Desalination and Water Treatment
www.deswater.com

28 (2011) 164–173
April

doi: 10/5004/dwt.2011.2216

Adsorption of reactive dye from aqueous solutions by compost

Gordon McKay[a], Mahdi Hadi[b,*], Mohammad Taghi Samadi[c], Ali Reza Rahmani[c],
Mehri Solaimany Aminabad[c], Fatemeh Nazemi[c]

[a]*Department of Chemical and Biomolecular Engineering, Hong Kong University of Science and Technology, Clearwater Bay, New Territory, Hong Kong, SAR*
[b]*Environmental Health Research Center, Faculty of Health, Kurdistan University of Medical Sciences, Pasdaran St., Sanandaj, Iran Tel. +98 9189061738; Fax: +98 8716626969; email: hadi_rfm@yahoo.com*
[c]*Department of Environmental Health Engineering, School of Public Health, Center for Health Research, Hamadan University of Medical Sciences, Hamadan, Iran*

Received 9 August 2010; Accepted 2 November 2010

ABSTRACT

The adsorption of a reactive dye, Ariazol Scarlet 2G (AS2G) (C.I.: Reactive Red 234), onto compost, from aqueous solutions, was studied in a batch system. The effects of initial dye concentration, initial pH and sorbent mass have been studied. Four two-parameter isotherm models–Langmuir, Freundlich, Temkin and Harkins Jura – were used to fit the experimental data using a nonlinear trial-and-error method. The best fit of the adsorption isotherm data was obtained using the Langmuir model (X^2 = 1.97E−03). A comparison of kinetic models applied to the adsorption of AS2G on compost was evaluated using the pseudo-second order, Elovich and Lagergren first-order kinetic models. Results showed that the pseudo-second order kinetic model was found to agree well with the experimental data. An intra-particle diffusion model analysis showed multi-linearity with two steps and a non-zero intercept which indicated the intra-particle diffusion model is not a dominant rate controlling mechanism in the sorption of AS2G by compost.

Keywords: Adsorption; Adsorption isotherms; Reactive dye; Kinetic models; Compost

1. Introduction

Improper treatment and disposal of dye-contaminated wastewaters from textile, dyeing, printing, ink and related industries have provoked serious environmental concerns all over the world [1]. Different types of dyes are currently manufactured and the largest consumers of these dyes are the textile industries [2], paper and pulp industries [3], pharmaceutical industries [4], tannery [5], and Kraft bleaching [6] industries. Dyes, as they are intensively colored, cause special problems in effluent discharges, their effects are aesthetically more displeasing rather than hazardous, and can prevent sunlight penetration thus decreasing photosynthetic activity in aquatic environments. Furthermore, some azo dyes that cause the effluent color have been implicated as being mutagenic/carcinogenic as well as toxic to aquatic life [7,8]. Dye concentrations may be well below 1 ppm, i.e., lower than many other chemicals found in wastewaters, but are still visible even at such low concentrations [9]. Hence, the removal of dyes from such wastewaters is the major environmental concern of much research papers.

Among many structural varieties of dyes that fall into either the cationic, non-ionic, or anionic type, anionic dyes are the direct, acid and reactive dyes [10]. Brightly colored water-soluble reactive and acid dyes are the most problematic, as they tend to pass through conventional treatment systems unaffected with relative ease [11]. The color fastness, stability and the resistance

---

*Corresponding author.

of dyes to degradation have made color removal from industrial wastewaters difficult. They are not readily degraded under the aerobic conditions prevailing in biological treatment plants [12] and therefore effluents, in most cases are colored upon leaving the plant.

In general, there are four main methods of reducing color in textile effluent streams: physical methods, chemical methods, biological methods and emerging technologies [13]. Among the physico-chemical processes, adsorption technology is considered to be one of the most effective and proven technologies having potential application in both water and wastewater treatment [14]. Activated carbon is the most commonly used sorbent of organics removal by adsorption [15]. Although commercial activated carbon is the preferred sorbent for color removal, its widespread use is restricted due to high cost. As such, alternative non-conventional sorbents have been investigated. It is well known that natural materials such as soil, waste materials from industry and agriculture and biosorbents can be obtained and employed as inexpensive sorbents [16]. Sorption of polycyclic aromatic compounds to colloid dispersions of humic substances [17], adsorption of herbicides [18–20] and pesticides [21–23] in soils are some interesting examples.

Many investigations have studied the feasibility of using inexpensive alternative materials like date pit [24], mansonia wood sawdust [25], bamboo carbon [26], hydrolyzed oak sawdust [27], eucalyptus bark [28] and pine-cone [29,30] as carbonaceous precursors for the dye removal. Compost is a porous, solid matrix that is capable of adsorbing various organic and inorganic compounds [31], and appears to be a feasible alternative to activated carbon. The objectives of the present study were to assess the ability of compost to remove a reactive dye, Reactive Red 234(AS2G) from aqueous solution and to evaluate adsorption kinetic models. In one study Tsui et al. [32] reported the capacities of a compost for the sorption of several acidic, basic, direct and reactive dyes. They reported compost has relatively low sorption capacity for the removal of reactive dyes in comparison with acidic and basic dyes. Our study for the sorption of another reactive dye, Reactive Red 234, shows the compost has considerably more effectiveness for this reactive dye.

This study is the first kinetic study on the use of compost to treat of dye-contaminated water with the regards to the study of several isotherm models (Langmuir, Freundlich, Temkin and Harkins-Jura) and several kinetic models (pseudo-second order, first-order and Elovich) and intra-particle diffusion model. The factors studied include the influence of initial dye concentration, initial solution pH, and mass of sorbent on the sorption kinetics. Pearson's chi-square statistic was used to evaluate the goodness-of-fit of isotherm and kinetic models to experimental data. Residual mean square error (RMSE) was also used as a measure of the differences between model predicted values and the values actually observed from the experimental data. The isotherm and kinetic models parameters were determined by the nonlinear, trial-and-error method using OriginPro 8 SR1 Software.

2. Materials and methods

2.1. Adsorbent and dye

The cheap and widely available sorbent used in this study is compost, obtained from Kermanshah municipal solid waste recovery and composting company in the west of Iran. The compost was derived from the thermophilic processing of organic municipal solid wastes. The compost passed through an 8 mesh sieve and the residuals on 30 mesh sieve were used as sorbent in this study. The chemical characteristics of the compost are shown in Table 1. The N2-BET surface area of compost is approximately 3 m^2/g [33]; such low surface area measurements are subject to some inaccuracy. One reactive dye, Ariazol Scarlet 2G (C.I.: Reactive Red 234), was used in this study. This reactive dye is based on the vinyl sulphonyl reactive system. AS2G was bought from Alvansabet Co. in Hamadan.

