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Removal of carbofuran from aqueous solution by orange peel

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ABSTRACT

In this paper, orange peel was utilized as low-cost adsorbent to remove carbofuran from aqueous solution by adsorption. All the experiments were conducted at 30˚C to investigate the effects of initial concentration, adsorbent dosage, contact time, ionic strength, and pH on carbofuran adsorption. The results showed that it was effective to remove carbofuran in the alkalic medium and the equilibrium adsorption was practically achieved in 60 min. The presence of NaCl inhibited the adsorption of carbofuran onto orange peel. Langmuir model provided the better correlation of the experimental data and could interpret the adsorption process and the maximum monolayer adsorption capacity was found to be 84.49 mg/g at the temperature of 30˚C. The pseudo-second-order kinetic model could describe the adsorption kinetics rationally and the rate-limiting step was the intraparticle diffusion process. It was implied that orange peel may be suitable as adsorbent material for adsorption of N-methyl carbamate insecticides from aqueous solution.

Keywords: Orange peel; Adsorption; Carbofuran; Adsorption isotherms; Adsorption kinetics

1. Introduction

Carbofuran (2,3-dihydro-2,2-dimethylbenzofuran-7-ylmethyl-carbamate) is a broad spectrum carbamate insecticide, which has been used against various foliar pests observed in fruit, vegetable, and forest crops. It is widely used in agricultural cultivations and presents a high persistence in raw milk [1], water [2], soil [3], atmosphere [4], or plants [5], etc., due to its chemical stability. As stated above, the removal of carbofuran from water is necessary, and the development of effective and inexpensive techniques for their removal from water has generated increased research interests in recent years [6–16]. Of the several treatment methods used for the removal of water contaminants including chemical coagulation, filtration, photo oxidation, sedimentation, disinfection, and adsorption, adsorption seems to be the most effective method. Besides the conventional adsorbents, such as active carbons, more and more by-products of agriculture activities have been successfully adopted in water treatment. For example, several literatures have studied the removal of water contaminants using various kinds of these nonconventional materials that have been reported, such as yellow passion fruit wastes [17], rice straw [18], cotton fiber [19], marine alga [20], sunflower seed shells [21], corncobs [22], peanut husk [23], etc.

Orange peel, an agricultural waste available in large quantity in China [24], is often burned or discarded directly into the farm lands, which would produce waste gas and dust or unpleasant smell. Fortunately, orange peel was previously utilized as

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low-cost adsorbent to remove contaminants from wastewater, such as: Acid Violet 17 [25]; methylene blue, rhodamine B, methyl orange, and methyl violet [26]; and Direct Red 23 and 80, Cu(II), Ni(II), and Cd (II) [27–29]. It will solve both the problems we concern about above, and bring economic and environmental benefits to the industrial wastewater treatment.

In our research, the focus is fixed on the removal of carbofuran, which is one of the most widely used carbamates in China, from aqueous solution onto orange peel to simulate the conditions of natural water. The effects of initial carbofuran concentration, contact time, adsorbent dosage, ionic strength, and pH on carbofuran adsorption were studied. The isotherms and kinetics of carbofuran adsorption were studied to understand the adsorption mechanism of carbofuran onto orange peel.

2. Materials and methods

2.1. Preparation of carbofuran solution

Carbamates used in this study was carbofuran (99.5%) purchased from Jiangsu Jialong Chemical Co., Ltd., and used as received without further purification. Stock solution was prepared by dissolving accurately weighted carbofuran in distilled water to the concentration of 200 mg/L. The experimental solutions were obtained by diluting the stock solution accurately to the required concentration. All chemicals used throughout the study were analytical-grade reagents. All the adsorption experiments were carried out at the laboratory temperature of 30℃.

2.2. Preparation of adsorbent

Crude orange peel (OP) was collected from market as solid waste. They were washed with distilled water for several times, and dried in a hot air oven at 55℃ until a constant weight was reached. The dried peels were chipped off to particles with diameters between 0.15 and 0.20 mm by a metal ball mill. The granules were preserved in a desiccator before use.

