

## Sorption of *p*-nitrophenol onto sediment in the presence of cetylpyridinium chloride and $\text{Pb}(\text{NO}_3)_2$ : Influence of pH

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### Abstract

pH and the presence of compounds have a great effect on the sorption of organic contaminants. In this study, batch equilibrium experiments were carried out to investigate the influence of pH on the sorption of *p*-nitrophenol (PNP) onto sediment in the presence of  $\text{Pb}(\text{NO}_3)_2$  and cetylpyridinium chloride (CPC) cationic surfactant. Results indicated that in the multi-solute system with PNP,  $\text{Pb}(\text{NO}_3)_2$  and CPC, the sorption of PNP increased with the increasing pH and the amount of sorbed PNP at equilibrium was much higher than in the single-solute system. This can be attributed to the presence of  $\text{Pb}(\text{NO}_3)_2$  and CPC. It is believed that the main reason for that was the larger sorption of CPC at higher pH allowing higher sorption of PNP. The results are believed to provide a useful insight into describing the transport and fate of PNP in natural environments.

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**Keywords:** pH; Surfactant; *p*-Nitrophenol; Heavy metal; Sorption

### 1. Introduction

Sorption of organic pollutants onto sediment is known to be a key process in respect to the fate in environmental systems. Sorption of nonionic organic compounds onto sediments is due primarily to the partitioning into sediment organic matter (SOM) [1–3]. Besides the soil organic matter, sorption of ionizable organic compounds (IOCs), including phenols, carboxylic acids, and amines, is highly influenced by solution pH, which determines if the IOCs exist in either ionic or neutral forms. The effect of pH on IOC sorption onto soil and sediment has been widely studied and it is generally accepted that sorption of IOC is largely controlled by the pH, as ionized species are much more soluble and thus less hydrophobic than their neutral counterparts [4–8]. Consequently, the sorption potential of the ions is much lower than that of the neutral ones.

In addition to organic pollutants, industrial and municipal wastewater generally contain heavy metals and surfactants, which cause experiences obtained from single-solute systems

to be inadequate when describing sorption of organics in multi-solute systems. This is a result of various interactions, such as competition with heavy metals for adsorption site or formation of complexes [9–11]. In additions, surfactants can cause significant changes of the sorption of organic contaminants onto soil and sediment [3,12,13]. Hence, it is necessary to take these phenomena into consideration when describing the influence of pH on the sorption of organic contaminants in multi-solute systems.

*p*-Nitrophenol (PNP) and  $\text{Pb}(\text{NO}_3)_2$  were chosen as the reference organic contaminant in this study. PNP in wastewater mainly came from industrial sources such as high-temperature coal conversion, petroleum refining, resins and plastics. Pb is the most common heavy metal contaminant in the environment according to the environmental protection agency (EPA) [14]. It is a nonessential element in metabolic processes and may be toxic or lethal to organisms even when absorbed in small amounts [15]. Through solid/aqueous interfacial sorption and settling, PNP, heavy metal and surfactant in river coming from industrial and municipal effluent can finally move into sediment. Previous studies focusing on the sorption of PNP onto sediments or soils in simple systems found that sorption was greatly influenced by pH [4–8], as well as the surfactants and heavy metals present [9–13]. However, matters become more complicated

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when PNP, heavy metal and surfactant are mixed. Therefore, the influence of pH on the sorption of PNP onto sediment in the presence of cetylpyridinium chloride (CPC) and  $\text{Pb}(\text{NO}_3)_2$  onto sediment was investigated in this study. The objective of this study was to investigate the sorption characteristics of PNP onto sediment at varying pH values in multi-solute system.

## 2. Materials and methods

### 2.1. Materials

Sediment was collected in the depth of 0–20 cm at the bottom of Yong River, China.

