Porogen effect on characteristics of banana pith carbon and the sorption of dichlorophenols

M. Sathishkumar [a,*], K. Vijayaraghavan [b], A.R. Binupriya [a], A.M. Stephan [c], J.G. Choi [d], S.E. Yun [a]

[a] *Division of Biotechnology, Department of Food Science and Technology, Institute of Agricultural Science and Technology, Chonbuk National University, Jeonju 561-756, Republic of Korea*
[b] *Division of Environmental and Chemical Engineering, Research Institute of Industrial Technology, Chonbuk National University, Jeonju 561-756, Republic of Korea*
[c] *Central Electrochemical Research Institute, Karaikudi 630006, Tamilnadu, India*
[d] *National Agricultural Products Quality Management Service, Jeonju 561-823, Republic of Korea*

Abstract

Banana pith was used as precursor material to prepare carbon with and without porogens. Characterization of the carbons showed higher BET surface area (1285 m^2/g) for $ZnCl_2$-treated carbon, comparatively. Adsorption experiments were conducted to study the removal of 2,4-dichlorophenol (DCP) from aqueous solutions using the carbons under varying experimental conditions. Decrease in pH increased the percentage removal. All the carbons studied showed greater percentage of DCP removal with decrease in the initial concentration of DCP. Kinetic studies showed that the adsorption of DCP on the carbons was a rapid process. Nonlinear forms of pseudo-first-order and pseudo-second-order models were used to fit the experimental data. Among these the pseudo-first-order model described the data with high correlation coefficients and low percentage error values. Four nonlinear isotherm models including the Langmuir, Freundlich, Toth, and Sips were used to analyze the experimental DCP isotherms under different pH (2–4) conditions. Adsorption capacities (Q_{max}) from the Langmuir model were found to be 129.4, 67.7, and 49.9 mg/g for $ZnCl_2$-treated, KOH-treated, and porogen-free carbon, respectively, at pH 2. From desorption studies it seemed that chemisorption played a major role in the adsorption process. The results indicated that $ZnCl_2$-treated carbon could effectively remove phenols from wastewater.

1. Introduction

Organic pollutants have been a major factor of environmental problems for a number of years. Among these organic pollutants, chlorophenols are most common and have been highlighted as priority pollutants. In drinking water, phenols form chlorophenols in the presence of chlorine, imparting a medicinal taste that is quite pronounced and objectionable [1]. Chlorophenols are used in petrochemical refinery, plastic, pesticide, herbicide, fiberglass manufacturing, and coal conversion industries and hence are present in the effluents. General weakness, fatigue, ataxia, headache, anorexia, sweating, hyperpyrexia, nausea, vomiting, tachycardia, abdominal pain, terminal spasms, and death characterize acute poisoning by dichlorophenol [1]. Removal of phenolic compounds from wastewater is therefore of utmost importance for preventing pollution of water in the receiving watercourse. It is recommended that their concentration should be decreased up to 0.1 mg/L in wastewaters, if complete removal is not possible before their discharge into water streams as they are toxic even at low concentrations [2]. Many industrial wastes contain organics which are difficult, or impossible, to remove by conventional biological treatment processes [3]. The removal of organic refractory pollutants by catalytic wet peroxide ox-

idation [4], photocatalytic degradation using TiO_2 [5], and sonophotochemical [6] and ultrasonic degradation [7] has been investigated. However, in water treatment the most widely used method is adsorption onto the surface of activated carbon. The adsorption of phenol from aqueous solution onto carbons has received a great deal of attention and an exhaustive review has been published by Radovic et al. [8]. But its high running cost inhibits its application on large scale. Due to these problems, investigation of some new, indigenous, and cheaper sorbents especially from agricultural wastes for the removal of these contaminants is a focus of intense research these days. Palm pith carbon [1], palm seed coat carbon [9], olive stones [10], fruit seed hulls [11], wood pulp [12], coconut coir pith carbon [13], and rice husk [14] are some adsorbents that have been studied for the removal of chlorophenols. But most of these adsorbents are industrially unsuitable due to their low adsorption capacity. Efficiency of sorbent is mainly dependent on surface area and binding forces present within the particles of sorbents, as well as chemical characteristics of sorbate. The surface area of any carbon can be increased by increasing its porosity. Porosity in carbonaceous materials can be generated with the use of several chemical activation agents such as Na_2CO_3, K_2CO_3, NaOH, KOH, H_3PO_4, $AlCl_3$, $MgCl_2$, LiCl, and $ZnCl_2$.

The objective of this work was to increase the surface area of carbon prepared from an agricultural waste, banana pith, using chemical porogens like KOH and $ZnCl_2$ for activation and to study their adsorption characteristics for the removal of 2,4-dichlorophenol (DCP) from aqueous solutions.

2. Materials and methods

2.1. Preparation and characterization of adsorbent

High-quality banana pith fibers were obtained from agricultural fields in Kerala, India. Sheets of the herbaceous stems were dried in the sun and fibers were mechanically drawn from them. The fibers were then soaked in water, washed, and dried. The brownish white dry fibers were then treated with concentrated solutions of $ZnCl_2$ or KOH for 5 days at 110 °C at a fiber:porogen ratio of 1:5 by weight, and dried. Pyrolysis was carried out by heating under flowing nitrogen at 800 °C at a heating ramp of 10 °C/min for a hold period of 1 h [15]. Pyrolytic carbons were also obtained without treatment with the porogen, in which case the fibers were simply heat-treated under the above conditions. Elemental analysis was done by a Perkin–Elmer CHN 2000 elemental analyzer. Powder X-ray diffraction patterns were recorded between 10° and 80° on a Jeol X-ray diffractometer (Model D/Max 2500) fitted with a nickel-filtered $CuK\alpha$ radiation source [15]. The morphologies of the pyrolytic carbons were examined by a scanning electron microscope (FESEM S-4700, Hitachi). BET surface area measurements were carried out on a surface area analyzer (Micromeritics ASAP2010). FTIR spectra were recorded on a Perkin–Elmer Paragon 500 FTIR.