2.3. Fourier transform infrared study

Fourier transform infrared (FTIR-8400, Shimadzu) analysis was applied on the unused OP and carbofuran-adsorbed-OP to determine the surface functional groups, and the spectra were recorded from 4,000 to 400 cm^{-1}.

2.4. Batch adsorption experiments

Adsorption experiments were carried out in an isothermal rotary shaking at 150 rpm and 30℃ using a series of 500 mL conical flasks containing 200 mL of different initial concentrations of carbofuran solution. The initial pH values of the solutions were previously adjusted with 0.1 mol/L HCl or NaOH. Before determining optimum pH, the experiments were carried out at the original pH of the carbofuran solution (pH = 7.81). Meanwhile, the effects of adsorbent dosage and ionic strength on the adsorption reaction were also studied. The adsorbent was added to each flask, and then the flasks were sealed up. After shaking the flasks for predetermined time intervals, the samples were withdrawn from the flasks and the carbofuran solutions were separated from the adsorbent by filtration with microfilter (0.45 μm). The residual concentrations of carbofuran were measured by high-performance liquid chromatography (Agilent 1200, SHISEIDO C_{18} column 250 mm × 4.6 mm, 5 μm) which used a mobile phase of redistilled acetonitrile:deionized water = 40:60 (v/v) at a flow rate of 1 mL/min throughout the analysis. The wavelength of 280 nm and the column temperature of 30℃ were also selected. The adsorption capacity of the adsorbent was calculated as follows:

$$q_t = \frac{(C_0 - C_t)V}{W} \tag{1}$$

where q_{t} (mg/g) is the amount of carbofuran adsorbed on adsorbent at time t, C_0 (mg/L) and C_t (mg/L) are the carbofuran concentration at time 0 and t, V (L) is the initial volume of carbofuran solution, and W (g) is the amount of adsorbent used. The percentage of carbofuran removal R (%) was calculated using the following equation:

$$R\ (\%) = \left(\frac{C_0 - C_t}{C_0}\right) \times 100 \tag{2}$$

3. Results and discussion

3.1. FTIR of OP

The FTIR spectrum of OP (Fig. 1 and Table 1) shows that some peaks were shifted or disappeared and that new peaks were also detected. In unused OP spectrum, the broad and intense absorption peaks at 3,419 cm^{-1} correspond to the O–H stretching vibrations of alcohols, phenols, and carboxylic acids. The peaks at 1,799, 1,762, and 1,726 cm^{-1} can be assigned to the carbonyl stretching vibration of the carboxyl groups of pectin, hemicellulose, and lignin. The peaks at 1,643 cm^{-1} are due to the C=C stretching vibration that can be attributed to the aromatic C–C bonds and

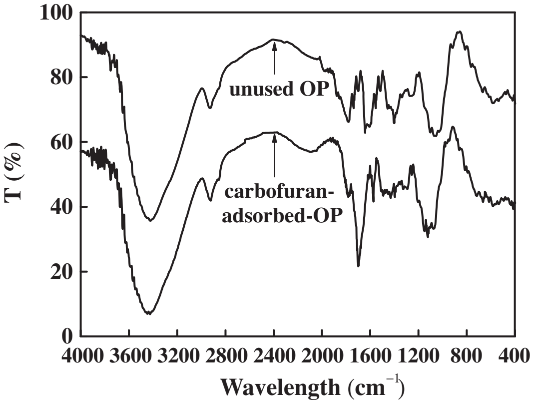

Fig. 1. FTIR of unused OP and carbofuran-adsorbed-OP adsorbents.

to COO− asymmetric stretchings. The peaks at 1080 cm^{-1} could be assigned to C–O stretching vibrations of carboxylic acids and alcohols [30]. Comparing the spectra before and after adsorption, some changes can be seen. It shows that weakened free carboxyl band at 1,799 cm^{-1} and movement of asymmetric C=O band at 1,787 cm^{-1} indicate some carboxyl binding, and the peak 1,762, 1,726 cm^{-1} was appeared after adsorption. Shifting of symmetric C=O band was also seen, and this shift is relatively large [30].

