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ORIGINAL PAPER

Effect of heavy metals and surfactants on the adsorption of phenolic compounds on sediment

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Abstract The effects of different heavy metals (copper and mercury), cationic surfactants cetylpyridinium chloride, anionic surfactant sodium dodecylbenzenesulfonate and the chemistry of the solution (pH value) on the adsorption of three selected phenolic compounds (2, 4-Dichlorophenol, 2, 4-Dinitro-phenol and 2, 4-Dimethyphenol) on sediment were studied. Results indicated that in the sediment-water system with phenolic compounds: (1) all of the data could be simulated by Freundlich equation; (2) the experiments studying pH effects showed that the adsorption capacity of 2, 4-Dichlorophenol and 2, 4-Dimethyphenol were quite potentia Hydrogenii dependent and increased with decrease in potentia Hydrogenii, while 2, 4-Dinitrophenol followed the different trend; (3) As the concentration increased from 0 to 0.2 mM for Cu^{2+}, the Freundlich capacity coefficient constant varied from 62.84 to 325.1 for 2, 4-Dichlorophenol, from 13.1 to 82.179 for 2, 4-Dinitrophenol and from 29.433 to 7.976 for 2, 4-Dimethyphenol, respectively. The Freundlich capacity coefficient constant of 2, 4-Dichlorophenol, 2, 4-Dinitrophenol and 2, 4-Dimethyphenol varied from 62.84 and 421.43, 13.1 and 138.1, 29.433 and 1.381, respectively, with concentration of Hg^{2+} increased from 0 to 0.04 mM, respectively; (4) the adsorption of 2, 4-Dichlorophenol and 2, 4-Dimethyphenol were accentuated by cetylpyridinium chloride but suppressed by sodium dodecylbenzenesulfonate, whereas the adsorption of 2, 4-Dinitrophenol on sediment was enhanced by both cationic and anionic surfactants, effects that are consistent with electrostatic and hydrophobic interactions among ionic surfactants, phenolic compounds and sediment. The results are believed to provide a useful insight into describing the transport and fate of phenolic compounds in natural environments.

Keywords Environmental fate · Freundlich isotherm · pH value · River sediment · Sorption

Introduction

The surficial sediment is considered as main carriers and potential sources of both organic and inorganic pollutants in aquatic environments. The adsorption behaviors of compounds by sediment played an important role in determining their transport, fate, and potential biological effects. There were a large number of factors which can affect the adsorption behavior, including adsorption isotherms, adsorption thermodynamics. Therefore, to understand the effects and the mechanism is important for helping us to predict the fate of some toxic materials in the aquatic environment. Phenolic compounds in the aquatic environment could arise from natural substance degradation, agricultural practices and industrial activities (for example pulp and paper industry, petrochemical works). Phenolic compounds have been found to be toxic and lethal to fish and most types of microorganisms, and also causes

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several dreaded acute and chronic toxic effects on human health (inducing a wide range of symptoms: headache, vomiting, fainting, liver and kidney damage and other mental disorders) (ATSDR 1998; Agarry et al. 2009; Subramanyam and Das 2009). So far, attention has primarily been drawn to nitrophenols, methyphenol and chlorinated phenols as priority pollutants (USEPA 2004). Because phenolic compounds exhibit complex speciation behaviors with varying potentia Hydrogenii (pH), phenolic compounds adsorption on the sediment were likely to be highly pH-dependent (Fytianos et al. 2000; Amiri et al. 2004; Cea et al. 2007; Rahman and Worch 2005). In addition, the performance of many phenolic compounds in water environment might be strongly influenced by interactions with other compounds (for example heavy metals and surfactants). The environmental fate of these contaminants in the aquatic environment (Mohiuddin et al. 2010; Sciera et al. 2004; Muchuweti et al. 2006; Brandt et al. 2008) were partly governed by their adsorption on sediment, and numerous studies have focused on the adsorption of these contaminants in isolation from each other (Xu et al. 2005; Ying 2006; Sekabira et al. 2010; Mahvi 2008). However, it was commonly accepted that these contaminants would be in practice coexist as complex mixtures in real contaminated sediment, such as being found in the aquatic environment accepted with wastewater. Previous study observed that nickel or chromium decreased the adsorption of phenol to activated sludge. This was attributed to a mechanism that competition between the metal and the polar organic compound for the deprotonated functional group binding sites (Aksu and Akpinar 2000, 2001). Xu et al. (2005) also found that the added Cu^{2+} reduced the solid-phase concentration of propisochlor on humic acids, and Cu^{2+} might compete with propisochlor for the sorption sites of humic acids, such as carboxylic and phenolic groups.

Others works have shown that surfactants affect the physical, chemical, and biological properties of sediment, including sediment-water balance, sediment structure, adsorption processes (Fendinger et al. 1994; Rao and He 2006; Ying 2006). For instance, when 0.28 mM of cationic surfactant cetyltrimethylammonium bromide was added, the amount of bisphenol A sdsorbed increases by 3.12-folds, a while it was inhibited by anionic surfactant sodium dodecylb enzenesulfonate (Li et al. 2007). The Songhua River was the major freshwater source for industry and agriculture, as well as the source of the drinking water of millions of residents living along it. Coexistence of heavy metal, surfactant and phenolic compounds were common in the Songhua River, but little has been known about how they interact with each other, and whether the presence of such contaminants may affect individual contaminant adsorption and their ultimate fate in the water environment (Lin et al. 2007; Zhai 2004; Liu 1995, Liu and Zhai 1998). The objective of this study is to investigate the effect of cationic/anionic surfactants, heavy metals on the adsorption of three phenolic compounds on natural sediment, and to elucidate the underlying adsorption mechanism related to the distribution and transport of phenolic compounds in the aquatic environment. All the adsorption experiments were carried out in 2010 on the laboratory of Department Environmental Science and Engineering, Harbin Institute of Technology.

