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ORIGINAL ARTICLE

Biosorption of diazinon by a pre-treated alimentary industrial waste: equilibrium and kinetic modeling

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Abstract This study explores the feasibility of pre-treated coffee waste (PCW) as biosorbent for the removal of diazinon. The effect of the pesticide concentration (6–20 mg L^{-1}), contact time, adsorbent dose (0.2–1.2 g L^{-1}), solution pH (3–11.5), temperature (15–40 °C) and co-existing inorganic ions ($H_2PO_4^-$, NO_3^-) on the diazinon biosorption over PCW is investigated. The experimental results indicate an optimal pH of 7.3 for the diazinon elimination on PCW (1 g L^{-1}). The Langmuir model describes well the isotherm data with a high regression coefficient ($R^2 > 0.990$) and a maximum monolayer biosorption capacity of 18.52 mg g^{-1} at 15 °C. It is also observed that the intra-particle diffusion is not the rate-controlling step. A comparison is evaluated between the pseudo-second-order and intra-particle diffusion kinetic models; the experimental data are well fitted by the pseudo-second-order kinetic model. The biosorption capacity decreases with increasing temperature for a diazinon concentration of 10 mg L^{-1}. The negative enthalpy $\Delta H°$ (−63.57 kJ/mol) indicates that the diazinon biosorption onto PCW is exothermic. Under optimal conditions, the biosorption reaches 95% after 90 min. The removal efficiency decreases from 95 to 65.67 and 48.9% for the diazinon alone and in the presence of NO_3^- and $H_2PO_4^-$ (100 mg L^{-1}), respectively.

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Introduction

Among newly developed pesticides, organophosphorous compounds are most commonly used. Diazinon (*O*,*O*-diethyl *O*-[6-methyl-2-(1-methylethyl)-4- pyrimidinyl] phosphorothioate) is an organo-phosphorus insecticide classified by the World Health Organization (WHO) as "moderately hazardous" belonging to Class II. It is an organophosphate insecticide formerly employed for the fleas control, but remains toxic for the aquatic organisms at concentration as low as 350 ng L^{-1} (Li et al. 2002) while fetal human doses were found to be extremely high in the range (90–445 mg kg^{-1}) (Zhang and Pehkonen 1999). Toxic effects of diazinon are attributed to its inhibition for the enzyme acetylcholinesterase (Shemer and Linden 2006). High diazinon residues were found in urban wastewaters and effluents from sewage treatment plants (Bailey et al. 2000; Li et al. 2002); hence, it is necessary to reduce its concentration before landfills. In this respect, several techniques are used for the pesticides removal such as advanced oxidation processes (Zhang and Pehkonen 1999), aerobic degradation (Nandagopal and Antony 2015), nanofiltration membranes (Mehta et al. 2017), ozonation (Shemer and Linden 2006) and biosorption (El Bakouri et al. 2009). However, the biosorption remains one of the most used techniques (Cortina et al. 2003) and has proven its effectiveness in the elimination of organic pollutants in aqueous medium (Zhang and Pehkonen 1999).

Suitable adsorbents must possess high removal efficiencies with economical, ecological and technological advantages. In this regard, activated carbons are currently

favored because they can efficiently remove pesticides, organic compounds and metal ions. However, the high cost of activated carbons and their production are limiting factors, leading us to use inexpensive raw materials as adsorbents. Therefore, there is a need for the development of low-cost materials which adsorb organic pollutants. Natural biosorbents such as wood bark, peat, fly ash (Shemer and Linden 2006), acid-treated date stones (El Bakouri et al. 2009) are available in large quantities and may have a great potential in the water treatment. The utilization of an abundant residual biomass, namely the apricot stone, as a raw material for activated carbons gives an additional economical interest to the technical studies.

In this paper, we report the biosorption of diazinon onto pre-treated coffee waste (PCW). Several sets of experiments are conducted to determine the influence of biosorbent dose, initial diazinon concentration, temperature, solution pH as well as the effect of some anions on the diazinon biosorption. Equilibrium and kinetic analysis were conducted to determine the factors controlling the adsorption rate, the optimization of various parameters and to find out the possibility of using this material as low-cost adsorbent for pesticide removal.

Materials and methods

Waste coffee is obtained from industrial coffee production; it is thoroughly washed with deionised water and dried at 50 °C for 24 h. Then, it is oxidized with NaOCl solution (1%) in order to remove the organic matter (Yeddou and Bensmaili 2006). The powder is washed, dried and screened through a set of sieves to get geometrical size in the range (50–210 µm). The chemical composition of PCW determined by X-ray fluorescence (XRF) using Horiba equipment is given in Table 1. The sample is mounted on a piece of metal, coated with ~60 nm thickness of gold and observed by scanning electron microscopy (SEM, JEOL, JSM-6360LV).

The biosorbate is the diazinon which is a commercial pesticide ($C_{12}H_{21}N_2O_3PS$, Fig. 1). All chemicals are of analytical reagent grade used without any further purification. The solutions are prepared from distilled water and the initial pH of the solution is adjusted with NaOH and HCl solutions.

