



Journal of Environmental Science and Technology

ISSN 1994-7887

science
alert

ANSI*net*
an open access publisher
<http://ansinet.com>

Adsorption Behavior of *p*-chlorophenol on the Reed Wetland Soils

Ding Cheng, Li Zhaoxia, Yan Jinlong and Jin Jianxiang

Department of Chemical and Biological Engineering, Yancheng Institute of Technology,
Jiangsu Province 224003, China

Abstract: Investigation of the adsorption behavior of organic pollutants by soils is fundamental to simulating and eventually predicting their transport in environmental compartments. The adsorption behavior of *p*-chlorophenol by soils from Yancheng reed wetland was studied in a series of batch equilibration experiments and experiments were analyzed by Langmuir and Freundlich isotherm equation. Results showed that the adsorption process could be described with both Freundlich and Langmuir isotherms. But the empirical Freundlich equation fit the behavior better and the highest correlation coefficient, $r = 0.9690$, was obtained. Parameters affected the adsorption property of *p*-chlorophenol, such as solution pH, ionic strength and soil organic matter, were also studied. Adsorption capacity increased with lower pH, higher ionic strength and soil OC.

Key words: Adsorption, isotherm, *p*-chlorophenol

INTRODUCTION

The production and usage of man-made in industry has led to the entry of many xenobiotics into the environment. The environmental fate of such organic micropollutants is strongly influenced by their sorption in natural sorbents. Investigation of their sorption behavior is fundamental to simulating and eventually predicting their transport in environmental compartments. One such group of xenobiotics is chlorophenols, which have become of environmental concern due to their acute toxicity and resistance to degradation. Chlorophenols are widely present as environmental pollutants. They belong to a class of polarizable hydrophobic compounds with relatively high n-octanol/water (K_{ow}) coefficients (Fingler *et al.*, 2004). They are weak organic acids, (pK_a 5-9). The sorption of such partially ionized but still highly hydrophobic compounds comprise both molecular and ionic forms.

Constructed wetlands have been widely used on treating different types of wastewater, such as sewage, industrial wastewater, agricultural runoff and landfill leachate. Such naturalized treatment systems have been shown to have a significant capacity for both wastewater and resource recovery (Yang *et al.*, 2001). The physical, chemical and biological characteristics of the wetland soil, as well as the chemical properties of the organic compounds will influence their fate and transport. The adsorption properties of chlorophenols are controlled largely by their degree of substitution and the resultant hydrophobicity. In the normal soil pH, most chlorophenols will adsorption, transport and change their bioavailability (Kookana and Rogers, 1995). Several investigators have noted that pH plays an important role in the adsorption properties of compounds with acidic functional groups on activated carbon and soil because the neutral and ionic forms display very different adsorption behavior (Hyun *et al.*, 2003). In the absence of significant Organic Carbon (OC) content, the adsorption maximum for weak organic acids on hydrous Fe- and Al-oxide surfaces often occurs at or near their pK_a -due to the combined effects of pH on oxide surface charge and acid dissociation. Chlorophenols adsorption in soils have been described assuming hydrophobic partitioning of the neutral species to

Corresponding Author: Ding Cheng, Department of Chemical and Biological Engineering,
Yancheng Institute of Technology, Jiangsu Province 224003, China Tel: +86-515-88168322

soil organic matter or as described by He *et al.* (2006) as a hole-filling adsorption mechanism into the soil organic matter, facilitated by H-bonding (Schwertmann *et al.*, 1986; Di Vincenzo and Sparks, 2001; He *et al.*, 2006).

The main objective of the present study was to evaluate the adsorption behavior of *p*-chlorophenol on reed wetland soils with different physicochemical properties as a function of pH and ion strength.

MATERIALS AND METHODS

Soil

p-chlorophenol adsorption behavior was studied on reed wetland soils on March of 2007 from Yancheng, located in China (Table 1). Four soil samples were collected representing depth of 0-20 cm from different area, air dried at room temperature and then passed through a 2 mm sieve prior to their use in this study. Various soil properties thought to impact *p*-chlorophenol adsorption were measured.