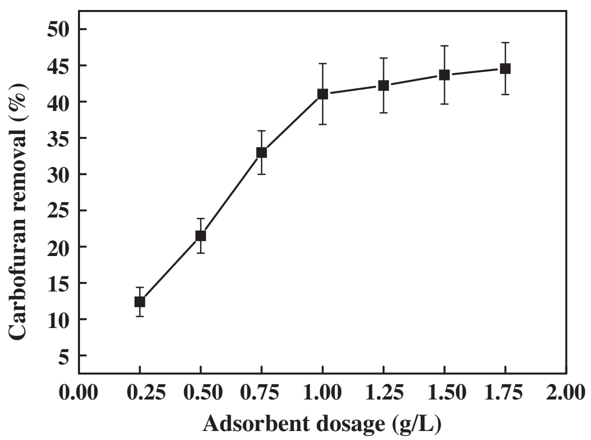

Fig. 2. Effect of adsorbent dosage on carbofuran removal (%) by OP (carbofuran concentration: 40 mg/L; temperature: 30° C; pH: 7.81; shaking speed: 150 rpm; and contact time: 60 min).

3.2. Effect of adsorbent dosage

The effect of adsorbent dosage (0.25, 0.50, 0.75, 1.00, 1.25, 1.50, and 1.75 g/L) on the carbofuran adsorptions by OP was carried out in this study. The percentage (%) of carbofuran removal by varying adsorbent dosage is shown in Fig. 2. It can be seen that at 1.0 g/L of adsorbent dosage, the removal percentage of carbofuran was found to be 41.04% and it was increased to be 43.56% at the adsorbent dosage of 1.75 g/L. Increase in the percentage of carbofuran removal with adsorbent dosage could be attributed to an increase in the adsorbent surface area, which increased the availability of more adsorption sites [31,32]. Therefore, the following experiments were carried out at adsorbent concentration of 1.0 g/L when the concentration of carbofuran is 40 mg/L.

Table 1
FTIR changes of OP adsorbent at the temperature of 30℃

IR peak	Frequency (cm^{-1})		Differences	Assignment
	Before adsorption	After adsorption		
1	1,799	1,787	−12	C=O stretching
2	1,762	–	–	C=O stretching
3	1,726	–	–	C=O stretching
4	1,643	1,704	61	C=O stretching
5	1,618	–	–	C=O stretching
6	1,546	–	–	C=N stretching
7	1,558	1,575	2	Bonded C=C
8	1,556	–		C=N stretching
11	1,406	1,454	49	in-plane—OH bending and C—O stretch of dimmers
12	1,284	1,213	29	C—O stretching
13	1,218	1,274	56	C—N stretching
14	1,110	1,149	39	C—O—C asymmetrical stretching
15	1,080	1,128	48	C—O—C asymmetrical stretching

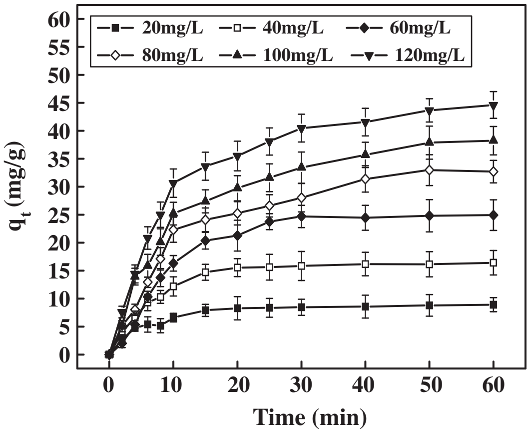

Fig. 3. Effect of initial concentration on removal of carbofuran by OP (adsorbent dosage: 1.0 g/L; temperature: 30℃; pH: 7.81; shaking speed: 150 rpm; and contact time: 60 min).

