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Kinetics adsorption process of mercury on sediment affected by aquatic dissolved organic matters

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ABSTRACT

In this experiment, *Ruditapes philippinarum* and *Phragmites communis*, the common species in aquatic ecosystems, were used to get two kinds of dissolved organic matter (DOM_c and DOM_r). These DOM were applied in this study to confirm the influence of DOM prepared from aquatic organisms in kinetics of adsorption of mercury on sediment collected from Jiaozhou bay. The results indicated that the adsorption amount of sample $1^{\#}$ was higher than that in sample $2^{\#}$ in all treatments, due to the higher content of organic matter in sample $1^{\#}$. The employ of DOM had increased the amount of mercury adsorption into sediment in comparison with that in the groups dealt with de-ionized water, obviously. In the condition of lower mercury concentrations (Hg^{2+}=10 mg/L) and higher mercury concentrations (Hg^{2+}=40 mg/L), the maximum amounts of mercury adsorption of sample controlled with DOM_c were137% to 113% higher than these in the same samples dealt with de-ionized water, respectively. And for the treatment of DOM_r, the data was 120% to 107%, respectively. The fitting results indicated that the mercury kinetics adsorption process onto sediment better fitted to the equation of y = a-b*c^x in all treatments. Generally, DOM originated from the organism living in the aquatic ecosystem could increase the adsorption amount of mercury onto sediment, which may result in the re-emit of mercury in the sediment up to the overly water body, accordingly increasing the mercury risk in aquatic ecosystem.

KEYWORDS

Mercury; DOM; Aquatic environment; Heavy metal; Sediment.

INTRODUCTION

Mercury (Hg) and its compounds, mainly in methyl mercury (MeHg), are the venomous global pollutants, with the comprehensive attention in the world. Dissolved organic matter (DOM) composed of a series of molecules with their different size and structure in soil and water, which can pass through 0.45 μm membrane and dissolve in water[1]. DOM exists widely in aquatic and terrestrial ecosystems, and organic matter in soil and water could be the cosolvent and migration carrier for the difficult soluble pollutants, which would tremendously affect the toxicity and mobility of pollutants[2,3]. DOM can increase the adsorption and fixation to heavy metal by the increase of the number of adsorption points on the solid surface[4]. However, DOM contains a lot of functional groups, which can form the organic metal complexes with heavy metal in soil by complexation, and then enhance the solubility of heavy metals[5,6]. In general, the influence of DOM to Hg adsorption onto sediment/soil was affected by both the physicochemical properties of adsorption carrier and external condition. Moreover, DOM from different sources would have the different influence on Hg adsorption to sediment/soil due to their different molecular weight and functional groups contained.

The previous studies have focused on the influences of terrestrial DOM to Hg adsorption in soil. Therefore, the research on the effects of DOM from organism in aquatic ecosystem to Hg adsorption in sediments is still rare. The Jiaozhou bay sea area is a famous seafood culture zone, with aquaculture area of reaching 145 km^2, output value being 1.93 billion yuan, and *Ruditapes philippinarum* is its main product, accounting for 95% of aquaculture production in the whole bay. The purpose of this study was to clear the effect of DOM, which prepared from *Ruditapes philippinarum* and *Phragmites communis*, on Hg adsorption in sediment from Jiaozhou bay, and was to provide the theory basis for the prevention and control of aquatic products from Hg pollution and the reduction of health risk to populations by Hg exposure.

MATERIALS AND METHODS

Collection and preparation of experimental materials

The two experimental sediments were collected in Jiaozhou bay with their location being longitude 120°11' 18.4", latitude 36°7' 55.8" for sample 1$^{\#}$, and longitude 120°9' 11.2", latitude 36°9' 5.4" for sample 2$^{\#}$. The sediments samples were air drying and grinding to use in this experiment and their basic physical and chemical properties were listed in TABLE 1.