It was air-dried and grounded to less than 100 meshes with a diameter of 0.15 mm prior to sediment characterization and sorption studies. The analysis of sediment clay minerals were performed by X-ray diffraction (X' Pert MPD Philips instrument). The organic carbon content was measured using LECO CS-344 type carbon-sulfate analyzer at the condition of 50% relative humidity and 25 °C. The BET- $\text{N}_2$  surface area was determined using Coulter-100CX surface area analyzer. The cation-exchange capacity was analyzed using ion exchange methods [16]. The characteristics of the sediment are shown in Table 1.

The cationic surfactant CPC contains one hydrophilic and hydrophobic group. CMC and molecular weight of CPC are  $297 \text{ mg L}^{-1}$  and 358, respectively [17].

PNP and  $\text{Pb}(\text{NO}_3)_2$  were of analytical grade. All of the reagents were purchased from Shanghai Chemical Co., China and used without further treatment. The water solubility ( $S$ ) and octanol–water partition coefficient ( $K_{ow}$ ) of PNP are  $1.6 \times 10^4 \text{ mg L}^{-1}$  and 93, respectively [18].

### 2.2. Analytical methods

The aqueous concentrations of PNP and CPC were quantified by UV-2401 PC ultraviolet spectrophotometer (Shimadzu) at absorbance wavelength 317 and 259 nm, respectively. The pH values of analyte solutions were fixed at 3 for PNP in order to eliminate the pH effect on the PNP [13].

### 2.3. Batch experiment procedure

Sorption experiments were carried out using a conventional batch equilibrium technique. A batch equilibrium method is

Table 1  
Characteristics of the sediment<sup>a</sup>

Foc	0.39%
SA ( $\text{m}^2 \text{ g}^{-1}$ )	14
CEC ( $\text{cmol kg}^{-1}$ )	15.8
Clay mineral content	11.5%
Bentonite content	4.8%
Illite content	2.4%
Kaolinite content	1.9%

<sup>a</sup> Foc is the organic carbon content; SA the BET- $\text{N}_2$  surface area; CEC the cationic exchange capacity.

useful for studying the reaction mechanism in the solid/water interface. An appropriate amount of solute was added to the 100 mL Erlenmeyer flasks with glass caps, which contained 1.0 g sediment in 25 mL solution with given concentrations of other solutes. The flasks were shaken for 12 h at  $25 \pm 0.5$  °C in a gyratory shaker at 150 rpm, as preliminary studies indicated that this was sufficient time to establish equilibrium. The solution and solid phase were separated by centrifugation at 3000 rpm for 30 min to completely separate the undissolved solute. After this, the equilibrium concentration in the supernatants was determined, and the adsorbed amount of solute was calculated from the concentration difference.

The pH range studied was 2–8, obtained by adding 0.1 M  $\text{HNO}_3$  or 0.1 M  $\text{NaOH}$  each hour. The ionic strength was maintained at 1 mM in order to eliminate the possible influence during the pH conditioning.

Sediment blank experiments without solutes were simultaneously carried out in order to correct the results. In addition, control experiments containing solutes without sediment were carried out to evaluate solute losses due to volatilization and uptake by the glass flasks and it was found that the losses were negligible. Six replicates of each experiment were performed.

## 3. Results and discussion

The effect of pH on PNP sorption in a multi-solute system containing CPC and  $\text{Pb}(\text{NO}_3)_2$  are unclear, although several influencing factors have been identified. First, the influence of pH on the sorption of PNP [4–8]; second, the influence of pH on the competitive sorption of  $\text{Pb}(\text{NO}_3)_2$  which may affect the sorption of PNP [19]; finally, adsorption of CPC is influenced by pH which change the sorption of PNP [17]. Therefore, in the multi-solute system containing PNP,  $\text{Pb}(\text{NO}_3)_2$  and CPC, all these effects are simultaneously involved.

