Effects of Solute and Soil Concentrations on the Distribution of Chlorophenols in the Water-Soil System

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Abstract: The distribution of chlorophenols in the soil-water system has received great attention by many researchers. However, most of research was conducted at low organic concentrations. In fact, chlorophenols might be spilled to soil at high concentrations and the water content of most soils varies unpredictably. The objective of this study, therefore, was to analyze and illustrate the effects of solute concentration and soil concentration on the distribution of chlorophenols between the aqueous and soil phases. Batch sorption experiments were conducted with 4-chlorophenol and 2,4,6-trichlorophenol at various soil to solution ratios (by weight) ranging from 1:5 to 1:100. The initial concentrations of organic compounds ranged from 0.04Cs to 0.5Cs with Cs being the saturation water solubility. Langmuir model was employed as a general expression without the specific characteristics and molecular structures of the soil. According to experimental results of two target compounds, the adsorption density, q, increases with increasing the equilibrium concentrations, C, and both adsorption curves could be well fitted to the Langmuir model. Langmuir isotherms appropriately simulated the distribution behaviors of 4-chlorophenol and 2,4,6-chlorophenol throughout the whole range of saturation solubility. The fitted K values of individual chlorophenols maintained constant that implied an identical driving force, i.e. the hydrophobicity of chlorophenols, under different environmental conditions (pH values and soil concentrations). The higher soil concentration decreases the adsorption capacity of chlorophenols, which could be in analogy to the relevance between force and pressure. The magnitude order of adsorption capacities of 4-chlorophenol and 2,4,6-chlorophenol follows pH 5 > pH 7 > pH 9 > pH 11 > pH 3.

Keywords: sorption; chlorophenols; solute concentration; soil concentration; contamination.

1. Introduction

Among many contaminants, pesticides have been used in the countryside for several decades and most pesticides contain chlorophenols. In addition, other industries such as the oil refinery, paper manufacture, coal factories would discharge the wastewater containing the chlorophenols. Consequently, chlorophenols become the environmental concerns and have been listed in the known priority pollutants in the USA. In fact, chlorophenols possess the stability in the nature system and have bioaccumulation effect, which hazard the soil and groundwater dramatically [1]. In order to remediate the contaminated soil and groundwater, understanding the distribution behaviors of chlorophe-

nols between water and soil materials is important. The distribution mechanisms also play a critical role about the assessment of the transport and fate of pollutants in the environment. In this study, the distribution characteristics of chlorophenols between the water and soil surface were established.

In general, the partition process has been considered a major mechanism on the distribution of organic compounds in water-soil system. This partition mechanism is analogical to the dissolution, which the organic chemical (solute) dissolves into the soil (solvent). Hence, the distribution of organic chemicals has no relationship with the specific sites on the soil but with the organic solubility [2]. The organic matters of the soil have been regarded as the solvent and the minerals in the soil have little effect on the distribution [3]. Due to the partition, the distribution of organics in water-soil system has always been expressed by a linear function [4]. However, Mingelgrin and Gerstl argued that linearity could not completely explain the distribution of organic compounds [5]. In addition, some researchers reported that chlorophenols distributed in water and soil system performed a nonlinear behavior [6,7]. Haderriein et al. reported that the nitrobenzens sorption is nonlinear and Langmuir model could simulate the experimental results [8]. Liu stated that the linear sorption behavior appeared when trichlorophenols concentrations range from 5-7 mg/L and Freundlich model was suitable when trichlorophenols concentrations range from 5-30 mg/L [6]. The above description shows that the solute concentration of organic contaminants has the significant effect on the distribution in the water-soil system.

