Concentration of 2-Phenylphenol by Organoclays from Aqueous Sucrose Solution

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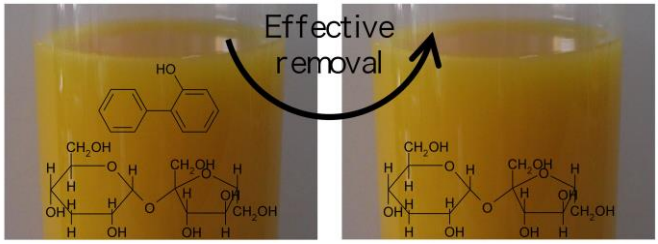
Abstract

The adsorption of 2-phenylphenol, which is an antifungal agent, onto organically modified clay from aqueous sucrose solution was investigated. 2-Phenylphenol was effectively adsorbed on neostigmine-modified smectites and octadecyltrimethylammonium modified smectites even in the presence of sucrose in the starting aqueous solution. Two smectites (a natural montmorillonite, Kunipia F, and a synthetic saponite, Sumecton SA) were used to find clay minerals with lower layer charge density gave larger adsorption capacity for 2-phenylphenol. The result showed the potential application of the organically modified clays to remove 2-phenylphenol from orange extracts.

Keywords

molecular recognition; smectite; organoclay; 2-phenylphenol

Graphic abstract



1. Introduction

The concentration of certain molecular species from environments by the adsorption onto solids is a topic of a wide range of scientific and practical interests such as the removal of toxic compounds and the concentration of the noble elements. Since the target species to be concentrated, noble metals in sea water and herbicide and pesticide in ground water for example, are normally mixed with other species, selective adsorption of target species from the mixtures are prerequisites for the practical application. Several inorganic-organic hybrid materials have been designed for this purpose (Lagaly, 1981; Barrer, 1989; Ogawa and Kuroda, 1997; Xu et al., 1997; Stein et al., 2000; Okada et al., 2012; Okada et al., 2014), in addition to the well established such nanoporous materials as zeolites with molecular sieving effects (Breck, 1974; Barrer 1978). We have recently achieved the selective (molecular recognitive) adsorption of certain kind of organic compounds on organically modified layered titanate and silicate from aqueous mixtures (Wei and Nakato, 2006; Ide and Ogawa, 2007; Ide et al., 2011) and molecular recognitive photocatalytic decomposition on layered titanates (Ide et al., 2010). These successes motivated us to study selective adsorption from aqueous mixtures for environmental purification and food safety.

In this article, 2-phenylphenol (which is also known as 2-hydroxybiphenyl and named 2PP in this study), a well-known antifungal agent used for oranges, was concentrated from aqueous sucrose solutions using organically-modified smectites (Tayama et al., 1989; Cheng et al., 2005). On site removal of 2PP would be a way to improve the safety of fresh orange juice. In the previous study, we successfully concentrated 2PP from aqueous solutions using organically-pillared clays (Seki and Ogawa, 2010) with appropriate interlayer organic cation. In this study, 2PP adsorption from aqueous sucrose solutions was investigated. Organically-modified smectites were used because of the tunable adsorption characteristics thanks to the materials' variation (Lee et al., 1989; Lawrence et al., 1998; Okada and Ogawa, 2003; Okada et al., 2004; Okada and Ogawa, 2004; Okada et al., 2005; Okada et al., 2010). Smectites are layered clay minerals with negatively-charged layers and charge-compensating interlayer cations (Theng, 1974; van Olphen, 1977) have possible applications as adsorbents for

radioactive ions in nuclear wastes (Kozai et al., 1993) as well as heavy metals (Mercier and Detellier, 1995), and photo/electro functions (Ogawa and Kuroda, 1995). When interlayer cations are replaced with organoammonium cations, the surface properties can be modified to enhance the sorption of various nonionic organic species (Jordan, 1949; Barrer and Perry, 1961a, 1961b; Barrer, 1978; Ogawa et al., 1994; Jaynes and Vance, 1999; Chun et al., 2003; Hayashi, et al., 2003; Nir et al., 2006; Seki and Ogawa, 2010). We have recently shown the possible roles of interlayer cations and layer charge in controlling adsorption capacity (Seki and Ogawa, 2010). In this study, two pillared and one organophilic organically-modified clay minerals were used to concentrate 2PP from aqueous sucrose solutions. Octadecyltrimethylammonium-exchanged montmorillonite was used as an example of organophilic clay. Neostigmine-smectites were used as adsorbents because they were suitable 2PP sorbents according to the previous investigation (Seki and Ogawa, 2010). The effects of sucrose in water on the 2PP adsorption are discussed in this paper.