Chemicals

p-Chlorophenol (M_w (g mol⁻¹): 128.56) was purchased from Shanghai Chemical Co. With reported purities of >95%. Relevant physical and chemical properties such as water solubility (S_w), octanol/water partition coefficient ($\log K_{ow}$) and acid dissociation constant (pK_a) are 26 300, 2.93 and 9.2, respectively.

Kinetics Experiments

The time needed for the attainment of equilibrium between the liquid and the solid substrates was measured by batch experiments. Precisely weighted amounts of adsorbent were placed in glass vials. The vials were shaken for set periods of time between 30 min and 24 h (30, 60 min and 3, 4, 5, 6, 7, 8, 9, 12 and 24 h). After this time interval, sufficient for the solid substrates to reach equilibrium at the experimental ionic strength, equal volumes of stock *p*-chlorophenol solution were added to the vials. The presence of the same initial concentrations of *p*-chlorophenol and a constant liquid-to-solid mass ratio were thus achieved. The time interval of *p*-chlorophenol solution addition was recorded and the vials were placed again in the chamber for mixing at constant temperature. The vials were opened at random time intervals and the suspensions were centrifuged and filtered by 0.2 μ m PTFE membranes. The *p*-chlorophenol in water was extracted with *n*-hexane. Some quantity of internal standard was added and the samples were analyzed by gas chromatography with FTD detector. All experiments were done at least in duplicate. The amount adsorbed by soil was calculated from the difference between the initial and final concentrations of *p*-chlorophenol in solution.

Equilibrium Adsorption Experiments

All equilibrium adsorption experiments were conducted in duplicate in 50 mL glass vials containing 0.2 g soil. The soil samples were equilibrated with 20 mL of 0.1 mol L⁻¹ NaCl with range of *p*-chlorophenol concentrations at pH values of 5.0, 6.0, 7.0, 8.0 and 9.0 (adjusted as needed with 0.1 mol L⁻¹ HCl or 0.1 mol L⁻¹ NaOH before equilibration) on a reciprocating shaker for 24 h at 25°C. After equilibration, the samples were analyzed as above.

Table 1: Physicochemical characteristic of the four soil samples

Parameters	Soil samples			
	S1	S2	S3	S4
pH (water)	8.920	8.970	8.440	8.640
Organic Matter (OM) (%)	2.995	1.961	3.686	1.874
Soil density (g mL ⁻¹)	1.098	1.276	1.119	1.038

The effect of iron strength on *p*-chlorophenol adsorption was examined by adding CaCl₂ solution. The amount adsorbed was quantified according to the same procedure described above.

RESULTS AND DISCUSSION

Significant adsorption of *p*-chlorophenol was found with the wetland soil substrate. The rate of the processes was too high to measure accurately because adsorbed *p*-chlorophenol on soils reached its final amount almost instantly. More than 80% of *p*-chlorophenol was transformed in 6 h. A plateau value was attained in about 12 h as may be seen in Fig. 1.

This study sets out to find simple predictive relationships between soil properties and the rate of adsorption. To facilitate this, rate laws that contained only one rate constant were used: Firstly a rate law for a reversible first-order process (Amacher, 1991), henceforward described as the distance-from-equilibrium rate law.

$$\ln(C_{eq} - C_t) = \ln(C_{eq}) - kt$$

where, C_t is the amount of *p*-chlorophenol adsorbed at time t , C_{eq} is the amount of *p*-chlorophenol adsorbed at equilibrium, k is rate constant. The rate law of *p*-chlorophenol on the soils is accord with $\ln C_{eq} = 3.5082 - 0.018 t$ and the correlation coefficients is 0.7822.