Based on the Boehm titration [34] results, the equivalent numbers of each basic and acidic groups based on the solution neutralization were calculated. As shown in Table 2, small concentrations of basic groups and considerable concentrations of acidic groups are present on the surface of compost. If the acidic groups are divided into three individual groups, large concentrations of phenolic groups are found on the surface of compost sorbent. Compared to phenolic and lactonic groups, carboxylic groups are less abundant on compost surface.

2.2. Batch equilibrium method and dye concentration measurement

Adsorption processes were studied in 100 ml Erlenmeyer flasks inside an incubator container (Model TS

Table 1
Chemical composition of the compost sorbent

Parameter	Level	Parameter	Level (mg g^{-1})
N	1.43%	Fe	12.6
P	0.53%	Mn	0.40
K	1.60%	Zn	0.38
Organic C	16.31%	Cu	0.85
pH (1:2.5)[a]	8.5	Pb	0.42
Ec × 10^{-3} (1:2.5)[a]	18	Cd	0

[a] Mass of compost (g): volume of dionized water (ml).
Source: Kermanshah municipal solid waste recovery and composting company in the west of Iran.

Table 2
Surface functional groups of compost

Group	Value (eq g^{-1})
All basic groups	2.16×10^{-3}
All acidic groups	4.58×10^{-3}
Carboxylic	0.83×10^{-5}
Lactonic	1.75×10^{-3}
Phenolic	2.75×10^{-3}

606/2-i). The contents of all Erlenmeyer flasks were mixed thoroughly using magnetic stirrers with a fixed setting to achieve a constant speed; the reproducibility of the agitation was confirmed by checking duplicate samples. The variables studied were initial dye concentration, initial pH solution and adsorbent mass. The balance used was a Sartorius ED124S and the pipettes were Precicolour HGB Germany.

To measure dye concentrations in all experiments, 2 ml samples were taken at irregular intervals and at the equilibrium time for doing kinetic and equilibrium studies, respectively. After the agitation was stopped most, but not all, of the suspended adsorbent material settled. Consequently, a 2 ml sample was taken for final clarification. A volume of 2 ml distilled water was added to each sample and all samples were centrifuged at 3800 rpm (Model – 301 Sigma) for 30 min. It should be noticed that the adsorption time was not included in length of centrifugation time in this study. A range of centrifugation times were tested to remove small amounts of residual solids and it was found that optical density measurement values only changed a small amount on average about 5%. Then the dye concentrations in the samples were measured spectrophotometrically at the wavelength corresponding to the maximum absorption wavelength (λ_{max}), 505 nm, using a UV-1700 Pharmaspec Shimadzo spectrophotometer. The amount of dye adsorbed onto the compost sorbent, q_e (mg g^{-1}) was calculated as follows:

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{1}$$

where C_0 (mg l^{-1}) and C_e (mg l^{-1}) are the initial and equilibrium concentrations of dye, respectively. q_e (mg g^{-1}) is the amount of dye sorbed, W (g) the mass of the compost sorbent and V (l) is the volume of the liquid phase. The residual centrifuged sample was found to contain a very small yellow discharge from the compost which did not interfere with the dye adsorption band.

2.3. Effects of initial dye concentration

The effect of initial dye concentration on the sorption was studied in three Erlenmeyer flasks at a fixed temperature, 20.3°C, and initial pH 7.5 ± 0.2. A 2 g sample of compost with 30 mesh size was added to each 100 ml volume of AS2G dye solution. The initial concentrations of dye solutions were 202.3, 150 and 97.3 mg l^{-1}.

2.4. Effects of compost mass

Various amounts of compost sorbent of 0.5, 2 and 4 g were added to each 100 ml dye solution (100 mg l^{-1}) at pH 7.4 ± 0.3. The flasks were sealed and the contents stirred for 45 h at 20.3°C.

2.5. Effect of initial solution pH

The initial pH of the solution is an important factor which must be considered during sorption studies. A 4 g mass of compost was added to each 100 ml flask of dye solution (98.13 mg l^{-1}) at 20.3°C. The experiments were carried out at pH 2.3, 5, 7 and 9.5 using H_2SO_4 (0.1 M) and NaOH (0.1 M) for pH adjustment. A 100 ml micropipette (Model Transferpette) and a digital pH meter (Model Sartorius Professional Meter PP-50) were used for pH adjustment.

2.6. Chi-square and residual error analysis

To evaluate the fit of kinetic and isotherm equations to the experimental data, the residual root mean square error (RMSE) analysis was used to measure the kinetic and isotherm constants. RMSE can be defined as:

$$\text{RMSE} = \sqrt{\frac{1}{N-2}\sum_{i=1}^{N}\left(q_{e,\exp} - q_{e,calc}\right)^2} \tag{2}$$

The chi-square test [35] is given as

$$X^2 = \sum_{i=1}^{N}\frac{\left(q_{e,\exp} - q_{e,calc}\right)^2}{q_{e,calc}} \tag{3}$$

If data from the model are similar to the experimental data, X^2 will be a small number; if they are different, X^2 will be a large number.

The subscripts "exp" and "calc" show the experimental and calculated values and N is the number of observations in the experimental data; the smaller the RMSE value, the better the curve fitting.

3. Results and discussion

3.1. Equilibrium modeling

Equilibrium data are employed for representing the equilibrium states of an adsorption system. These data can give useful information regarding the adsorbate, the adsorbent, and the adsorption process.

Four adsorption isotherm models, Langmuir [36], Freundlich [37], Temkin [38] and Harkins-Jura [39] were used to describe the equilibrium between adsorbed dye on the adsorbent and dye in solution at constant temperature.

The Langmuir equation, which is valid for monolayer sorption onto a surface with a finite number of identical sites, is given by Eq. (4):

$$q_e = \frac{abC_e}{1 + bC_e} \tag{4}$$

where C_e (mg l^{-1}) is the equilibrium concentration of dye in solution, a (mg g l^{-1}) is the maximum amount of adsorbed dye per unit mass of compost sorbent corresponding to complete coverage of the adsorptive sites, q_e (mg l^{-1}) refer to the amount of dye adsorbed at equilibrium time and b (l mg^{-1}) is the Langmuir constant related to the energy of adsorption.