2. Experimental

2.1. Reagents and materials

Natural Na-montmorillonite (Kunipia F obtained from Kunimine Ind. Co., Japan; hereafter abbreviated as KF; $(Na_{0.53}Ca_{0.09})^{0.71+}[Al_{3.28}Fe_{0.31}Mg_{0.43})(Si_{7.65}Al_{0.35})O_{20}(OH)_4]^{0.71-}$) and a synthetic saponite (Sumecton SA from Kunimine Ind. Co., Japan; hereafter abbreviated as SA; $(Na_{0.49}Ca_{0.14})^{0.77+}[Mg_{5.97}Al_{0.03})(Si_{7.20}Al_{0.80})O_{20}(OH)_4]^{0.77-}$) were used. Neostigmine bromide $(CH_3)_3N^+(C_6H_4)CO_2N(CH_3)_2Br^-$ (abbreviated as CONH) and octadecyltrimethylammonium (abbreviated as C_{18}TMA) chloride were purchased from Tokyo Kasei Ind. Co. and used as received. The molecular structures of 2PP, CONH, and C_{18}TMA are shown in Figure 1.

2.2. Preparation of adsorbents

Organoammonium-clays were prepared from KF and SA by cation exchange in aqueous solutions as previously reported (Ogawa et al., 1993; Ogawa et al., 1995 Seki and Ogawa, 2010). Adsorbed organic cation amounts of 111 meq/100 g for C_{18}TMA-KF, 115 meq/100 g for

CONH-KF, and 73 meq/100 g for CONH-SA were determined from the organic carbon contents, which confirmed quantitative cation exchange. The basal spacing of 2.17 nm for C_{18}TMA-KF indicates a *pseudo*-trimolecular arrangement of C_{18}TMA (Ogawa et al., 1993; Ogawa et al., 1995). On the other hand, the basal spacings of CONH-KF and CONH-SA were 1.73 and 1.51 nm, respectively, which is indicative of the microporous structures (organic pillared clay) as reported previously (Seki and Ogawa, 2010). Figure 2 shows the nitrogen adsorption/desorption isotherms of KF and SA before and after the pillaring. It is not straight forward to derive microporous structure from the isotherms due to the expected complex geometry as well as the difficulty to remove adsorbed water completely. In addition, due to the nature of finite particles, the contribution of external surface on the BET surface area is not negligible (Michot, and Villiéras, 2013). From the nitrogen adsorption isotherms, BET surface area was determined and the values (CONH-SA: 144 m^2 g^{-1} and CONH-KF: 14 m^2 g^{-1}) are slightly larger than those of original clay minerals (SA: 112 m^2 g^{-1} and KF: 13 m^2 g^{-1}).

2.3. Adsorption tests

Adsorption of 2PP from 15 mM (5.13 g/L) aqueous sucrose solutions was conducted as follows: adsorbents (25 mg) were reacted with 50 mL of aqueous 2PP solution in 50 mL-glass vessels for 1 day at room temperature in the dark. Initial concentration of 2PP was 0.05-1.0 mM (0.085-0.17 g/L). Blank samples without adsorbents, were also prepared to estimate vaporization losses and the adsorption on the glass vessel. After the adsorbents were separated by centrifugation, the concentration of the remaining 2PP in supernatant was determined by UV absorption spectroscopy (absorption λ_{max} of 2PP at 282 nm). Adsorption isotherms were obtained by plotting the adsorbed amounts of 2PP versus the equilibrium concentrations.

Insert Fig.s 1 and 2

3. Results and discussion

The adsorption isotherms of 2PP from water on the CONH-SA and KF were reported previously (Seki and Ogawa, 2010). In the present study, the adsorption isotherms of 2PP from water and aqueous sucrose solution on the CONH-SA and KF were obtained as shown in Figure 3. Adsorption isotherms of 2PP from water and aqueous sucrose solutions for CONH-SA and CONH-SA were fitted to the Langmuir equation ($1/W = 1/W_s + (1/aW_s)(1/C)$ by plotting $1/C$ versus $1/W_s$), where W is 2PP adsorbed to the organoclays and C is equilibrium 2PP concentration (Figure 3). The sucrose did not significantly affect 2PP adsorption. The adsorption constant (a), the amounts of 2PP adsorbed as a monolayer (W_s), and the R^2 values (measure of linearity) were determined for each isotherm. A large affinity between the CONH aromatic ring and the 2PP aromatic ring is thought to occur. The 2PP adsorption constant (a) values of 20.0 for CONH-KF with sucrose and 20.7 without sucrose (Table 1) were almost the same. The 45.3 adsorption constant (a) value for 2PP adsorption to CONH-SA from sucrose was larger than the 36.1 value from water. This means that CONH/2PP interactions were strong enough for effective adsorption even in the presence of sucrose.