3.3. Effect of contact time and initial carbofuran concentrations

The effect of contact time and initial concentrations of carbofuran (20, 40, 60, 80, 100, and 120 mg/L) on the capacity of adsorption onto OP was studied. Fig. 3 shows that the adsorption capacity increased with an increase in initial concentration and remained constant after reaching equilibrium time. The concentration provides an important driving force to overcome all mass transfer resistance between the aqueous and solid phases. Hence, a higher initial concentration will enhance the adsorption efficiency [30]. Along with the increase of initial carbofuran concentrations from 20 to 120 mg/L, the adsorption capacity increased from 8.91 to 44.62 mg/g; however, the removal percentage decreased from 44.54 to 37.18%. A similar observation was reported for the adsorption of dyes and heavy metals on OP [25,28,33].

Fig. 3 also indicates that the carbofuran removal was rapid in the initial stages of contact time and gradually decreases with lapse of time until saturation. The rapid adsorption at the initial contact time is due to the availability of the positively charged surface of the OP for adsorption of carbofuran. The slow percentage of carbofuran adsorption is probably due to the electrostatic hindrance or repulsion between the adsorbed negatively charged sorbate species onto the surface of OP and the available anionic adsorbate species in solution as well as the slow pore diffusion of the solute ions into the bulk of the adsorbent. The equilibrium was found to be nearly 60 min when the maximum cefradine adsorption onto OP was reached. The similar trend was also observed for methyl blue adsorption onto pineapple stems [30].

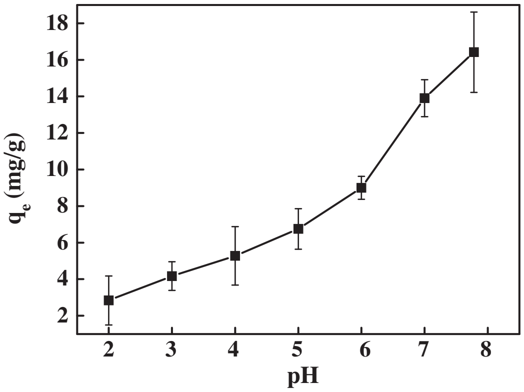

Fig. 4. Effect of pH on removal of carbofuran by OP (carbofuran concentration: 40 mg/L; adsorbent dosage: 1.0 g/L; temperature: 30℃; shaking speed: 150 rpm; and contact time: 60 min).

3.4. Effect of pH

The effects of pH, ranging from 2.00 to 7.81, on the adsorption of carbofuran by OP were studied and the results are shown in Fig. 4. Within 60 min, the adsorption capacity increased from 2.84 to 16.42 mg/g with increasing initial pH values, which indicates that an acidic medium will inhibit the absorption. The effect of pH can be explained considering the surface charge on the adsorbate. The results showed significant variation in the amount of carbofuran adsorbed with increase in pH, in the pH range studied. This could be associated to the ionizable nature of carbofuran in the pH range studied, having a pK_a value of 11.95 ± 0.46 [34]. At lower pH, the carbofuran molecule has become a positively charged ion, thus it tended to be compete with protons for positively charged sites of OP, which resulted in a decrease in the adsorption capacity. At higher pH, the surface of OP maybe negatively charged which enhance the positively charged carbofuran cations through electrostatic force at attraction [35,36]. A similar trend was reported for the adsorption of dyes and heavy metals on OP [35].

3.5. Effect of ionic strength

The effect of ionic strength on the on the adsorption of carbofuran by OP was examined over a range of concentrations of NaCl from 0 to 17.5×10^{-3} M. As elucidated in Fig. 5, the presence of NaCl significantly inhibited the adsorption of carbofuran, and the removal capacity (q_e) decreased from 16.42 mg/g to 2.24 mg/g. The interpretation of the phenomenon was that [37]: in the pH of 7.81, Na^+ as an inhibitor competing with ionizable nature of carbofuran for the limited active sites on the surface of OP reduce the