The other important factor for the chlorophenols distribution is the soil to solution ratio, i.e., soil concentration, which influences the distribution behavior in spite of any kind of contaminants. Routson and Serne [9] and Weiss and Colombo [10] have found that the partition coefficient of low-level radioactive element decreases with an increase of the soil to solution ratio. Fotoval et al. have reported that a decreasing soil to solution ratio increases the amount of cations adsorbed per unit weight of soil [11]. Puls et al. also found K_d, namely partition coefficient, increases with decreasing soil to solution ratio for Pb and Cd sorption on kaolinite [12]. The objective of this study, therefore, was to analyze and illustrate the effects of solute concentration and soil concentration on the distribution of chlorophenols between the aqueous and soil phases.

2. Materials and methods

Soil samples were collected from three different sites located in Taichung County, Taiwan. The characteristics of soil including soil texture, pH, organic matter, and soil moisture contents were determined. Table 1 shows the results and their analytical methods. According to Table 1, three samples were sandy and neutral pH soils. The water contents ranged from 1.9% to 6.1%. The contents of the organic matter range from 1.4% to 2.5%. The target compounds were 4-chlorophenol and 2,4,6-trichlorophenol for experiments. Table 2 lists the basic physico-chemical properties of the target compounds. All chemicals were purchased from Fluka Co, and the purity is greater than 97.0%.

Batch sorption experiments were conducted with 4-chlorophenol and 2,4,6-trichlorophenol at various soil to solution ratios (by weight) ranging from 1:5 to 1:100. The initial concentrations of organic compounds range from 0.04Cs to 0.5Cs with Cs being the saturation water solubility. The pH of solution was controlled at 3, 5, 7, 9 and 11 by the addition of NaOH or H_2SO_4 solution, respectively.

Table1. Basic physical and chemical properties of the soils

Properties	No.1 soil	No. 2 soil	No. 3 soil	Analysis Methods
Texture	sandy	sandy	sandy	ASTM D2217-85
Soil pH	7.0	7.2	7.7	NIEA S410.60T
Water content	1.9%	6.1%	4.4%	NIEA S280.61C
Organic matter	2.2%	2.5%	1.4%	Handbook of Soil Mechanics

Table 2. Basic physico-chemical characteristics of chlorophenols

| Basic characteristics	4-chlorophenol	2,4,6-trichlorophenol
Molecular formula	C_6H_5ClO	$C_6H_3Cl_3O$
Molecular weight (g)	128.56	246
Melting point (oC)	9	69
Boiling point (oC)	173	246
Saturation solubility (g/L)	28	0.8
pKa	8.11	6.23

To a series of glass bottles, a desired amount of soil and organic compound in solution of constant ionic strength electrolyte (0.05M NaNO3) were added. The bottles were placed in a shaker and shaken constantly for 24 hours to reach the equilibrium condition, which was determined by preliminary tests. The mixtures were then centrifuged at 3,000 rpm (1,000 *g*) using a Hettich Zentrifugen Co. model EBA12 centrifuge to separate the soil from the solution. The residual concentration of the chlorophenols in the centrifugate was analyzed. For 4-chlorophenol and 2,4,6-trichlorophenol analyses, the samples were extracted one time in hexane then determined with a GC/ECD, Varian CP3800. Figure 1 is the schematic of the experimental procedures.

3. Results and discussion

In general, the distribution behaviors of organic contaminants between water and soil phases have been expressed by either the linear or nonlinear equations empirically. If using the linear equation, the partition process is regarded as a major distributive mechanism, which assumes the soil as the solvent. When the nonlinear equation was applied, the adsorption mechanism served as the controlling factor for the contaminants distribution. Among a number of nonlinear adsorption models, Langmuir and Freundlich adsorption isotherms could properly fit most of data [13, 14, 15]. In addition, Langmuir model is valid to describe the linear distribution of contaminant concentrations versus adsorption. densities under low aqueous concentrations. Freundlich adsorption was differentiated from the Langmuir adsorption only by assuming the heterogeneous surface of the soil. As a consequence, Langmuir adsorption was chosen to describe the distribution behaviors of chlorophenols between the aqueous and soil phase in this study.