Kinetic studies

PCW (1 g L^{-1}) is mixed with 100 mL of the diazinon concentration (6–20 mg L^{-1}) in conical flasks. The initial pH is adjusted at ~7 before mixing the adsorbent solution. The flasks are covered with aluminum foil and agitated on a shaker at constant temperature. The aliquots are withdrawn and separated from the biosorbent by centrifugation (10,000 rpm, 20 min); their concentrations are determined using UV–Vis spectrophotometer (Shimadzu 1800, $\lambda_{max} = 248$ nm).

Table 1 Chemical components of pre-treated coffee waste

Component	%
Na_2O	0.4
MgO	0.419
Al_2O_3	0.11
SiO_2	0.299
P_2O_5	0.289
SO_3	0.031
K_2O	0.019
CaO	3.19
ZnO	0.014
Sr	0.026
Cl	7.995
Volatile matter	84.607

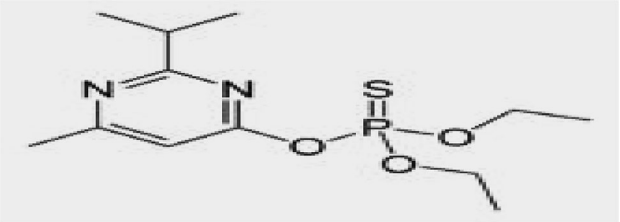

Fig. 1 Chemical formula of the diazinon

Equilibrium studies

Effect of adsorbent dose

The equilibrium data are obtained by addition of (0.02–0.12 g) of PCW into a series of conical flasks filled with 100 mL of diazinon solution (10 mg L^{-1}). The flasks covered with aluminum foil are placed in a thermostatic shaker for 2 h at 15 °C.

Effect of pH and initial concentration

The biosorption tests are performed with different diazinon solutions over the pH range (3–11.5) on PCW (100 mg). The experiments are carried out by addition of 0.1 g of PCW to 100 mL of solutions over the concentrations range (3–20 mg L^{-1}, pH 7.3).

Effect of temperature

The thermal variation of the biosorption is investigated in the range (15–40 °C). The flasks containing 0.1 g of diazinon (pH 7.3) are placed in a thermostatic shaker at 15, 25, 30 and

40 °C. The removal efficiency (E) of the diazinon degradation on PCW, the biosorption capacity (q) and the distribution ratio (K_d) are calculated from the relations:

$$E = \frac{C_0 - C_f}{C_0}, \quad (1)$$

$$q = \frac{V(C_0 - C_f)}{m}, \quad (2)$$

$$K_d = \frac{\text{amount of diazinon on adsorbent}}{\text{amount of diazinon in solution}}, \quad (3)$$

where C_o and C_f are the initial and final concentrations (mg L^{-1}), respectively, V is the volume of the solution (L) and m is the weight of the adsorbent (g).

Results and discussion

Effect of the initial concentration on the diazinon biosorption

The effect of initial concentration of diazinon (C_o) on the biosorption rate by PCW is shown in Fig. 2. The quantity of biosorbed pesticide increases with time for all concentrations. As the concentration C_o increases from 6 to 20 mg L^{-1}, the loading capacity of PCW increases from 4.81 to 15.39 mg g^{-1} during the first hour, attributed to the increased biosorbate quantity. The rapid pesticide uptake for the first 10 min is due to the occurrence of molecule transfer ascribed to diazinon–biosorbent interactions with negligible interference solute–solute. The enhanced biosorption may also be due to the fact that initially, the sites on the PCW surface are vacant and the solute concentration gradient is high. The extent of diazinon uptake decreases over the contact time, because of the gradual decrease in the number of the surface sites. The remaining vacant sites become difficult to be reached due to repulsive forces between the solute molecules on the surface and bulk phase, thus leading to saturation (Al-Qodah et al. 2007; Ramanaiah et al. 2007). When the biosorption involves a surface reaction, the initial step is rapid.

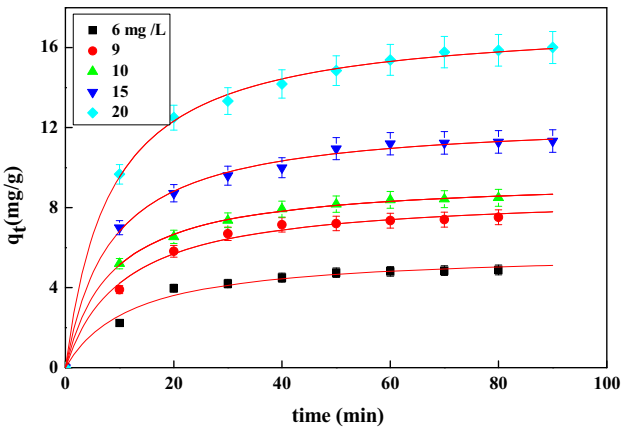

Fig. 2 Biosorption on pre-treated coffee waste at different diazinon concentrations

Effect of temperature

The thermal effect on the diazinon biosorption on PCW (Fig. 3) shows that the uptake capacity (q_e) decreases with raising temperature, indicating an exothermic biosorption, which is inhibited at high temperatures. An explanation of the decreased biosorption with temperature may be attributed to low number of polar groups of carbons (i.e., carboxylic oxygen).

