

INTRODUCTION

It is well established that the adsorption of organic cations to clays results in a modification of its surface properties from hydrophilic to hydrophobic or organophilic [1]. Adsorption of non polar volatile or leachable herbicides to such organoclays can be used as mean of extending the biological activity of these agrochemicals under field conditions, resulting in a reduction of the environmental threat of contamination of soils and ground water [2]. The peculiar "gallery structure" of pillared clays makes them also potential candidates for sorbents of compounds of agricultural and environmental interest. It is expected that the adsorptive capacity of a pillared clay towards organic molecules can be increased by replacing the remaining exchangeable inorganic cations by organic cations such as quaternary ammonium derivatives, similarly to what has been done in the case of regular clays [1]. Since the intensive experiments are being carried out to study the sorption mechanism of cations by these soil components and to improve the knowledge of the soil organo-mineral complexes as buffer substances for plant herbicides or pesticides, pollutants [3-7]. The aim of this work is to study the adsorption of phenol and chlorophenols, on pillared and organopillared-clays as model of organic compounds of environmental interest usually present in wastewaters at relatively low concentrations and for which a biological degradation is rather difficult. The results can be extended to molecules of agricultural interest as the pentachlorophenol.

MATERIALS AND METHODS

The cationic surfactant benzyl tetradecyl dimethyl ammonium chloride (BTDDMAC) used in this work was provided by Sigma Chimie. The trimethyl ammonium chloride was from Aldrich. The pillared clay used was the ALFULCAT-2C (PILCS) prepared by the National Technical University of Athens. The pillars were the Aluminium ions. A general revue on PILCS is given in reference [8]. The phenols were products from Sigma Chimie, and were used as received. Their principal characteristics are given in Table I. For the preparation of the BTDDMAC pillared-organo complex, ten grams of PILCS was dispersed in two liters of BTDDMAC calibrated solution of 8.10^{-3} mol.kg⁻¹. Then the suspension was allowed to equilibrate during one week on a rotary shaker. The amount adsorbed after the equilibration time was $4.4 \cdot 10^{-4}$ mol.g⁻¹. A part of BTDDMAC adsorbed by physical interactions was desorbed by simultaneous washing and centrifugation at 6000 tours.min⁻¹ during 15 min. The final amount of BTMAC remained on PILCS was close to $3. \cdot 10^{-4}$ mol.g⁻¹. For the BTMAC, the initial concentration was $4. \cdot 10^{-4}$ mol.kg⁻¹, the same solid ratio and equilibration time than above was used. After washing, the amount of the BTMAC adsorbed was close to $2.3 \cdot 10^{-4}$ mol.g⁻¹, and then they were dried at 60°C. In table II, we summerized the physico-chemical characteristics of these clays.

Compound	Abre	λ_{\max} (nm)	ϵ (mol ⁻¹ cm ²)	pKa*	water* solubility (g.kg ⁻¹)
phenol	PHE	270	1480	9.9	77
2,6 Dichlorophenol	DCP	275	1880	8	4.5
2,4,5 Trichlorophenol	TCP	289	2555	7.7	0.8
Pentachlorophenol	PCP	318	3576	4.7	0.14

* indicatives values

Table I: Physicochemical properties of phenol and chlorophenols.

	PILCS	BTMA-PILCS	BTDDMA-PILCS
Specific surface area N ₂ BET (m ² .g ⁻¹)	315	234	43
Pore specific volume (cm ³ .g ⁻¹)	0.332	0.256	0.109
d001 (Å)	17.3 (broad)	16.6 (charp)	15.8 (charp)

Table II: Physicochemical properties of PILCS and organo-PILCS adsorbents

The rest method was used for performing adsorption **isotherms** on PILCS and **organo-PILCS**. They were obtained by weighing **100 mg** quantities of the clay or organo-clay complexes into **150 ml** polyethylene flasks and adding 20 ml of appropriate calibrated solution of each phenol derivatives without reaching the solubility limit of the product. The suspensions were then **shaked** during 24 hours at **20°C**. After the equilibrium time, the suspensions were centrifuged at **18000 tours.min⁻¹** during **30 min**. For non adjusted pH suspension, the equilibrium pH of supernatants was 4 to 5. The analysis of the appropriate compound in the solution phase were made by using spectrophotometer ACTA MTV utilizing an appropriate absorption band in the **ultraviolet** region (table I).

RESULTS

Adsorption of phenols on PILCS

Figure 1 shows adsorption **isotherms** of phenols and its chlorine derivatives from water on untreated PILCS. For the phenols the **pKa** is close to superior to 9, at pH 5 to 6 of experimental conditions, **all** these phenols are in protonated **form**. The isotherms exhibit some differences for the various chlorinated phenols. The phenol which is more polar, and have high **affinity** for water molecules, remain in bulk and is not adsorbed at all by the **Al-PILCS** in the all range of concentrations studied, same results are obtained by Mortland and al on Wyoming bentonite [9]. Hence **Al-PILCS** have no polar sites in their structure and the hydrophilicity of the initial clay was more reduced by the intercalation of the metal oxide aggregates of alumina cations. As the number of chlorine atoms on