It is necessary to understand the theory of Langmuir adsorption to get insight to the distribution phenomenon. Langmuir adsorption model was derived on the basis of an reaction of contaminant molecules with water molecules on the soil surface. The exchange process and the mathematic expression shown as follows [16]:

Soil to Solution Ratio
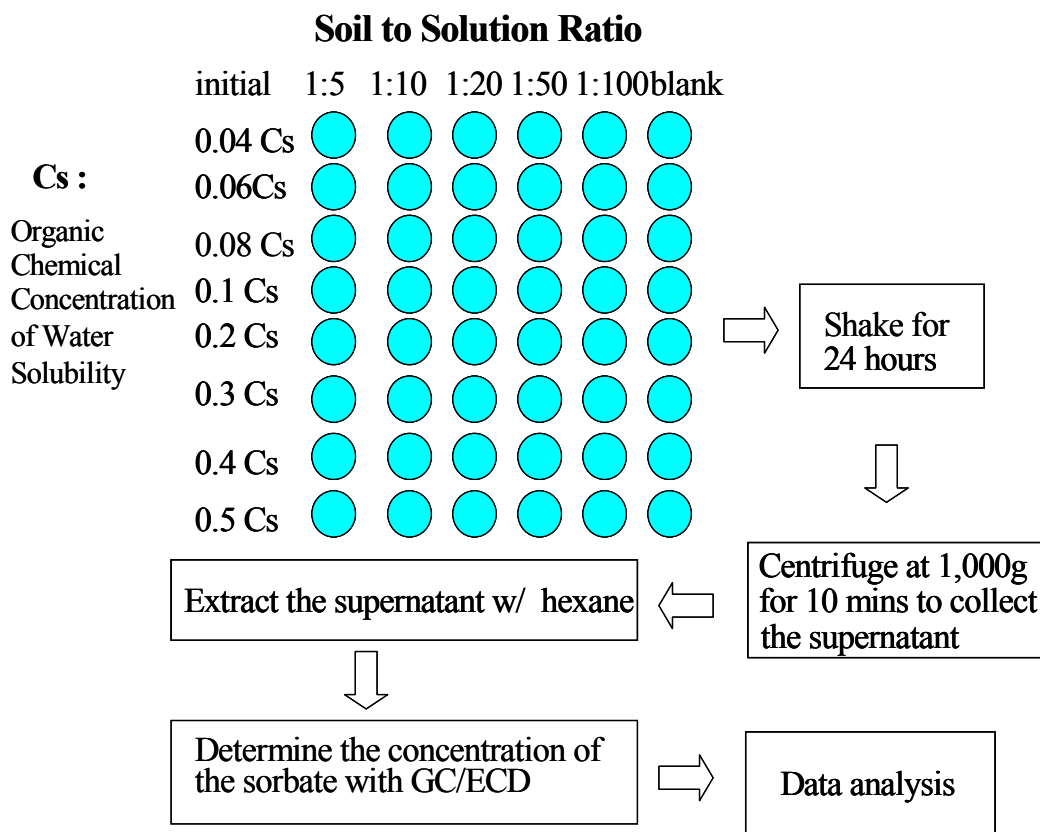
Figure1. Adsorption Experimental procedures for chlorophenols

Solute (adsorbed on surface, mol fraction xsi) + Water (in solution, mole fraction xw)

$$q = \frac{KbC}{1 + KC} \qquad (1)$$

where q is the solute concentration on the soil (mg/kg), C is the solute concentration in the water (mg/L), b is the adsorption capacity (mg/kg), and the K is the equilibrium constant of the exchange reaction. Through the analysis of K and b values under various experimental conditions, the driving force of distribution may be illustrated appropriately. For applying Langmuir model to the distribution of chlorophenols in the water-soil system, there exists some other reasons such as: (1) Since the soil organic matters (SOMs) are the dominant components for the adsorption of organic contaminants, adsorption sites are valid to regard as homogeneous. (2) the limited adsorption capacity of Langmuir model can reflect the saturation solubility of the organic contaminant in the soil when the soil serves as the solvent (i.e., the partition mechanism). (3) Many adsorption models including Freundlich, Frumkin-Fowler-Guggenhein, and BET isotherms were derived on the basis of Langmuir model. Therefore, Langmuir model is suitable to serve a general expression when the specific characteristics or molecular structures of the soil are unclear.