Effect of pH on the biosorption equilibrium

The biosorption is strongly dependent on pH through the functional groups of the biosorbent. Figure 4 shows that the removal efficiency of diazinon increases with pH, an abrupt variation is found in the pH range (3.0–7.3). The maximum biosorption (9.5 mg g^{-1}) is obtained at pH 7.3 and decreases for higher pHs due to the ionic form of the diazinon (aromatic structure, polar groups) in solution and the electrical charge of PCW. The weak removal at high

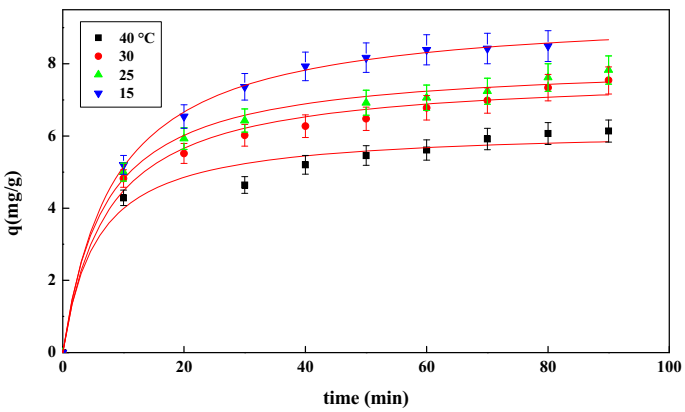

Fig. 3 Diazinon biosorption on pre-treated coffee waste at different temperatures

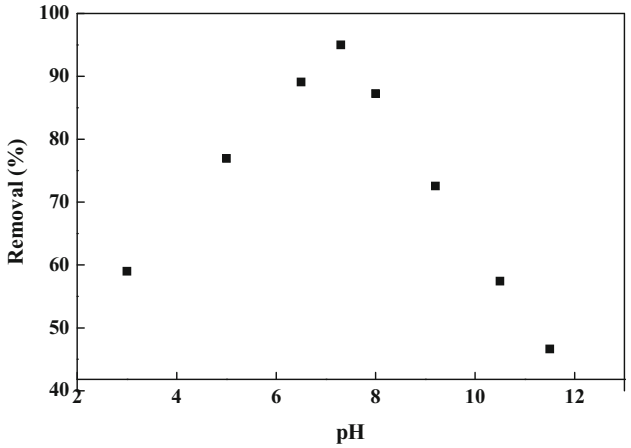

Fig. 4 Diazinon biosorption on pre-treated coffee waste (PCW) at different pHs

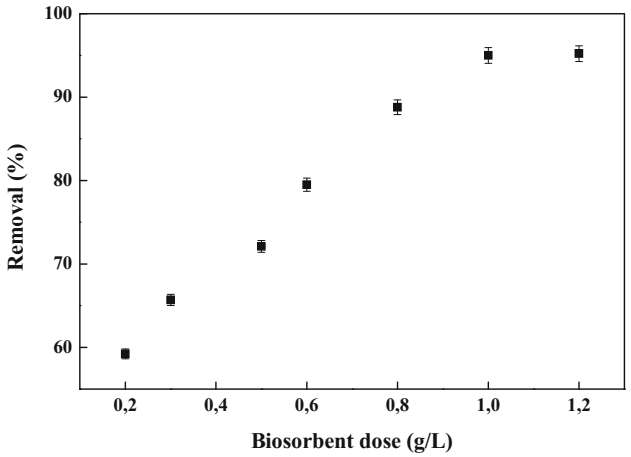

Fig. 5 Effect of the biosorbent dose on the diazinon removal

(>7.3) and low pHs (<5) may be due to the diazinon hydrolysis. So, the pH appears to be a key factor affecting the diazinon biosorption. The optimal pH leads to a high surface potential, allowing a better biosorption.

Effect of the biosorbent dose

To determine the biosorbent quantity for a maximal removal of diazinon, the effect of the PCW dose on the biosorption equilibrium is illustrated in Fig. 5 which shows the uptake of diazinon for five doses over the range (0.2–1.2 g L^{-1}). For a concentration of 10 mg L^{-1}, PCW dose of 1 g L^{-1} is found to be optimal. This is probably due to the resistance to the mass transfer of the pesticide from the bulk liquid to the PCW surface, which becomes important at high biosorbent doses; this optimal dose is used for further experiments.