Insert Fig. 3 and Table 1

Monolayer 2PP adsorption to CONH-KF was 0.041 g/g of clay (Table 1), which was not affected by sucrose. Monolayer 2PP adsorption to CONH-SA was 0.067 g/g with sucrose and 0.062 g/g without sucrose. Thus, 2PP concentration from aqueous sucrose solution was more efficient than that from 2PP solution. Though this phenomenon is presently difficult to explain, differences of the 2PP solubility in water and in sucrose solution might be concerned. While the presence of sucrose resulted in increasing monolayer 2PP adsorption on CONH-SA, the adsorbed 2PP amount was smaller when the initial concentration of 2PP was higher (Figure 3). The correlation coefficient of Langmuir equation (R^2 in Table 1) was smaller in the case of co-existence of sucrose (0.9552 without sucrose and 0.9327 with sucrose). Generally, on partitioning between adsorbent and solvent, relative contribution of both

adsorbate-solvent and adsorbate-adsorbent interactions determines the adsorption capacity. In the CONH-SA system, adsorbent-solvent interactions may be affected by the presence of sucrose in the solution to give the observed difference. Larger amounts of 2PP were adsorbed to CONH-SA than those to CONH-KF (Table 1 and Figure 3). One explanation is that the relatively low-layer charge saponite led to relatively larger interlayer pore volumes (Seki and Ogawa, 2010). On the other hand, the presence of sucrose did not affect the 2PP adsorption on CONH-KF, probably due to the smaller pore size and volume of CONH-KF than CONH-SA.

The adsorption isotherms of 2PP onto C_{18}TMA-KF are shown in Figure 4. The 2PP adsorption isotherms were type C according to the Giles classification (Giles et al., 1974), where 2PP uptake resulted from partitioning. For this type of isotherm, the following equation has been proposed: $W = K_p C$, where W, K_p, and C denote adsorbed amount, partition coefficient, and equilibrium concentration, respectively. From this equation, a K_p value of 1.80 was determined for 2PP sorption to C_{18}TMA-KF with or without sucrose. The higher adsorption efficiency for C_{18}TMA-KF was shown by comparing with the adsorption isotherms on CONH-smectites (Figure 3). These results suggest that 2PP adsorption to C_{18}TMA-KF occurred by hydrophobic interactions between 2PP and the alkyl chains of the interlayer C_{18}TMA, and the interactions play a dominant role in the 2PP adsorption. Accordingly, sucrose had no effect on the adsorption.

Insert Fig. 4 and Fig. 5

The removal of 2PP by C_{18}TMA-KF was effective with % removal values larger than 60% (Figure 5). When the initial 2PP concentration was lower than 0.085 g/L (0.5 mM), more than 80% of 2PP adsorbed to C_{18}TMA-KF. This means that the 2PP that remained in 1 L of sucrose solution after treatment with 25 mg of C_{18}TMA-KF was < 17 mg. This value is lower than the 20 mg/50 kg/day 2PP

intake set by the World Health Organization. These findings motivate further study on 2PP removal from foods.

4. Conclusions

The antifungal agent, 2-phenylphenol, was effectively sorbed by neostigmine-modified smectites and octadecyltrimethylammonium-modifed montmorillonite from aqueous sucrose solutions. Sucrose did not affect 2-phenyphenol concentration for the organically modified montmorillonites, suggesting that the future possibility to remove toxic compounds from foods and drinks.

Acknowledgments

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Table and figure captions

Table 1. Adsorption parameters obtained from the isotherms.

Fig. 1. Structure of 2-phenylphenol (a) neostigmine (b), and octadecyltrimethylammonium (c).

Fig. 2. Nitrogen adsorption (filled symbols)/desorption (open symbols) isotherms for KA (a) and SA (b) before (circles) and after (squares) pillaring with CONH.

Fig. 3. Adsorption isotherms of 2PP from water in the presence (open symbols) or absence (filled symbols) of sucrose on CONH-SA (squares) and CONH-KF (circles).

Fig. 4. Adsorption isotherms of 2PP on C_{18}TMA-KF from water in the presence (×) or absence (○) of sucrose.

Fig. 5. Efficiency of 2PP removal from aqueous sucrose solution on C_{18}TMA-KF (×), CONH-SA (○), and CONH-KF (□).