Materials and methods

Materials

High performance liquid chromatography (HPLC)-grade of phenolic compounds 2, 4-Dichloro-phenol (2, 4-DCP), 2, 4-Dinitrophenol (2, 4-DNP) and 2, 4-Dimethyphenol (2, 4-DMP) (97.4 %) were purchased from Dikma Chemical Co. and used as-received (properties listed in Table 1). Heavy metals (Cu^{2+} and Hg^{2+}) were supplied as reagent-grade chloride. Cetylpyridinium chloride (CPC) (analytical reagent grade) and sodium dodecylbenzene sulfonate (SDBS) (analytical reagent grade) were purchased from Central Chemical Factory in Shanghai Chemical Reagent Station, China. The literature critical micelle concentration (CMC) of CPC and SDBS were 322 and 522 mg/L, respectively (Monticone et al. 1994).

Sediments were collected in the depth of 0–20 cm at the Jiamusi stream of the Songhua River. It was cool-dried and sieved to less than 100 meshes with a diameter of 0.15 mm prior to sediment characterization and adsorption studies.

Table 1 Physico-chemical propertied of three selected phenolic compounds

Common name	Molecular formula molecular weight	Water solubility (mg/L)	Log Kow	pKa
2, 4-Dichlorophenol	163.001	4,500	3.08	7.80
2, 4-Dinitrophenol	184.106	5,600	1.54	3.94
2, 4-Dimethyphenol	122.164	7,929	2.30	10.10

Table 2 Physico-chemical properties of the river sediment used in this study

Physico-chemical parameters	Jiamusi sediment
pH	7.33
Cation-exchange capacity (cmol/g)	12.56
Total C (%)	11.175
BET surface area (m^2/g)	31.219
Zeta potential at pH 7.18 (mV)	−11.5

The organic carbon content of the sediment sample was measured using an NC analyzer (Flash EA 1112, Thermo Electron Co., Waltham, MA, USA), while cation exchange capacity (CEC) was measured using ion exchange methods (Hu et al. 2000). The zeta potential was measured using a zeta potential analyzer (Nano Zen2600, UK). The BET-N2 surface area was determined using Coulter-100CX surface area analyzer. The basic properties of the sediment used here were listed in Table 2.

Adsorption experiments

Adsorption experiments were carried out using a conventional batch equilibrium technique. A batch equilibrium method was useful for studying the reaction mechanism in the solid/water interface. Briefly, 0.1 g of sediment and 25 mL solution with given concentrations (0.324, 0.452, 0.675, 0.781, and 0.946 mg/L) of three solutes (2, 4-DCP, 2, 4-DNP and 2, 4-DMP) were added in 50 mL glass centrifuge tubes sealed with Teflon-lined screw caps. A background solution containing 0.001 M $CaCl_2$ and 100 mg/L of NaN_3 were to maintain a constant ionic strength and to inhibit microbial activity, respectively (Kile et al. 1999). The glass centrifuge tubes were shaken by a 2D-shaker at 150 rpm in an incubator at 10 ± 1 °C for 30 h, as preliminary studies indicated that this is sufficient time to establish equilibrium. After 30 h of equilibration, the solution and solid phase were separated by centrifugation at 3,000 rpm for 10 min to completely separate the un-dissolved solute. After this, the equilibrium concentration of 2, 4-DCP, 2, 4-DNP and 2, 4-DMP in the supernatants were determined by HPLC analysis, and the adsorbed amount of solute was calculated from the concentration difference. The HPLC (LC-10AD VP series, Shimadzu, Kyoto, Japan) system equipped with a 5-mm ODS column (VP-ODS, Shimadzu, Kyoto, Japan), a UV/vis absorbance (SPD-10A VP, Shimadzu, Kyoto, Japan). The UV/vis absorbance detector was used to monitor 2, 4-DCP, 2, 4-DNP and 2, 4-DMP at wavelengths of 295, 278 and 280 nm, respectively. A ultrapure water and acetonitrile (90:10 volume%) were used as an isocratic mobile phase for 2, 4-DMP, while ultrapure water and methanol (70:30 and 45:55 volume%) was used for the 2, 4-DCP and 2, 4-DNP. 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.

Effect of environmental factors on the adsorption of phenolic compounds

Batch equilibration method was also carried out for the effect of environmental factors on adsorption experiments. For the effect of pH value, the pH was varied from 2.0 to 11.8 for sediment-2, 4-DCP system by addition of HCl or $NaHCO_3$. And for the effect of heavy metal, various concentrations of 2, 4-DCP (0.324, 0.452, 0.675, 0.781, and 0.946 mg/L) and Cu^{2+} (0, 0.05 and 0. 2 mM) or Hg^{2+} (0, 0.01 and 0.04 mM) as chloride in 50 mL glass centrifuge tubes sealed with Teflon-lined screw caps. And for the effect of surfactant, in sediment-2, 4-DCP-surfactant system, the concentrations of surfactant were for CPC (33.2, 99.6, 166 mg/L) and for SDBS (53.2, 106.4, 212.8 mg/L), representing 0.1, 0.3, 0.5 of CMC for surfactant, respectively. The CMC is defined as the concentration of surfactants above which micelles form and almost all additional surfactants added to the system go to micelles (McNaught and Wilkinson 1997). The CMC is an important characteristic of a surfactant. Before reaching the CMC, the surface tension changes strongly with the concentration of the surfactant. After reaching the CMC, the surface tensions remains relatively constant or changes with a lower slope. As described above the effect of environmental factors on 2, 4-DNP and 2, 4-DMP was in the same experiment condition.

