cm^3/g)	0.30	0.13
Meso + macro volume (cm^3/g)	0.47	0.73
Average pore diameter (4V/A by BET) (nm)	2.22	8.42
Average pore diameter (4V/A by BJH)[b] (nm)	2.42	19.42

  [a] Only meso.
  [b] [37].

is 61%. It can be seen in Fig. 2 that CZn5 does not contain macropores. The total surface area of PETNa8 is 410 m^2/g, of which 59% and 41% is contained in micropores and in meso + macropores, respectively. The total volume of CZn5 is 0.77 cm^3/g, of which 43% is contained in micropores, the amount of mesopores is 57%. The total volume of PETNa8 is 0.86 cm^3/g of which 15% is contained in micropores. PETNa8 have 85% meso + macropores. It is seen that porous carbon was prepared by $ZnCl_2$ have a well-developed microporosity and lower pore size (2.22, 2.42 nm), and larger pore (8.42, 19.42 nm) will be gained by NaOH activation. Previous studies have demonstrated that porous carbons prepared by $ZnCl_2$ have a well-developed microporosity [33,34].

3.2. Effect of initial dye concentration on the adsorption of MG

The influence of the initial dye concentration of malachite green in the solutions on the rate of adsorption on CZn5 and PETNa8 was studied. The experiments were carried out at fixed adsorbent dose (0.1 g/25 ml) in the test solution at 26 °C temperature, and natural pH and at different initial concentrations of malachite green. The effect of initial concentration of dye is shown in Fig. 3. Percent adsorption efficiency of CZn5 and PETNa8 decreased with increase in initial dye concentration. Similar results have been reported for the removal of MG by different activated carbons in the litera-
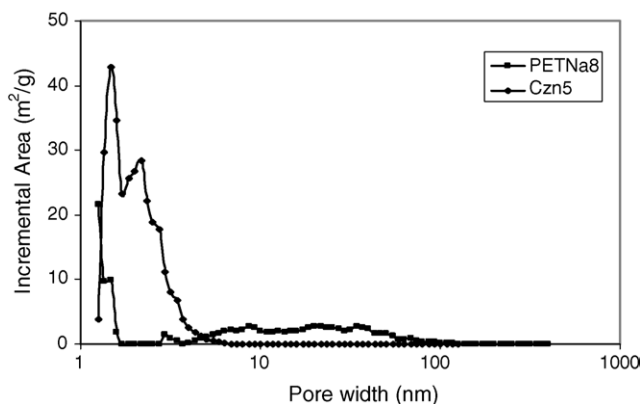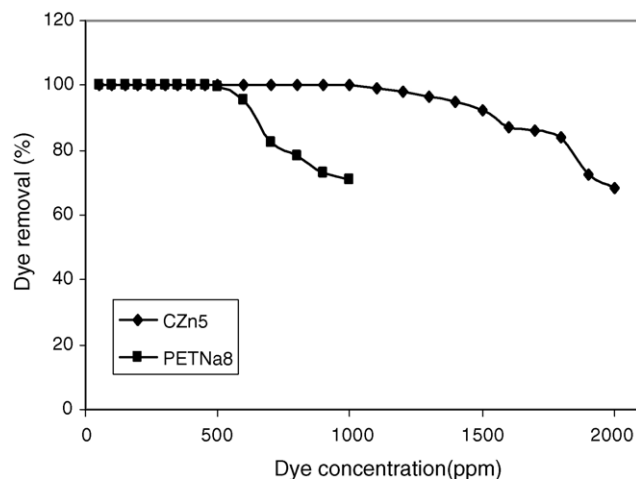

Fig. 3. Effect of initial dye concentration on malachite green removal by CZn5 and PETNa8 (adsorbent dosage = 0.1 g/25 ml; contact time = 3 h; temperature = 26 °C; pH, natural).

ture [19,20,22,23,25,38]. The percent dye removal decreased from 100 to 71.14 as the dye concentration was increased from 50 to 2000 mg/l and from 100 to 68.39 as the dye concentration was increased from 50 to 1000 mg/l for CZn5 and PETNa8, respectively.