### 3.1. Influence of pH on the sorption of PNP in presence of CPC and $\text{Pb}(\text{NO}_3)_2$

Influence of pH on sorption of PNP onto sediment in multi-solute system was investigated. The initial concentration of PNP was  $300 \text{ mg L}^{-1}$ ,  $\text{Pb}(\text{NO}_3)_2$  was  $200 \text{ mg L}^{-1}$  and CPC was  $2500 \text{ mg L}^{-1}$  and the results are depicted in Fig. 1. Preliminary studies indicated that the isotherms of PNP is linear, consequently, the solid–water partition coefficient of PNP ( $K_d$ ) is defined as the ratio of sorbed and equilibrium aqueous concentration of PNP. Sorption of PNP increased with increasing pH, and the  $K_d$  values obtained were in the range of  $15\text{--}75 \text{ mL g}^{-1}$ . However, preliminary studies indicated that in the single-solute system,  $K_d$  values of PNP with the initial concentration of  $300 \text{ mg L}^{-1}$  was less than  $10 \text{ mL g}^{-1}$ , which was negligible with the pH ranging from 2 to 8. Therefore it can be assumed that the distinct sorption behavior of PNP in multi-solute system was due to the presence of  $\text{Pb}(\text{NO}_3)_2$  and CPC, while the influence of pH on the PNP sorption was insignificant. The influence of  $\text{Pb}(\text{NO}_3)_2$  and CPC at various pH values in multi-solute system will be further discussed in the following.

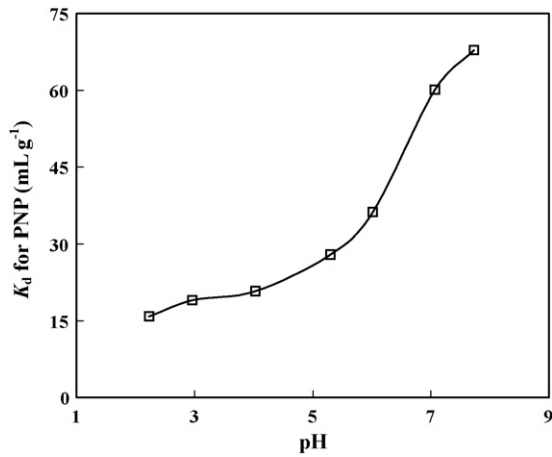


Fig. 1. Sorption of PNP at various pH values in multi-solute system with the initial concentration of PNP 300 mg L<sup>-1</sup>, Pb(NO<sub>3</sub>)<sub>2</sub> 200 mg L<sup>-1</sup> and CPC 2500 mg L<sup>-1</sup>.

### 3.2. Influence of Pb(NO<sub>3</sub>)<sub>2</sub> at various pH values in multi-solute system

Johnston et al. suggested that the sorption of nitroaromatic compounds is attributed to two kinds of surface interaction: non-specific van der Waals' interactions between the neutral portion of the organic guest species and the clay siloxane surface; and the site-specific interactions between cations and organic substituents carrying partial negative atomic charge [20]. Thus, the presence of Pb(NO<sub>3</sub>)<sub>2</sub> had two competitive effects on the sorption of PNP: (i) enhancing the adsorption of PNP by interaction between adsorbed Pb and –OH or –NO<sub>2</sub> of PNP; (ii) competing with the sorption of PNP by occupying more space due to the large hydrated radius 0.401 nm [21] which would lead to the decrease of sorption of PNP. So the sorption of PNP onto sediment depends on the net effect of these two effects. The net effect of Pb(NO<sub>3</sub>)<sub>2</sub> can be calculated from the difference in  $K_d$  values of PNP in the presence and absence of Pb(NO<sub>3</sub>)<sub>2</sub>. At examined pH values, the sorption of PNP onto sediment in a multi-solute system was inhibited by the presence of Pb(NO<sub>3</sub>)<sub>2</sub> as shown in Fig. 2. This indicated that competitive adsorption of Pb(NO<sub>3</sub>)<sub>2</sub> played the major role in the influence of Pb(NO<sub>3</sub>)<sub>2</sub> on the sorption of PNP onto sediment.