Adsorption Isotherms

The adsorption data of *p*-chlorophenol by soils was analyzed with Langmuir and Freundlich models to evaluate the parameters in the adsorption process. Langmuir and Freundlich isotherms have been extensively used for the adsorption of organic and inorganic matter on suspended cell, activated carbon, sediment and peat, etc. (Jain and Ram, 1997; Li and Ye, 1997; Tanjore and Viraraghavan, 1997). Langmuir model assumes uniform energies of adsorption onto the surface and no remotion of adsorbate on the surface. The linear form of Langmuir isotherm equation is represented by equation:

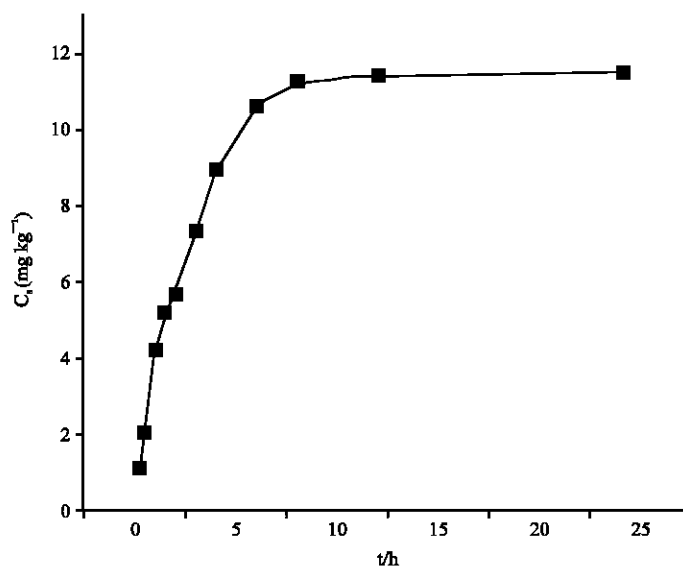


Fig. 1: Kinetics of *p*-chlorophenol on soil

Table 2: Calculated adsorption parameters and correlation coefficients with two isotherms

Soil samples	Langmuir equation			Freundlich equation		
	K	B	r	K _f	1/n	r
S1	0.965	0.6718	0.9429	0.0351	20.325	0.9527
S2	0.743	0.7019	0.9649	0.0260	20.408	0.9690
S3	0.728	0.6822	0.9458	0.0310	17.182	0.9608
S4	0.875	0.6791	0.9272	0.0220	21.692	0.9434

$$C/C_s = 1/KB + C/B$$

where, C_s is the amount of *p*-chlorophenol adsorbed from the beginning of the experiment per mass of adsorbent (mg g⁻¹) and C is the corresponding *p*-chlorophenol concentration in solution (mg L⁻¹). Parameters B and K are Langmuir constants related to maximum adsorption capacity (monolayer capacity) and energy of adsorption, respectively, which are functions of the characteristics of the system as well as time. The Langmuir parameters, B and K, were obtained by linearly regressing the data with the equation (Table 2). These values were used for comparison and correlation of the sorption properties of soils. The correlation coefficient (r) between 1/C_s and 1/C indicated that a straight line with slope 1/KB and intercept 1/B was obtained, which showed that the adsorption of *p*-chlorophenol on the soils followed the Langmuir isotherm model.

Freundlich isotherm equation:

$$C_s = K_f C^{1/n}$$

where, C_s is the amount of adsorbate adsorbed by adsorbent (mg g⁻¹), C is the equilibrium concentration of the adsorbate (mg L⁻¹) and K_f and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. The correlation coefficients (r) between log C_s and log C were given in Table 2. When log C_s was plotted against log C; a straight line with slope 1/n and intercept log K_f was obtained. It indicated the Freundlich isotherm model fitted for the adsorption of *p*-chlorophenol. The parameters K_f and 1/n (which are functions of the characteristics of the system as well as time) were obtained by linearly regressing the data with the equation. The Freundlich parameters for the adsorption of the *p*-chlorophenol were demonstrated in Table 2 too.