From here on for simplicity, porogen-free carbon will be referred as PFC, KOH-treated carbon as KTC, and $ZnCl_2$-treated carbon as ZTC.

2.2. Biosorption experiments

Adsorption isotherm experiments were carried out by agitating 100 mg of carbon with 50 ml of 0–300 mg/L DCP solution under various pHs (2–4) at 200 rpm, 35 °C in a thermostated rotary shaker (ORBITEK). DCP concentration was estimated spectrophotometrically by monitoring the absorbance at 284 nm using a UV–vis spectrophotometer (Hitachi U-3210). The solution pH was measured using a pH meter (Elico LI-107). The DCP solutions were separated from the adsorbent by centrifugation at 20,000 rpm for 20 min and its absorbance was measured. Kinetic experiments were conducted by fixing initial DCP concentration at 100 mg/L and pH at 2 with adsorbent dosage fixed at 2 g/L. The samples were collected at different time intervals and the remaining estimation procedure was the same as that of isotherm experiments.

2.3. Adsorption isotherm modeling

The Langmuir, Freundlich, Toth, and Sips models were used to describe the nonlinear equilibrium relationship between the solute sorbed onto the sorbent (Q) and that left in solution (C_f). The model equations can be represented as

Langmuir model,

$$Q = \frac{Q_{max} b C_f}{1 + b C_f}; \tag{1}$$

Freundlich model,

$$Q = K_F C_f^{1/n}; \tag{2}$$

Toth model,

$$Q = \frac{Q_{max} b_T C_f}{[1 + (b_T C_f)^{1/n_T}]^{n_T}}; \tag{3}$$

Sips model,

$$Q = \frac{K_S C_f^{\beta_S}}{1 + a_S C_f^{\beta_S}}; \tag{4}$$

where Q_{max} is the maximum DCP uptake (mg/g), b is the Langmuir equilibrium constant (L/mg), K_F is the Freundlich constant (L/g), n is the Freundlich constant, b_T is the Toth model constant, n_T is the Toth model exponent, K_S is the Sips model isotherm constant (L/g), a_S is the Sips model constant (L/mg), and β_S is the Sips model exponent. All isotherm and kinetic model parameters were evaluated using nonlinear regression employing the Sigma Plot (version 4.0, SPSS, USA) software [16]. The average percentage error between the experimental and the predicted values was calculated using

$$\varepsilon(\%) = \frac{\sum_{i=1}^{N}(Q_{exp,i} - Q_{cal,i}/Q_{exp,i})}{N} \times 100, \tag{5}$$

where Q_{exp} and Q_{cal} represent the experimental and calculated uptake values, respectively, and N is the number of measurements.

Table 1
The atomic hydrogen to carbon ratio (H/C), average pore diameter, and BET surface area of the pyrolytic carbons

Sample	H/C ratio	Pore diameter (Å)	BET surface area (m^2/g)
PFC	30	19	37
KTC	24	24	751
ZTC	26	57	1285

2.4. Desorption experiments

Desorption studies were conducted using the DCP-loaded adsorbent, which was previously exposed to 300 mg/L of DCP solution at pH 2. The DCP-loaded adsorbent was filtered using Whatman filter paper and washed gently with distilled water to remove any unadsorbed DCP. Several such samples were prepared. Then the spent adsorbent was agitated for 120 min with 50 ml of distilled water, adjusted to different pH values. The desorbed DCP was estimated as noted earlier. Similarly desorption experiments were also carried out in 50 ml of 1 N NaOH solution.

All experiments were duplicated and the reported values were the average of two data sets.

3. Results and discussion

3.1. H/C ratio and surface area

Table 1 gives values of H/C ratio, average pore diameter, and BET surface area of the pyrolytic carbons. It can be seen that the H/C ratio of the porogen-treated fiber carbons is less than that of the untreated one. The heat generated during the decomposition of the porogen or any chemical reaction of the products formed during decomposition of the porogen in the fibers might have altered the chemical composition of the carbonaceous products. Despite a large volume of literature on chemical activation, the mechanisms of the processes are yet to be fully elucidated. It is, however, generally believed that ZnCl$_2$ acts as a dehydrating agent [17–19] and on carbonization leads to charring and aromatization of the carbon skeleton and creation of pore structure [17,19]. ZnCl$_2$ at high concentrations is known to give Bronsted acidity to the activation solution, and to dissolve cellulosic constituents of biomass [20]. In the case of KOH, the oxygen in the alkali removes the cross-linking and stabilizes the carbon atoms in crystallites [21]. Metallic potassium obtained at the pyrolysis temperature may intercalate and force apart the lamellae of the crystallites [21]. Removal of metallic potassium by washing creates microporosity in the new structure [21,22]. Furthermore, the surface area and pore diameter of the products are greatly varied due to the action of the porogens. For example, the pore diameter increased from 19 Å for the untreated fiber carbon to 24 and 57 Å for the products obtained by treatment with KOH and ZnCl$_2$, respectively. The attendant increase in the BET surface area was from 37 to 751 and 1285 m^2/g for the ones after treatment with KOH and ZnCl$_2$, respectively. Thus, the pore size was increased up to threefold, and the surface area increased 35 times because of the action of the porogens. The microstructural evolutions can significantly

influence the adsorption behavior of the carbons. Wu et al. [23] reported that the BET surface area of carbons prepared from KOH-treated fir wood ranged between 891 and 2794 m^2/g.