The essential characteristics of the Langmuir isotherm can be expressed in terms of the dimensionless constant separation factor or equilibrium parameter, R_L [40] which is defined by Eq. (5):

$$R_L = \frac{1}{1 + bC_0} \tag{5}$$

where b is the Langmuir constant and C_0 (mg l^{-1}) is the initial concentration of the sorbate in solution. The values of R_L indicates the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$).

The empirical Freundlich equation based on sorption onto a heterogeneous surface is given by Eq. (6):

$$q_e = k_f C_e^{1/n} \tag{6}$$

where C_e (mg l^{-1}) is the equilibrium concentration and q_e (mg g^{-1}) is the amount adsorbed dye per unit mass of the adsorbent. The constant n is the Freundlich equation constant that represents the parameter characterizing quasi-Gaussian energetic heterogeneity of the adsorption surface [41]. The Freundlich constant, n, gives an indication on the favorability of adsorption. It is generally stated that values of n in the range of 2–10 represent good, 1–2 moderately difficult, and less than 1 poor adsorption characteristics [42].

Various amounts of compost sorbent of 0.5, 1, 2, 3, 4, 5, 6 and 7 g were added to each 100 ml dye solution (37.0 mg l^{-1}) at pH 7.5. The flasks were sealed and the contents stirred for 3 d at 20.3°C. The adsorption isotherms and constant parameters of the isotherm equations were calculated by the nonlinear trial-and-error method [43]. Fig. 1 shows the theoretical and experimental adsorption data and the values of the isotherm parameters and related Chi-square values are shown in Table 3. As shown, the Freundlich and Langmuir isotherms were generally a satisfactory fit to the experimental data as indicated by coefficient of determination (R^2) and Chi-square statistic. However, the Langmuir isotherm shows a better fit to adsorption data than the Freundlich isotherm. The fact that the Langmuir isotherm fits the experimental data well may be due to homogeneous distribution of active sites on the compost

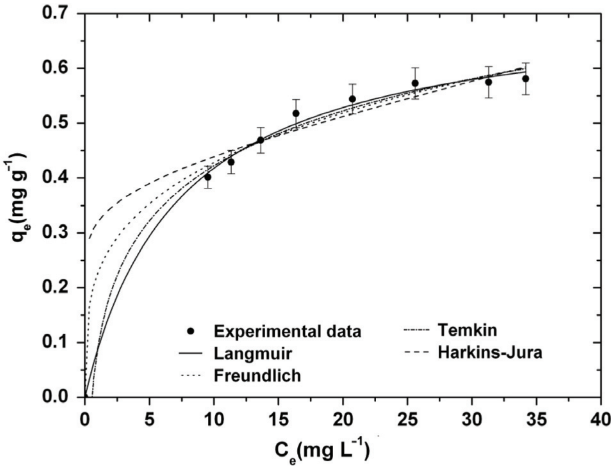

Fig. 1. Theoretical isotherms and experimental data.

Table 3
Two-parameter isotherms constants

Model	Parameter symbol	Parameter value	Standard error	R^2	X^2	RMSE
Temkin	b_T	16.90	1551	0.991	3.70E−03	1.45E−02
	K_T	1.867	0.610			
Harkins-Jura	B	4.915	0.286	0.981	4.79E−01	1.42E−01
	A_H	0.503	0.081			
Freundlich	K_F	0.226	0.022	0.988	5.28E−03	1.72E−02
	n	3.615	0.410			
Langmuir	a	0.718	0.020	0.995	1.97E−03	1.06E−02
	b	0.139	0.014			

surface; since the Langmuir equation assumes that the adsorbent surface is energetically homogeneous [36]. The parameters *a* and *b* for the Langmuir model were obtained 0.718 mg g^{-1} and 0.139 l mg^{-1}, respectively.

It is apparent that the value of the Freundlich constant, *n*, obtained indicates favourable adsorption characteristics, as it is equal to 3.61, and although the capacity is quite low. Moreover, R_L values indicate favorable adsorption of AS2G onto compost particles as it is decreased from 0.069 to 0.034 with an increase in concentration from 97.3 to 202.3 mg l^{-1} and lies between 0 and 1 at all concentrations tested (Table 4).

The derivation of the Temkin isotherm [38] assumes that the fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation [44]. The Temkin isotherm has generally been applied in the following form [45]:

$$q_e = \frac{RT}{\Delta Q} \ln \left(K_T C_e \right) \tag{7}$$

where, *T* (K) is the absolute temperature, *R* is the universal gas constant (8.314 kJ $kmol^{-1}$ K^{-1}), K_T is the equilibrium binding constant (l mg^{-1}), and ΔQ is the variation of adsorption energy (kJ mol^{-1}). These parameters were calculated by nonlinear regression fitting. The variation of adsorption energy, $\Delta Q = (-DH)$, is positive for AS2G dye and is 16.9 kJ mol^{-1}. This indicates the adsorption reaction is exothermic [46]. The theoretical isotherm curve is compared with the corresponding experimental data in Fig. 1 and the obtained error function values are presented in Table 3. The experimental equilibrium curve is relatively close to that predicted by the Temkin model. Consequently, the Temkin isotherm can describe the adsorption isotherms of AS2G onto compost acceptably. X^2 and RMSE values for the Langmuir and the Temkin models were obtained 0.002, 0.011 and 0.004, 0.015, respectively. The comparison of the error functions X^2 and RMSE show that the Langmuir model describes the experimental data better than Temkin model.

The Harkins-Jura [39] adsorption isotherm can be expressed as:

$$q_e = \left(\frac{A_H}{B - \log C_e} \right)^{1/2} \tag{8}$$

Table 4
Parameters of the langmuir isotherm

C_0 (mg l^{-1})	*a* (mg g^{-1})	*b* (l mg^{-1})	R_L
97.3	0.718	0.138	0.069
150	0.718	0.138	0.046
202.3	0.718	0.138	0.034

where A_H and *B* are the isotherm parameter and the constant, respectively. The isotherm equation accounts for multilayer adsorption and can be explained by the existence of a heterogeneous pore distribution. The theoretical and experimental isotherm data according to the Harkins-Jura [39] isotherm model for the sorption of AS2G dye onto compost are shown in Fig. 1. According to the obtained error functions in Table 3, this model shows the poorest agreement with experimental data and this result indicates adsorption of dye onto the compost cannot be described well the assumptions of the Harkins-Jura model.

