

THE EVALUATION OF FACTORS AFFECTING SORPTION OF PENTACHLOROPHENOL IN SOIL

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Abstract

The release of persistent organic pollutants (POPs) derived from different industrial processes represents an important source of environmental contamination. Pentachlorophenol (PCP) is a highly chlorinated organic compound that has been extensively used as a broad spectrum biocide, particularly in the wood preservation industry. Due to its stable aromatic ring structure and high chlorine content, PCP is persistent in the environment, and it has become one of the most widespread contaminants in soil, sediments and water. In soil, the fate of POPs is governed by their interactions with reactive soil colloids. The soil properties as well as the chemical properties of the pollutants, control its bioavailability and transport, thus, affecting further remediation processes. The main objective of the present work was to study the sorption of pentachlorophenol in soil, collected from Iasi area (Romania). The experiments were performed in batch mode. Interest was directed towards the effects of contact time (0-72 h), initial pollutant concentration (5 - 20 mg L⁻¹), pH and temperature (10 - 50°C). The sorbed amounts of PCP increased with increase in contact time and initial concentration and reached the equilibrium after 24 h. Pentachlorophenol sorption increase with temperature in the range of 10-25°C, suggesting an endothermic process, and decrease when the temperature increased from 25 to 50°C. The results indicated that lower temperature (i.e. 10 to 25°C) was favorable for the sorption process. The high temperature (50°C) might affect the physicochemical properties of soil therefore; the sorption PCP on soil was significantly reduced.

Key words: soil, pentachlorophenol, sorption, pesticides

Soil contamination is a problem discussed as a degraded process which importance exceeds in agricultural area. Soil systems play a key role in terrestrial ecosystem processes. It is a part of the global disturbance in the ecosystem in transport of energy and substances, and is a main effect of the soil degradation.

Pentachlorophenol (PCP) and its salt have been world-widely applied for more than 50 years as a biocide in industry, as wood preserving reagent and also in agriculture, which led to serious soil contamination. Due to its stable structure, slow biodegradation, the PCP may present a toxicity risk in contaminated soils for long periods of time, even if in low concentration (He Y., et al., 2006; Cea M., et al., 2007).

Elucidating the behavior of PCP requires an assessment of the processes influencing its fate, transport, sorption, desorption, volatilization, biodegradation, run-off and persistence in soils.

Several study regarding the sorption process of pentachlorophenol onto different type of soil such as silt loam (DiVincenzo J.P., Sparks D.L., 2001), allophanic soil (Cea M., et al., 2007; Cea M., et al., 2010), soil and silty loam soil (Pu X., Cutright T.J., 2006), on sediments (Chen Y.X., et al., 2004), on soil (regosol, fluvisol and chernozem) with organomineral complex (Dercova K., et al., 2006), on chernozem, protisol and allophanic soil (Smaranda C., 2011).

The evaluation of the rate and extent of sorption processes of persistent pollutants onto soil represent a key factor for understanding their behavior and fate in the soil matrix, and assessing their potential environmental impact. More studies are still need to elucidate the sorption of PCP on soil particles.

The objective of this research was to evaluate the main parameters, that affect the sorption of PCP in surface horizons of natural soil

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samples, collected from Iasi area (Splai Bahlui – Tudor Vladimirescu), NE of Romania.

MATERIAL AND METHOD

Soil

The soil used in this study was sampled in the surface layer (0-25 cm) from Splai Bahlui – Iasi county located in the North-Eastern of Romania. The soil was classified by Romanian System of Soil Taxonomy (SRTS-2003), as protisoil with the subtype entiantroisol urbic associated with aluviosoil molic/gleic/pelic. The characteristics of soil samples are shown in *tab. 1*. Triplicate air-dried <0.02 mm particle size samples were analyzed according to standard methods. The soil pH value was 5.88, determined by potentiometric method (soil:bidistilled water, 1/5 w/w; size fraction < 0.01 mm; contact time – 30 minutes), using a multimeter Corning Pinnacle Model 555. The redox potential was determined through direct method with a couple of platinum-calomel electrodes.