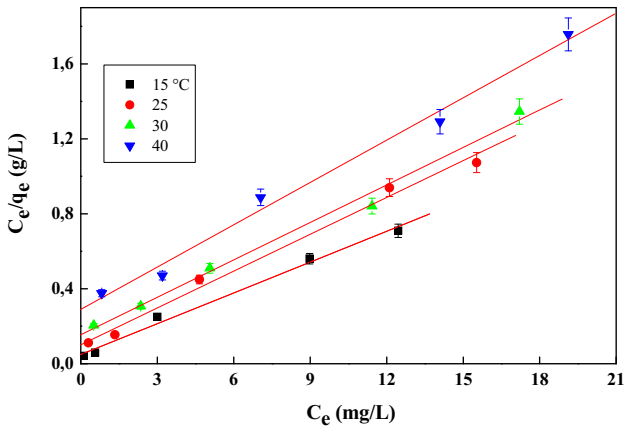

Fig. 6 The Langmuir adsorption isotherms for pre-treated coffee waste at various temperatures

Batch isotherm studies

The capacity of PCW to absorb the diazinon is determined by measuring the equilibrium isotherms to describe the interaction adsorbate (10 mg L^{-1})/adsorbent (1 g L^{-1}) at pH ~7.3. Thus, a correlation of the equilibrium data by either theoretical or empirical equations is essential for the practical operations to optimize the design of the biosorption system; so it is important to establish the most appropriate correlation for the equilibrium curves. The isotherm data are analyzed using the commonly used equilibrium models, namely the Langmuir and Freundlich ones (Hamdaoui et al. 2008; Akar et al. 2009; Al-Qodah et al. 2007). The mathematical expressions are, respectively, given by

$$q_e = q_{max} \frac{bC_e}{1 + bC_e}, \quad (4)$$

the linearized form gives

$$C_e/q_e = 1/(q_m b) + C_e/q_m, \quad (4')$$

$$q_e = K_f . C_e^{1/n}, \quad (5)$$

whose linearized form is

$$\ln q_e = \ln Kf + (1/n) \ln C_e, \quad (5')$$

where q_{max} (mg g^{-1}) is the maximum amount of diazinon per unit weight of PCW, to form a complete monolayer on the surface and b (L mg^{-1}) is a constant related to the affinity of the binding sites, determined from the linear plot of C_e/q_e versus C_e. The characteristic constant K_f (mg $L^{-1/n}$ g^{-1} $L^{1/n}$) and the dimensionless n are determined from the linearized form of Eq. (5).

Figures 6 and 7 show the plots of linearized forms; the best-fitted parameters deduced from Eqs. (4) and (5) by the linear regression analysis are listed in Table 2, along with

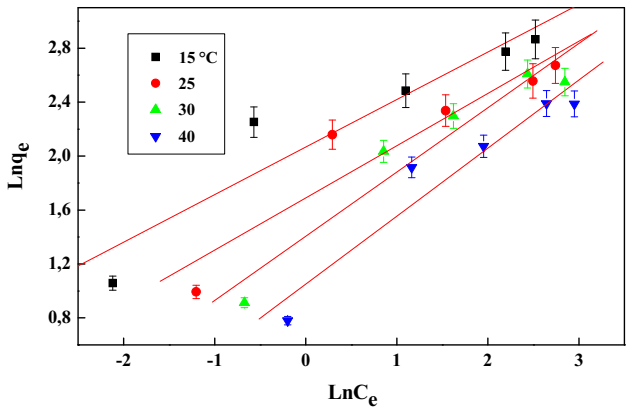

Fig. 7 The Freundlich adsorption isotherm for pre-treated coffee waste at various temperatures

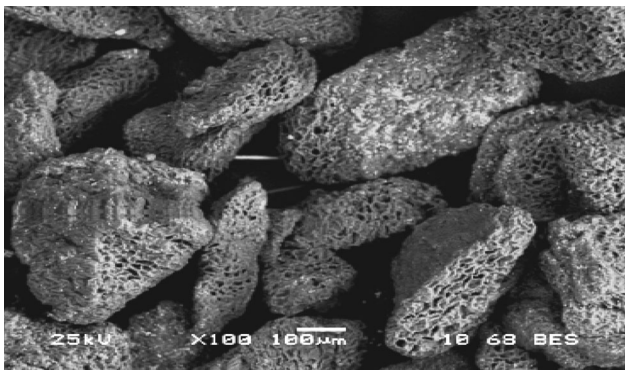

Fig. 8 SEM image of pre-treated coffee waste (PCW)

the regression coefficients (R^2), which provide a measurement of the model fitness. The R^2 coefficients of the Freundlich model are lower ($0.891 \leq R^2 \leq 0.925$) than those of Langmuir ($0.990 \leq R^2 \leq 0.992$). The n values are greater than unity ($1.980 < n < 2.840$; Table 2), indicating that the diazinon is favorably adsorbed on PCW. The constants K_f and n are obtained at 15 °C and this implies that the binding capacity reaches the maximal value and the affinity PCW/diazinon is higher at that temperature. The high regression coefficient shows that the Langmuir model is the most suitable for describing the biosorption over the studied concentrations range and suggests that some homogeneity in the PCW surface or inside the pores plays a role in the biosorption. The surface of PCW grains is regular with homogeneous porous structure as shown in the SEM image (Fig. 8). Similar results were obtained by Azouaou et al. (Azouaou et al. 2010) for the Cd^{2+} adsorption by untreated coffee residue. The maximum capacity q_{max}, determined from the Langmuir isotherm, was 18.52 mg L^{-1} at 15 °C and the large b value (=1.102) implies a strong interaction diazinon/PCW. The essential feature of the Langmuir isotherm can be expressed by a dimensionless separation factor (R_L), defined by (Chatzopoulos et al. 1993):

$$R_L = \frac{1}{1 + bC_0}. \quad (6)$$

The R_L value indicates the isotherm type: unfavorable ($R_L > 1$), linear ($R_L = 1$), irreversible ($R_L = 0$) or favorable ($0 < R_L < 1$); the separation factor (R_L) increases from 0.083 to 0.27 as the temperature increases from 15 to 40 °C (Table 2).

