



# Effect of humic acids on pentachlorophenol sorption to cetyltrimethylammonium-modified, Fe- and Al-pillared montmorillonites

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## ABSTRACT

Because natural organic matter is commonly present in surface water and might interfere with the removal of organic contaminants, we investigated the effect of humic acids (HA) on the adsorption of pentachlorophenol (PCP). The sorbents are synthetic clay compounds: surfactant-modified pillared montmorillonite (SMPM). First the cation exchange sites of an Algerian bentonite were blocked by intercalation of metallic polycations from either Fe(III) or Al(III); then cetyltrimethylammonium cations were adsorbed in order to obtain two hydrophobic and organophilic clay compounds. According to batch adsorption isotherms in single systems, both PCP and HA sorptions increased when pH decreased, especially for Fe-SMPM in comparison with inorganic pillared clays without cationic surfactant. The Fe-SMPM was more effective than the Al-SMPM for PCP sorption: at pH 6, the maximum PCP sorption capacities were 530 mg g<sup>-1</sup> vs. 300 mg g<sup>-1</sup>, respectively. From data treatment with an extended Freundlich model, in binary systems at pH 6 and at various PCP/HA ratio (ranging between 1/4 and 4/1 g g<sup>-1</sup>), the competition affected both forms of SMPM quite strongly. In addition, the competition between PCP and HA was more important for the Fe-SMPM than the Al-SMPM, with respective maximum PCP sorption capacities of 133 vs. 53 mg g<sup>-1</sup>. Due to their high thermal stability and efficiency towards organic compounds, SMPM may have environmental applications in treating surface water and wastewater for the removal of organic pollutants such as chlorinated phenols.

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## 1. Introduction

Organic chemicals in surface and groundwater supplies are major environmental and sanitary problems. The sorption of natural organic matter (NOM) to particle surfaces influences its environmental fate and affects both NOM reactivity with pollutants and its transport through soils, rivers, and lakes.

Humic acids (HA) constitute a major fraction of NOM in surface waters but their removal is difficult due to their water solubility and their wide range of distribution in molecular weight and size. For example, Martin-Mousset et al. (1997) have shown that these organic acid compounds arise from the decay of plant and animal residues and exist as a heterogeneous mixture of molecules with various functional groups such as phenolic, carboxylic, carbonyl, amino, etc. Water treatment through sorption onto activated carbon is often used to eliminate organic micropollutants from drinking water. In another way, many potential solid sorbents such as zeolites, resins, metal oxides and natural clays have been studied to describe the sorption phenomena of humic substances and phenolic compounds.

Clay particles are ineffective in removing many organic components from water, because clays are strongly hydrated in water and the clay surface is hydrophilic (Karickhoff et al., 1979; Schellenberg et al., 1984; Rebhun et al., 1992). However, the modification of clay materials by interaction with organic compounds leads to the formation of organophilic solid materials, the properties and uses of which were recently summarized (de Paiva et al., 2008). For example, a surfactant-modified bentonite with a long-chain quaternary alkyl ammonium cation can effectively sorb chlorophenols from water (Rawajfih and Nsour, 2006). Both adsorption and partition mechanisms contribute to their sorption, which can be related to their hydrophobicity order: phenol < 4-chlorophenol < 2,4-dichlorophenol. Unfortunately, such organoclays are thermally unstable.

The intercalation of metallic polycations into the interlamellar space between clay layers produces pillared clays with higher basal spacing and specific surface area (Zielke and Pinnavaia, 1988; Khalaf et al., 1997; Schoonheydt et al., 1999). Synthetic surfactant-modified pillared montmorillonites (SMPM) are obtained by co-adsorption of the pillared clay with large alkylammonium cations such as cetyltrimethylammonium (CTA). They showed an increased sorption capacity towards organic micropollutants, and a good thermal stability. In this way, numerous previous studies have clearly shown that organo-inorgano clays materials (which are characterised by their high hydrophobicity) could effectively remove organic compounds and especially chlorinated

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phenols from aqueous solutions (Mortland et al., 1986; Boyd et al., 1988; Srinivasan and Fogler, 1990a,b; Michot and Pinnavaia, 1991; Lawrence et al., 1998; Bouras et al., 1999, 2001; Jiang et al., 2002; Jiang and Zeng, 2003; Ake et al., 2003; Wiles et al., 2005). Thus SMPM represents an innovative and promising class of sorbent materials. Hydrophobic interactions between the non-polar organic molecules and the alkyl chains of surfactant can reduce the mobility in soil of some organic pollutants such as phenol derivatives which are characterised by low water solubility (see, among others: He et al., 2006).

Surfactant-modified pillared montmorillonite (SMPM) could be implemented for drinking water treatment or for decontamination of water resources. Up to now, only few studies have considered the influence of NOM on the sorption of organic pollutants by SMPM, and specifically concerning the sorption of chlorophenols. PCP was chosen as a model molecule because it is a persistent chlorinated organic compound with known cytotoxic and endocrine disruptive properties. Its dissemination has resulted from its extensive use as a pesticide. In order to understand the behaviour of SMPM towards pentachlorophenol (PCP) in environmental conditions (competition reactions), we investigated the influence on its sorption of NOM such as humic acids (HA). Moreover, selective sorption of a specific solute and competition between different solutes for sorption sites are of general interest.

The first part of this paper deals with PCP or HA sorption from aqueous solution and discusses their sorption isotherms. Thereafter, the sorption behaviour of surfactant-modified pillared montmorillonite (SMPM) in contact with an aqueous mixture of PCP and HA was studied at different PCP/HA ratios at pH 6.