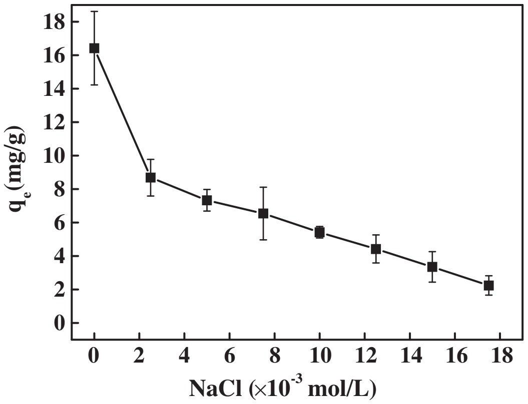

Fig. 5. Effect of ionic strength on removal of carbofuran by OP (carbofuran concentration: 40 mg/L; adsorbent dosage: 1.0 g/L; temperature: 30°C; shaking speed: 150 rpm; contact time: 60 min; and pH: 7.81).

adsorption percentages and capacity, whose mechanism has been reported by ion exchange.

3.6. Adsorption isotherm studies

To optimize the design of an adsorption system for the removal of adsorbate, it is important to establish the most appropriate correlation for the equilibrium data. Various isotherm equations have been used to describe the isotherm curve. The relative parameters of each equation are obtained using the residual sum of squares (RSS) between the calculated data and the experimental data by nonlinear regressive analysis. The calculated expression of RSS is given as Eq. (3):

$$\mathrm{RSS} = \sum (q_c - q)^2 \tag{3}$$

where q_c is the predicted (calculated) adsorption capacity of carbofuran onto OP according to the adsorption models and q is the experimental data.

The experimental data were tested with the Langmuir and Freundlich isotherm equations. Linear regression was frequently used to determine the best-fitting isotherm, and the applicability of isotherm equations was compared by judging the correlation coefficients.

3.6.1. The Langmuir adsorption isotherm

The Langmuir adsorption [38] model is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface. The Langmuir equation was described as follows:

$$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \tag{4}$$

where C_e (mg/L) is the concentration of the carbofuran at equilibrium, q_e (mg/g) is the amount of carbofuran adsorbed at equilibrium, Q_m is the maximum adsorption capacity, and K_L is Langmuir constant related to the affinity of the binding sites and energy of adsorption.

3.6.2. The Freundlich adsorption isotherm

The Freundlich isotherm [39] is the earliest known relationship describing the sorption equation. The fairly satisfactory empirical isotherm can be used for nonideal adsorption that involves heterogeneous surface energy systems and is expressed by the following equation:

$$q_e = K_F C_e^{\frac{1}{n}} \tag{5}$$

where K_F and $1/n$ are empirical constants and indicate adsorption capacity and intensity, respectively.

All relative parameters of the isotherm equations, the determined coefficients (R^2), and the values of

Table 2
Correlation isotherm parameters and correlation coefficients for adsorption of carbofuran onto OP adsorbent

Isotherm models	Correlation parameter		Correlation coefficient
	Name	Value	R^2
Langmuir isotherm	Q_m (mg/g)	84.49	0.9818
	K_L (L/mg)	0.0124	
	RSS	8.08	
Freundlich isotherm	K_F (L/mg)	2.7020	0.9413
	$\frac{1}{n}$	0.6167	
	RSS	26.11	

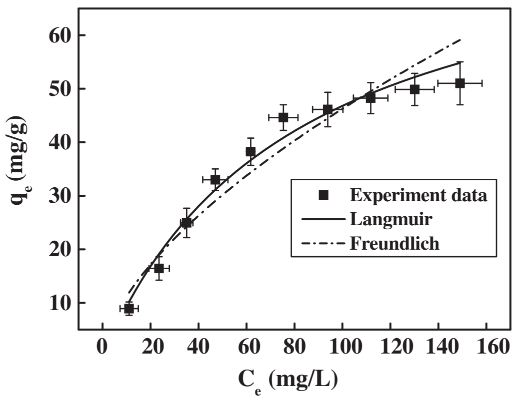

Fig. 6. Comparison of different isotherm models for carbofuran adsorption onto OP (adsorbent dosage: 1.0 g/L; temperature: 30℃; shaking speed: and 150 rpm; contact time: 60 min).

other parameters are listed in Table 2, respectively. Fig. 6 depicts the experimental equilibrium data and the fitted equilibrium curves by two various isotherms, respectively.