Biosorption kinetics

The biosorption rate gives information for the designing batch biosorption systems. To clarify the kinetics of diazinon biosorption onto PCW, the pseudo-second-order and intra-particle models are applied to the experimental data. The derived rate constants together with the regression coefficient R^2 are gathered in Tables 3 and 4. The effects of temperature and initial concentration (C_o) on the biosorption kinetics are also examined. The pseudo-second-order model gives the best fit with the kinetic data for the diazinon-PCW systems; all regression coefficients are high (>0.99, Table 3). In the case of the intra-particle model, the regression coefficients are between 0.812 and

Table 2 Isotherm constants for diazinon adsorption onto pre-treated coffee waste

	Temperature			
	15 °C	25 °C	30 °C	40 °C
Freundlich				
n	2.84	2.58	2.10	1.98
K_f (mg $L^{-1/n}$ g^{-1} $L^{1/n}$)	7.89	5.41	4.07	2.85
r^2	0.891	0.890	0.926	0.925
Langmuir				
q_{max} (mg/g)	18.52	15.38	15.15	13.33
b (L/mg)	1.102	0.643	0.428	0.259
r^2	0.992	0.990	0.990	0.990

Table 3 Parameters for the pseudo-second-order equation

	K_2 (g/mg min) × 10^3	Q_e (mg/g)	H (mg/g min)	R^2
C_o (mg/L)				
6	15.5	5.6818	0.50	0.993
9	11.28	8.9525	0.904	0.996
10	12.0	9.4339	1.153	0.999
15	9.566	12.5	1.494	0.998
20	6.31	17.86	2.012	0.999
T (°C)				
15	12.9	9.4339	1.153	0.999
25	14.05	8.333	0.975	0.995
30	12.26	8.13	0.8103	0.993
40	14.45	6.7567	0.660	0.991

Table 4 Parameters for intra-particle diffusion model

	K_i (mg/g $min^{1/2}$)	R^2	Di (cm^2/s) × 10^7	$T_{1/2}$ (min)
C_o (mg/L)				
6	0. 450	0.813	5.33	11.34
9	0.558	0.812	6.11	9.90
10	0.619	0.928	7.39	8.17
15	0.821	0.957	7.23	8.37
20	1.108	0.949	6.81	8.87
T (°C)				
15	0.619	0.928	7.39	8.17
25	0.409	0.954	7.08	8.54
30	0.404	0.986	6.03	10.03
40	0.321	0.950	5.91	10.24

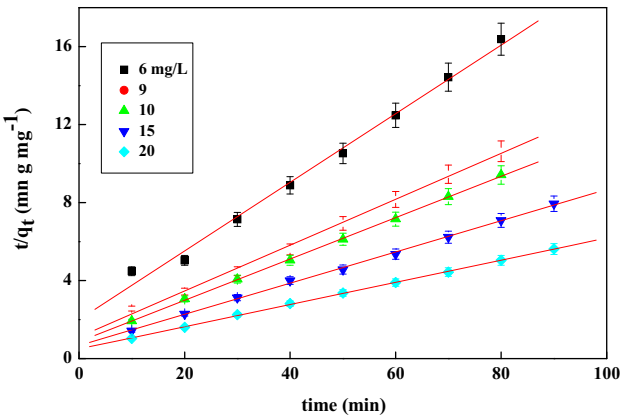

Fig. 9 Pseudo-second biosorption kinetics of preatreated coffee waste at various diazinon concentrations

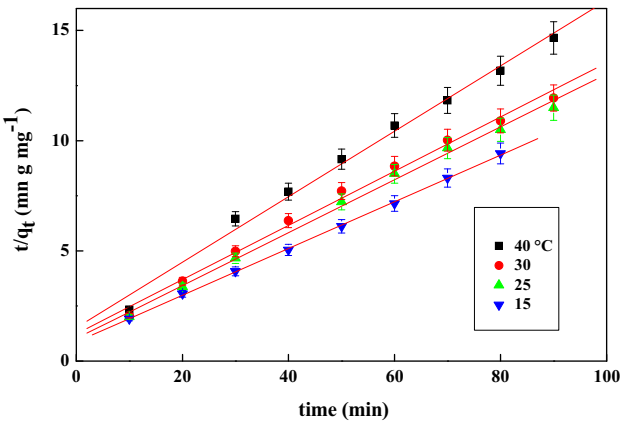

Fig. 10 Pseudo-second biosorption kinetics of pre-treated coffee waste at different temperatures

0.986 (Table 4), suggesting the inapplicability of the model for the diazinon biosorption on PCW.