3.3. Effect of contact time on the adsorption of MG

A plot of adsorption capacity versus adsorption time (min) was shown in Fig. 4. Contact time studies were carried out at 26 °C, natural pH with 0.1 g/25 ml adsorbent dosage. Very rapid adsorption is observed at 60 min for CZn5. This situation is explained by the activated carbon pore structure. It is seen in Fig. 2 that CZn5 have higher microporous structure (43%) than micropores (15%) of PETNa8 which may be due to increase of adsorption percentage for CZn5. After 60 min, increases in the amount of the dye adsorbed were observed slowly. Equilibrium is achieved in about 120 min at an MG concentration 1000 mg/l for CZn5 and in
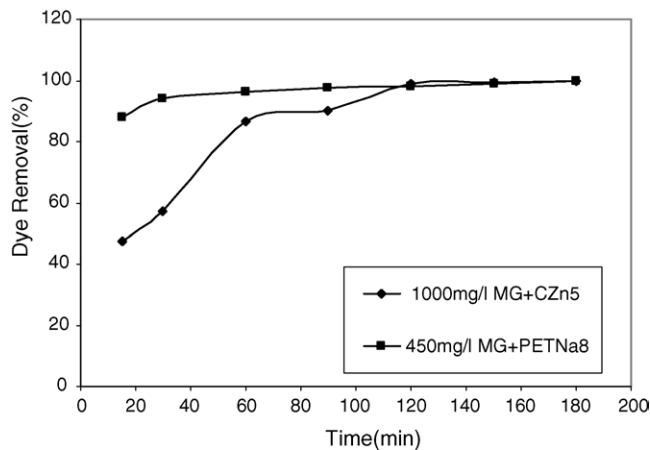

Fig. 2. Pore size distribution of CZn5 and PETNa8.

Fig. 4. Effect of contact time on malachite green removal by CZn5 and PETNa8 (adsorbent dosage = 0.1 g/25 ml; pH, natural; temperature = 26 °C.
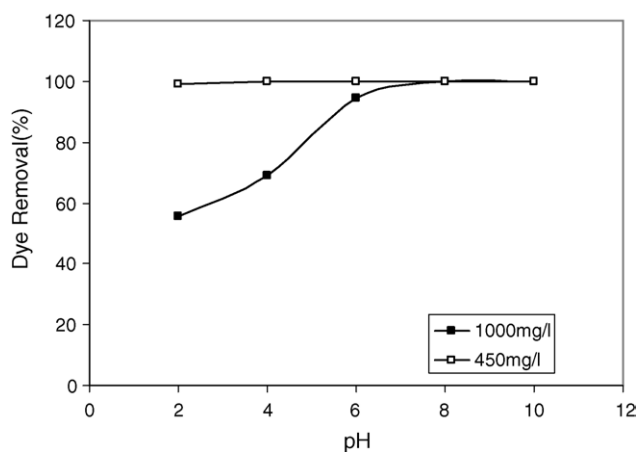
Fig. 5. Effect of pH on malachite green by PETNa8 (adsorbent dosage = 0.1 g/25 ml; temperature = 26 °C).

about 90 min at an MG concentration 450 mg/l for PETNa8; thereafter, it remains almost unchanged with respect to time.

3.4. Effect of pH on the adsorption of MG

The effect of pH on malachite green by PETNa8 and CZn5 is shown in Figs. 5 and 6, respectively. The pH experiments were studied at two different initial dye concentrations for both adsorbents. The adsorption percentage in the low concentration, (450 mg/l for PETNa8 and 1000 mg/l for CZn5) remained nearly constant in the pH range of 2.0–10.0, and therefore, the adsorption of MG on the PETNa8 and CZn5 might be attributed to weak electrostatic interactions between the dye molecules and the activated carbon surface. Adsorption of MG on the PETNa8 and CZn5 are dominantly pore diffusion at low initial dye concentration. Similar results have been reported by Garg et al. [19]. In this study, to study
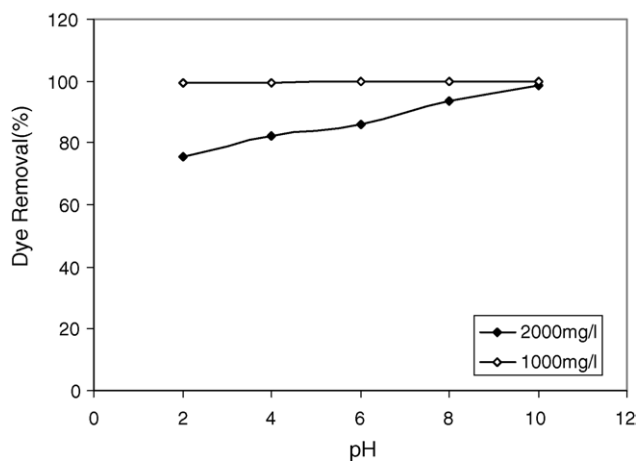