In paper by Tsui et al. [32] some values for the adsorption of reactive dyes on compost are presented. The highest adsorption value for Reactive Red 2 dye reported by using the experimental data as equal to antilog 0.5, which is about 0.003 mg g^{-1} (Fig. 3b of Ref. [24]). The maximum point adsorption capacities for other dyes on compost in Fig. 3b of Tsui et al. [32] are about 0.080, 0.014, 0.005 and 0.002 mg g^{-1} for Basic Blue 9, Acid Black 24, Acid Orange 74 and Direct Orange 39 dyes, respectively. These values are significantly lower than the data for the Reactive Red 234 dye obtained in the present study which is 0.718 mg g^{-1}. More work needs to be done to explain why this is the case.

3.2. Kinetic studies

For evaluating the adsorption kinetics of AS2G dye, pseudo-second order [46], first-order [48] and Elovich [49] kinetic models were used. The conformity between experimental data and the model-predicted values was expressed by the nonlinear Chi-square statistic.

3.2.1. Kinetic models

3.2.1.1. The pseudo-second order model. The pseudo-second order rate equation is expressed as Eq. (9):

$$q_t = \frac{q_e^2 k_2 t}{q_e k_2 t + 1} \tag{9}$$

where k_2 is the rate constant of pseudo-second order model (g $mg^{-1}$$min^{-1}$).

The pseudo-second order kinetic model considers the rate-limiting step as the formation of a chemisorptive bond involving sharing or exchange of electrons between the sorbate and the sorbent [50]. In contrast to the other kinetic models, it predicts the behavior over the whole range of studies supporting a pseudo-second order equation and is in agreement with chemisorption being the rate controlling step. An inverse relationship was observed in the values of the overall pseudo-second order reaction rate (k_2) and initial dye concentration based on Table 5 data. This was consistent with the observations reported by Low et al. [51] for the biosorption of basic dyes by water hyacinth roots and Waranusantigul et al. [52] for basic dye biosorption by giant duckweed (Spirodella Polyrrhiza).

An empirical correlation was made between pseudo-second order overall rate parameters, k_2 and the initial dye concentration [53,54]. A straight line logarithmic plot with a coefficient of determination of 0.769 was obtained between log k_2 and log C_0 can be expressed as:

$$\text{Log } k_2 = -0.725 \log C_0 + 2.362 \qquad (10)$$

The negative slope obtained in this relationship could be related to the inverse relationship in the values of the pseudo-second order rate constant and the initial dye concentration.

3.2.1.2. The Elovich model. The Elovich kinetic model is generally expressed as:

$$q_t = \frac{\ln \alpha\beta}{\beta} + \frac{1}{\beta} \ln t \qquad (11)$$

where α is the initial adsorption rate (mg g^{-1} min^{-1}), β is the desorption constant (g mg^{-1}) during any one experiment.

Table 5 shows the kinetic parameters and the values of Chi-square statistic for Elovich and first order models. Chi-square statistic values for Elovich model can be comparable with pseudo-second order model. Comparison of Chi-square statistic for Elovich and pseudo-second order models show that the latter described the rate of dye sorption onto compost better than the Elovich model.

3.2.1.3. Lagergren first-order model. The Lagergren first-order kinetic model is expressed as Eq. (10):

$$q_t = q_e - \exp\left(\ln q_e - k_1 t\right) \qquad (12)$$

where k_1 (g mg^{-1} min^{-1}) is the rate constant of the Lagergren first-order model.

As can be seen from Table 5, the values of the Chi-square statistic of the first-order model cannot be comparable with other models. The pseudo-first order equation of Lagergren did not fit well over the range of contact times and did not describe well the rate of dye sorption onto the compost.

3.2.2. Effects of compost mass

Fig. 2 shows the adsorption of AS2G as a function of compost mass. It seems that with an increased mass of compost, more surface area is made available and therefore the amount of absorbed dye per unit surface area of

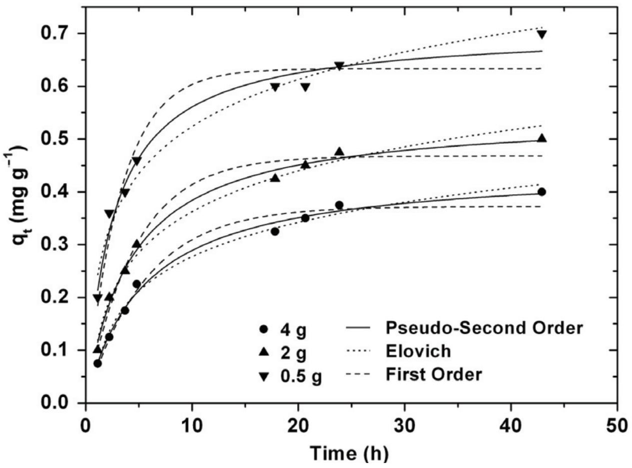

Fig. 2. Kinetics of AS2G dye adsorption onto compost at various sorbent masses (pH = 7.4 ± 0.3, Temperature = 20.3°C, Dye concentration = 100 mg l^{-1}).

Table 5
Kinetic parameters of dye uptake by compost

Experimental parameters				Elovich model				First-order model			Pseudo-second model		
m (g)	pH	C_0 (mg l^{-1})	q_e (mg g^{-1})	β	α	X^2	RMSE	k_1	X^2	RMSE	k_2	X^2	RMSE
0.5	7.4	100	0.69	7.7	0.75	4.14E−03	0.026	0.3	1.06E−02	0.042	0.543	3.81E−03	0.0251
2	7.4	100	0.49	8.9	0.28	1.68E−03	0.016	0.21	2.91E−03	0.022	0.433	8.95E−04	0.0122
4	7.4	100	0.39	10.6	0.18	9.95E−04	0.012	0.17	2.21E−03	0.019	0.408	7.41E−04	0.0111
2	7.5	97.3	0.38	45.1	17650	7.03E−04	0.01	1.3	2.09E−03	0.018	7.61	4.24E−04	0.0084
2	7.5	150	0.5	42.7	1.63	7.03E−04	0.01	1.52	1.69E−03	0.016	7.518	5.39E−05	0.0029
2	7.5	202.3	0.68	25.4	36240	1.48E−03	0.015	1.32	5.63E−03	0.03	4.302	5.32E−04	0.0094
4	2.3	98.1	1.45	6.8	118	1.23E−02	0.045	0.86	7.13E−02	0.109	0.937	9.57E−04	0.0451
4	4.7	98.1	0.77	13.1	72.2	4.69E−03	0.027	0.85	1.31E−02	0.046	1.779	9.57E−04	0.0126
4	7.1	98.1	0.44	25.8	146	1.61E−03	0.016	0.99	4.17E−03	0.026	3.757	6.16E−04	0.0101
4	9.2	98.1	0.35	25.5	10.7	2.27E−03	0.019	0.66	3.04E−03	0.022	3.087	7.06E−04	0.0108

absorbent decreases [54]. The pseudo-second order kinetic model fits well to experimental data at various compost masses and showed a better degree of fitness in comparison with the Elovich and the first-order kinetic models.