Pseudo-second-order model

Based on the equilibrium biosorption, the pseudo-second-order kinetic equation is expressed by the relation (Hamdaoui et al. 2008):

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}, \tag{7}$$

where K_2 is the rate constant (g/mg min):

$$h = K_2\, q_e^2, \tag{8}$$

h is the initial biosorption rate (mg/g min). According to Ho (Ho 2006), the advantage of this model is that there is no need to know the equilibrium capacity from the experiments, since it can be easily calculated. In addition, the initial biosorption rate can be obtained from the model. Reported studies (Walker et al. 2003) showed that the pseudo-second-order rate equation gives reasonably a good fit of the experimental data over the entire fractional approach to equilibrium and is extensively employed in the biosorption kinetics (Weber and Morris 1963). The application of the linear forms of the pseudo-second-order kinetic model on our experimental data is presented in Fig. 9 (for different concentrations) and Fig. 10 (different temperatures); the constants K_2 and q_e are determined from the intercept and slope of the straight line obtained by plotting t/q_t versus t, respectively. It can also be observed that the equilibrium biosorption capacity q_e increases with increasing the diazinon concentration C_o, from 6 to 20 mg L^{-1} (Table 3). In addition, it has been found that the biosorption rate h decreases with C_o according to the relation:

$$h = -0.102\, C_o - 0.022 \quad \left(R^2 = 0.976\right), \tag{9}$$

q_e can be expressed as a function of C_o by the following relation:

$$q_e = 0.824\,C_o + 0.995 \quad \left(R^2 = 0.984\right). \tag{10}$$

Substituting the values of q_e and h from Eqs. 9 and 10 into Eqs. 7 and 8, one can derive the rate law for the pseudo-second-order and the relationship of q_t, t and C_o:

$$q_t = \frac{0.08405C_0^2t - 0.08336C_0t - 0.0219t}{0.102C_0t - 0.022t + 0,824C_0 + 0.995}. \tag{11}$$

Equation (11) is used to derive the amount of biosorbed diazinon at any time and for any concentration. The variations of t/q_t versus t at various temperatures of the diazinon solution (10 mg L^{-1}) confirm the validity of the pseudo-second-order model. The parameters K_2, h and q_e at different temperatures are calculated from Eqs. (12) and (13); the results (Table 3) reveal that the fitted biosorption capacity at equilibrium q_e decreases from 9.43 mg g^{-1} at 15 °C to 6.75 mg g^{-1} at 40 °C, while the initial biosorption rate, h, decreases with increasing temperature:

$$h = -0.021\,T + 1.456 \qquad R^2 = 0.982, \tag{12}$$

$$q_e = -0.104\,T + 11.03 \qquad R^2 = 0.980. \tag{13}$$

Substituting the values of q_e and H from Eqs. (12) and (13) into Eqs. (7) and (8), one obtains the rate law for the pseudo-second-order and relationship of q_t, t and T:

$$q_t = \frac{0.00208T^2t - 0.372Tt + 16.06Tt}{-0.02Tt + 1.456t - 0.104T + 11.03}. \tag{14}$$

The data of the diazinon biosorption (Figs. 9 and 10) confirm the validity of the pseudo-second-order model with R^2 coefficient between 0.974 and 0.986. The confrontations of the experimental and predicted results are shown in Fig. 11a for the concentrations and Fig. 11b for the temperatures.

Intra-particle diffusion

The diffusion mechanism and the kinetic results are also analyzed by the intra-particle diffusion model developed by Weber and Morris (1963), and McKay and Poots (1980) where the initial rate of intra-particle diffusion is calculated by linearization of Eq. (15)

$$q_t = K_p t^{1/2} + C, \tag{15}$$

C (mg g^{-1}) is a constant related to the thickness of the boundary layer, attributed to the instantaneous utilization of the most readily available adsorbing sites on the adsorbent surface.

The diffusion rate constant K_p (mg/g $min^{1/2}$) is determined from the slopes of the linear plots of q_t versus $t^{1/2}$ for various diazinon concentrations and temperatures (Fig. 12). The R^2 coefficients are between 0.812 and 0.986 (Table 4). K_p increases from 0.45 to 1.108 mg g^{-1} $min^{1/2}$ with

