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Carbaryl Sorption by Porogen-treated Banana Pith Carbon

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ABSTRACT: This paper reports the adsorption ability of banana pith activated carbon, with ZnCl₂ as the porogen, towards carbaryl (1-naphthyl-N-methylcarbamate) from aqueous solution. The pH-edge experiments revealed that carbaryl adsorption onto ZnCl₂-treated banana pith activated carbon (ZTC) was a pH-dependent process with maximum adsorption occurring at pH 11. The adsorption isotherm obtained at pH 11 revealed that ZTC possessed a maximum adsorption capacity of 45.9 mg/g. The adsorption isotherms were well described by the Langmuir and Freundlich models. The kinetic data obtained at different initial carbaryl concentrations were modelled using pseudo-first- and second-order models. Acetone successfully desorbed carbaryl with a 99.8% elution efficiency.

1. INTRODUCTION

The application of pesticides in agricultural activities is well known; however, their extensive or improper application may pollute water resources. Although much benefit is obtained from their usage, they have some undesirable side-effects such as toxicity, carcinogenity and mutagenicity (Becker and Wilson 1980). Only part of the total amount of pesticide applied is bioactive, the rest is distributed in the environment. Maximum permissible limits of 0.1 µg/l for individual pesticides and related products, 0.5 µg/l for total pesticides in drinking water and 1–3 µg/l for surface waters have been recommended (EEC 1980; Akhtar et al. 2007). Carbaryl (1-naphthyl-N-methylcarbamate), a well-known carbamate pesticide, is used widely for pest control due to its low persistence and high effectiveness (Jury et al. 1987). However, carbaryl has a relatively low soil adsorption coefficient, indicating that it is likely to dissolve and be transported in water. It subsequently poses a potential hazard to health due to its high toxicity (Lin et al. 2007).

Several methods, either independently or in conjunction, have been used for the removal of pesticides from the environment, including adsorption (Gupta et al. 2002; Yang et al. 2004),
biodegradation (González et al. 2006), coagulation (Chen et al. 2007) and ozone treatment (Ormad et al. 1997). Of these, adsorption onto activated carbon (AC) is one of the most effective and emerging technology used to deal with the purification of water contaminated by pesticides. However, commercially available activated carbons are still considered as expensive materials due to the use of non-renewable and relatively expensive starting materials such as coal. As a consequence, this has prompted many researchers in recent years to produce activated carbons from renewable and cheaper precursors. These are mainly agricultural and industrial by-products, such as rice husk (Yalçın and Sevinç 2000), rubber wood sawdust (Praskash Kumar et al. 2005), activated sludge (Wang et al. 2008) and coconut coir pith (Namasivayam and Sangeetha 2008).

Our past research on the production of activated carbon using banana pith resulted in the development of highly porous and effective adsorbents for 2,4-dichlorophenol (Sathishkumar et al. 2008). Using ZnCl₂ as the porogen, the surface area of banana pith AC was enhanced from 37 m²/g to 1285 m²/g. Since surface area is a key indicator of the adsorptive power of ACs, this developed adsorbent should perform efficiently for a variety of different sorbates. Thus, this study examines the performance of ZnCl₂-treated banana pith AC for the removal from aqueous solution of carbaryl, a potent carcinogenic pesticide.

2. EXPERIMENTAL SECTION

2.1. Adsorbent and chemicals used

Carbaryl (with a purity of 99.5%) was purchased from Dr. Ehrenstorfer GmbH, Germany and used as received. High-quality banana pith fibres were obtained from agricultural fields in Kerala, India. Sheets of the herbaceous stems were dried in the sun and fibres were drawn mechanically from them. These fibres were then soaked in water, washed and dried. The resulting brownish-white dry fibres were then treated with concentrated solutions of ZnCl₂ for 5 d at 110°C at a fibre/porogen ratio of 1:5 by weight and dried (Sathishkumar et al. 2008; Stephan et al. 2006). The carbon thus prepared is designated as “ZTC” below.

2.2. Adsorption experiments

Experiments were conducted to obtain the pH dependency (pH edge), concentration dependency (isotherm) and time dependency (kinetics) of the adsorption process. Such experiments were performed employing a 250 mL Erlenmeyer flask into which was placed carbaryl at a desired concentration (10–100 mg/l) and a 2 g/l aqueous solution of ZTC at the desired pH value. The resulting suspensions were shaken at 200 rpm (at 30°C), the supernatants filtered (0.45 µm filter) and their carbaryl content determined by HPLC methods. The desorption experiments involved an initial period of adsorption (12 h contact time) followed by a desorption step, using acetone and ethanol.