As shown in Fig. 2, the net effect of Pb(NO<sub>3</sub>)<sub>2</sub> on the sorption of PNP was pH-dependent, and generally decreasing with increasing pH. This effect is believed mainly to be attributed to the increase interaction between adsorbed Pb and –OH or –NO<sub>2</sub> of PNP rendering the net effect decreased with increasing pH. This is related to the higher sorption capacity of Pb(NO<sub>3</sub>)<sub>2</sub> and the dissociation of PNP at higher pH. First, to confirm the higher sorption capacity of Pb(NO<sub>3</sub>)<sub>2</sub> at higher pH, the sorption of Pb<sup>2+</sup> onto sediment as a function of pH was determined at an initial Pb(NO<sub>3</sub>)<sub>2</sub> concentration of 200 mg L<sup>-1</sup>. The mean relative standard deviation was in the range of 0.5–1.0%. The results confirmed that increase of pH from 2 to 8 led to an increase in the sorption amount of Pb(NO<sub>3</sub>)<sub>2</sub> from 1.17 to 4.60 mg g<sup>-1</sup> (Fig. 3). This is related to that at higher pH, more Pb<sup>2+</sup> is adsorbed onto

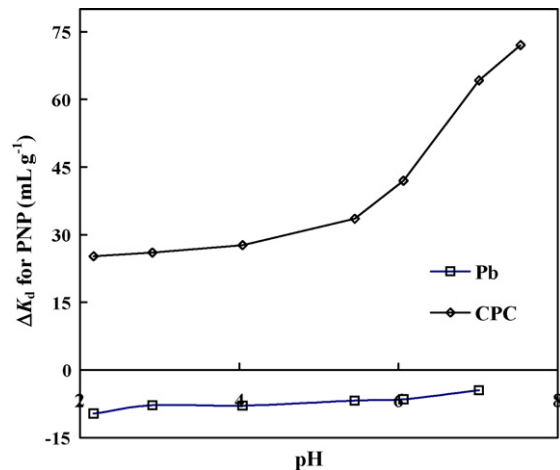


Fig. 2. Influence of Pb(NO<sub>3</sub>)<sub>2</sub> and CPC at various pH values in multi-solute system.

sediment owing to its facility to precipitation as many studies concluded that sorption of aqueous Pb is controlled by metal ions hydrolysis [22–25]. Secondly, as PNP is an ionizable organic compound with a  $pK_a$  of 7.16 [26], it can dissociate into protons and anions according to:



The degree of protonation ( $\alpha_0$ ) can be expressed as [27]:

$$\alpha_0 = \frac{1}{1 + 10^{(\text{pH} - \text{p}K_a)}} \quad (2)$$

where  $pK_a$  is the negative logarithm of the sorbate acidity constant.

Hence, PNP can occur both in ionic and neutral form depending on solution pH and sorbate  $pK_a$  values. In the pH range of 2–8, PNP had a higher degree of dissociation, the ionic form of PNP increased from 0 to 88%.

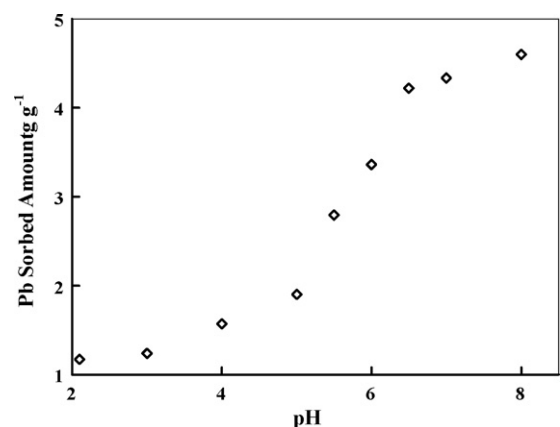


Fig. 3. Sorption of Pb<sup>2+</sup> onto sediment as a function of pH (initial concentration of Pb<sup>2+</sup> 200 mg L<sup>-1</sup>).