3.2. FTIR analysis

FTIR spectra for the carbons obtained with and without porogen treatment were studied. The characteristic peak around 1650 cm^{-1} is ascribed to νC=O (asymmetric stretching), the peak around 1400 cm^{-1} to δCH$_2$, and those around 1300 and 1000–1200 cm^{-1} to νC=O (symmetric stretching) and νC=O, respectively. The oxygen in the carbons is present in functional groups such as carboxyls, carboxyl anhydrides, phenols, carbonyls, lactones, quinines, quinine-like structures, etc. [24]. These functional groups appear at edge carbon atoms, and are formed during the pyrolysis process. Similar observations have been reported by Naoi et al. [25].

3.3. SEM examination

Fig. 1 depicts the SEM micrographs of banana pith carbons obtained with and without porogen treatment. The PFC shows a tube-like structure (Fig. 1a). On the other hand, the carbon from fiber treated with ZnCl$_2$ has large aligned fibrous stacks, parts of which seem to have been blown off by the emanating gases [15]. More interestingly, the KOH-treated fiber carbons have a loose, disjointed structure with no particular shape.

3.4. XRD analysis

Figs. 2a–2c show the XRD patterns of the carbon samples. They are typical of disordered carbons, although the characteristic (0 0 2) and (1 0 0) peaks of graphite are still discernible. The (1 0 0) reflections around 43° honeycomb structures are formed by sp^2 hybridized carbons, while the broad (0 0 2) reflections between 20° and 30° indicate small domains of coherent and parallel stacking of the grapheme sheets. According to Liu et al. [26] the empirical parameter, R, defined as the ratio of the height of the (0 0 2) Bragg reflection to that of background is a measure of the quantity of single layered carbon sheets in disordered carbons prepared by low-temperature pyrolysis. Low values of the R factor for the samples (PFC, 2.31; KTC, 2.02; ZTC, 2.27) suggest large concentrations of nonparallel single layers of carbon. The increase in the R value on treatment with the porogens suggests a breakdown of aligned structural domains in the carbon matrix.

3.5. Adsorption kinetic experiments

In the first stage to elucidate the performances of different forms of carbon samples on the removal of DCP, adsorption kinetic experiments were conducted. Sorption kinetics in wastewater treatment is significant as it provides valuable insights into the reaction pathways and into the mechanism of sorption reactions [27]. Also, the kinetics describes the solute uptake which in turn controls the residence time of sorbate uptake
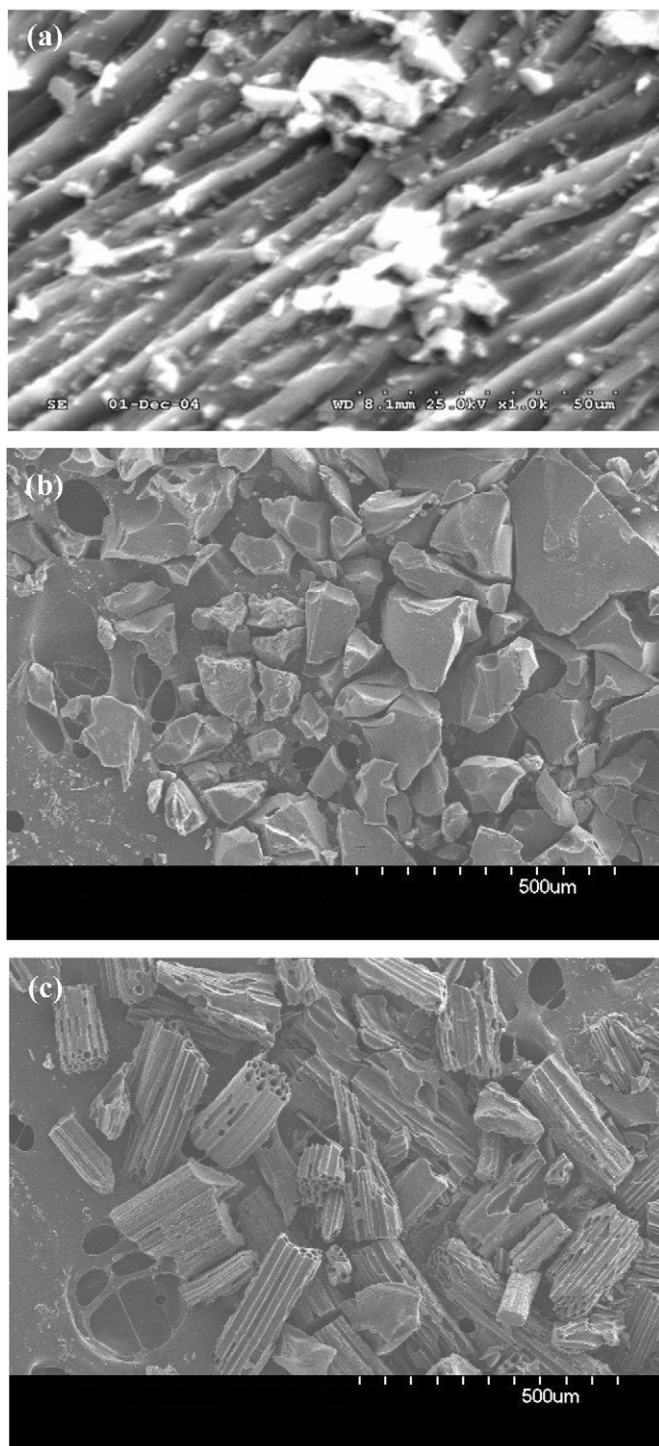
Fig. 1. SEM micrographs of pyrolytic carbons derived from: (a) PFC, (b) KTC, and (c) ZTC.