3.1. Effect of solute concentration

Figure 2 and Figure 3 show isothermal adsorption curves of 4-chlorophenol and 2,4,6-trichlorophenol under various soil to solution ratios at pH 5, respectively. According to

these two figures, the adsorption density, q, increases with increasing the equilibrium concentrations, C, and the adsorption curves could be well fitted to the Langmuir model. However, the adsorption curves of 4-chlorophenol possessed a downward curvature but those of 2,4,6-trichlorophenol were close to linear. This could be attributed to the hydrophobicity of organic solutes because higher hydrophobicity of organic chemicals performs the lower saturation solubility. The organic chemical with low saturation solubility could not occupy the soil sites in high percentage; namely, its adsorption density is much lower than the adsorption capacity. The chlorinated compounds with more chlorine atoms generally have higher hydrophobicity because chlorine atoms decrease the polarity of the phenolic organics. Therefore, the adsorption density of 2,4,6-trichlorophenol (saturation solubility is 0.8 g/L) could not approach the adsorption capacity. In contrast to 2,4,6-chlorophenol, 4-chlorophenol with the saturation solubility of 28 g/L could reach to the maximum of adsorption density.

Under other experimental conditions such as various pHs of the solution and soil types, the distribution behaviors of these two target compounds were similar to Figure 2 and 3, respectively. Our explanation is as follows: The partition mechanism plays a key role of the chlorophenols distribution, which means the adsorption should be linear theoretically. However, the linear relationship is based on the activity coefficient maintaining constant throughout whole range solubility. Roughly speaking, this constant activity coefficient is valid when the contaminant solubility is below 3% by weight [17]. When the SOMs exert a solvent, the contaminant concentration will easily reach up to 10% due to the SOMs content of only several percents in the soil. The activity coefficient of organic contaminant in the soil phase could not be an invarious value but that in the aqueous phase could

still be a constant. As a result, adsorption density increases with increasing solute concentration nonlinearly. Consequently, Langmuir isotherm is feasible to simulate the distribution of chlorophenols, i.e., a linear and a nonlinear mode could describe the organic adsorption during the relatively low and high concentrations, individuall.