Fig. 6. Effect of pH on malachite green by CZn5 (adsorbent dosage = 0.1 g/25 ml; temperature = 26 °C.

the effect of pH on malachite green adsorption on GAC, PCSDC (sulphuric acid treated prosopis cineraria sawdust), PCSD (formaldehyde-treated prosopis cineraria sawdust), the experiments were carried out at 250 mg/l initial dye concentration with 0.4 g/100 ml adsorbent mass at 27 °C for 3 h equilibrium time. The dye adsorption by GAC was unaffected by pH changes in the range of 2–10. Both adsorbents were found to be very effective in removing the dye in all the pH values at low initial dye concentration. But, the dye adsorption by PETNa8 and CZn5 was affected by pH at high initial dye concentration. At high concentration, adsorption percentage at the low pH values is lower than adsorption percentage in the low concentration. This may be attributed to over lapping or aggregation of adsorption sites resulting in decrease in total adsorbent surface area available to MG and an increase in diffusion path length. PETNa8 had maximum dye removal (99.84%) over the pH range of 6–10, which decreased to 55.72% at pH of 2.0. By CZn5, dye uptake was minimum (75.53%) at pH of 2.0, which increased to 98.75% at pH of 10. It was suggested that the increase in adsorption depended on the properties of the properties of the adsorbent surface and the dye structure. The dye adsorption by PETNa8 and CZn5 was significantly affected over the pH range of 2–6. The adsorption was increased with pH at high initial dye concentration for the each activated carbon which may be due to the increase of the negatively charge on the carbon surface; thus, the electrostatic attraction forces between carbon surface and the MG ions were increased [39]. This however did not explain the constant dye removal by PETNa8 and CZn5 at all the studied pH values and low initial dye concentration (450 mg/l for PETNa8 and 1000 mg/l for CZn5). It might be explained by other adsorption modes, e.g., ion exchange [40].

3.5. Adsorption isotherms and kinetics

The experimental data were evaluated by using Langmuir and isotherm equation. But experimental data did not fit the Freundlich model. That's why these results are not given. The Langmuir equation has been successfully applied and given by:

$$q_e = \frac{kbC_e}{1 + kC_e} \tag{1}$$

where b is the maximum amount of adsorption corresponding to complete monolayer coverage on the surface (mg/g), C_e the adsorbate equilibrium concentration (mg/g) and k is the Langmuir constant (l/g), and b represent a practical limiting adsorption capacity when the surface is fully covered with adsorbate molecules and assists in the comparison of adsorption performance. Eq. (1) can be rearranged to linear form:

$$\frac{C_e}{q_e} = \frac{1}{kb} + \frac{C_e}{b} \tag{2}$$

A linearised plot of C_e/q_e versus C_e is obtained for both CZn5 and PETNa8 as shown in Fig. 7. The fits are quite
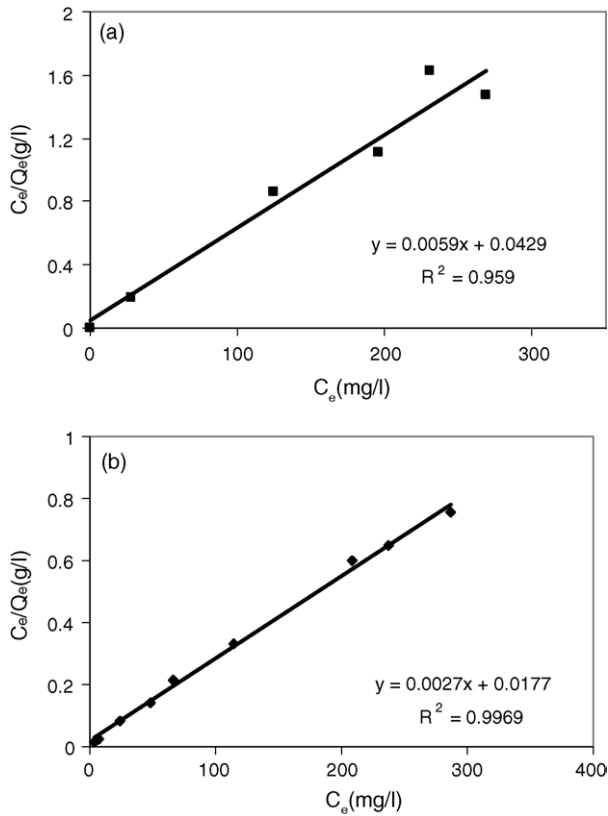
Fig. 7. Langmuir adsorption isotherms of PETNa8 (a) and CZn5 (b).