Fig. 2. XRD patterns of pyrolytic carbons derived from: (a) PFC, (b) KTC, and (c) ZTC.

at the solid–solution interface. It was observed that DCP up-take was rapid for the initial 30 min and then it proceeded at a slower rate and finally attained saturation (Fig. 3). The higher sorption rate at the initial period (30 min) may be due to an increased number of vacant sites available at the initial stage, which results in an increased concentration gradient between sorbate in the solution and sorbate in the adsorbent surface [1]. As time increases, this concentration gradient is reduced due
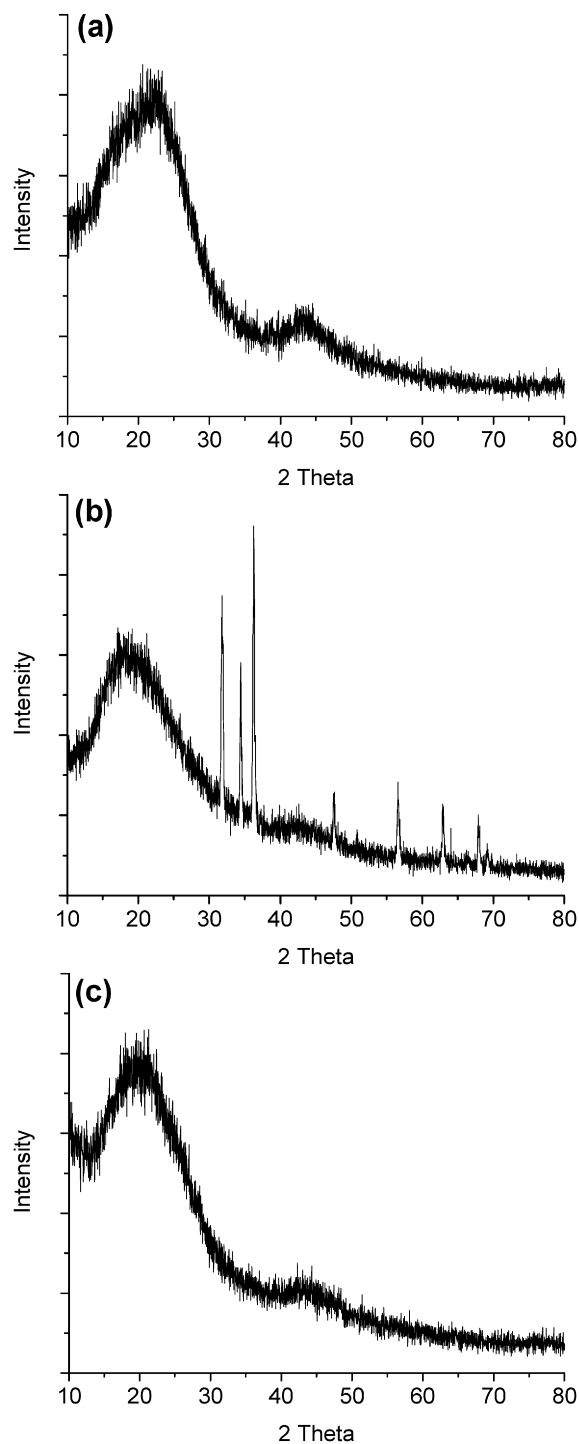
to the sorption of DCP onto vacant sites, leading to a decrease in sorption rate at later stages. On comparison, ZTC performed well in DCP adsorption.

The experimental adsorption kinetic data were modeled using pseudo-first- and pseudo-second-order kinetics. The nonlinear form of pseudo-first- and pseudo-second-order models are shown below as Eqs. (2) and (3), respectively [28],

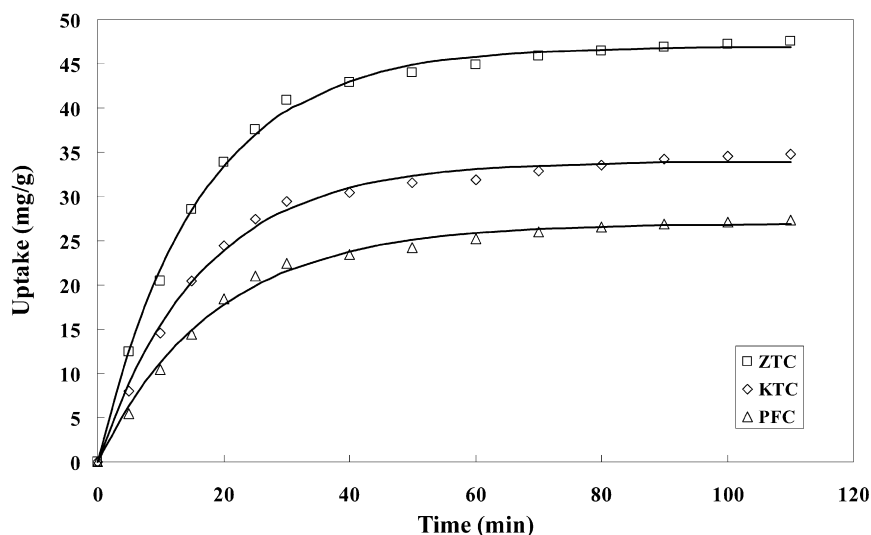$$Q_t = Q_e\big(1 - \exp(-k_1 t)\big), \tag{6}$$

Fig. 3. DCP adsorption kinetics onto different forms of carbon (initial DCP concentration = 100 mg/L and pH 2). Lines were predicted by a pseudo-first-order model.