Adsorption isotherms of Cu^{2+} and Hg^{2+} in the absence or presence of phenolic compounds

Sediment (0.10 g) was immersed in a 0.001 M $CaCl_2$ background electrolyte solution (25 mL) in 50 mL centrifuge tubes and Cu^{2+} or Hg^{2+} was added together with three selected phenolic compounds. Control samples were identical to other samples, except no phenolic compounds were added. The concentrations of heavy metal were (0.05, 0.1, 0.15, 0.2, 0.25, 0.3 and 0.35 mM) for Cu^{2+} and (0.01, 0.02, 0.03, 0.04, 0.05, 0.06 and 0.07 mM) for Hg^{2+}, whereas the initial concentrations of phenolic compounds

Table 3 Freundlich parameters of 2, 4-DCP, 2, 4-DNP and 2, 4-DMP adsorption on sediment as a Function of pH

Phenolic compounds	pH value	Log (K_F)	*n*	R^2
2, 4-Dichlorophenol	2.5	1.994	0.774	0.919
	3.1	1.916	0.709	0.99
	5.39	1.853	0.644	0.949
	7.16	1.798	0.945	0.961
	8.12	1.712	0.965	0.872
	10.5	1.291	0.844	0.786
2, 4-Dinitrophenol	2.14	1.291	0.491	0.946
	3.72	1.226	0.983	0.958
	4.08	0.866	0.937	0.981
	5.61	1.044	0.971	0.935
	7.25	1.117	0.96	0.946
	8.81	1.448	0.846	0.988
	10.02	1.507	0.704	0.946
2, 4-Dimethyphenol	4.02	2.026	0.885	0.995
	5.39	1.958	0.881	0.955
	6.65	1.865	0.636	0.913
	7.05	1.754	0.84	0.986
	7.81	1.469	0.925	0.981
	8.29	1.305	0.989	0.927
	10.84	1.17	0.964	0.854

were 0.675 mg/L. The pH of all sorbent solutions was maintained at 7.0 ± 0.2 by addition of HCl or $NaHCO_3$ during the equilibration period. The adsorption equilibration time was 24 h. After reaching equilibrium, the suspension was centrifuged at 3,000 rpm for 30 min to separate the liquid and solid phases, and the concentrations of Cu^{2+} and Hg^{2+} in the supernatants were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Adsorption experiments were carried out in triplicate.

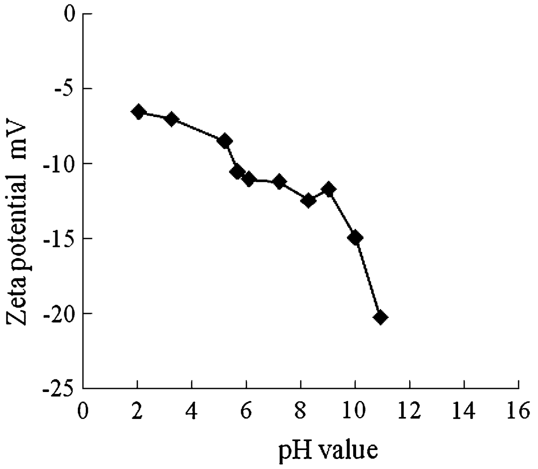


Fig. 1 Effect of pH value on the zeta potential of sediment surface

Adsorption isothermal modeling

The Freundlich (Eq. 1) model was used to fit the adsorption data of 2, 4-DCP, 2, 4-DNP and 2, 4-DMP on sediment, which can be expressed, respectively as.

$$q_e = K_F\, C_e^n \tag{1}$$

where q_e is the equilibrium sorption amount (ug/g), K_F is a constant representing the adsorption capacity ($mg^{1-N}/(kgL^N)$), C_e represents the equilibrium concentration (ug/mL) of three selected phenolic compounds in solution, and n is a constant depicting the adsorption intensity.

Results and discussion

Effects of pH on the adsorption of 2, 4-DCP, 2, 4-DNP and 2, 4-DMP

To evaluate the influence of pH on adsorption ability of three selected phenolic compounds on sediment, pH values ranging from 2.0 to 10.8 were set. Batch adsorption experiments were used to determine Freundlich capacity coefficient constant (K_F) values. The Zeta potential of sediment was measured as a function of pH. As predicted, the Zeta potential was more negative with increasing solution pH for sediment. This was because increasing the pH to greater than the point of zero charge in sediment increases negative surface charge, that is, the Zeta potential of sediment becomes more negative with increasing the solution pH. Results for adsorption of the three selected phenolic compounds on natural sediment as a function of pH value were shown in Fig. 1. In all cases, the measured phenolic compounds adsorption isotherms were well described by the Freundlich equation (Table 3). As shown in Table 3, after pH value increased from 2.5 to 10.5 (for 2, 4-DCP) and 4.02 to 10.84 (for 2, 4-DMP), the log (K_F) decreased from 1.994 to 1.291 and 2.026 to 1.171, respectively. The log (K_F) for 2, 4-DNP did not show a consistent trend, which the measured parameters decreased from 1.291 to 0.866 after pH value increased from 2.04 to 4.08, whereas parameters increased from 0.866 to 1.507 after pH value increased from 4.08 to 10.5.

Phenolic compounds were kind of the ionizable organic compounds, which were highly influenced by solution pH, which determined the ionizable organic compounds exist in either ionic anion or neutral molecular forms (Fabrega et al. 1998). Thus, varying pH had two competitive effects on the adsorption of phenolic compounds: (1) changing the adsorption of phenolic compounds by interaction between surface charged of sediment and substituent of phenolic compounds; (2) changing the existed form of phenolic compounds, which would lead to the changing of adsorption of phenolic compounds. So the adsorption of phenolic compounds onto sediment depended on the net effect of these two effects. The net effect of pH values could be calculated from the difference in log (K_F) values of phenolic compounds by varying the solution pH values. At examined pH values, the adsorption of phenolic compounds on sediment in a sediment-water system was inhibited or promoted by varying the solution pH values. In order to clarify the adsorption of phenolic compounds on sediment as a function of pH, the adsorption coefficients of the three phenolic compounds were shown along with the Zeta potential (the measurement of surface potential) of sediment (Fig. 1). Since it is assumed that the adsorption of phenolic compounds occurred by electrical attraction of countercharged phenolic compounds and sediment. The combined factors for phenolic compounds adsorption on sediment are presented in Fig. 2.