Table 2
R_L values of CZn5 and PETna8

Concentration (mg/l)	$R_L \times 10^3$
CZn5	
1000	6.29
1100	5.72
1200	5.25
1300	4.88
1400	4.50
1500	4.20
1600	3.94
1700	3.71
1800	3.50
PETNa8	
450	15.9
500	13.4
600	12.0
700	10.3
800	9.04
900	8.11
1000	7.25

well for both the activated carbons (correlation coefficients are 0.959 and 0.996 for PETNa8 and CZn5, respectively). The values of b and k are computed from the slope and intercepts. The b values determined are 169.49 and 370.37 mg/g for PETNa8 and CZn5, respectively. Data show that the CZn5 have higher adsorption capacity than that of PETNa8 and other activated carbons in the literature [41,42]. The k values determined are 0.137 and 0.158 l/mg for PETNa8 and CZn5, respectively.

One of the essential characteristics of the Langmuir isotherm could be expressed by dimensionless constant called equilibrium parameter, R_L [43]:

$$R_L = \frac{1}{1 + kC_0} \tag{3}$$

where C_0 is the initial solute concentration (mg/l). The values of R_L indicates the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 0$) or unfavourable ($R_L > 1$). Equilibrium parameters R_L are determined $0 < R_L < 1$ of PETNa8 and CZn5 for all initial solute concentration. R_L values are summarized in Table 2. The adsorption of MG on PETNa8 and CZn5 are favorable.

Several models have been proposed to express the adsorption mechanism of solute molecules onto an adsorbent: (a) pseudo-first-order kinetic model, (b) intraparticle diffusion model and (c) pseudo-second-order kinetic model.

A pseudo-first-order kinetic model of Lagergren [44] is given by:

$$\log(q_e - q) = \log q_e - \frac{k_1}{2.303}t \tag{4}$$

In this equation the average value of the rate constant, k_1 (min^{-1}) for adsorption of MG on PETNa8 and CZn5 can be calculated from this equation, where q_e and q are the amounts of the dye adsorbed at equilibrium and at time t, in mg/g, respectively and k_1 is the first-order rate constant. The half adsorption time, $t_{1/2}$ (min) is given by:

$$t_{1/2} = \frac{\ln 2}{k_1} \tag{5}$$

An intraparticle diffusion model of Weber and Moris [45] is shown as:

$$Q_t = k_{int}t^{1/2} + C \tag{6}$$

where Q_t is the amount of dye adsorbed (mol/g) at time t, C is the intercept. The values of intercept give an idea about the boundary layer thickness, i.e. the larger intercept, the greater is the boundary layer effect. k_{int} is the intra-particle diffusion rate constant (mol/(g min$^{1/2}$)). The plot may present multilinearity, indicating that a few steps take place. The first, sharper portion is attributed to the diffusion of adsorbate through the solution to the external surface of adsorbent or the boundary layer diffusion of solute molecules. The second portion describes the gradual layer adsorption stage, where intraparticle diffusion is rate limiting. The third portion is attributed to the final equilibrium stage.

A pseudo-second-order kinetic model of Ho and McKay [46,47] is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{7}$$

where k_2 (g/(mol min)) is the rate constant for pseudo-second-order model, q_e and q_t are amount of solute adsorbed per unit adsorbent at equilibrium and any time, in mol/g respectively. Herein, the initial adsorption rate (mol/(g min)), $h = k_2 q_e^2$.