Table 2
Pseudo-first- and pseudo-second-order model kinetic parameters obtained during DCP adsorption onto different forms of carbon

Carbon type	Experimental Q_e (mg/g)	K_1 (1/min)	Predicted Q_e (mg/g)	R^2	ε (%)	K_2 (g/mg min)	Predicted Q_e (mg/g)	R^2	ε (%)
ZTC	47.5	0.062	46.9	0.998	0.31	0.0013	54.9	0.988	1.68
KTC	34.8	0.061	33.9	0.995	0.94	0.0018	40.0	0.985	2.33
PFC	27.4	0.054	26.9	0.994	1.48	0.0018	32.3	0.984	2.99

$$Q_t = \frac{Q_e^2 kt}{1 + Q_e kt}, \tag{7}$$

where Q_e is the amount of DCP sorbed at equilibrium (mg/g), Q_t is the amount of DCP sorbed at time t (mg/g), k_1 is the first-order equilibrium rate constant (1/min), and k_2 is the second-order equilibrium rate constant (g/mg min). The rate constants predicted equilibrium uptakes and corresponding correlation coefficients for all forms of carbon tested have been calculated and summarized in Table 2.

On comparisons based on correlation coefficients and percentage error values, the pseudo-first-order model was found to describe the kinetic data more accurately than the pseudo-second-order model. Also, the pseudo-first-order model successfully simulated the kinetic curves (Fig. 3) and predicted the equilibrium uptake values (Table 2).

3.6. Adsorption isotherms and modeling

Next, experiments were conducted to examine the full saturation potential of the adsorbents. For this purpose, isotherm experiments were conducted under different pH conditions (pH 2–4) by varying initial DCP concentrations from 0 to 300 mg/L. Of the examined conditions, pH 2 was found to be suitable for the removal of DCP in the case of all three carbons. When pH is less than the pK_a (DCP: pK_a = 7.89), DCP primarily exists in its molecular form [29], and the amount of adsorption remains relatively constant. When the pH value is higher than the pK_a, the dissociation of chlorophenols to anions increases and the amount of adsorption decreases. When the pH

is less, the overall surface charge of carbon became positive and this led to the interactions between the aromatic rings of DCP activated by the OH⁻ and Cl⁻ and the groups of the carbon surface. At very low pH values, the surface of sorbent would also be surrounded by the hydronium ions which enhance the chlorinated phenols interaction with binding sites of the adsorbent by greater attraction forces [30]. Also, the isotherms at pH 2 exhibited the steepest initial isotherm slope, which is the measure of the sorbent–solute affinity, with the eventual highest uptake values of 117, 59.4, and 45.3 mg/g for ZTC, KTC, and PFC, respectively. Comparing the three forms of carbon, the isotherm of ZTC was the steepest and indicated the highest affinity of DCP toward binding sites (Fig. 4).

Adsorption isotherms were modeled using the Langmuir, Freundlich, Toth, and Sips models. The main reason for the extended use of these isotherm models was that they incorporate easily interpretable constants. The model coefficients along with correlation coefficients (R^2) and average percentage error (ε) values obtained from the four isotherm models are listed in Table 3.