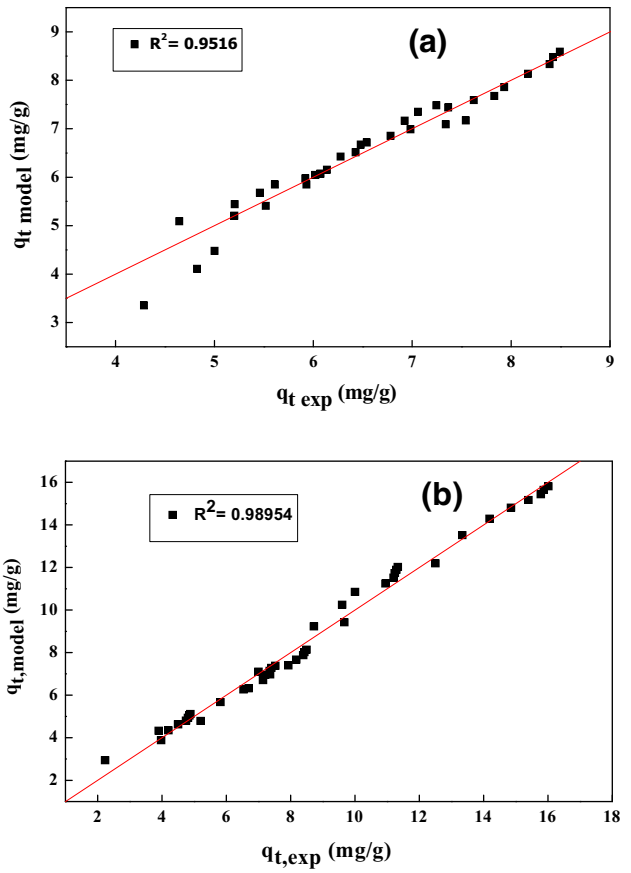

Fig. 11 Experimental versus predicted confrontations of the biosorption capacity for the diazinon-PCE for different concentrations (**a**) and different temperatures (**b**)

increasing the concentration C_o from 6 to 20 mg L^{-1} and this can be explained by the increased driving force which reduces the diffusion of diazinon in the boundary layer and enhances the diffusion in the solid. In addition, raising the temperature reduces the pore diffusion in the biosorbent particles, resulting in a reduction in the intra-particle diffusion rate (Moussa and Trari 2015). The corresponding constants K_p vary from 0.619 to 0.321 mg/g $min^{1/2}$ in the range (15–40 °C) (Table 4). The straight lines do not pass by the origin (Fig. 12), implying that the intra-particle diffusion is not the only rate-controlling step. In addition, the diffusion coefficients (D_p, cm^2/s) for the intra-particle transport of diazinon in the pores of biosorbent particles have been calculated from Eqs. (16) and (17) (Shemer and Karl 2006),

$$D_P = \frac{0.03\,r_0^2}{t_{1/2}}, \tag{16}$$

$$t_{\frac{1}{2}} = \frac{1}{k_2 q_e}, \tag{17}$$

where $t_{1/2}$ is the time for half-biosorption of diazinon; the average radius (r_o) of the adsorbent particle (cm) is found to be 11 × 10^{-3} cm, assuming spherical particles. With

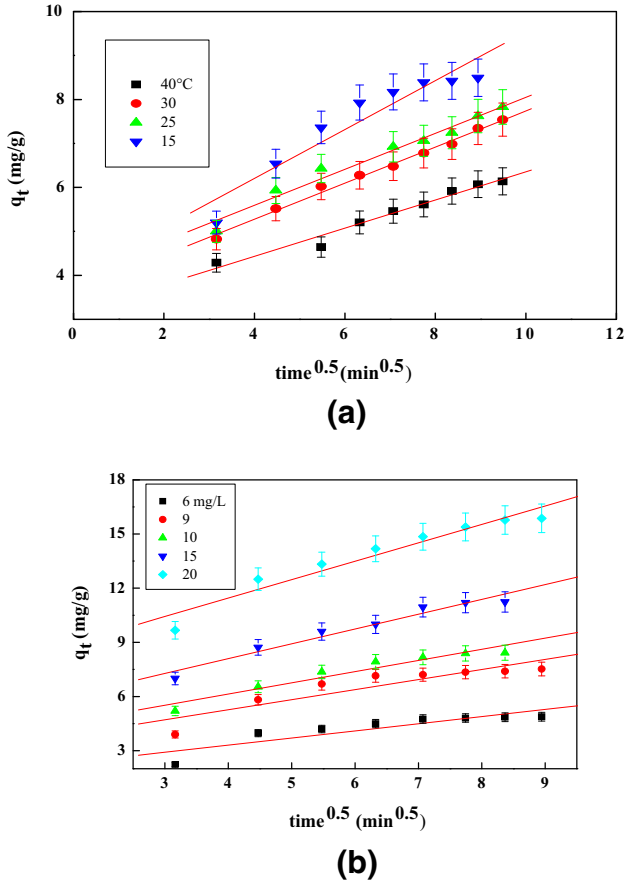

Fig. 12 Plot of intra-particle diffusion modeling of diazinon onto PCW at various temperatures (**a**) and concentrations (**b**)

increasing the diazinon concentration C_o from 6 to 10 mg L^{-1}, the coefficient D_p increases from 5.33×10^{-7} to 7.39×10^{-7} cm^2/s and then decreases to 6.81×10^{-7} cm^2/s in the concentration range (10–20 mg L^{-1}). This concentration dependence of the diffusivity agrees with the literature (Moussa and Trari 2015). It is also observed that D_p decreases as the temperature increases from 15 to 40 °C. The D_p values (Table 4) are within the magnitudes reported in the literature (Hamdaoui et al. 2008), and confirm that the intra-particle diffusion is not the only rate-controlling step.