Table 5 shows the pseudo-second order kinetic model parameters of AS2G sorption by compost at several experimental conditions. It can be seen that the dye removal efficiency increases from 3.5% to 16 % and the amount of adsorbed dye per unit of compost mass decreases from 0.7 to 0.4 mg g^{-1} with the increase of compost sorbent mass from 0.5 to 4 g for a given initial dye concentration and pH.

3.2.3. *Effects of initial dye concentration*

As shown in Fig. 3, the amount of absorbed dye per unit mass of compost increased rapidly in the first five hours and slowly until equilibrium. In addition, equilibrium data in Table 5 reveals that, the percent of removal efficiency decreased from 15.50% to 13.28 % with the increase of initial dye concentration from 97.3 to 202.3 mg l^{-1}. This may be due to the fact that increased bulk liquid phase dye concentration increases with increasing C_0 and therefore increases the rate of chemisorption at the surface adsorption sites of the compost [55]. The pseudo-second order kinetic model showed satisfactory fits with the experimental data with low Chi-square values (Table 5). The equilibrium sorption capacity (q_e) increased from 0.377 to 0.672 mg g^{-1} with the increase of initial dye concentration from 97.3 to 202.3 mg l^{-1}.

3.2.4. *Effects of initial solution pH*

The results showed that the adsorption capacity decreases significantly with the increase in the pH. This trend can be explained by the fact that low acid pH range might correspond to the rate of dissociation of the AS2G dye with maximum ionization of the molecule which enhances the electrostatic attraction between anionic and cationic species of both sorbate and adsorbate [56]. Moreover, high pH ranges may be attributed to the increase of hydroxyl ions leading to formation of aqua complexes thereby retarding the dye sorption [57]. As seen from Fig. 4 the pseudo-second order kinetic model shows well fits with experimental data at various pH values. The values of the rate constant, the equilibrium capacity, and the removal efficiencies are shown in Table 5. Sorption capacity decreased from 1.453 to 0.349 mg g^{-1} with the increase of initial pH from 2.3 to 9.2.

Based on the results obtained from the analysis of the sorption data with pseudo-second order kinetic model it can be suggested that the pseudo-second order kinetic model described the sorption of AS2G onto compost better than the other models tested.

3.2.5. *Intra-particle diffusion study*

In spite of the kinetic analyses demonstrating that the mechanism appears to follow pseudo-second order kinetics, it is still important to assess the contribution of intra-particle diffusion on the rate controlling process.

The most commonly used simplified technique for identifying the mechanism involved in the adsorption process is by using an intra-particle diffusion model [58–60] as:

$$q_t = k_d t^{1/2} \tag{13}$$

where k_d (mg g^{-1} h$^{-1/2}$) is the intra-particle diffusion rate parameter. If intra-particle diffusion occurs, then q_t against $t^{1/2}$ will be linear and the line will pass through

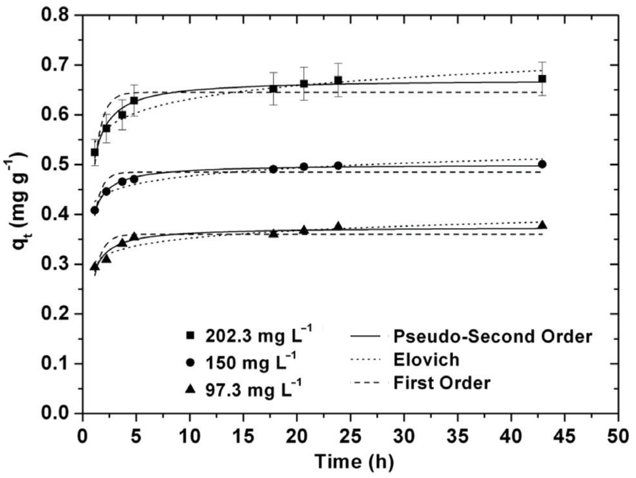

Fig. 3. Kinetics of AS2G dye adsorption by compost sorbent at several initial dye concentrations (pH = 7.5 ± 0.2, Temperature = 20.3°C, Sorbent mass = 2g).

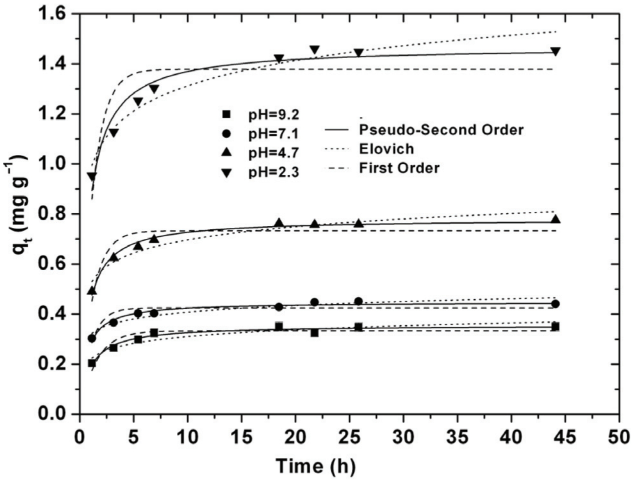

Fig. 4. Kinetics of AS2G dye adsorption by compost sorbent at several initial pH (Mass of sorbent = 4g, Temperature = 20.3°C, Dye concentration = 98.13 mg l^{-1}).

the origin, if the intra-particle diffusion was the only rate limiting parameter controlling the process [59,60]. Otherwise, some other mechanism is also involved [61]. Figs. 5 and 6 illustrate intra-particle plots for AS2G sorption onto compost for different dye concentrations and initial pH values, respectively. The figures show two linear portions. Different linear sections have been attributed to diffusion control through different pore size ranges, for example, mesopores, micropores and mesopore–micropore transition. But there are serious problems interpreting the mechanism as pure intra-particle diffusion because: (i) the root time plots do not go through the origin and demonstrate a significant intercept, (ii) for a pure homogeneous pore distribution the slope of the linear plot should be reciprocal 0.5 [60], (iii) the time to reach equilibrium is too short for conventional intra-particle adsorption diffusion processes which are typically 10–30 d [61], (iv) agricultural wastes do not have a significant porous structure therefore an intra-particle diffusion rate controlling process is most unlikely. Recent studies have identified the importance between the pore size distribution and molecular size of the adsorbent and the diffusion time to reach equilibrium [62,63]. The values of the intercept give an idea about the thickness of the boundary layer, the greater the intercept the greater the boundary layer effect [64].