As indicated in Table 2, this adsorption process could be described with both Freundlich and Langmuir isotherms. But the empirical Freundlich equation fit the behavior better. In all cases the isotherms are nonlinear with slopes (1/n)>1. The K_f values indicate that the adsorption is highest on S2 followed, in the order, by S3, S1, S4, which is also the order of decreasing value of organic matter content. Despite the small number of samples, linear regressing analyses between selected soil properties and the Freundlich constant, K_f, were performed. But there is no significant correlation between K_f and soil properties.

Effect of pH

The dependence of *p*-chlorophenol adsorption on soil solution pH was also tested (Fig. 2). The pH value is an important factor which can influence the electricity amount on soil surface and the form of pollutant. *p*-Chlorophenol was in the dissociated and undissociated forms in solutions with the pH range in these experiments. When pH decreased, H⁺ ion concentration increased and undissociated forms of *p*-chlorophenol increased in proportion. The undissociated *p*-chlorophenol was high hydrophobic, it was easier to be adsorbed than its dissociated form (Wang *et al.*, 2002). Other authors (Karimi-Jashni and Narbaitz, 1997) have reported the impact of pH on the adsorption kinetics of 2-nitrophenol on activated carbons. At pH 13 the prevalent dissociated form of 2-nitrophenol

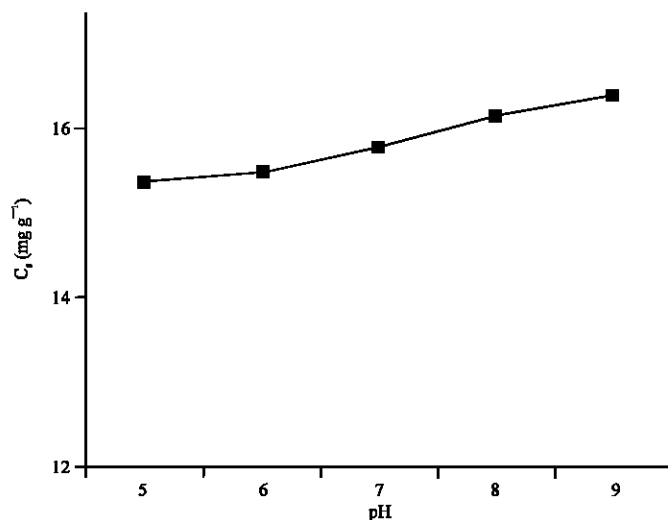


Fig. 2: Effect of pH on the adsorption of *p*-chlorophenol on soil

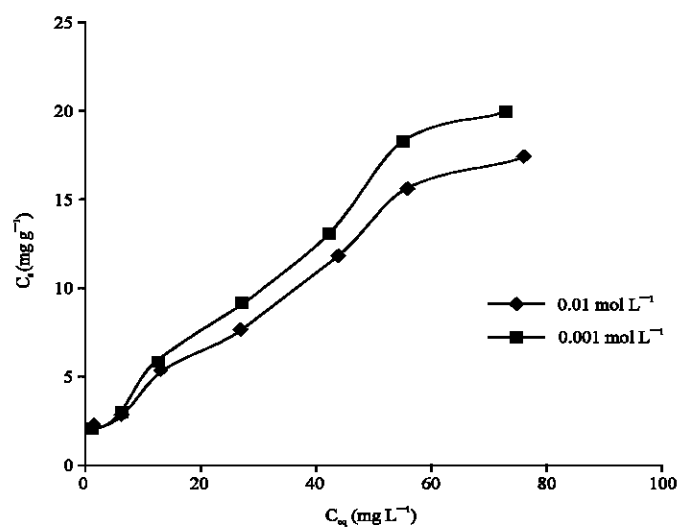


Fig. 3: Effect of ionic strength on the adsorption of *p*-chlorophenol on soil

leads to the lower adsorption capacity. Actually, it was found that the *p*-chlorophenol adsorption increase as the pH value of the soil solution decrease. The decrease of pH was useful for *p*-chlorophenol adsorption on soils.