With a pKa of 7.8, 2, 4-DCP adsorption on sediment was affected by the electrostatic properties of sediment. Adsorption of 2, 4-DCP on sediment, which was negatively charged above its zero point of charge (ZPC), was maximum at low pH 2.5 and then gradually decreased as pH increased. Thus, as the 2, 4-DCP became more anionic form at high pH 10.5, the adsorption on sediment became minimum (Fig. 2). For 2, 4-DMP (pKa = 10.6), at pH below 10.6 the molecule was dominant. At pH higher than 10.6, the negatively charged form of 2, 4-DMP dominated. The highest adsorption of 2, 4-DMP to sediment occurred at a pH around 4.02 which 2, 4-DMP was existed in the form of neutral molecules; meanwhile, the zeta potential of sediment was the lowest in this study (Fig. 2).

Johnston et al. (2002) suggested that the adsorption of substituents aromatic compounds (especially for nitro-aromatics) is attributed to two kinds of surface interaction: non-specific vander Waals' interactions between the organic pollutants and the sediment surface; and the site-specific interactions between surface charged of sediment and organic substituent carrying partial negative atomic charge. Due to its pKa of 3.94, 2, 4-DNP existed in molecular or cationic form in the solution at pH blew 3.94 and negatively charged form at pH above 3.94. The adsorption of 2, 4-DNP on sediment started to decrease at pH = 2.14 (Fig. 2), the same trend with 2, 4-DCP until solution around pH 4.08. After around pH 4.08, the adsorption was beginning to increase to the maximum point at pH around 10.84, which was in the area where the 2, 4-DNP existed negatively charged (anion form). Thus, 2, 4-DNP was unable to interact electrostatically with sediment, but non-specific vander Waals' interactions between 2, 4-DNP and the sediment surface are also possible, provided that electrostatic repulsion was overcome.

Effect of Cu^{2+} and Hg^{2+} on the adsorption of phenolic compounds

The dominant mechanism of heavy metal adsorption on sediment was the site-specific interactions between the high affinity adsorption sites and heavy metal. The

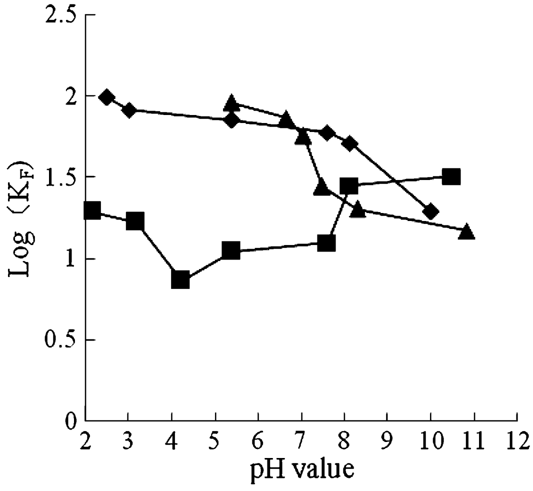


Fig. 2 pH-adsorption profiles of 2, 4-DCP (*filled diamond*), 2, 4-DNP (*filled square*) and 2, 4-DMP (*filled triangle*) to sediment are shown along with the pH-dependent zeta potential of sediment

Fig. 3 Adsorption curves of 2, 4-DCP on sediment in the presence of Cu^{2+} (*filled diamond* 0 mM, *filled square* 0.05 mM, *filled triangle* 0.2 mM) and Hg^{2+} (*filled diamond* 0 mM, *filled square* 0.01 mM, *filled triangle* 0.04 mM)

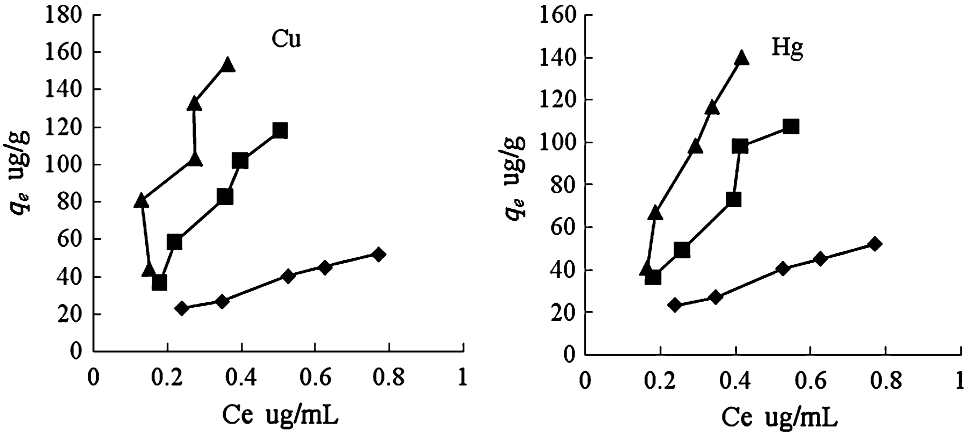


Fig. 4 Adsorption curves of 2, 4-DNP on sediment in the presence of Cu^{2+} (*filled diamond* 0 mM, *filled square* 0.05 mM, *filled triangle* 0.2 mM) and Hg^{2+} (*filled triangle* 0 mM, *filled square* 0.01 mM, *filled triangle* 0.04 mM)