The specific surface area of the soils was measured using the Brunauer–Emmet–Teller (BET) method. Results were obtained by means of N₂ adsorption at 77 K using Quantachrome Autosorb Automated Gas Sorption System analyser (Quantachrome, USA). Prior to analysis, all soil samples were outgassed at 80°C for 6 h, under vacuum.

Soil morphological features of soil samples and quantification elemental analysis to identify the weight percentage of major and minor elements present in the samples were done using Scanning Electron Microscope (SEM) equipped with an Energy Dispersive X-Ray system for qualitative and quantitative analysis and elemental mapping. The analyses were performed by soil samples fixed on copper supports. The microphotographs were recorded using an Environmental Scanning Electron Microscope (ESEM) type Quanta 200, at an accelerating voltage of 15 kV with secondary electrons in low vacuum mode (LV).

Chemicals

Pentachlorophenol (PCP) was used as the model contaminant in this study. Pentachlorophenol with the molecular formula C₅Cl₅OH and molecular weight of 266.5 g mol⁻¹, solubility of 3.0 μg ml⁻¹ at 25°C, pKa of 4.75, and log Kow of 5.01, purchased from Sigma Aldrich, was first purified with dichloromethane through a silica gel column and then the solvent was removed on a rotary evaporator (Gmb H, Germany). A stock solution of PCP (1000 mg L⁻¹) was prepared by dissolving 1 g of the pesticide in methanol, the stock solution were kept at 4° C. Calcium chloride (CaCl₂) was purchased from Fluka. Methanol, 99% purity was purchased from Sigma Aldrich (Germany).

Experimental procedure

The sorption experiments were carried out in batch mode. 20 mL of pesticide solution was added to an accurately mass of soil and agitated in a thermostatic shaker (IKA KS 4000 IC Control, Germany) at 150 rpm, in the dark and 25°C.

The experimental solutions with different concentration were obtained by diluting the stock solution to a set concentration with an electrolyte of 0.01 M CaCl₂. Solutes were added via methanol carrier, keeping the methanol percentage in the range of 0.5–1%, methanol in water solution has no significant effect on sorption.

All the glass vials containing soil and PCP solutions were shaken in darkness until the measurement time was reached. For each batch experiment, blank samples were prepared and monitored (PCP solutions without soil). The blanks did not indicate any significant PCP degradation or sorption losses during the course of the experiment.

Batch samples were equilibrated on a temperature controlled rotating shaker at 10, 25 and 50 °C. The pH of the solutions was adjusted with HCl or NaOH (0.1 mol L⁻¹).

An equilibration period of 72 hours was chosen after preliminary experiments lasting up to 96 h indicated that such duration was sufficient to achieve equilibrium. At the end of the sorption period, the solution was separated from the adsorbent by centrifugation at 6000 g for 20 minutes (Hettich EBA 20 Centrifuge, Germany). The supernatant was filtered through membrane filter 0.2 μm pore size (OlimPeak) and the PCP concentration in the supernatant was determined by HPLC (high pressure liquid chromatography). pH was measured using a pH meter (Hanna Instruments).

The HPLC instrument equipped with a VARIANO 9010 pump, a Waters 717 Plus injector, a Waters 486 (Tunable Absorbance Detector) detector operating at 220 nm, and a reversed-phase ZORBAX SB-C18 column made by Agilent (USA) was used. The mobile phase was made of methanol and 0.1 N sulfuric acid solutions, the flow rate was 0.5 ml min⁻¹. Instrument calibrations and quantifications were performed against pure reference standards.

The amount of PCP sorbed onto soil particle at time *t*, *q_t* (mg g⁻¹), were obtained by mass balance, according to equations (1):

$$q = \frac{(C_i - C_e)V}{m} \quad (1)$$

where, *C_i* and *C_e* are the initial and equilibrium liquid phase concentrations of pesticide (mg L⁻¹), *V* is the solution volume (L) and *m* is the mass of soil (g).