the phenol structure was increased, the hydrophilic character of these molecules decreases, and their solubility in water molecules decreases leading to an **increase** in the adsorption. For DCP, the isotherm is nearly linear, indicating that the partition rate of these molecules is close to be equal between the surface and the aqueous bulk phase [10]. The adsorption amount of DCP reaches $80 \mu\text{mol.g}^{-1}$. For TCP isotherm, it is of **Langmuir** type up to equilibrium concentration equal to $10^{-3} \text{ mol.kg}^{-1}$, and after this, the adsorption increases **linearly** with the increase of the **equilibrium** concentration. The adsorbate-adsorbent interaction was relatively strong, **which** is due to the strong interaction of this sorbent with the surface than that with the water solvent molecules. For the PCP, all the quantities of this sorbent added up to initial concentration equal to $2.6 \cdot 10^{-5} \text{ mol.kg}^{-1}$ was adsorbed, the lower concentration used was due to its lower solubility limit which does not exceed $5 \cdot 10^{-5} \text{ mol.kg}^{-1}$. The amount adsorbed for **TCP** and DCP on Al-PILCS are greater than that obtained by **Zielke** and **al** on alumina delaminated Laponite [11].

Adsorption of phenols on organo-PILCS

The adsorption of phenols on BTDDMAC-PILCS and BTMAC-PILCS are respectively given in Figures 2 and 3. When the sorbent was the BTDDMAC-PILCS complex, the adsorption amount of the phenols increases with the number of chlorine atoms on the phenol structure as found for adsorption on **TMPA⁺** smectite [9]. Otherwise, as the hydrophilic nature of these molecules decreases the adsorption increases via hydrophobic interactions. The phenol sorbent was not adsorbed at all up to **equilibrium** concentration close to $8 \cdot 10^{-4} \text{ mol.kg}^{-1}$. After these equilibrium concentration, adsorption occurs and small increase of the amount adsorbed was obtained with the increase of adsorption isotherm. The quantity of the sorbent retained does not exceed $40 \mu\text{mol.g}^{-1}$. At weak equilibrium concentration, the phenol molecule is hydrophilic and is more solubilised in water phase, as the concentration increases, some phenol molecules are trapped into interior of the porous galleries where they are retained by the **alkyl** chains. In this case, once molecule of phenol is adsorbed, however, a cooperative adsorption takes place, and adsorbent-adsorbent forces promote the adsorption of more molecules. For DCP and TCP **isotherms** of **Langmuir** type are obtained indicating, relative strong adsorbent-adsorbed hydrophobic interaction [5]. All the PCP added is retained by the organo-PILCS complex. For the BTMAC-PILCS system, the adsorption of phenol from water is quite different than on untreated PILCS and BTDDMAC-PILCS complex. However, for higher equilibrium concentrations, the adsorption of phenol is equivalent to the adsorption of DCP on BTDDMAC-PILCS complexes and reaches $100 \mu\text{mol.g}^{-1}$. For DCP and TCP, the adsorption increases with the number of the chlorine atoms, and both type of these molecules exhibit adsorption amounts intermediate between their adsorption on **PILCS** and BTDDMAC-PILCS. The feature of DCP adsorption isotherm is linear, indicating a same sorbent partition between the aqueous bulk phase and the **solid** phase [5].

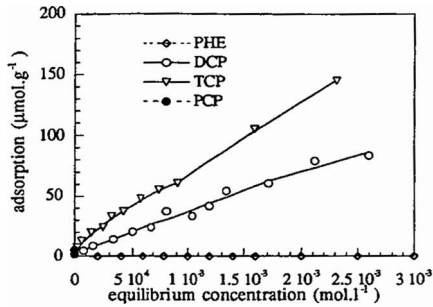


Figure 1: Adsorption of phenols on Al-PILCS

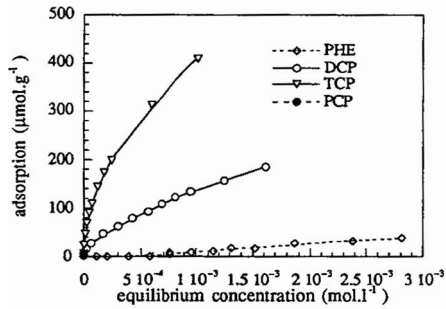


Figure 2: Adsorption of phenols on BTDDMAC-Al-PILCS

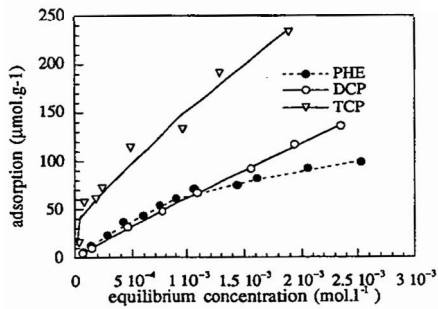


Figure3: Adsorption of phenols on BTMAC-Al-PILCS

CONCLUSION

The proposed research was designed to experimentally determine the role of **surfactants** to enhance the retention of organic molecules by the Al-pillared clays. Specific effects to be investigated were impacts of the surfactants in the sorption **efficiency**. The degree of partitioning of hydrophobic organic pollutants to particles depend on the hydrophobicity of the organic molecule and the type of organic ammonium treated particle. The adsorption of chlorophenols is considerably increased by the treat of the **Al-PILCS** by the quaternary **alkyl** ammonium. The phenol not adsorbs on the untreated **Al-PILCS** and **unsignificantly** adsorb on the BTDDMAC-PILCS. However, its adsorption is noteworthy increased on the **BTMAC-Al-PILCS organo-clay**.

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