The data indicate that the intra-particle diffusion model is not a good representative model but because of the linearity of the plots it could be involved in part of the operative mechanism in the sorption of AS2G by compost.

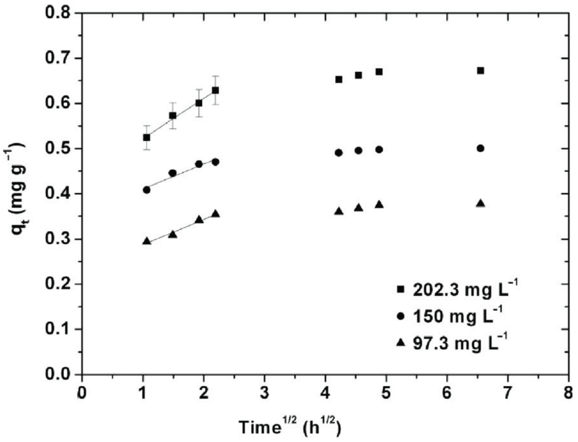

Fig. 5. Intra-particle diffusion plots for the sorption of AS2G onto compost sorbent at different dye concentrations (pH = 7.5 ± 0.2, Temperature = 20.3°C, Sorbent mass = 2 g).

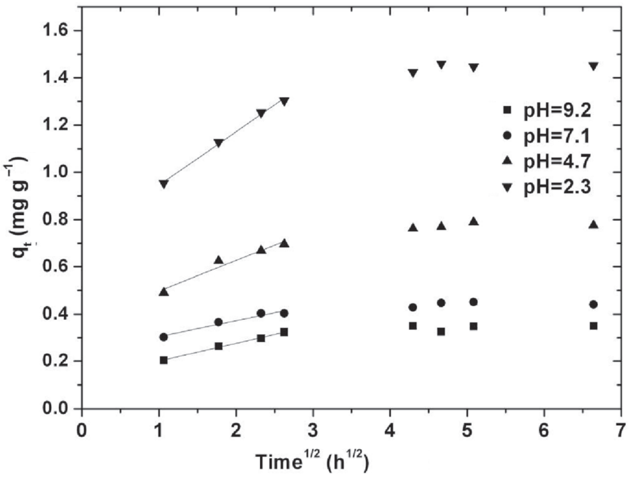

Fig. 6. Intra-particle diffusion plots for the sorption of AS2G onto compost sorbent at different pHs (Mass of sorbent = 4 g, Temperature = 20.3°C, Dye concentration = 98.13 mg l^{-1}).

4. Conclusion

The results of the present investigation showed that the mature, thermophilic compost has a relatively considerable capacity (0.718 mg g^{-1}) for the removal of reactive dye, AS2G, from aqueous solution over a wide range of concentrations. The results showed that the adsorption equilibrium data fitted well to the Langmuir and Temkin models. The value of the Chi-square statistic for the Langmuir, Temkin, Freundlich and Harkins-Jura isotherms were 1.97E−03, 3.70E−03, 5.28E−03 and 4.79E−01, respectively. The high value Chi-square statistic for the Harkins-Jura model shows this model could not described the experimental data well. The adsorption process was dependent on initial dye concentration, mass of sorbent and the pH. Intra-particle diffusion does not play a significant role in the sorption of AS2G onto the compost in the present study. The pseudo-second order kinetic model showed the best model fits with the experimental data with the lowest Chi-square values and is important in the sorption of AS2G onto the compost. The adsorption of dye was highly pH-dependent and the results showed that the adsorption capacity decreases significantly with increase in the pH. The optimum pH for the dye removal was found to be 2.3.

Based on our study it is apparent that the adsorption capacity of compost for reactive dyes is low, even though our capacities were an order of magnitude greater than the previous work. The search for waste agricultural products as adsorbents is driven by their low cost which in the case of compost is effectively zero. But the mass required to remove a commercial quantity of reactive dye effluent is very large and raises further issues of handling problems.

Acknowledgment

The authors thank the Hamadan University of medical sciences for financial support. The support of Kurdistan

University of medical sciences for providing search facilities is also gratefully acknowledged.

Symbols

b — Langmuir constant (l mg^{-1})
a — Maximum adsorption capacity in Langmuir model (mg g^{-1})
I — Intercept of the intraparticle diffusion model (mg g^{-1})
C_0 — The initial concentration of the solute in the bulk solution (mg l^{-1})
C_e — The equilibrium concentration of the solute in the bulk solution (mg l^{-1})
k_d — The intraparticle diffusion rate constant (mg g^{-1} min$^{-1/2}$)
k_1 — Lagergren pseudo-first-order rate constant (min^{-1})
k_2 — the pseudo-second-order rate constant (g mg^{-1} min^{-1})
K_F — Freundlich constant indicative of the relative sorption capacity of the sorbent (mg1$^{-1/n}$ l$^{-1/n}$ g^{-1})
n — Freundlich constant indicative of the intensity of the sorption
K_T — The Temkin equilibrium binding constant (l mg^{-1})
b_T — The variation of adsorption energy in Temkin model (kJ mol^{-1})
A_H — The Harkins-Jura isotherm parameter
B — The Harkins-Jura isotherm constant
α — The initial adsorption rate of Elovich model (mg g^{-1}min^{-1})
β — Elovich model desorption constant (g mg^{-1})
q_t — The amount of solute sorbed at any time t (mg g^{-1})
q_e — The amount of solute sorbed per unit weight of sorbent at equilibrium (mg g^{-1})
q_m — The maximum sorption capacity (mg g^{-1})
R^2 — coefficient of determination
X^2 — The chi-square statistic
RMSE — Residual root mean square error
N — Number of observations in the experimental data
R_L — Dimensionless separation factor of Hall
t — Time (min)
W — Sorbent mass (g)
V — Volume of dye solution (l)

References

[1] C. Allegre, P. Moulin, M. Maisseu and F. Charbit, Treatment and reuse of reactive dyeing effluents, J. Membrane Sci., 269 (2006) 15–34.