Thermodynamic study

The type of the biosorption can be determined through the thermodynamic functions, i.e., the free energy ($\Delta G°$), the enthalpy ($\Delta H°$) and entropy ($\Delta S°$) for the diazinon biosorption on PCW:

$$\Delta G^{\circ} = -RT \ln K_d, \quad (18)$$

$$\ln K_d = -\frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R}, \quad (19)$$

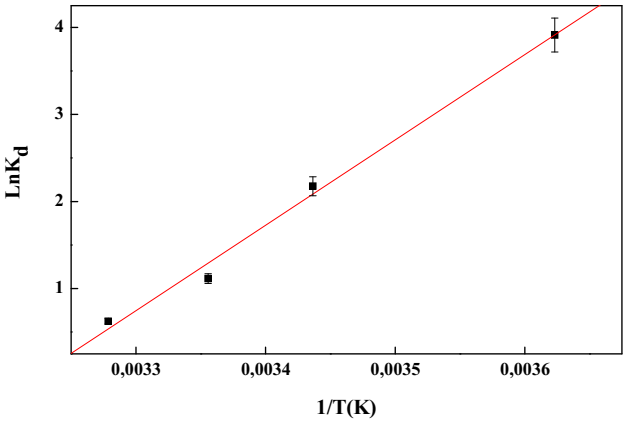

Fig. 13 The thermal variation of K_d of diazinon adsorption onto PCW

Table 5 Thermodynamic parameters of the diazinon biosorption

Temperature (°C)	$-\Delta G°$ (kJ/mol)	$-\Delta S°$ (kJ/mol)	$\Delta H°$ (kJ/mol)
10	6.73	57.01	−63.57
15	4.62	58.99	
20	2.97	59.58	
30	1.96	61.96	

where T is the absolute temperature and R is the universal gas constant. Figure 13 shows a linear relationship between the logarithm of rate constant and T^{-1}. The values of $\Delta H°$ (−63.57 kJ mol^{-1}) and $\Delta S°$ (−0.198 kJ mol^{-1}) are determined from the slope and intercept of the plot of ln K_d versus T^{-1}. The negative entropy reflects the decreased randomness at the solid/solution interface during the diazinon biosorption while the negative free energy ($\Delta G°$) (Eq. 12) indicates a feasible biosorption onto PCW. $\Delta G°$ increases from −6.73 to −1.96 kJ/mol in the range (10–40 °C, Table 5), thus suggesting more biosorbed diazinon at low temperature. The negative enthalpy indicates an exothermic process controlled by chemical mechanism (>40 kJ mol^{-1}) where the interaction diazinon-PCW is mainly electrostatic (Coulombic interactions). The heat of the biosorption involves relatively strong intermolecular forces and mainly electrostatic interaction as well as hydrogen bond.

Effect of co-existing inorganic ions

The presence of inorganic ions was found to influence the kinetics and mechanism of the catalytic degradation of organic pollutant (Muhamad 2010). The uptake of pesticides from wastewaters is different from that of a simple pesticide in solution. Indeed, the real effluents

contain not only organic contaminants but also many inorganic ions and heavy metals which change the ionic strength of the solution and affect the biosorbent capacity. Therefore, the diazinon biosorption onto PCW (10 mg L^{-1}) was carried out in the presence of two inorganic ions (NaH_2PO_4 and $NaNO_3$). Hence, the effect of $H_2PO_4^-$ and NO_3^- on the biosorption is investigated by varying the concentrations of $H_2PO_4^-$ and NO_3^- over the range (50–100 mg L^{-1}) at pH 7.3 and 15 °C. The surface coverage by inorganic ions is competitive with the adsorption of the pesticides which is directly related to their occupation fraction and consequently has a negative impact on the biosorption. It is worth mentioning that the pH does not change significantly; it remains nearly constant with neutral ion NO_3^- while it increased to pH $\sim$10. So with H_3PO_4, the pH increase also accounts for the decreased degradation.

The result shows that $H_2PO_4^-$ is a more powerful inhibitor than NO_3^-. As the ion concentration increases, the removal efficiency of diazinon decreases from 86 to 48.9% and from 94.56 to 65.67%, respectively, with $H_2PO_4^-$ and NO_3^-. Such behavior is due to the interaction between the biosorbent surface and added solutes which may compete for the active sites and consequently block the diazinon biosorption. In addition, the inhibition of these ions is probably due to the existence of repulsive forces anion/diazinon.

Conclusion

Pre-treated coffee waste showed a good biosorption for the diazinon and, therefore, can serve as a low-cost alternative for costly activated carbon. Diazinon is classified as a hazardous insecticide and its biosorption on pre-treated coffee waste is of great potential. The effect of the insecticide concentration, contact time, adsorbent dose, solution pH, temperature and inorganic ions on the biosorption was studied. The biosorption increases until pH 7.3 and then decreases at higher pHs. The Langmuir isotherm model gave the best fitting of the experimental data. Batch studies showed that the pseudo-second-order kinetic model can adequately predict the diazinon biosorption. Moreover, it is observed that the intra-particle diffusion is not the rate-controlling step. The kinetic parameters were of the same order of magnitude of those reported in the literature. The thermodynamic study showed a spontaneous and exothermic biosorption onto PCW with chemical diazinon–PCW electrostatic interactions. The diazinon removal efficiency was lower in the presence of inorganic ions NO_3^- and $H_2PO_4^-$ and decreased with increasing their concentrations because of their competitive coverage on the PCW surface.

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