From Table 2, it is observed that the equilibrium data were fitted to two isotherm equations (the Langmuir and Freundlich expressions), with R^2 values of 0.9818 and 0.9413, respectively. By comparing between the experimental data and fitted curves, it was found the Langmuir isotherms can predict equilibrium adsorption behavior. The values of RSS of the Langmuir and Freundlich expressions were 8.08 and 26.11, respectively. The higher coefficient of 0.9818 and the lower RSS of 8.08 for the Langmuir isotherm predicted the monolayer coverage of carbofuran onto OP. A similar observation had been reported in previous literature when orange peel was utilized as low-cost adsorbent to remove dyes from colored textile wastewater [33].

From Table 2, it can be seen that the values of Q_m from Langmuir models was 84.49 mg/g. The reported values of Q_m, the Langmuir constant related to saturated monolayer adsorption capacity of carbofuran for granular activated carbon [9], date seed activated carbon [10], and clayey soil [8] are 96.15, 137.04, and 4.85 mg/g, respectively. Furthermore, orange peel has been utilized as low-cost adsorbent to remove Violet 17 [25], methyl orange [26], Cu(II), Ni(II), and Cd(II) [27,28] from aqueous solution in previous paper and the values of Q_m obtained from Langmuir was 19.88, 20.50, 52.08, and 80.00 mg/g, respectively. In the present study, the carbofuran adsorption capacity of OP estimated from Langmuir isotherm is 84.49 mg/g, which indicated that OP is competitive to other adsorbents for the uptake of carbofuran from their aqueous solutions. Furthermore, as an agricultural by-product, orange peel is vast and cheap, and therefore, it can be used to remove carbofuran from solution.

3.7. Adsorption kinetics studies

Adsorption kinetics give information about adsorption capacity and rate of the biosorption process occurs. It is important to determine appropriate kinetic model that provides best fitting with the experimental data. In this study, common used models, pseudo-first-order, second-order models, and intraparticle diffusion model were applied to analyze experimental data and the kinetic adsorption process was elucidated.

3.7.1. Pseudo-first-order model

The equation form of pseudo-first-order model was described by Lagergren [40]:

$$q_t = q_e(1 - e^{-k_1 t}) \tag{6}$$

Above equation can be linearized in following reciprocal form:

$$\log(q_e - q_t) = -\frac{k_1 t}{2.303} + \log q_e \tag{7}$$

where q_e is the amount of carbofuran adsorbed at equilibrium (mg/g), q_t is the amount of carbofuran adsorbed at time t (mg/g), and k_1 is the rate constant of pseudo-first-order adsorption (min^{-1}). The value of k_1 for carbofuran adsorption was determined from the plot of $\ln(q_e - q_t)$ against t.

3.7.2. Pseudo-second-order model

Also, the pseudo-second-order equation based on adsorption equilibrium capacity can be expressed as follows [41]:

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{8}$$

A linear form of pseudo-second-order model is as follows:

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

where k_2 (g/mg min) is the equilibrium rate constant of pseudo-second-order model. The value of k_2 can be

Table 3
Comparison of the pseudo-first-order, pseudo-second-order adsorption rate constants, and calculated and experimental q_e value obtained at different initial carbofuran concentrations

C_0 (mg/L)	Pseudo-first-order kinetic model				Pseudo-second-order kinetic model		
	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	K_1 (min^{-1})	R_1^2	$q_{e,cal}$ (mg/g)	K_2 (g/mg min)	R_2^2
20	8.91	5.69	0.0801	0.9350	9.29	0.0242	0.9974
40	16.42	10.96	0.0900	0.9173	18.21	0.0102	0.9955
60	24.93	20.95	0.1149	0.9424	27.62	0.0047	0.9917
80	32.99	27.66	0.0820	0.9442	34.84	0.0027	0.9893
100	38.23	32.20	0.0801	0.9454	40.16	0.0026	0.9902
120	44.62	37.38	0.0709	0.9794	46.95	0.0026	0.9961