[2] S. Rajgopalan, In: R.K. Trivedy (Ed.), Pollution Management in Industries, Karad., India, (1995) 21–44.

[3] M. Ali and T.R. Sreekrishnan, Aquatic toxicity from pulp and paper mill effluents – a review, Adv. Environ. Res., 5 (2001) 175–196.

[4] D.W. Koplin, E.T. Furlong and M.T. Meyer, Pharmaceuticals, hormones and other organic wastewater contaminants in US streams, Environ. Sci. Technol., 36 (1999–2000) 1202–1211.

[5] T. Routh, Anaerobic treatment of vegetable tannery waste water by UASB process, Ind. J. Environ. Prot., 20 (1998) 115–123.

[6] Q. Zhang and T.K. Chuang, Adsorption of organic pollutants of Kraft Pulp mill on activated carbon and polymer resin, Adv. Environ. Res., 3 (2001) 251–258.

[7] A. Gottlieb, C. Shaw, C. Smith, A. Wheatle and S. Forsyth, Toxicity of textile reactive azo dyes after hydrolysis and decolorisation, J. Biotec., 101 (2003) 49–56.

[8] N. Mathur, P. Bhavnagar, P. Nagar and P.K. Bijarnia, Assessment of effluents from textile/dye industries of Sanganer, Jaipur (India): a case study, Ecotoxicol. Environ. Saf., 61 (2005) 105–113.

[9] H. Zollinger, Color Chemistry: Synthesis, Properties, and Applications of Organic Dyes and Pigments, Helvetica Chimica Acta, 2003.

[10] G. Mishra and M. Tripathy, A critical review of the treatments for decolouration of textile effluent, Colourage, 40 (1993) 35–38.

[11] N. Willmott, J. Guthrie and G. Nelson, The biotechnology approach to colour removal from textile effluents, Dyes Colour., 114 (1998) 38–41.

[12] B. Waters, In: P. Cooper (Ed.), Society of Dyers and Colourists, The Alden Press, Oxford (1995) 22–30.

[13] Y. Anjaneyulu, C.N. Sreedhara and D.S.S. Raj, Decolourization of industrial effluents – available methods and emerging technologies – a review, Rev. Environ. Sci. Biores. Technol., 4 (2005) 245–273.

[14] S. Venkat Mohan, S. Krishna Mohan and J. Karthikeyan, in: S. Jayarama Reddy (Ed.), Analytical Techniques in Monitoring the Environment, Student offset printers, Tirupathi, India, (2000) 97–103.

[15] M.M. Nassar and M.S. El-Geundi, Comparative cost of colour removal from textile effluents using natural adsorbents, J. Chem. Technol. Biotechnol., 50 (1991) 257–264.

[16] C. Grégorio, Non-conventional low-cost adsorbents for dye removal: A review, Bioresource Technol., 97 (2006) 1061–1085.

[17] M. Arias-Estévez, D. Fernández-Gándara, M.S. García-Falcón, L. García-Río, J.C. Mejuto and J. Simal-Gándara, Sorption of PAHs to colloid dispersions of humic substances in water, Bull. Environ. Contam. Toxicol., 29 (2007) 251–254.

[18] M. Pateiro-Moure, C. Pérez-Novo, M. Arias-Estévez, E. López-Periago, E. Martínez-Carballo and J. Simal-Gándara, Influence of copper on the adsorption and desorption of Paraquat, Diquat, and Difenzoquat in vineyard acid soils, J. Agric. Food Chem., 55 (2007) 6219–6226.

[19] M. Pateiro-Moure, C. Pérez-Novo, M. Arias-Estévez, R. Rial-Otero and J. Simal-Gándara, Effect of organic matter and iron oxides on quaternary herbicide sorption–desorption in vineyard-devoted soils, J. Colloid Interface Sci., 333 (2009) 431–438.

[20] M. Pateiro-Moure, M. Arias-Estévez and J. Simal-Gándara, Competitive and non-competitive adsorption/desorption of paraquat, diquat and difenzoquat in vineyard-devoted soils, J. Hazard. Mater., 178 (2010) 194–201.

[21] M. Arias, A.C. Torrente, E. López, B. Soto and J. Simal-Gándara, Adsorption−desorption dynamics of cyprodinil and fludioxoznil in vineyard soils, J. Agric. Food Chem., 53 (2005) 5675–5681.

[22] M. Arias, M. Paradelo, E. López and J. Simal-Gándara, Influence of pH and soil copper on adsorption of metalaxyl and penconazole by the surface layer of vineyard soils, J. Agric. Food Chem., 54 (2006) 8155–8162.

[23] M. Arias-Estévez, E. López-Periago, E. Martínez-Carballo and J. Simal-Gándara, Carbofuran sorption kinetics by corn crop soils, Bull. Environ. Contam. Toxicol., 77 (2006) 267–273.

[24] N. Bouchemal and F. Addoun, Adsorption of dyes from aqueous solution onto activated carbons prepared from date pits: The effect of adsorbents pore size distribution, Desalination and Water Treatment, 7 (2009) 242–250.