First, the values of $\log(q_e - q)$ were calculated from the kinetic data of Fig. 4 and plotted against time in Fig. 8. The plots of PETNa8 (Fig. 8a) and CZn5 (Fig. 8b) are found to be linear, indicating that Lagergren's equation is applicable to the dye adsorption and the adsorption is a first-order process. First-order rate constants calculated from slope of the plots (Fig. 8) are found to be 4.46×10^{-2} and 3.06×10^{-2} l/min for CZn5 and PETNa8, respectively.

Second, the plots of Q_t versus $t^{1/2}$ for intraparticle diffusion model given in Eq. (5) is shown in Fig. 8. The external surface sorption (stage 1) is absent because of completion before 5 min. The plots of Q_t versus $t^{1/2}$ are found to be straight line (stage 2). The straight line refers to intraparticle diffusion effects [48]. The k_{int} values for CZn5 (from Fig. 8c) and PETNa8 (from Fig. 8d) are determined as 2.3×10^{-6} and 1.11×10^{-7} (mol/(g s$^{1/2}$)), respectively. At a certain time limit (about 20 min), the curves reveal a linear characteristic that the intraparticle diffusion controls the adsorption process.

Third, the values of the rate constants for MG onto PETNa8 (from Fig. 8e) and CZn5 (from Fig. 8f) were cal-
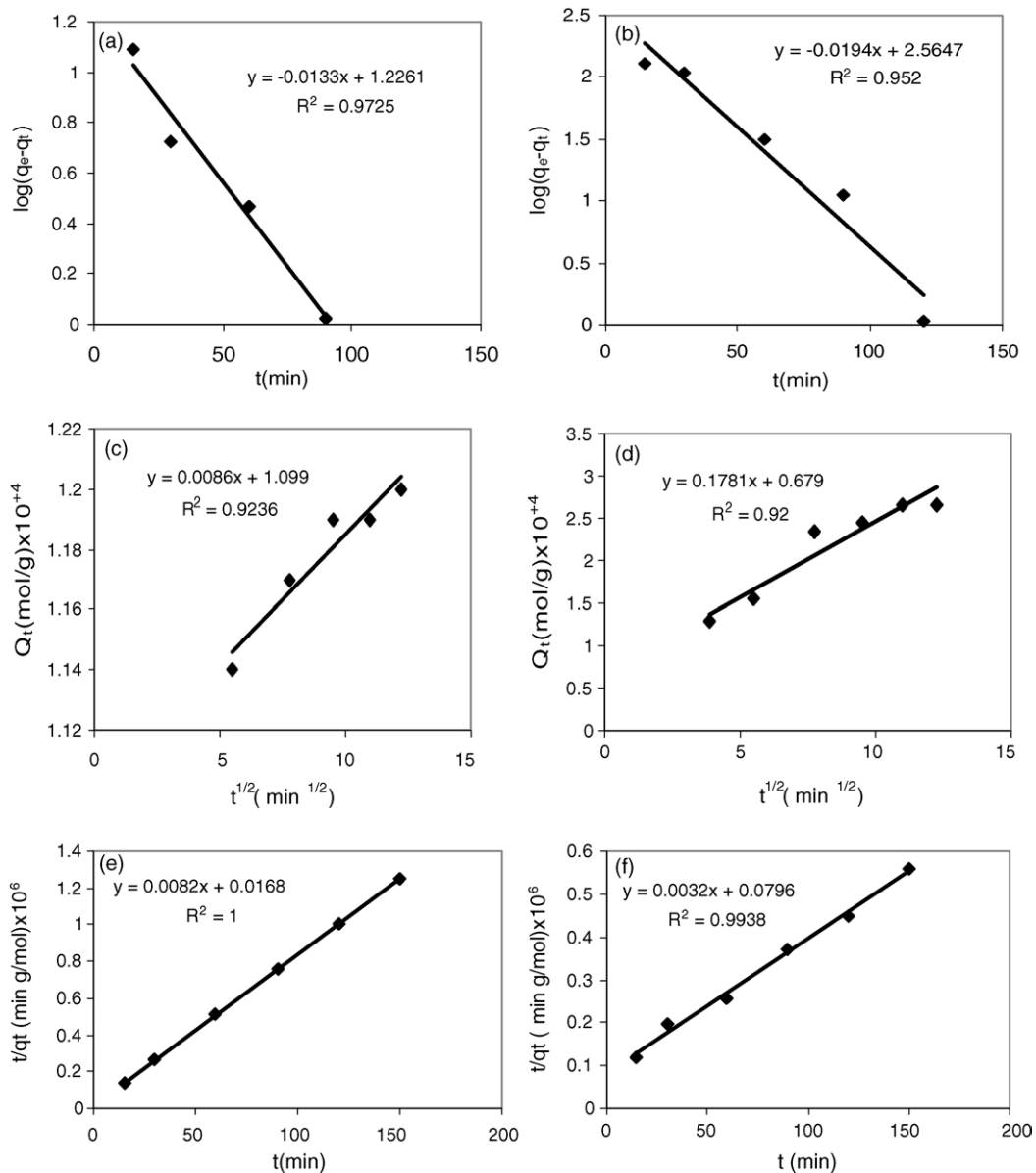