## 2. Materials and methods

### 2.1. Reagents

All chemicals were of analytical grade. The different solutions were prepared in high purity de-ionised water (HPW) (Milli-Q system: resistivity 18.2 M $\Omega$  cm, TOC < 10  $\mu$ g L<sup>-1</sup>). All glassware and containers were previously soaked in 10% (v/v) nitric acid for at least 24 h and then rinsed with HPW.

### 2.2. Sorbents

All these preparations were already optimized in previous studies (Khalaf et al., 1997; Bouras et al., 2007). The natural material used for the preparation of sorbents was a sample of bentonite (from Maghnia, western Algeria) whose chemical composition was previously studied (Khalaf et al., 1997). The < 2  $\mu$ m fraction of the clay was converted into the homoionic form by adding appropriate amounts of 1 mol L<sup>-1</sup> NaCl solution to replace all exchangeable cations with the single cation Na<sup>+</sup>. After five successive treatments, the homoionic clay was dialysed several times in HPW until free of anions.

Two pillaring solutions of iron(III) and aluminium(III) hydroxides were prepared and were kept in darkness for ageing (Bouras et al., 2007): the iron pillaring solution which gives Fe-hydroxy polymer was aged at room temperature (20  $\pm$  2  $^{\circ}$ C) for 10 days; solutions of Al-polyhydroxy species were aged at room temperature for 48 h at least.

The given pillaring solution was dropped into Na-montmorillonite suspensions (0.4% w/w). The intercalation of Na-montmorillonite by the pillaring solutions was obtained with the final concentrations [Fe]<sub>f</sub> = 0.2 mol L<sup>-1</sup> or [Al]<sub>f</sub> = 0.1 mol L<sup>-1</sup>. After vacuum filtration and washing several times with HPW the solid product obtained was dried at 40  $^{\circ}$ C in the air to a constant weight for at least 72 h, ground for homogenisation and sheltered from light.

The surfactant-modified pillared montmorillonites (SMPM) synthesis method consisted in modifying an Fe- or Al-pillared clay by co-adsorption of long-chain CTA cations. A 0.2% (w/w) aqueous solution

of CTA bromide was prepared by dissolution of the appropriate amount in HPW.

Aliquots of each dried solid were dispersed in HPW in order to obtain a 0.5% w/w suspension, to which a solution of quaternary ammonium salt was added and the mixture was mechanically stirred. The final solid products were separated by vacuum filtration. The excess of physically adsorbed CTA cations was removed by several washing with HPW. Then, the samples of each solid organophilic SMPM were dried at 40  $^{\circ}$ C for at least 72 h, powdered for homogenisation and then sheltered from light before use.

### 2.3. Batch isotherm experiments

#### 2.3.1. Solutions of adsorbates

A stock PCP solution ( $C_0 = 13$  mg L<sup>-1</sup>) was prepared by dissolving the appropriate amount of PCP in HPW at room temperature, shaken for several days and then filtered through Sartorius cellulose nitrate membrane (0.45  $\mu$ m) before use. Then this stock solution was diluted to prepare a series of standard solutions. All these solutions were kept at 4  $^{\circ}$ C in the dark to prevent any possible photodegradation (Bouchard, 1998).

HA were extracted from commercial humic acid sodium salt (purchased from Aldrich), following the standard procedure of purification onto Amberlite XAD-7 resins described by Martin-Mousset et al. (1997). A solution with initial concentration  $C_0 = 5$  mg L<sup>-1</sup> was diluted as appropriate. The sorption behaviour of HA to pillared clays or SMPM was examined because no published data were available.

For the sorption selectivity studies, the volumes of each solution were chosen in order to obtain PCP/HA ratio between 1/4 and 4/1 g g<sup>-1</sup>. These experiments were conducted at pH = 6 only. Supernatants from the PCP/HA mixtures were obtained by filtration and the final concentration of PCP in the binary systems was determined by UV absorbance in the same conditions as described below.

#### 2.3.2. Experimental conditions and analysis

The sorption behaviour of each SMPM sorbent in contact with diluted aqueous solutions of the two organic compounds (PCP and/or HA) was studied in several test series. The sorption equilibrium isotherms were carried out using batch reactor. For each isotherm, various sorbent amounts (0 to 100 mg SMPM) were accurately weighed into 250 mL brown glass flasks, followed by the addition of 100 mL aliquot of PCP or/and HA solution. One flask without sorbent served as a blank in order to check that there was no sorption onto the glass walls. All flasks were closed and shaken overnight at 20  $\pm$  2  $^{\circ}$ C on an orbital shaker (Ikalabortechnik model KS501) at 200 rpm.

Previous kinetic experiments (Bouras et al., 1999) with chlorophenols such as PCP indicated that the sorption of PCP onto SMPM was not totally reversible. Using equilibration times varying from 0 to 48 h also showed that the sorption process was very fast and that a pseudo equilibration time was reached in approximately 8 h. In the present study, we maintained the contact time for all experiments at 24 h, because other phenomena, such as microporous diffusion can probably take place after sorption (Bouberka et al., 2005; Anirudhan and Ramachandran, 2006). After a 24-hour equilibration, the content of each flask was filtered on 0.45  $\mu$ m Sartorius cellulose nitrate filters and the concentrations in the supernatant were determined from the UV absorbance at  $\lambda_{\text{max}}$  for each organic compound. These analyses were performed using a 1 cm quartz cell with a computer-controlled Agilent model 8543 UV-visible spectrophotometer. The maximum wavelengths for each organic compound were obtained directly by automatic sweeping between 200 and 800 nm:  $\lambda_{\text{max}} = 320$  nm for PCP;  $\lambda_{\text{max}} = 254$  nm for HA.

All experiments were carried out in duplicate and each point on the isotherm was the average value of two data sets.

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