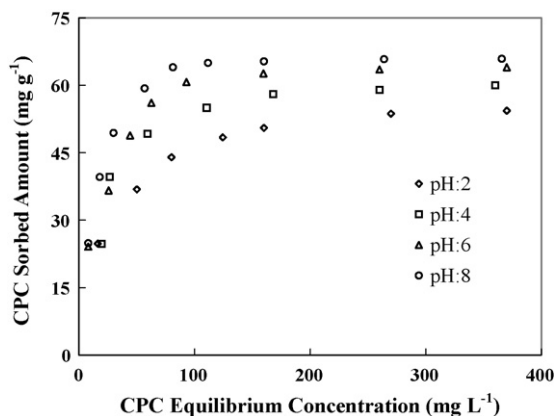


Fig. 4. Adsorption isotherms of CPC at different pH values.

### 3.3. Influence of CPC at various pH values in multi-solute system

Influence of CPC at various pH values in multi-solute system are demonstrated in Fig. 2. Influence of CPC can be calculated from the difference in  $K_d$  values of PNP with and without CPC. Compared to the competitive effect of  $\text{Pb}(\text{NO}_3)_2$ , the presence of CPC can enhance the sorption of PNP in the multi-solute system. It is believed that the enhancement of CPC on the sorption of PNP follows different mechanism to neutral and anion PNP. For the neutral PNP, CPC enhance the sorption of PNP by forming a bulk-like medium that behaves essentially as a partition phase [28–30]. As for the anion PNP, CPC enhance the sorption of PNP by forming a thin film which increase the interaction between cation of CPC and anion of PNP [20]. As shown in Fig. 2, the enhancement of CPC increased with the increasing pH and was greater than competitive effect of  $\text{Pb}(\text{NO}_3)_2$ . This effect is believed mainly to be attributed to the fact that increasing pH enhanced the adsorption of CPC which lead to higher sorption of PNP. To confirm the above reasoning, the adsorption isotherms of CPC under different pH (2–8) values are illustrated in Fig. 4. All adsorption isotherms were nonlinear, reaching a maximum in adsorbed amount at CPC equilibrium concentration above CMC. It is noted that increase of pH from 2 to 8 led to an increase in the maximum adsorption amount of CPC from 60.3 to 66.4  $\text{mg g}^{-1}$ . This indicated that increasing pH can enhance the adsorption of CPC onto sediment, which is in agreement with previous studies [17,31,32]. This behavior is believed to be related with that increase of pH lead to higher surface charge as a result of deprotonation of surface groups. This explains the observation that the cationic surfactant adsorption increased at increasing pH where the electrostatic interactions between positively charged cationic heads of surfactant and negatively charged sediment facilitated.

The results presented in Section 3.1 indicated that system containing PNP, CPC and  $\text{Pb}(\text{NO}_3)_2$ , the influence of pH on the sorption of PNP is related to the competitive effect of  $\text{Pb}(\text{NO}_3)_2$  and the enhancement of CPC. And the results from Sections 3.2 and 3.3 showed that in the multi-solute system sorption of PNP is controlled by the presence of CPC due to larger sorption of

CPC onto sediment at higher pH allowing higher sorption of PNP.

## 4. Conclusions

In the single-solute system, sorption of PNP was negligible. On the other hand, in multi-solute system where influence of  $\text{Pb}(\text{NO}_3)_2$  and CPC were simultaneously involved, sorption of PNP was much higher, and increased with increasing pH in the examined pH range. It is believed that the main reason for that was the larger sorption of CPC at higher pH allowing higher sorption of PNP. Therefore, the presence of  $\text{Pb}(\text{NO}_3)_2$  and CPC should be generally considered when describing the influence of pH on sorption of PNP onto sediment.

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