[25] A.E. Ofomaja, Equilibrium sorption of methylene blue using mansonia wood sawdust as biosorbent, Desalination and Water Treatment, 3 (2009) 1–10.
[26] A. Maximova and B. Koumanova, Equilibrium and kinetics study of adsorption of basic dyes onto perfil from aqueous solution, J. Univ. Chem. Technol. Metall., 43 (2008) 101–108.
[27] M.M. Abd El-Latif and A.M. Ibrahim, Adsorption, kinetic and equilibrium studies on removal of basic dye from aqueous solutions using hydrolyzed Oak sawdust, Desalination and Water Treatment, 6 (2009) 252–268.
[28] S. Boutemedjet and O. Hamdaoui, Sorption of malachite green by eucalyptus bark as a non-conventional low-cost biosorbent, Desalination and Water Treatment, 8 (2009) 201–210.
[29] M. Hadi, M.R. Samarghandi and G. McKay, Equilibrium two-parameter isotherms of acid dyes sorption by activated carbons: Study of residual errors, Chem. Eng. J. 160 (2010) 408–416.
[30] M. Hadi, M.R. Samarghandi and G. McKay, Water Air Soil Pollut., (2010) DOI: 10.1007/s11270-010-0635-2.
[31] R.E. Hinchee, B.C. Alleman, R.E. Hoeppel and R.N. Miller, Hydrocarbon Bioremediation, CRC Press, 1994.
[32] L.S. Tsui, W.R. Roy and M.A. Cole, Removal of dissolved textile dyes from wastewater by compost sorbent, Color. Technol., 119 (2003) 14–18.
[33] Lo. Tsui and W.R. Roy, The potential applications of using compost chars for removing the hydrophobic herbicide atrazine from solution, Biores. Technol., 99 (2008) 5673–5678.
[34] H.P. Boehm, Some aspects of the surface chemistry of carbon blacks and other carbons, Carbon, 32 (1994) 759–769.
[35] Y.S. Ho, Selection of optimum sorption isotherm, Carbon, 41 (2004) 2115–2116.
[36] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica, and platinum, J. Am. Chem. Soc., 40 (1918) 1361–1403.
[37] H.Z. Freundlich, Over the adsorption in solution, J. Phys. Chem., 57A (1906) 385–470.
[38] M.I. Temkin, Adsorption equilibrium and the kineticsof processes on non-hemogeneous surfaces and in the interaction between adsorbed molecules, Zh. Fiz. Chim., 12 (1941) 296–332.
[39] W.D. Harkins and G. Jura, The decrease (p) of free surface energy (g) as a basis for the development of equations for adsorption isotherms; and the existence of two condensed phases in films on solids, J. Chem. Phys., 12 (1944) 112–113.
[40] K.R. Hall, L.C. Eagleton, A. Acrivos and T. Vermeulen, Pore and solid-diffusion kinetics in fixed-bed adsorption under constant-pattern conditions, Ind. Eng. Chem. Fund., 5 (1966) 212–223.
[41] R.C. Bansal and M. Goyal, Activated Carbon Adsorption, CRC Press, Taylor & Francis Group, 2005.
[42] R.E. Treybal, Mass Transfer Operations, 3rd ed, McGraw-Hill, 1981.
[43] Y.S. Ho and C.C. Wang, Pseudo-isotherms for the sorption of cadmium ion onto tree fern, Process Biochem., 39 (2004) 759–763.
[44] C. Aharoni and M. Ungarish, Kinetics of activated chemisorption part 2. Theoretical models, J. Chem. Soc. Far. Trans., 73 (1977) 456–464.
[45] C. Aharoni and D.L. Sparks, in: D.L. Sparks and D.L. Suarez (Eds.), Rates of Soil Chemical Processes, Soil Science Society of America, Madison, WI (1991) 1–18.
[46] O. Hamdaoui and E. Naffrechoux, Modeling of adsorption isotherms of phenol and chlorophenols onto granular activated carbon: Part I. Two-parameter models and equations allowing determination of thermodynamic parameters, J. Hazard. Mater., 147 (2007) 381–394.
[47] Y.S. Ho and G. Mckay, Pseudo-second order model for sorption processes, Process Biochem., 34 (1999) 451–465.
[48] S. Lagergren, Zur theorie der sogenannten adsorption gelöster stoffe, Kungliga. Svenska Vetenskapsakademiens., 24 (1898) 1–39.
[49] M.J.D. Low, Kinetics of chemisorption of gases on solids, Chem. Rev., 60 (1960) 267–312.
[50] Y.S. Ho and G. McKay, Sorption of dye from aqueous solution by peat, Chem. Eng. J., 70 (1998) 115–124.
[51] K.S. Low, C.K. Lee and K.K. Tan, Biosorption of basic dyes by water hyacinth roots, Biores. Technol., 52 (1995) 79–83.
[52] P. Waranusantigul, P. Pokethitiyook, M. Kruatrachue and E.S. Upatham, Kinetics of basic dye (methylene blue) biosorption by giant duckweed (Spirodela polyrrhiza), Environ. Pollut., 125 (2003) 385–392.
[53] Y.S. Ho and G. McKay, Kinetic model for lead(II) sorption on to peat, Adsorp. Sci. Technol., 16 (1998) 243–255.
[54] G. McKay and Y.S. Ho, A kinetic study of dye sorption by biosorbent waste product pith, Res. Cons. Recycl., 25 (1999) 171–193.
[55] M. Özacar and I.A. engil, Adsorption of metal complex dyes from aqueous solutions by pine sawdust, Bioresource Technol., 96 (2005) 791–795.
[56] M.C. Ncibi, B. Mahjoub and M. Seffen, Adsorptive removal of textile reactive dye using posidonia oceanica(L.) fibrous biomass, Int. J. Environ. Sci. Tech., 4 (2007) 433–440.
[57] S.V. Mohan, N.C. Rao and J. Karthikeyan, Adsorptive apple pomace and wheat straw, Water Res., 36 (2002) 2824–2830.
[58] G. Crank, The Mathematics of Diffusion, Clarendon Press, 1933.
[59] G. McKay, The adsorption of dyestuffs from aqueous solutions using activated carbon: external mass transfer processes, J. Chem. Technol. Biotechnol., 33A (1983) 205–218.
[60] W.J. Weber and J.C. Morris, Kinetics of adsorption on carbon from solution, J. Sanit. Eng. Div. Am. Soc. Civ. Eng., 89 (1963) 31–40.
[61] V.J.P. Poots, G. McKay and J.J. Healy, The removal of acid dye from effluent using natural adsorbents–I. Peat, Wat. Res., 10 (1976) 1061.
[62] A.W.M. Ip, J.P. Barford and G. McKay, A comparative study on the kinetics and mechanisms of removal of Reactive Black 5 by adsorption onto activated carbons and bone char, Chem. Eng. J., 157(2010) 434–442.
[63] M.F.F. Sze and G. McKay, An adsorption diffusion model for removal of para-chlorophenol by activated carbon derived from bituminous coal, Environ. Pollut., 158 (2010) 1669–1674.
[64] N. Kannan and M. Sundaram, Kinetics and mechanism of removal of methylene blue by adsorption on various carbonsda comparative study, Dyes Pigm., 51 (2001) 25–40.