Effect of Ionic Strength

Adsorption isotherms of *p*-chlorophenol on soils at 25°C and for ionic strength values ranging from 0.001 to 0.01 mol L⁻¹ NaCl are shown in Fig. 3. As may be seen, the *p*-chlorophenol surface concentrations increased with increasing ionic strength of the solution. This suggests that the role of electrostatic interactions in the adsorption process is significant. The dependence on ionic strength has been reported on several occasions.

CONCLUSION

The rate law of *p*-chlorophenol on the soils is accord with $\ln C_{eq} = 3.5082 - 0.018t$ and the correlation coefficients is 0.7822. The adsorption process could be described with both Freundlich and Langmuir isotherms. But the empirical Freundlich equation fit the behavior better and the highest correlation coefficient, $r = 0.9690$, was obtained. Adsorption capacity increased with lower pH, higher ionic strength and soil OC.

ACKNOWLEDGMENTS

This study was supported by the National Natural Science Foundation of China (No. 20607018) and the Natural Science Foundation of Jiangsu Province (No. BK2006063).

REFERENCES

- Amacher, M.C., 1991. Methods of Obtaining and Analysing Kinetic Data. In: Rates of Soil Chemical Processes, Sparks and Suarez (Eds.). Chap. 2, Soil Sci. Soc. Am. Spec. Publ. 27., S.S.S.A., Madison, Wisconsin.
- DiVincenzo, J. and D.L. Sparks, 2001. Sorption of the neutral and charged forms of pentachlorophenol on soil: Evidence for different mechanisms. *Arch. Environ. Contam. Toxicol.*, 40 (4): 445-450.
- Fingler, S., S. Stipicevic and V. Drevenkar, 2004. Sorption behaviour of chlorophenols and triazine herbicides in reference EURO-soils. *Int. J. Environ. Anal. Chem.*, 84 (1/3): 83-93.
- He, Y., J. Xu and H. Wang, 2006. Detailed sorption isotherms of pentachlorophenol on soils and its correlation with soil properties. *Environ. Res.*, 101 (3): 362-372.
- Hyun, S., L.S. Lee and P.S. Rao, 2003. Significance of anion exchange in pentachlorophenol sorption by variable-charge soil. *J. Environ. Qual.*, 32 (3): 966-976.
- Jain, C.K. and D. Ram, 1997. Adsorption of lead and zinc on bed sediments of the river Kali. *Water Res.*, 31 (1): 154-162.
- Karimi-Jashni, A. and R.M. Narbaitz, 1997. Impact of pH on the adsorption and desorption kinetics of 2-nitrophenol on activated carbons. *Water Res.*, 31 (12): 3039-3044.
- Kookana, R.S. and S.L. Rogers, 1995. Effect of pulp mill effluent disposal on soil. *Rev. Environ. Contamin. Toxicol.*, 144: 13-64.
- Li, T. and C. Ye, 1997. Experimental research of adsorption of phenolic compounds on suspended particulates in water. *Environ. Chem.*, 16 (3): 227-232.
- Schwertmann, U., H. Kodama and W.R. Fischer, 1986. Mutual Interactions Between Organics and Iron Oxides (Mutual Interactions Between Organics and Iron Oxides). In: *Interactions of Soil Microbes with Natural Organics and Microbes*, Huang, P.M. and M. Schnitzer (Eds.). 2. Soil Science Society of America, Madison, pp: 3-250.
- Tanjore, S. and T. Viraraghavan, 1997. Effect of oxygen on the adsorption of pentachlorophenol by peat from water. *Water Air Soil Pollut.*, 100 (1-2): 151-162.
- Wang, W.J., W.H. Wang and X.L. Zhang, 2002. Adsorption of *p*-chlorophenol by biofilm components. *Water Res.*, 36 (3): 551-560.
- Yang, L., H.T. Chang and M.L. Huang, 2001. Nutrient removal in gravel and soil-based wetland microcosms with and without vegetation. *Ecol. Eng.*, 18 (1): 91-105.