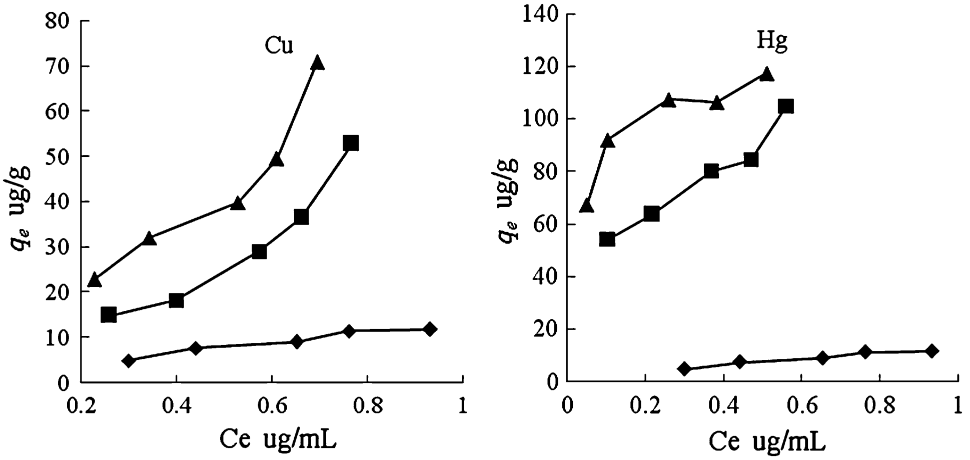
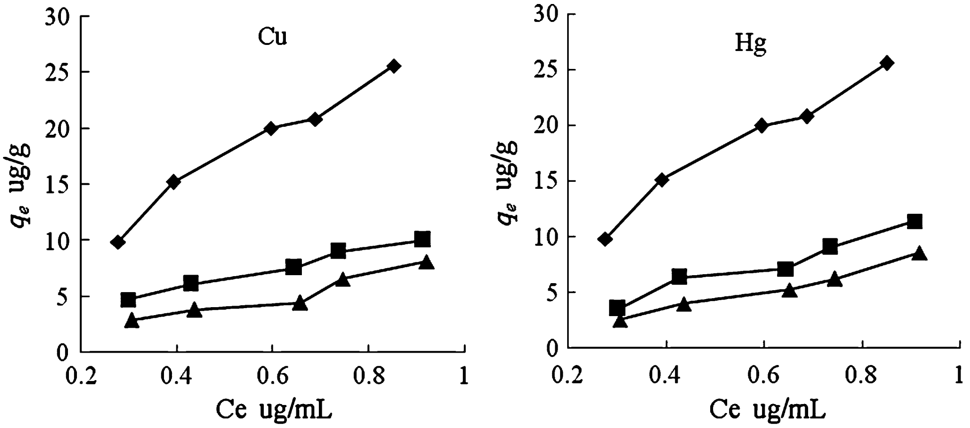


Fig. 5 Adsorption curves of 2, 4-DMP on sediment in the presence of Cu^{2+} (*filled diamond* 0 mM, *filled square* 0.05 mM, *filled triangle* 0.2 mM) and Hg^{2+} (*filled diamond* 0 mM, *filled square* 0.01 mM, *filled triangle* 0.04 mM)



adsorption of three selected phenolic compounds on sediment was attributed to physical adsorption (static effect, hydrogen bond and vander Waals' interactions). In general, the adsorption energy of site-specific interaction was higher than that of physical adsorption. Figs. 3, 4, 5 showed the adsorption curves of three selected phenolic compounds in the absence and presence of Cu^{2+} and Hg^{2+}, respectively. Nonlinear equilibrium adsorption of phenolic compounds in the presence of Cu^{2+} and Hg^{2+} were observed from Table 4. Experimental data was well fitted by Freundlich equation. As shown in Figs. 3 and 4, the promoted effect of Cu^{2+} and Hg^{2+} on the adsorption of 2, 4-DCP and 2, 4-DNP were concentration-dependent, and generally increased with increasing the concentration of

Table 4 Freundlich parameters of 2, 4-DCP, 2, 4-DNP and 2, 4-DMP adsorption on sediment in the absence and presence of Cu^{2+} and Hg^{2+}

(mM)	2, 4-Dichlorophenol			2, 4-Dinitrophenol			2, 4-Dimethyphenol		
	K_F	n	R^2	K_F	n	R^2	K_F	n	R^2
Cu^{2+}									
0	62.84	0.691	0.98	13.1	0.709	0.99	29.433	0.76	0.996
0.05	239.92	0.987	0.944	50.013	0.92	0.939	10.66	0.681	0.989
0.2	325.1	0.763	0.888	82.179	0.892	0.915	7.976	0.897	0.914
Hg^{2+}									
0	62.84	0.691	0.98	13.1	0.709	0.99	29.433	0.76	0.996
0.01	206.7	1.023	0.954	117.13	0.3579	0.93	12.173	0.9625	0.937
0.04	421.43	1.201	0.93	138.1	0.2183	0.913	8.82	1.039	0.981

K_F ($mg^{1-N}/(kgL^N)$)

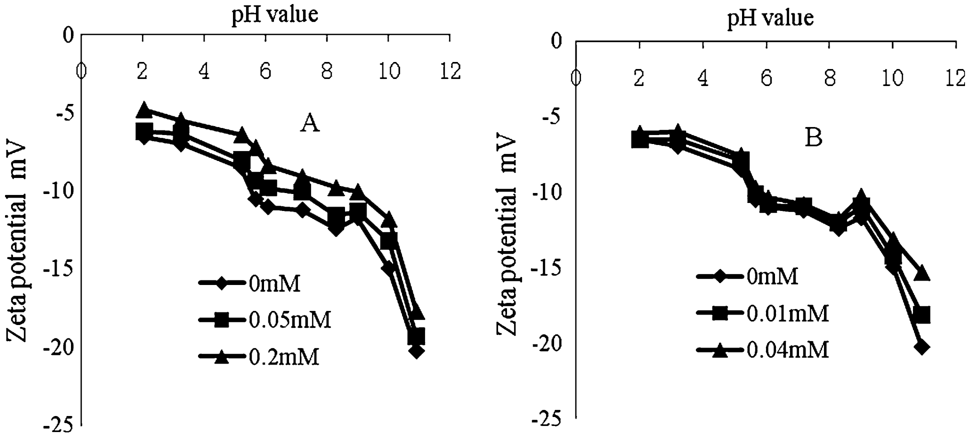


Fig. 6 Zeta-potential as a function of pH for sediment with Cu^{2+}(**a**) and Hg^{2+} (**b**)