RESULTS AND DISCUSSIONS

Characterization of soil samples

Chemical and mineralogical composition of soil particles was analyzed and the results are depicted in the *table 2*. The mineralogical - chemical analysis relived that the main percent of the investigated soil is represented by clay minerals 47,62 %, silica 28.42 % and organic mater 7.19 %, carbonated 4.86%, oxides and hydroxides of iron 3.54 %

The BET surface area, total pore volume and pore diameter, obtained by nitrogen adsorption isotherms were given in *table 3*. The surface area, pore volume and mean pore diameter of the

protisoil were 26.26 m²g⁻¹, 4.80 10⁻² cm³g⁻¹, and 73.17 Å, respectively. In accordance with the BET analysis, the soil particles are covered by micropores, which increase the surface by a factor of 1.36 compared with macroscopically measured

surface area (Smaranda C., 2011). The soil micropores have a special importance in chemical and physical sequestration of pollutants in the environment, as well as in the selectivity of the cation exchange.

Tabel 1

General characteristics of soil sample	
Sample characteristics	Soil
Area	Splai Bahlui-Iași
Sampling deep (cm)	0 - 25
Soil type/subtype*	Protisoil / Entiantrosoil urbic associated with aluviosol mollic-gleic / pelic
Soil horizon*	Apk / Bvk
Soil utilization	Green area (ruderal plants - <i>Gramineae</i>)
Anthropic soil transformation	Intense
Pollution degree**	Weak to medium
pH	5.88
E _h	580.13
CTSC	10.61

Tabel 2

Chemical and mineralogical composition of soil sample (% w/w)*			
Chemical-mineralogical composition		IS-T	
Clay minerals (%. w / w)	Smectite	15.29	
	Illite	9.87	
	Kaolinite	19.20	
	Amorphous	3.24	
	<i>Total</i>	47.62	
Carbonates	Crystalline	3.17	
	Amorphous	1.73	
	<i>Total (% w / w)</i>	4.91	
Iron oxides and oxihydroxides (%. w/w)	Crystalline	1.50	
	Amorphous	2.04	
	<i>Total</i>	3.54	
Silica (SiO ₂) (%. w / w)	Crystalline	6.64	
	Amorphous	4.42	
	<i>Total</i>	11.06	
Others minerals** (%. w / w)		6.13	
Organic matter (%. w / w)	Humic substances	Humic acids	3.19
		Fulvic acids	1.72
		Humic	0.42
		<i>Total</i>	5.33
	Others non-humic organic compounds	1.86	
<i>Total</i>	7.19		
Undecomposed vegetal matter % (w / w)		0.73	
Coarse fraction*** % (w / w)		1.51	

*Reported at raw soil sample.
 **Sulfates, phosphates, heavy minerals and relicts (from parent material). *Organic compound unbound to humus substances.
 ***Granulometric fraction $\Phi > 2,00$ mm (raw fraction; includes fragments of unmodified minerals and rocks parentale).

Tabel 3

Soil porosity characteristics	
BET parameters	Value
BET surface area (m ² /g)	26.26
Total pore volume (cm ³ /g)	4.805 * 10 ⁻²
Average pore diameter (Å)	73.17
Micro-pore volume (cm ³ /g)	3.087 * 10 ⁻³
Micro-pore surface area (m ² /g)	7.015
External surface area (m ² /g)	19.25

The surface morphology of the soil particles, analyzed by scanning electron microscopy (SEM) at 1000X is presented in figure 1. The morphology of the soil samples show an

internal structure relatively dense, homogeneous, formed by conglomerates of particles, characterized through crystal structure hexagonal and pseudo-hexagonal layered, this kind of texture is characteristic to mineral clays (Smaranda C., 2011).

The EDX elemental analysis shows the presence of the usual components of aluminosilicate minerals - Si, O, Al, K and Ca, as can be seen in the EDX spectrum presented in figure 2. Silica, oxygen and aluminum are elements present in high percent and are distributed in bunch, mostly at the surface of soil

particles. Calcium, potassium and magnesium are present in small quantity, and they are also, distributed in bunch. The heavy toxic elements Cd and Cr are present in soil sample.