HPLC was performed using Agilent LC systems connected to a G1322A degasser, a G1311A quaternary pump, a G1313A auto sampler and a G1321A FL detector. A Gemini 5 microC18 110A (Phenomenex) column (250 mm length × 4.6 mm i.d.) was employed at room temperature, with a mobile phase consisting of a 45:55 (v/v) water/acetonitrile mixture at a flow rate of 1 ml/min. The sample volume was 10 µl.
2.3. Modelling the experimental data

The adsorption isotherms obtained were fitted using the Langmuir and Freundlich isotherms, which can be expressed in their non-linear forms as:

**Langmuir model:**

\[ Q_e = \frac{Q_m b C_i}{1 + b C_i} \]  

(1)

**Freundlich model:**

\[ Q_e = K_F C_i^{1/n} \]  

(2)

where \( Q_m \) is the maximum uptake (mg/g), \( b \) is the Langmuir equilibrium coefficient (L/mg), \( K_F \) is the Freundlich constant \([\ell/g]^{1/n}\) and \( n \) is the Freundlich coefficient.

The pseudo-first- and pseudo-second-order kinetic models were used to describe the adsorption kinetic data. These models may be expressed in their non-linear forms as:

**Pseudo-first order:**

\[ Q_t = Q_e \left[ 1 - \exp(-k_1 t) \right] \]  

(3)

**Pseudo-second order:**

\[ Q_t = \frac{Q_e^2 k_2 t}{1 + Q_e k_2 t} \]  

(4)

where \( Q_e \) is the amount of solute sorbed at equilibrium (mg/g), \( Q_t \) is the amount of solute sorbed at time \( t \) (mg/g), \( k_1 \) is the pseudo-first-order rate constant (1/min) and \( k_2 \) is the pseudo-second-order rate constant [g/(mg min)]. All the model parameters were evaluated by non-linear regression using Sigma Plot (version 4.0, SPSS, U.S.A.) software. All experiments were performed in duplicate. The data are expressed as the mean values of two replicate experiments.

3. RESULTS AND DISCUSSION

3.1. Effect of pH

Sorption of the pesticide as a function of pH (see Figure 1) clearly showed that solution pH played an important role in the adsorption of carbaryl by ZTC. Experiments conducted over the pH range 2–11 indicated that adsorption increased with an increase in pH to attain a maximum at pH 11. Comparison of the percentage removal of pesticide from aqueous solution at pH values of 2 and 11 showed an increase in adsorption of 42%. However, this increase is small in comparison to the pH range considered. This confirms the presence of both anionic and cationic groups on the surface of the carbon. Adsorption at lower pH is believed to take place through the aromatic ring of the pesticide and also via ionic interaction involving the negative charge associated with the carboxyl group of the pesticide (Ania and Beguin 2007). Adsorption at higher pH is believed to be due to interaction between the –NH+ group in the pesticide and negative groups in the carbon. In addition, porosity is believed to play a major role in the uptake of the pesticide. The 3D image of carbaryl (Figure 2) implies that the distances between the atoms in the molecule are much smaller than the average pore size of the activated carbon, i.e. 57 Å (Sathishkumar et al. 2008). This would facilitate the uninterrupted movement of carbaryl into the carbon pores. Since the
carbon used in the present study had a very high surface area due to the increased porosity brought about by porogen treatment (Sathishkumar et al. 2008), a high uptake of carbaryl was achieved.

3.2. Adsorption isotherm

To evaluate the maximum adsorption potential of ZTC, isotherm experiments were conducted at pH 11 (Figure 3). A typical L-shaped isotherm (Limousin et al. 2007) was observed, which
implies that the ratio between the carbaryl concentration in solution and that sorbed onto the solid decreased with increasing initial carbaryl concentration, leading to a convex curve without a distinct plateau. A steep initial isotherm slope (which is a measure of the sorbent–solute affinity) and an eventual maximum uptake of 45.9 mg/g were observed at pH 11. The Langmuir and Freundlich models were used to evaluate the adsorption isotherm. The Langmuir sorption model allowed the maximum uptake values to be estimated when they could not be attained experimentally. The constant b represents the affinity between the sorbent and sorbate. Values of $Q_m$ and b of 68.6 mg/g and 0.24 $\ell$/mg, respectively, were obtained. The Freundlich model constants, $K_F$ and n, were 14.5 $\ell$/g and 1.74, respectively. Both models were able to simulate the adsorption isotherm with a very high correlation coefficient ($R^2 = 0.99$) and a low percentage error (< 3.9%).