Cu^{2+} and Hg^{2+} increasing. The K_F for 2, 4-DCP increased from 62.84 in the absence of Cu^{2+} and Hg^{2+} to 325.1 and 421.43, after the addition of Cu^{2+} and Hg^{2+}, respectively. The same trend was also appeared for 2, 4-DNP, which the K_F for 2, 4-DNP increased from 13.10 in the absence of Cu^{2+} and Hg^{2+} to 82.179 and 138.1, after the addition of Cu^{2+} and Hg^{2+}, respectively. This effect was mainly attributed to the surface complex formation of Cu^{2+} and Hg^{2+} on sediment changes the properties of sediment, which further affected the adsorption of ionizable 2, 4-DCP and 2, 4-DNP on the negatively charged surface of sediment. The possible mechanisms that may be responsible for enhanced adsorption of 2, 4-DCP and 2, 4-DNP in the presence of Cu^{2+} and Hg^{2+} are discussed below: the added Cu^{2+} and Hg^{2+} change the properties of sediment by formation the surface complex on sediment (for example Cu^{2+} and the –COOH of sediment surface can format the surface complex by chelation), which further affects the adsorption of anionic 2, 4-DCP and 2, 4-DNP on the negatively charged surface of sediment. The Zeta potential of sediment were measured as a function of pH at different Cu^{2+} and Hg^{2+} concentrations adsorbed (Fig. 6). As expected, the zeta-potential was more negative with increasing solution pH. This is because increasing the pH to greater than the point of zero charge in sediment systems increases negative surface charge, that is, the zeta-potential becomes more negative (Fig. 6). The surface charge has a marked influence on the adsorption of cations and anions from the solution phase. Increasing negative surface charge decreases the adsorption of anionic 2, 4-DCP and 2, 4-DNP and increases the adsorption of Cu^{2+} and Hg^{2+}. In turn, when Cu^{2+} and Hg^{2+} were adsorbed on sediment, the Zeta potential is less negative; thus, more anionic 2, 4-DCP and 2, 4-DNP was adsorbed on sediment. In contrast, at around pH 7, the adsorption of 2, 4-DMP onto sediment was inhibited by the presence of Cu^{2+} and Hg^{2+}, which the K_F for 2, 4-DMP decreased from 29.433 in the absence of Cu^{2+} and Hg^{2+} to 7.976 and 8.82, after the addition of Cu^{2+} and Hg^{2+} (Fig. 5). At examined pH around 7, 2, 4-DMP was mainly existed in cationic form, which indicated that electrostatic interactions suppress the adsorption of 2, 4-DMP onto sediment.

The adsorption curves of Cu^{2+} and Hg^{2+} with or without three selected phenolic compounds were shown in

Fig. 7. This indicated that heavy metal and phenolic compounds competed for the same adsorption sites on sediment. Significantly more Cu^{2+} and Hg^{2+} were adsorbed onto sediment, mainly because of the organic matter content and cationic exchange capacity of sediment. As can be seen from Fig. 7; 2, 4-DNP had a little effect on the adsorption of Cu^{2+} and Hg^{2+} on sediment, but 2, 4-DCP decreased the adsorption of Cu^{2+} and Hg^{2+} slightly (K_F decreased from 0.119 to 0.092 for Cu^{2+} and from 0.0064 to 0.0055 for Hg^{2+}). 2, 4-DMP strongly suppressed the adsorption of heavy metal, where K_F decreased from 0.119 to 0.065 for Cu^{2+} and from 0.0064 to 0.0029 for Hg^{2+}. Cu^{2+} and Hg^{2+} were heavy metal with high electronegativity and may form outer- and inner-sphere complexes on the sediment surface (Pei et al. 2008). When an inner-sphere complex was formed, Cu^{2+} and Hg^{2+} were bound directly to the sediment surface, and the surrounded water molecules were partially displaced by –OH groups of soil or sediment minerals and organic matter (Flogeac et al. 2004) and by –COOH groups of soil or sediment organic matter (Xia et al. 1997). As shown in Table 4, the competitive effect between Cu^{2+} or Hg^{2+} and 2, 4-DMP for the same adsorption sites was occurring, and this was responsible for the observed mutual suppression of adsorption of both 2, 4-DMP and Cu^{2+} or Hg^{2+}.

Effect of surfactant on three selected phenolic compounds adsorption

The mechanism by which surfactant affected the adsorption of three selected phenolic compounds on sediment was complex. According to the type and concentration of surfactant and the charges of the sorbent (soil and sediment) surface and coexisted contaminant, the latter may exhibit