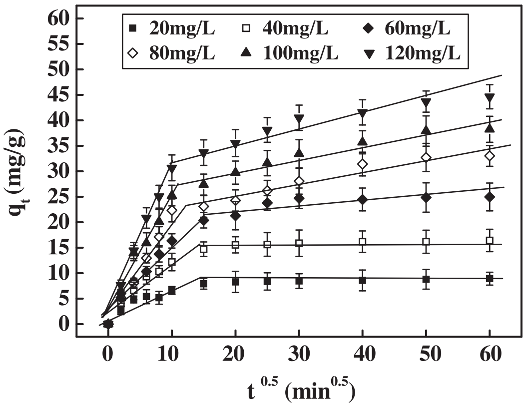

Fig. 7. Intraparticle diffusion plot for the adsorption and different initial carbofuran concentrations (adsorbent dose: 1.0 g/L; temperature: 30℃; shaking speed: 150 rpm; contact time: 60 min; and pH: 7.81).

calculated from the slope and intercept of the plots t/q_t vs. t.

The values of k_1, k_2, R_1^2 (correlation coefficient for pseudo-first-order kinetics) and R_2^2 (correlation coefficient for pseudo-second-order kinetics) were calculated and shown in Table 3. According to Table 3, the correlation coefficients (R_2^2) were found to be in the range 0.98–0.99, which indicated that the data conformed well to the pseudo-second-order kinetic model. The high agreement that exist between the calculated and experimental q_e values of the pseudo-second-order kinetic model over the other model renders it best in adsorption of carbofuran on OP. This confirms that the adsorption data are well represented by the pseudo-second-order kinetics for the entire adsorption period. The increase in values of the adsorption capacity, q_e, with an increase in the initial carbofuran concentration could be attributed to the increase in the driving force for mass transfer, allowing more cefradine molecules to reach the surface of the adsorbents in the whole process.

3.7.3. Intraparticle diffusion model

The kinetic results were further analyzed by the intraparticle diffusion model to elucidate the diffusion mechanism on the OP surfance [42]:

$$q_t = K_{\mathrm{id}} t^{\frac{1}{2}} + C \tag{10}$$

where C is the intercept, K_{id} is the intraparticle diffusion rate constant (mg/g min$^{0.5}$), which can be evaluated from the slope of the linear plot of q_t vs. $t^{0.5}$ (Fig. 7). If the regression of q_t vs. $t^{0.5}$ is linear and passes through the origin, then intraparticle diffusion is the sole rate-limiting step [23]. For intraparticle diffusion plots, the first, sharper region is the instantaneous adsorption or external surface adsorption. The second region is the gradual adsorption stage where intraparticle diffusion is the rate limiting. As seen from Fig. 7, the plots were not linear over the whole time range, implying that more than one process affected the adsorption.

4. Conclusions

This study confirmed that orange peel, a low-cost agricultural waste, could effectively remove carbofuran from wastewater. The results showed that it was effective to remove carbofuran in the alkalic medium and the equilibrium adsorption was practically achieved in 60 min. The presence of NaCl inhibited the adsorption of carbofuran onto orange peel. The equilibrium adsorption data were analyzed by Langmuir and Freundlich models. The results indicated that the Langmuir model provided the better correlation of the experimental data and and the maximum monolayer adsorption capacity was found to be 84.49 mg/g at the temperature of 30℃. The kinetic study of carbofuran by orange peel performed based on pseudo-first-order, pseudo-second-order, and intraparticle diffusion equations. The adsorption kinetics followed pseudo-second-order kinetic model very well and the rate-limiting step was the intraparticle diffusion process. Based on this research, an application of orange peel on wastewater treatment could efficiently remove carbamates from aqueous solution and solve the problems of solid waste as well.

Acknowledgments

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