### 3.3. Kinetics

The time profiles for carbaryl adsorption onto ZTC at different initial carbaryl concentrations and at pH 11 are presented in Figure 4. In general, carbaryl uptake by ZTC was strongly dependent on the initial carbaryl concentration, with high uptakes being observed for high initial carbaryl concentrations. On changing the initial carbaryl concentration from 20 mg/$\ell$ to 80 mg/$\ell$, the amount adsorbed increased from 9.7 mg/g to 37.4 mg/g. However, the removal efficiency of carbaryl decreased from 97.0% to 93.5% as the carbaryl concentration increased from 20 mg/$\ell$ to 80 mg/$\ell$. This is because, at the lower concentration, the ratio of the initial moles of solute to the available surface area is low and subsequently the fractional sorption becomes independent of the initial concentration (Vijayaraghavan and Yun 2008). However, at higher concentrations, the available sorption sites become fewer in number compared to the number of moles of solute present, and hence the percentage removal of carbaryl is dependent upon the initial concentration. It may also be observed from Figure 4 that the uptake of carbaryl was rapid for the initial 100 min, but thereafter proceeded at a slower rate and finally attained saturation. The higher sorption rate over the initial period may be due to an increased number of vacant sites available at this stage of the process, which results in an increased concentration gradient between the sorbate in solution and the sorbate at the adsorbent surface. However, with increasing time, this concentration
gradient is reduced due to the sorption of carbaryl molecules onto the vacant sites, leading to a decrease in the sorption rate in the later stages.

The experimental adsorption kinetic data were modelled using the pseudo-first- and pseudo-second-order kinetic equations. Initially, the validity of the two models was checked by studying the kinetics under different initial carbaryl concentrations. The rate constants, predicted equilibrium uptakes, corresponding correlation coefficients and percentage error values for all the concentrations examined were calculated and are summarized in Table 1. With the pseudo-first-order model, very high correlation coefficients (> 0.99) and low percentage error values (< 1.2%) were obtained. In addition, the model was capable of predicting the uptake values over the entire time period, with the predicted equilibrium uptake values closely coinciding with the experimental values. On the other hand, the pseudo-second-order model, which is based on the sorption capacity on the solid phase, over-predicted the equilibrium uptake values. Despite the high correlation coefficients (R² > 0.99) and low percentage error values (< 0.9%), this model gave a poor correlation with the experimental data.

### 3.4. Desorption

In order to regenerate the adsorbent for possible re-use, it is important to identify a proper eluent for a given system. Desorption is also important, especially in those cases where sorbent preparation/generation is costly, since its efficiency will diminish the dependency of the process on a continuous supply of adsorbent. Consequently, two eluants (ethanol and acetone) were used to study the desorption possibilities in the present system. The results obtained (see Figure 5) reveal that increasing the solvent strengths improved their respective elution efficiencies. Thus, eluent solutions of pure acetone and ethanol (at 100% concentration) exhibited elution efficiencies of 99.8% and 53%, respectively. However, when the strength of the eluent was reduced to 50%, the elution efficiencies of acetone and ethanol decreased to 45.3% and 15%, respectively. The possibility of recovering the solvents by distillation and re-using them in the next desorption cycle
has been demonstrated by Binupriya et al. (2007), which should make this process even more economical and eco-friendly.

4. CONCLUSIONS

The following conclusions can be drawn from the present study.

1. Banana pith carbon treated with ZnCl₂ (yielding ZTC) was found to be an effective adsorbent for the removal of carbaryl from aqueous solution.
2. Experiments at different pH values revealed that pH 11 provided the optimum conditions for carbaryl adsorption.
3. The adsorption isotherm obtained at pH 11 indicated that ZTC possessed a maximum carbaryl uptake of 45.9 mg/g. Both the Langmuir and Freundlich models were capable of describing the adsorption isotherms with high correlation coefficients and low percentage error values.
4. The pseudo-first-order kinetic model gave a better prediction of the adsorption data for carbaryl onto ZTC compared to pseudo-second-order kinetic model.
5. Desorption of carbaryl from carbaryl-loaded ZTC was possible by employing pure (100%) acetone, which performed well with a desorption efficiency of 99.8%.
6. Overall, this study has demonstrated the possible application of ZnCl₂-treated banana pith carbon for the remediation of carbaryl-contaminated waters. Since the precursor material — banana pith — is inexpensive, indigenous and easily available as waste material, its use as an adsorbent would significantly lower treatment costs and can be viewed as a waste management strategy.

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