Fig. 8. Plots adsorption kinetic equation for adsorption of MG onto PETNa8 and CZn5, the pseudo-first-order adsorption kinetics of MG onto (a) PETNa8 and (b) CZn5; intraparticle diffusion kinetics of MG for (c) PETNa8 and (d) CZn5; the second-order adsorption kinetics of MG onto (e) PETNa8 and (f) CZn5.

Table 3
The kinetic parameters for adsorption MG onto CZn5 and PETNa8

Sample	k_1[a]	$t_{1/2}$[b]	$R_1^{2\,c}$	k_{int}[d]	$R_{int}^{2\,e}$	k_2[f]	h[g]	$R_2^{2\,h}$
CZn5	4.46×10^{-2}	15.51	0.952	2.3×10^{-6}	0.920	1.29×10^8	12.56	0.994
PETNa8	3.06×10^{-2}	22.63	0.972	1.11×10^{-7}	0.924	4.00×10^9	59.53	1

[a] The rate constant of the pseudo-first-order reaction (min^{-1}).
[b] The half adsorption time (min).
[c] Correlation coefficient from pseudo-first-order equation.
[d] Intraparticle diffusion rate constant ($\text{mol}/(\text{g s}^{1/2})$).
[e] Correlation coefficient from intraparticle diffusion equation.
[f] The rate constant of the pseudo-second-order reaction ($\text{g}/(\text{mol min})$).
[g] Initial adsorption rate from the pseudo-second-order kinetics ($\text{mol}/(\text{g min})$).
[h] Correlation coefficient from the pseudo-second-order equation.

culated from slopes and intercepts of the pseudo-second-order plots. The second-order rate constant values are determined as 1.29×10^8 and 4×10^9 g/(mol min) for CZn5 and PETNa8, respectively. The initial adsorption rate values of CZn5 and PETNa8 are 12.56 and 59.53 mol/(g min) (from $h = k_2 q_e^2$).

The R^2 values obtained from pseudo-second-order kinetic model are greater than those of other rate laws. Also, as shown in Table 3, the values of R^2 are higher than 0.99. These indicate that the adsorption perfectly complies with pseudo-second-order reaction [16].

The kinetic parameters for adsorption MG onto CZn5 and PETNa8 are summarized in Table 3.

4. Conclusion

Adsorptions of MG on to activated carbon have been carried out by other investigators in the literature. Those investigations have been studied at low initial dye concentration. The results of present investigation showed that CZn5, PETNa8 prepared from pine sawdust and polyethyleneterephatalate (PET) have higher efficiency than other activated carbon used to remove MG in literature. Adsorption percentage decreases while initial dye concentration increase, but CZn5 has high adsorption efficiency than PETNa8 at high dye concentration. Maximum dye was removed within 120 and 90 min for CZn5 and PETNa8, respectively. Initial dye solution pH over the range of 6–10 was optimum for dye removal by CZn5 and PETNa8. Adsorption followed the Langmuir model. Batch studies indicated that removal kinetics are second-order expressions, however, the intraparticle diffusion of the dye molecules within the particles was found to be rate controlling in these adsorption processes after 20 min contact. The present work revealed that the pine sawdust and PET were the promising materials for the removal of dyes from aqueous solution.

Acknowledgement

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