The Langmuir sorption isotherm is a two-parameter isotherm model, which has traditionally been used to quantify and contrast the performance of different sorbents. In its formulation, binding to the surface was primarily by physical forces and implicit in its deviation was the assumption that all sites possess equal affinity for the sorbate [16]. Its use was extended to empirically describe the equilibrium relationships between the bulk liquid and the solid phases [31]. In this study, the Langmuir model produced reasonably good agreement with the sorption
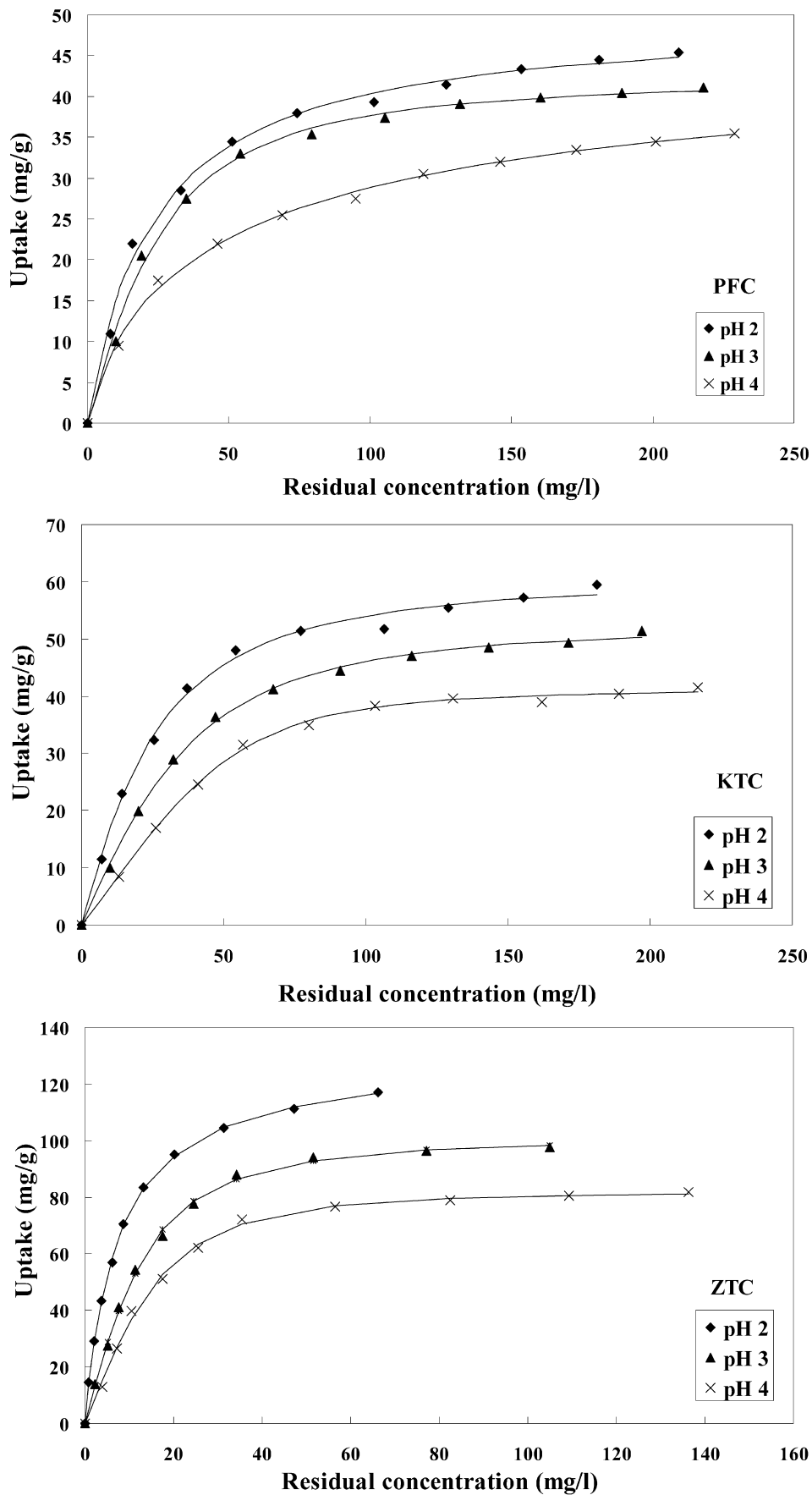
Fig. 4. Adsorption isotherms under different pH conditions. Lines were predicted by the Toth model.

Table 3
Isotherm model parameters under different pH conditions for different forms of carbon

pH	Carbon type	Langmuir model				Freundlich model				Toth model					Sips model				
		Q_{max} (mg/g)	b (L/mg)	R^2	ε (%)	K_F $(l/g)^{1/n}$	n	R^2	ε (%)	Q_{max} (mg/g)	b_T $(L/mg)^{1/\beta}_{RP}$	n_T	R^2	ε (%)	K_S $(L/g)^{1/\beta}_S$	a_S $(L/mg)^{1/\beta}_{RP}$	β_S	R^2	ε (%)
2	ZTC	129.4	0.13	0.999	0.33	29.9	2.88	0.955	11.26	130.4	0.13	1.02	0.999	0.15	17.8	0.14	0.99	0.999	0.09
3	ZTC	114.8	0.08	0.992	3.57	22.1	2.89	0.921	12.79	101.1	0.06	0.60	0.999	0.13	9.3	0.08	0.97	0.991	3.99
4	ZTC	94.1	0.07	0.986	5.26	18.9	3.12	0.910	12.34	82.3	0.05	0.52	0.998	1.24	6.9	0.07	0.96	0.984	5.73
2	KTC	67.7	0.04	0.993	2.15	10.3	2.88	0.951	6.59	60.9	0.03	0.68	0.996	0.57	3.1	0.04	0.93	0.991	2.70
3	KTC	61.9	0.03	0.993	2.94	7.4	2.63	0.950	6.78	52.4	0.02	0.56	0.999	0.76	2.1	0.03	0.92	0.990	3.56
4	KTC	51.8	0.02	0.982	3.97	5.8	2.61	0.931	7.42	41.1	0.02	0.36	0.998	0.38	1.5	0.03	0.91	0.976	4.67
2	PFC	49.9	0.04	0.996	0.90	9.2	3.23	0.965	4.17	49.7	0.04	0.99	0.996	0.86	1.9	0.04	1.03	0.995	0.73
3	PFC	46.6	0.04	0.993	2.09	8.5	3.27	0.947	5.20	42.2	0.03	0.66	0.997	0.90	2.4	0.05	0.90	0.990	2.60
4	PFC	40.4	0.03	0.996	0.53	5.5	2.85	0.986	2.10	49.7	0.04	1.53	0.998	0.36	1.5	0.03	0.89	0.997	0.07

isotherm data (Table 3). The Langmuir model served to estimate the maximum uptake values where they could not be reached in the experiments. The coefficient b represents the affinity between the sorbent and the sorbate. Both Q_{max} and b increase with decreasing pH from 4 to 2. High b values indicate that the sorbent can remove DCP even at trace levels and high Q_{max} values show a desirable high capacity of DCP binding [31]. From Table 3, it can be inferred that ZTC exhibited the highest Q_{max} and b values compared to other forms of carbon examined.