Effect of initial pesticide concentration

Four different concentrations 5, 10, 15 and 20 mg L⁻¹ were selected to investigate the effect of initial concentration (C_0) on the sorption of PCP onto studied soil. The experiments were performed at 25°C and natural pH of solution (5.8). The results obtained are shown in *fig. 3*. The maximum sorption capacity increased from 0.09 mg/g to 0.22 mg/g with the increase of pesticide concentration from 5 to 20 mg L⁻¹. For lower

initial concentration the rate of pesticide adsorbed is faster; while for higher concentrations the available sorption sites become fewer and the rate of uptake onto soil matrix decrease (Dercova K., et al., 2006).

Effect of contact time

The amount of sorbed pesticides per unit of soil mass (mg g⁻¹) enhances with contact time increasing and reached the apparent equilibrium after 24 hours. A large quantity of pesticides has been sorbed onto soil after a relatively short contact time where the uptake more than 40% of the molecules was noticed within the first 2 hours of the experiments (*figure 3*).

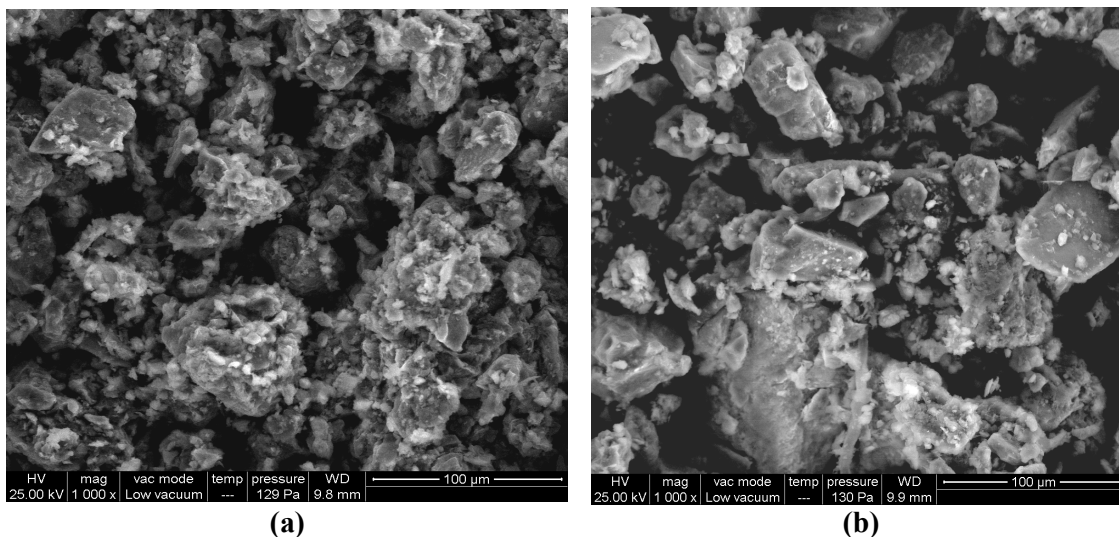


Figure 1 Scanning electron micrograph of soil particles (a) before sorption process and (b) after PCP sorption