3.2. Effect of soil concentration

Figure 4 and 5 show Isothermal adsorption curves of 4-chlorophenol and 2,4,6-chlorophenol respectively under various soil to solution ratios at pH=9. The adsorption capacities of these organic compounds increase with decreasing the soil concentration (1:5 is the highest soil concentration). Under the various pH and soil types conditions, this phenomenon always appeared which was called the "soil concentration effect". One explanation for the soil concentration effect is that there exist colloids in the aqueous phase. Since the solute adsorbed on the colloid surface, there leads to an overestimation of the aqueous phase concentration [18]. In fact, incomplete separation process truly produces colloids in the aqueous phase. However, Servos and muir reported that the effect of soil concentration still occurred under no colloid situation (18). Our postulation is that the organic pollutants would be favor to enter the soil at low soil concentration compared to that at high soil concentration. Considering the relationship between the force and pressure system, a surface with smaller area will makes a high pressure. In the water-soil system, the hydrophobicity of chlorophenols creates an identical force from the water phase to the soils. When the soil concentration was decreased (small surface area), the adsorption ability increases (high pressure). As a result, the soil concentration has the significant effect on the solute distribution in the water-soilsystem in spite of any kind of solute.
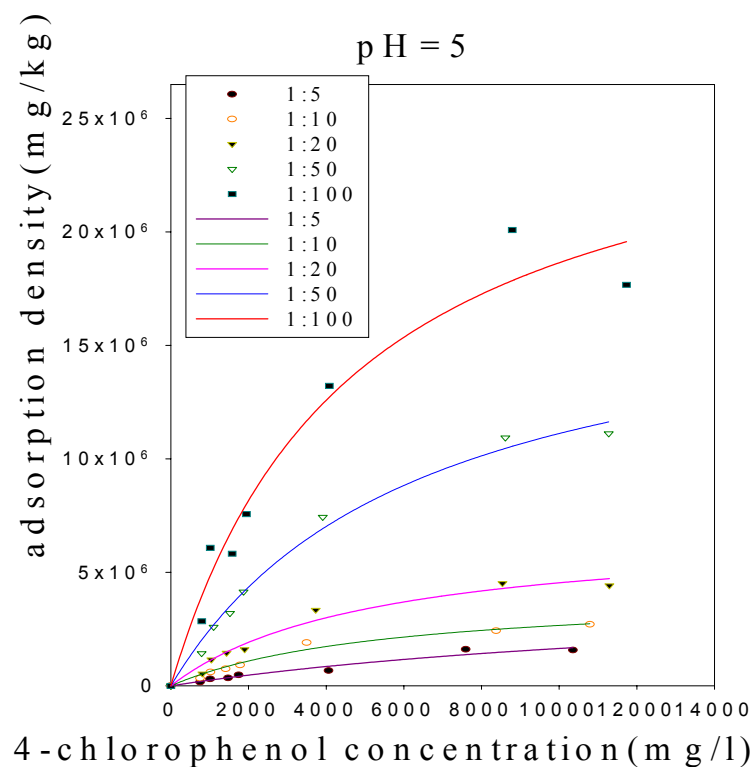
Figure2. Isothermal adsorption curves of 4-chlorophenol under various soil to solution ratios at pH= 5.
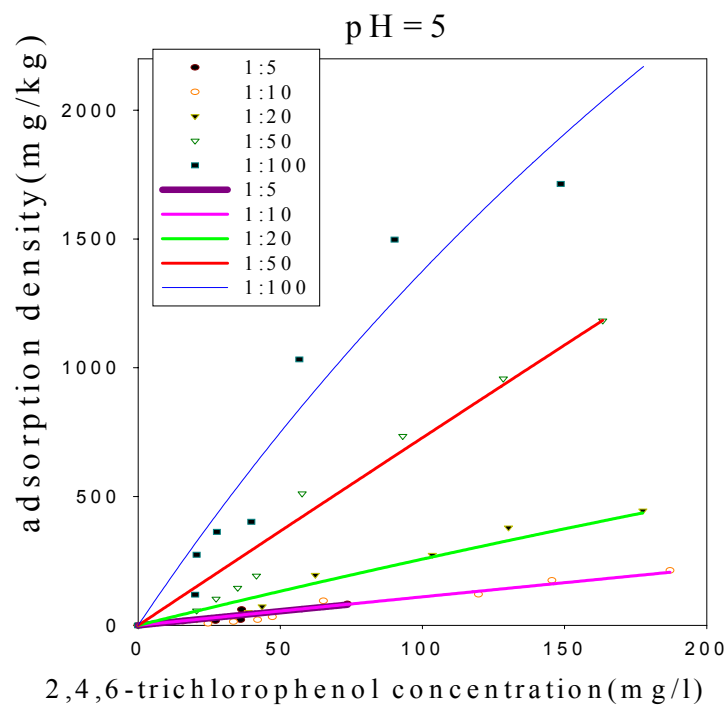
Figure 3. Isothermal adsorption curves of 2,4,6-trichlorophenol under various soil to solution ratios at pH=5.
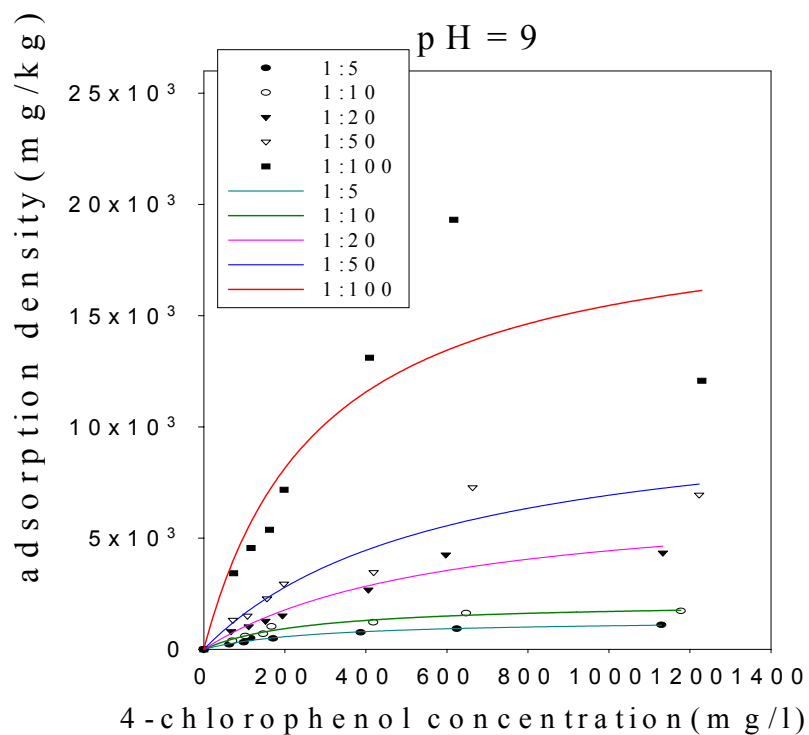
Figure 4. Isothermal adsorption curves of 4-chlorophenol under various soil to solution ratios
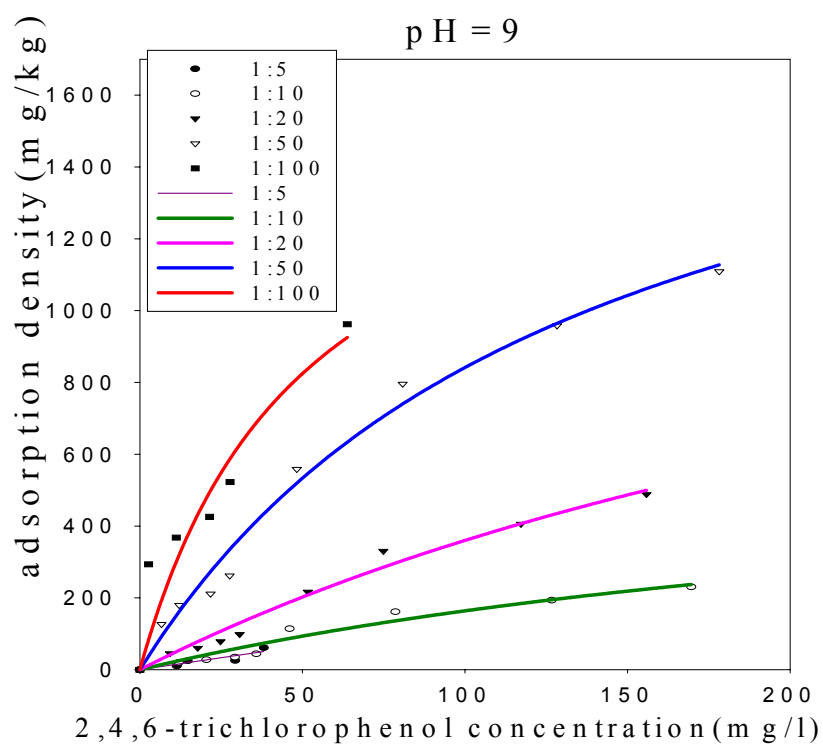