Table 1

		R^2	a (adsorption constant)	Ws (adsorbed amount of 2PP as monolayer, g/g clay)
CONH-KF	without sucrose	0.9818	20.0	0.041
	with sucrose	0.9856	20.7	0.041
CONH-SA	without sucrose	0.9552	36.1	0.062
	with sucrose	0.9327	45.3	0.067

Fig. 1

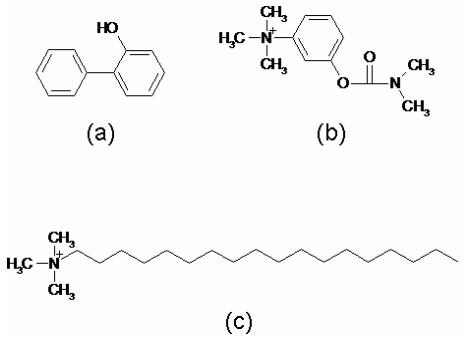


Fig. 2

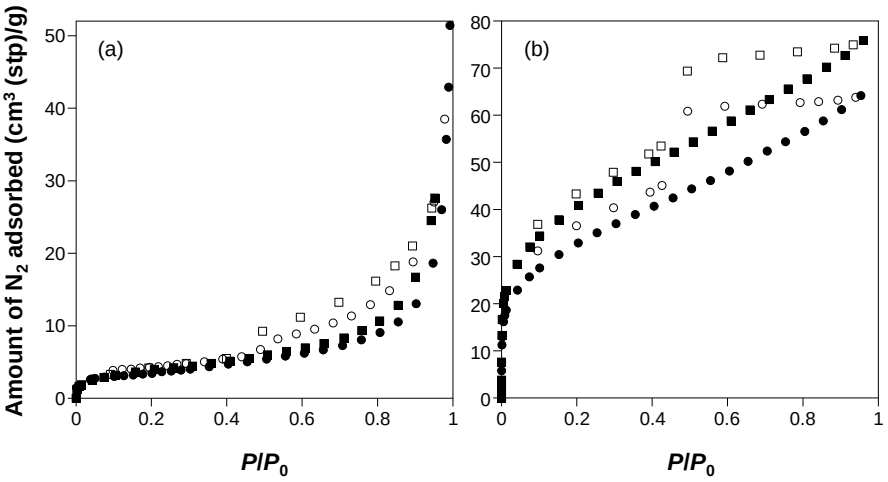
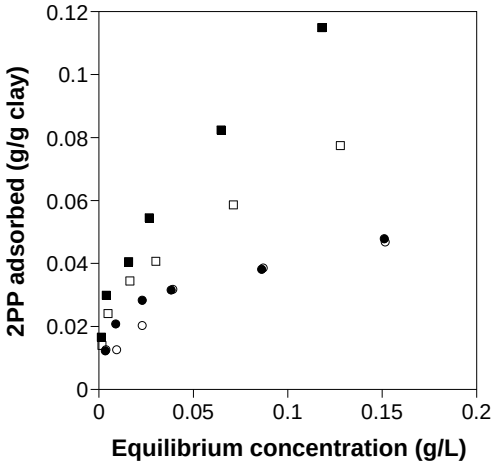


Fig. 3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Equilibrium concentration (g/L)

Fig. 4

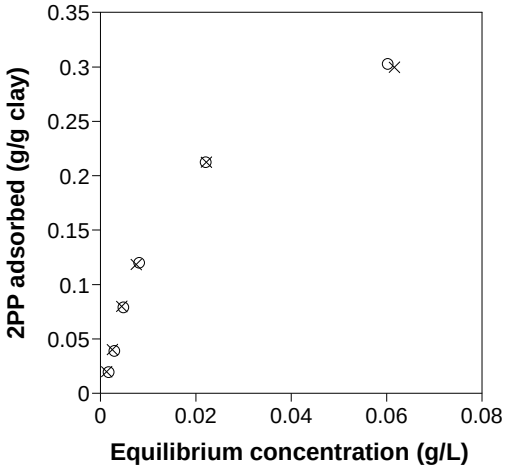
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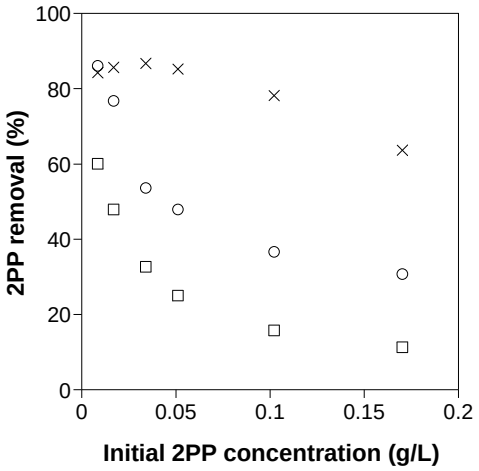
Fig. 5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