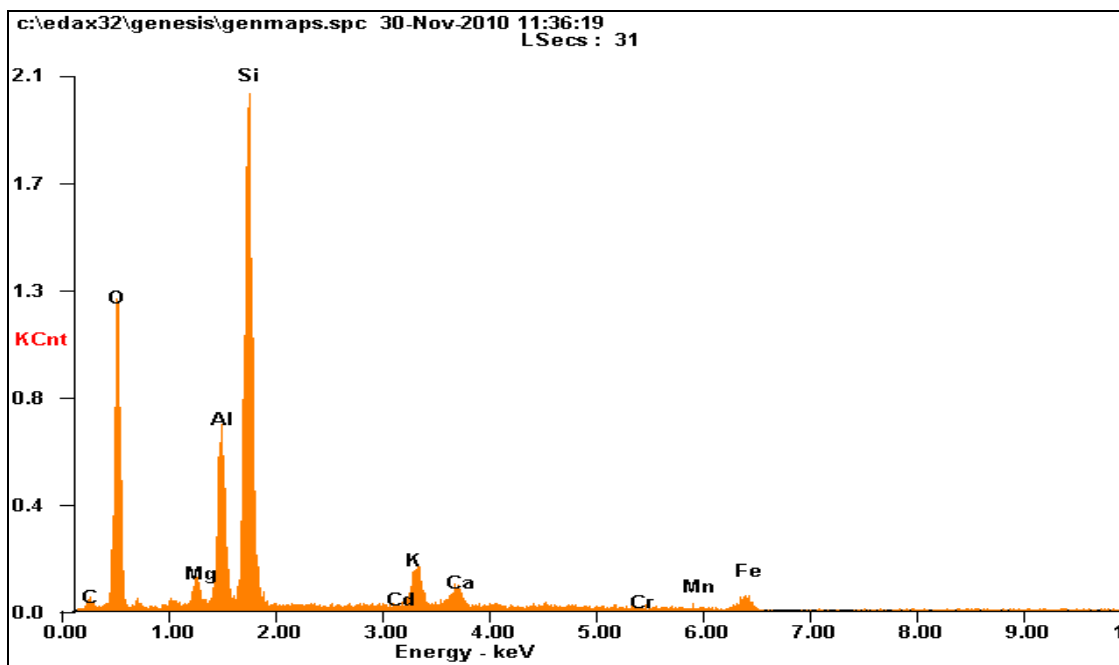


Figure 2 EDX spectrum of soil sample

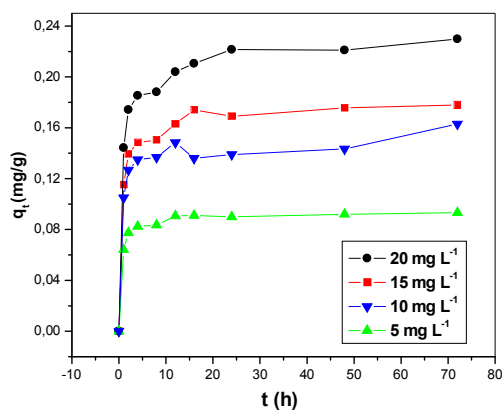


Figure 3 Effect of the initial concentration of PCP on sorption onto soil ($m_{\text{soil}} = 1 \text{ g}$; $C_{\text{PCP}} = 5 - 20 \text{ mg L}^{-1}$; $T = 25^\circ\text{C}$)

Sorption continued slowly reaching an apparent equilibrium after 24 h, reflecting 90-95% of the sorption maximum, observed after 72 h. These results are in accordance with the other sorption study (DiVincenzo J.P., Sparks D.L., 2001) where 78% of PCP was sorbed on soil, other study reported 60% of PCP uptake in the first 7 hours (Cea M., et al., 2010). The difference of the amount of PCP adsorbed can be attributed to the differences in soil properties, the organic content of the Iasi soil is 5.33% (tab. 1) and 1.7% for first reported study and 7.9 % for the second. In fact, soil organic matter plays an important role in the sorption of highly hydrophobic compounds such as PCP. The rapid sorption of the pollutant at the beginning of the process indicates a surface phenomenon.

Effect of pH

The effect of pH was studied carrying out at both pH 4 and pH 8 to compare the protonated and ionized forms of PCP, and also at pH 6 (soil natural pH is 5.88). The experimental results are depicted in fig. 4. The higher sorption capacity was obtained at pH 4, when q_e value was $0,214 \text{ mg g}^{-1}$, and the lowest sorption capacity was obtained at pH 8.

At pH 4, the PCP exists mainly (50%) in protonated form and in ionized form at pH 8. With the increase of pH, proportion of neutral PCP decreases and proportion of ionized species increases.

At low pH, PCP should be predominantly protonated and adsorb or partition more to soil particles (He Y., et al., 2006). In general, as the pH comes closer to the pK_a of the compounds, the adsorption increases due to the hydrophobicity of their neutral form.

Because the change of pH is the colligated results of special soil properties, it may indicate again the combined contributions of soil properties on the sorption of PCP. Also, deprotonation of the polar functional groups on the surface of soil increases with pH, sorption of PCP is decreasing due to electrostatic repulsion and it favored hydrophobic effect.