Figure 5. Isothermal adsorption curves of 2, 4, 6-trichlorophenol under various soil to solution ratios

Langmuir parameters fitted to experimental results (pH=5) were listed in Table 3. Under other experimental conditions, there existed the similar fitted phenomena as those of pH=5. To the consideration of 4-chlorophenol in the soil 1, the K constant was pertaining to 0.0001 under different experimental conditions (e.g., soil concentrations). The K constant of 2,4,6-chlorophenol in the soil 1 was around 0.003. This indicated that the there existed an identical driving force of the adsorption reaction and the force has no relationship with soil concentration. In addition, it can be seen that the adsorption capacity, b, becomes twice for the three soils when soil concentration decreases to half roughly. This special proportionality supported our postulation about the effect of soil concentration (similar to the relationship between force and pressure). Therefore, it can be implied that the hydrophobicity was the only driving force

for the distribution of chlorophenols between aqueous and soil phase. For the consideration of pH influence, the magnitude order of adsorption capacities for both 4-chlorophenol and 2,4,6-chlorophenol was pH 5 > pH 7 > pH 9 > pH 11 > pH 3 under the same experimental conditions. The pKa of 4-chlorophenol and that of 2,4,6-chlorophenol is around 9.2 and 6.23, respectively. When the pH of the solution exceeded the pKa value, more chlorophenols with negative charge exits in water and the soil surface possessed stronger negative electric potential. Therefore, chlorophenols presented high affinity to the soil at low pH conditions. However, the adsorption capacity became lowest at pH 3 among all experimental results. This may imply that strong acid would destroy the soil organic matter, which results in the low adsorption.

Table 3. The fitted parameters of Langmuir isotherm for chlorophenols

4-chlorophenol soil to solution ratio	soil 1			soil 2			soil 3		
PH 5	K	b	R2	K	b	R2	K	b	R2
1:5	0.0001	34,559	0.8529	0.001	22,783	0.9215	0.0001	7,387	0.9354
1:10	0.0001	76,485	0.9281	0.001	49,616	0.9613	0.0001	37,219	0.9391
1:20	0.0001	95,954	0.8976	0.001	75,979	0.9025	0.0001	89,468	0.9266
1:50	0.0001	229,568	0.9793	0.001	130,794	0.9685	0.0001	157,591	0.9487
1:100	0.0001	434,568	0.9633	0.001	226,257	0.9320	0.0001	377,742	0.9674
2,4,6-trichlorophenol soil to solution ratio	soil 1			soil 2			soil 3		
PH 5	K	b	R2	K	b	R2	K	b	R2
1:5	0.0041	5,137	0.8312	0.0047	2,731	0.8862	0.0053	2,701	0.8639
1:10	0.0029	7,524	0.9699	0.0045	4,139	0.9436	0.0047	3,388	0.9769
1:20	0.0035	18,953	0.8876	0.0035	7,577	0.9484	0.0057	12,221	0.9904
1:50	0.0027	42,380	0.9516	0.0044	20,156	0.9635	0.0088	25,861	0.9014

4. Conclusions

According to experimental results and theoretical analysis, several conclusions can be drawn:

1. Langmuir isotherm is appropriate to describe the distribution behaviors of 4-chlorophenol and 2,4,6-chlorophenol throughout the whole range of the saturation solubility.

2. Under various experimental conditions of pH and soil concentrations, the fitted K values for chlorophenols maintained constant implied that the identical adsorption ability controlled the distribution behaviors.

3. The identical adsorption ability could be attributed to the hydrophobicity of chlorophenols.

4. For the effect of soil concentration, the high soil concentration decreased the adsorption capacity, which could be analogy to the relationship between force and pressure.

5. The magnitude order of adsorption capacities of 4-chlorophenol and 2,4,6-chlorophenol was pH 5 > pH 7 > pH 9 > pH 11 > pH 3 because more nonionic chlorophenols presented under the low pH conditions.

Acknowledgments

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