The DCP adsorption capacity observed in this study was superior when compared to the results of other agricultural wastes published in the literature. Coir pith carbon [13] exhibited 19.12 mg DCP/g and Palm pith carbon [1] adsorbed 19.16 mg DCP/g compared to 129.4 mg DCP/g by ZTC in this study.

The Freundlich isotherm, again a two-parameter isotherm model was originally empirical in nature, but later became interpreted as sorption to heterogeneous surfaces or surfaces supporting sites with varied affinities [16]. The Freundlich coefficient K_F of ZTC reached its corresponding maximum value at pH 2, implying that the binding capacity had reached its highest value compared to the other conditions investigated (Table 3).

To improve the fitness of sorption isotherm data, two three-parameter isotherm models, Sips and Toth, were also used. The Sips or Langmuir–Freundlich isotherm was employed in the present study. At low sorbate concentrations this model effectively reduces to the Freundlich isotherm and thus does not obey Henry's law. At high sorbate concentrations, it predicts a monolayer sorption capacity characteristic of the Langmuir isotherm [16,32]. The results indicated that ZTC outperformed all other forms of carbon with maximum K_S, a_S, and β_S values at pH 2 (Table 3). The exponent β_S values were close to unity. It means that DCP sorption data obtained in this study are more of a Langmuir rather than a Freundlich form, which was also confirmed in Table 3.

The Toth isotherm, derived from potential theory, has proven useful in describing sorption in heterogeneous systems such as phenolic compounds on carbon. It assumes an asymmetrical quasi-Gaussian energy distribution with a widened left-hand side; i.e., most sites have sorption energy less than the mean value [16,32]. All three Toth model constants were found maximum in the case of DCP adsorption by ZTC (Table 3). The fitness of adsorption isotherm data was improved, in all cases, when the Toth model was applied (Fig. 4). The isotherm data described by the Toth model indicate that the surface of the adsorbent is heterogeneous and contains different functional groups.

3.7. Desorption

The attractiveness of the adsorption process is enhanced when a possibility of recovery of the adsorbed solute exists. Desorption was initially attempted by varying the pH from 2 to 11 and the results suggested that elution efficiency was not even 35% (Fig. 5). This indicates that chemisorption has played a major role in the adsorption process [33]. Hence desorption was attempted in 1 M NaOH solution. NaOH reagent results in the formation of sodium salt of phenol which may facilitate desorption of phenol from carbon surfaces [9]. Very encouraging results were obtained with 1 M NaOH which was able to elute 98.1% of DCP from the DCP-loaded ZTC.

The regeneration experiments were aimed to explore the adsorption potential of ZTC for DCP over three sorption–desorption cycles. The adsorbent approximately retained their first cycle DCP uptake (95 mg/g) throughout the three cycles examined, which consistently reached high elution efficiencies around 98% by 1 M NaOH. Most importantly, the weight loss was insignificant (<6%) at the end of three consecutive cycles.

4. Conclusions

From the present study on the adsorption of DCP from aqueous solution, using chemically treated banana pith carbon, the following conclusions are suggested:

- Among the chemical agents used, $ZnCl_2$ used as porogen increased the adsorbent surface area from 37 to 1285 m^2/g.
- SEM micrograph confirmed the formation of porous structures on the carbon probably due to emanating gases.
- Lower pH proved to be efficient for DCP adsorption onto all forms of banana pith carbon.
- Kinetic studies revealed that DCP uptake was rapid for the initial 30 min and thereafter it proceeded at a slower rate and finally attained saturation. The nonlinear form of pseudo-first-order kinetic model described and simulated the kinetic data well.
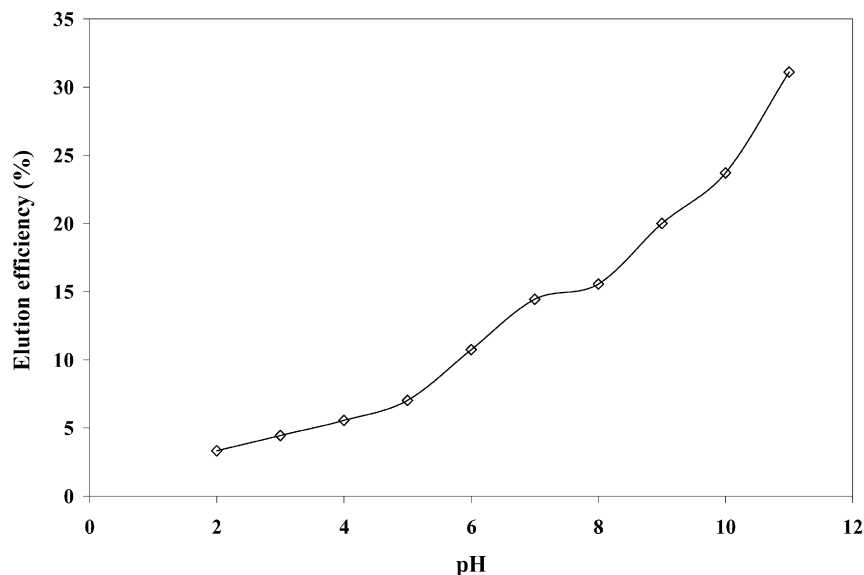
Fig. 5. Elution of DCP under different pH conditions (sorbent = 95 mg/g loaded ZTC).