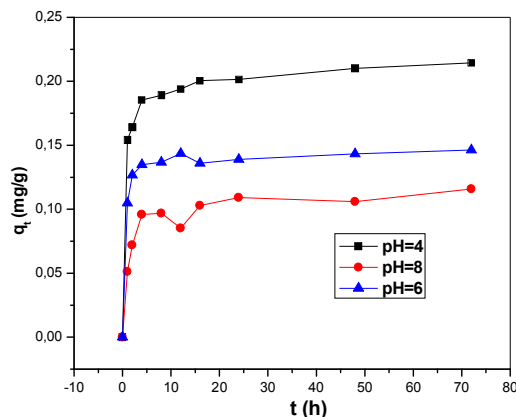


Figure 4 Effect of the pH on the sorption of PCP on soil ($C_{\text{PCP}} = 10 \text{ mg L}^{-1}$; $m_{\text{soil}} = 1 \text{ g}$)

Effect of temperature

In order to determine the effect of temperature on PCP sorption in soil, the experiments were carried out at three different values of temperature - 10, 25 and 50°C . The results are summarized in fig. 5. In general, the increasing of temperature increases the rate of diffusion of solute molecules from the solution to the external or internal surface of the sorbent.

Over the studied temperature range, the results indicated that temperature has important influence on sorption processes; it was observed an increase of the sorption capacity with increasing temperature in the range of 10 to 25°C . Over 25°C the quantity sorbed decreased with increasing temperature.

These results indicate that the process is exothermic over 25°C . Comparable results were reported on PCP sorption on carbon nanotubes and activated carbon (Salam M.A., Burk R.C., 2010).

The result suggests that low temperature regime is favorable for sorption of PCP in soils. This effect indicates that the mechanism of PCP sorption on studied soil involves a physical process. It is possible that temperature to affect the bound linkage between soil and PCP if the sorption process is attributed to interaction of functional groups.

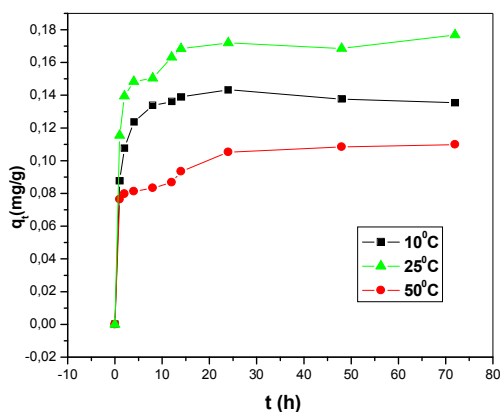


Figure 5 Effect of the temperature on the sorption of PCP on soil ($C_{PCP}=10 \text{ mg L}^{-1}$; $m_{\text{soil}} = 1 \text{ g}$; T - 10, 25, 50°C)

Also, high temperatures, such as 50°C, may modify physical-chemical properties of soil. Similar results were reported by Pang K.M., et al., (2007) at sorption of PCP onto magnetite-immobilized chitin, when the adsorption capacity decreased over 25°C, the lowest values of q_e were obtained at 50°C. Marouf R., et al., (2006) studied the effect of temperature on the sorption of pentachlorophenol onto dolomite, and observed the same effect in decreasing of sorption capacity with temperature increasing, in the range 25-50°C.

CONCLUSIONS

The sorption process of pentachlorophenol on protisoil was studied under different reaction conditions, in batch equilibrium mode. The amount of PCP sorbed increased with the contact time and with initial pesticide concentration. The sorption is rapid at the beginning of the process, indicates a surface phenomenon.

The temperature is another important factor that affects pesticide behavior in soil. The results show that low temperature regime is favorable for sorption of PCP onto studied soil, while at high temperature the sorption process onto soil particle is unfavorable; the temperature affect the mobility of PCP and leaching potential into groundwater.

The acid-base behavior of PCP and the soil properties contribute to the complexity of PCP retention in the soil-water system. At low pH (4), PCP is predominantly in protonated form and is sorbed or partitioned to soil. The increase of pH, proportion of ionized species increases and sorption of PCP molecules on soil particles is reduced.

The uptake and mobility of PCP in protisoil is highly influenced by soil pH. The PCP – soil sorption system can be used as model in the design of soil remediation systems and the methodology developed for PCP may be considered to extend to other POPs.

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