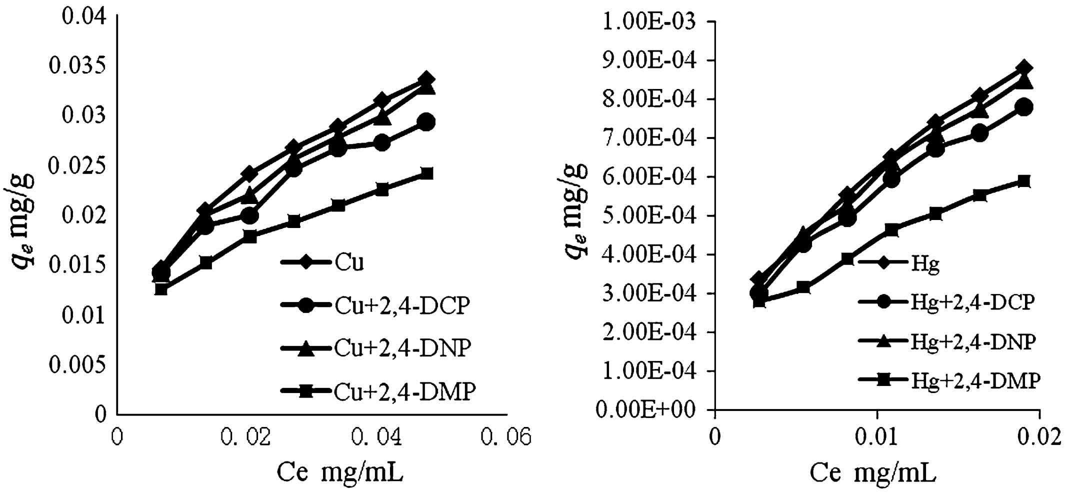
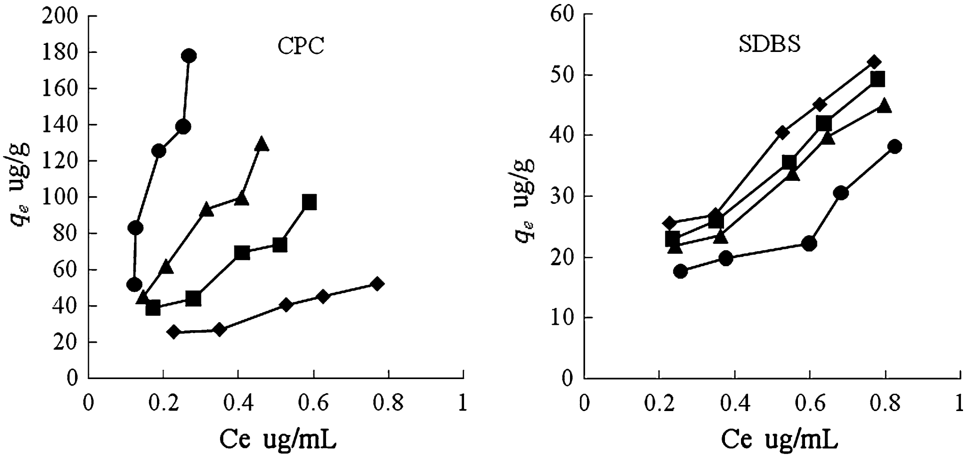


Fig. 7 Adsorption curves of Cu^{2+} and Hg^{2+} on sediment in the absence and presence of three selected phenolic compounds (C0 = 0.675 g/L)

Fig. 8 Adsorption curves of 2, 4-DCP on the sediment of Jiamusi stream in the presence of CPC and SDBS (*filled diamond* 0, *filled square* 0.1, *filled triangle* 0.3, *filled circle* 0.5 CMC) solution



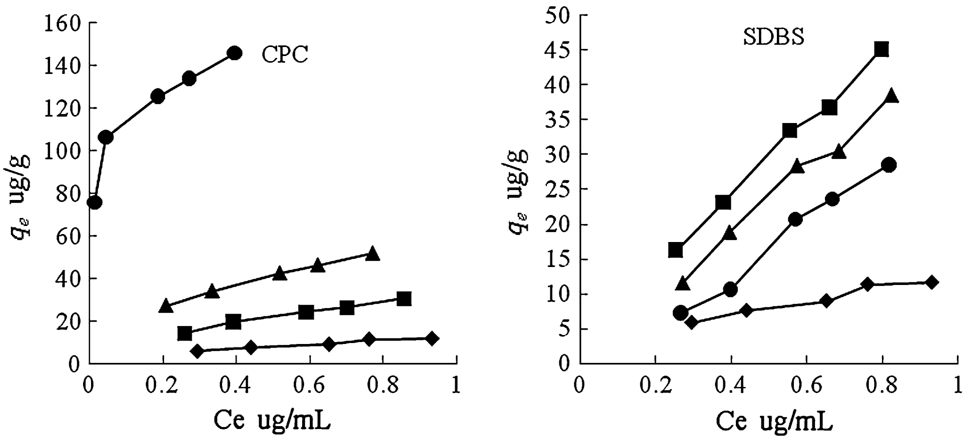


Fig. 9 Adsorption curves of 2, 4-DNP on the sediment of Jiamusi stream in the presence of CPC and SDBS (*filled diamond* 0, *filled square* 0.1, *filled triangle* 0.3, *filled circle* 0.5 CMC)

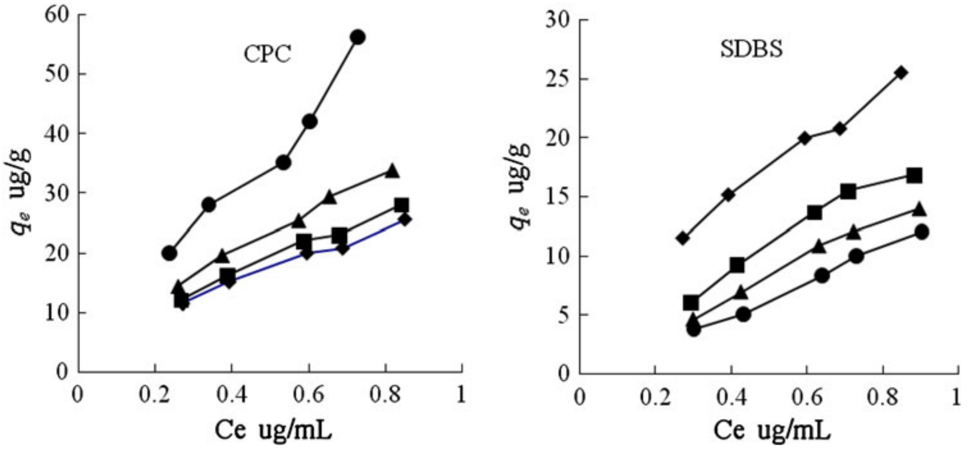


Fig. 10 Adsorption curves of 2, 4-DMP on the sediment of Jiamusi stream in the presence of CPC and SDBS (*filled diamond* 0, *filled square* 0.1, *filled triangle* 0.3, *filled circle* 0.5 CMC)

Table 5 Freundlich parameters of 2, 4-DCP, 2, 4-DNP and 2, 4-DMP adsorption on sediment in the absence or presence of CPC and SDBS