- Adsorption isotherms were modeled using the Langmuir, Freundlich, Sips, and Toth models. ZTC exhibited a DCP uptake of 129.4 mg/g compared to the KTC and PTC uptakes of 67.7 and 49.9 mg/g, respectively, according to the Langmuir model. Based on the correlation coefficients and percentage error values, the Toth model better simulated the DCP adsorption isotherms under all examined conditions.
- Desorption was possible with 1 M NaOH with elution efficiency of 98%. The adsorption potential of ZTC remained effective for the three sorption–desorption cycles with <6% weight loss.

Thus it could be concluded that ZTC can be used as a potential adsorbent for removal of 2,4-DCP. Since the precursor material, banana pith, is inexpensive, indigenous and easily available in plenty as waste, its use as adsorbent would significantly lower treatment costs and can be viewed as a waste management strategy.

Acknowledgments

References

[1] M. Sathishkumar, A.R. Binupriya, D. Kavitha, S.E. Yun, Biores. Technol. 98 (2007) 866.
[2] M.A. Massa, P.A. Ayude, R.J. Fenoglio, J.F. Gonzalez, P.M. Haure, Lat. Am. Appl. Res. 34 (2004) 133.
[3] H.B. Crauford, G. Cline, Water Treatment Plant Design, McGraw–Hill, New York, 1990, p. 457.
[4] A. Santos, P. Yustos, A. Quintanilla, F. Garcia-ochoa, J.A. Casas, J.J. Rodriquez, Environ. Sci. Technol. 38 (2004) 133.
[5] A.G. Agrios, K.A. Gray, E. Weitz, Langmuir 19 (2003) 1402.
[6] I.Z. Shirgaokar, A.B. Pandit, Ultrason. Sonochem. 5 (1998) 53.
[7] A.B. Pandit, P.R. Gogate, S. Mujumdar, Ultrason. Sonochem. 8 (2001) 227.
[8] L.R. Radovic, C.D. Moreno-Castilla, J. Rivera-Utrilla, in: P. Thrower (Ed.), Chemistry and Physics of Carbons, Dekker, New York, 2000, pp. 227–405.
[9] S. Rengaraj, M. Seung-Hyeon, R. Sivabalan, B. Arabindoo, V. Murugesan, J. Hazard. Mater. 89 (2002) 185.
[10] F. Caturla, J.M. Martinez, M.M. Sabio, F.R. Reinoso, R. Torregrosa, J. Colloid Interface Sci. 124 (1988) 528.
[11] H. Sajilkan, B. Cetinkaya, Chim. Acta Turcica 19 (1991) 257.
[12] S.J. Severston, S. Benarjee, Environ. Sci. Technol. 30 (1996) 1961.
[13] C. Namasivayam, D. Kavitha, Sep. Sci. Technol. 39 (2004) 1407.
[14] M. Akhtar, M.I. Bhanger, S. Iqbal, S.M. Hasany, J. Hazard. Mater. 128 (2006) 44.
[15] A.M. Stephan, T.P. Kumar, R. Ramesh, S. Thomas, S.K. Jeong, K.S. Nahm, Mater. Sci. Eng. 430 (2006) 132.
[16] M. Sathishkumar, A.R. Binupriya, K. Vijayaraghavan, S.I. Yun, J. Chem. Technol. Biotechnol. 82 (2007) 389.
[17] F. Caturla, M.M. Sabio, F.R. Reinoso, Carbon 29 (1991) 999.
[18] F.R. Reinoso, M.M. Sabio, Carbon 30 (1992) 1111.
[19] S. Balci, T. Dogu, H. Yucel, J. Chem. Technol. Biotechnol. 60 (1994) 419.
[20] M.M. Sabio, F.R. Reinoso, Colloids Surf. A 241 (2004) 15.
[21] H. Marsh, D.S. Yan, T.M. O'Grady, A. Wennerberg, Carbon 22 (1984) 603.
[22] M.A.F. García, J.R. Utrilla, J.R. Gordillo, I.B. Toledo, Carbon 26 (1988) 363.
[23] F.C. Wu, R.L. Tseng, R.S. Juang, Sep. Purif. Technol. 47 (2005) 10.
[24] P. Ehrburger, A. Addoun, F. Addoun, J.B. Donnet, Fuel 65 (1986) 1447.
[25] K. Naoi, N. Ogihara, Y. Igarashi, A. Kamakura, Y. Kusachi, K. Utsugi, J. Electrochem. Soc. 152 (2005) 1047.
[26] Y. Liu, J.S. Xue, T. Zheng, J.R. Dahn, Carbon 34 (1996) 193.
[27] Y.S. Ho, G. McKay, Proc. Biochem. 34 (1999) 451.
[28] C.S. Ku, M. Sathishkumar, S.P. Mun, Chemosphere 67 (2007) 1618.
[29] K.J. Kennedy, J. Lu, W.W. Mohn, Water Res. 26 (1992) 1085.
[30] Z. Aksu, J. Yener, Water Manage. 21 (2001) 695.
[31] T.A. Davis, B. Volesky, A. Mucci, Water Res. 37 (2003) 4311.
[32] Y.S. Ho, J.F. Porter, G. McKay, Water Air Soil Pollut. 141 (2002) 1.
[33] C. Namasivayam, D. Kavitha, J. Environ. Sci. Eng. 46 (2003) 217.