CMC	2, 4-DCP			2, 4-DNP			2, 4-DMP		
	K_F	n	R^2	K_F	n	R^2	K_F	n	R^2
CPC									
0	62.84	0.691	0.98	13.10	0.709	0.99	29.433	0.76	0.996
0.1	129.8	0.73	0.93	33.53	0.61	0.929	31.41	0.71	0.99
0.3	239.2	0.86	0.98	58.7	0.49	0.991	39.45	0.74	0.99
0.5	839.1	1.2	0.86	173.7	0.19	0.962	66.78	0.85	0.96
SDBS									
0	62.84	0.691	0.98	13.10	0.709	0.99	29.433	0.76	0.996
0.1	55.33	0.65	0.97	54.66	0.89	0.997	20.48	0.95	0.98
0.3	50.68	0.65	0.95	48.01	1.06	0.988	16.48	1.02	0.99
0.5	37.3	0.61	0.83	36.25	1.33	0.982	13.58	1.08	0.99

K_F (mg^{1-N}/(kgL^N))

either enhanced sorption or enhanced solubilisation (Jones-Hughes and Turner 2005; Hari et al. 2005; Turner and Xu 2008). The influence of surfactant on compound adsorption to sediment might be explained by considering the following two impacts. When a surfactant was added to the sediment-water system, two contaminants interacted, either directly or indirectly. On the one hand, the surfactant in monomer form might be adsorbed onto the sediment and increased the affinity between the phenolic compounds substituents which carrying partial negative atomic charge and the sediment. On the other hand, due to its special surface properties, the surfactants would increase the water solubility of some organic chemicals (Margesin and Schinner 1999). That is, the surfactants might increase the solubility of three selected phenolic compounds, hence increase partition of the three selected phenolic compounds into the solution and decrease the adsorption of phenolic compounds on sediment. Since both actions gave rise to opposite influences on the organic contaminants adsorption, the net influence of the surfactant on the phenolic compounds adsorption would depend on the balance of both of them.

In the presence of surfactant at concentrations below the CMC, the adsorption of three selected phenolic compounds on sediment was noticeably affected (Figs. 8, 9, 10). The Freundlich parameters of three selected phenolic compounds in the presence of surfactants of CPC and SDBS with different CMC were shown in Table 5. As shown in Table 5, the K_F of 2, 4-DCP and 2, 4-DNP increased with increasing CPC concentration. When 0.1 CMC CPC was added, the K_F of phenolic compounds adsorbed increased by the value of 2.07-folds for 2, 4-DCP, 2.56-fold for 2, 4-DNP and 1.07-folds for 2, 4-DMP. Larger increase was seen for higher CPC concentration. The K_F of three selected phenolic compounds increased by 13.35-fold for 2, 4-DCP, 13.26-fold for 2, 4-DNP and 2.27-folds for 2, 4-DMP with the CPC of 0.5 CMC, respectively. The results clearly indicated that the adsorption of three selected phenolic compounds on sediment was greatly enhanced in the presence of CPC. The cationic surfactant CPC was favorably sorbed by the sediment because the sediment surface is negatively charged and hence the amount of CPC sorbed by the sediment was highly greater relative to the amount of CPC in the solution phase. Hence, as compared to the increase in solubility of phenolic compounds, the adsorption of CPC was significantly greater and led to the enhancement of phenolic compounds adsorption on sediment.

Conversely, as indicated in Figs. 8, 9, 10, the addition of anionic SDBS caused a slight reduction in the adsorption capacity of 2, 4-DMP and 2, 4-DCP but enhanced 2, 4-DNP. The reason was that the electrostatic repulsion between anionic SDBS and negative sediment surface inhibits the adsorption of SDBS on sediment significantly and the SDBS predominantly exists as monomers in solution. As a result, the solubiliazation of 2, 4-DMP and 2, 4-DCP in solution outweighed the increase on adsorption of phenolic compounds and decreased the amount of 2, 4-DMP and 2, 4-DCP adsorbed onto sediment. Compared to 2, 4-DMP and 2, 4-DCP, the effect of SDBS on the adsorption of 2, 4-DNP was concentration dependent. When adding the SDBS, it increased the adsorption of 2, 4-DNP sediment, which was in agreement with previous studies (Talbot et al. 2003; Pura and Atun 2005). However, when SDBS concentration increased to 0.3 CMC and 0.5 CMC from 0.1 CMC, SDBS slightly reduced the adsorption of 2, 4-DNP (K_F values decreased from 48.01 to 36.25). We postulated that with the increasing the CMC of SDBS, the solubilization of 2, 4-DNP is increased but suppressed hydrophobic property. The concentrations of CPC and SDBS in the environmental aqueous system were normally lower than CMC. Therefore, the presence of CPC would increase the adsorption of phenolic compounds to sediment and reduced the concentration of phenolic compounds in water. This could decrease the mobility of phenolic compounds and lowered the risk of the exposure to phenolic compounds. In contrast, the presence of SDBS could reduce the adsorption of phenolic compounds to sediment and facilitated the transport of phenolic compounds in environment.

Conclusion

It was observed that the adsorption of ionizable phenolic compounds is strongly dependent on the system pH, the phenolic compounds properties (pKa), and the nature of the surface charge (point of zero charge). At different pH value, electrostatic forces were the main acting force involved in sediment-2, 4-DCP/2, 4-DNP interaction, while in the adsorption of 2, 4-DMP was mainly governed by vander Waals' interactions. This study has clearly demonstrated that adsorption of phenolic compounds are suppressed by SDBS but accentuated by CPC, effects that are consistent with electrostatic and hydrophobic interactions between ionic surfactants and natural sediment. The Cu^{2+} and Hg^{2+} remarkably enhanced the adsorption of 2, 4-DCP and 2, 4-DNP to the sediment by electrostatic interactions. The Cu^{2+} and Hg^{2+} had suppressing impacts on the adsorption of 2, 4-DMP.

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