TABLE 1 : Physical and chemical properties of the tested sediments

Samples	Hg (mg/kg)	pH	Organic matter (g/kg)	SO_4^{-2}/ (cmol/kg)	TN (g/kg)	Sediment particle size distribution（%）			
						>0.01mm	0.01~0.005mm	0.005~0.001mm	<0.001mm
1$^{\#}$	0.049	7.64	10.43	3.74	0.104	12%	43%	24%	21%
2$^{\#}$	0.053	7.31	6.18	1.19	0.127	21%	37%	27%	15%

Preparation for DOM used in this experiment

DOM_c was prepared from *Ruditapes philippinarum* based on the method used by Barricuso et al.[7]. *Ruditapes philippinarum* was gathered from the aquatic product market in Chengyang District, Qingdao City, and sea water gathered from Yangkou. A mixture of *Ruditapes philippinarum* and sea water (1:4, m:m) was cultivated for a period of a week at room temperature. And then, that mixture was filtered through a 0.45μm membrane filter to obtain DOM_c. DOM_r from *Phragmites communis* was prepared by the same method, except for the ratio being 1:15, with plastic film covering. The basic properties of DOM were listed in TABLE 2.

TABLE 2 : The basic properties of DOM

Type of DOM	Hg/(mg/L)	TOC/(g/L)	Electrical conductivity/(mS/cm)	pH
DOM_c	0.002	1.78	3.12	7.03
DOM_r	0.003	1.56	2.98	8.47

Kinetics adsorption test

In this experiment, the addition Hg content was much higher than that in the sediment samples and DOM, with the limited added amount of DOM, which resulted in the neglect of disturbance of Hg in sediment samples and DOM to the results in this experiment. And a balance method was used in this experiment. Two Hg contents, set as the lower initial Hg content (Hg^{2+}=10 mg/L) and higher initial Hg content (Hg^{2+}=40 mg/L) in solution were used in this experiment. The background ion concentration was adjusted as 0.01mol/L, after the different type of DOM added, with a ratio of solid/liquid being 1:80. At the room temperature, the mixture solution was taken out at the time of 5, 10, 30, 60, 120, 240, 360, 720, 1440 min, and then, the supernatant was detected for their Hg content after centrifugation for 10 minutes.

Measurement for Hg content and data analysis

Hg content in solution was detected by a mean of cold atomic absorbent spectrophotometry with the application of an F732-V cold atomic absorbent instrument and following the standard method in China. The F732-V cold atomic absorbent instrument has a measuring range of 0 to 10.0 μg/L and a sensitivity of not less than 0.05 μg/L. All chemicals used in this experiment were produced by Sinopharm Chemical Reagent Co. Ltd., and all glassware were dipped in a mixture of HNO_3:H_2O (1:3, v/v) for a whole night to eliminate the interference of ions attached to the glass walls. A three parallel experiment was carried out in this test and the average Hg value was used. All data were analysed using SPSS 17.0 for windows and figures were drawn using origin 7.0.

RESULT AND DISSCUSS

Effect of DOM to kinetic adsorption characteristics of Hg in sediments

Figure 1 and 2 showed that the amount of Hg adsorption to sediment increased with passage of time under the condition of the different Hg concentrations, and this adsorption rate slowed down at point of high Hg equilibrium concentration. This was because there are many special adsorption points for Hg^{2+} under the station of low Hg concentrations in solution, thus Hg^{2+} in solution could be adsorbed to those points quickly. The adsorption speed was reduced when those special adsorption points were filled. In this experiment, the addition of two kinds of exogenous DOM promoted Hg adsorption in the two sediments. The promoting effect caused by DOM_c was higher than that cause by DOM_r and the law of DOM influencing Hg adsorption in sediment was as following: DOM_c>DOM_r>CK. In sample $1^{\#}$, DOM_c and DOM_r maximized Hg adsorption capacity increased by 137% and 118% compared with CK under the condition of lower Hg content, and by 116% and 112% under the condition of higher Hg content, respectively. And to $2^{\#}$, the data was 135% and 120% under the condition of lower Hg content, and 113% and 107%under the condition of higher Hg content, respectively.

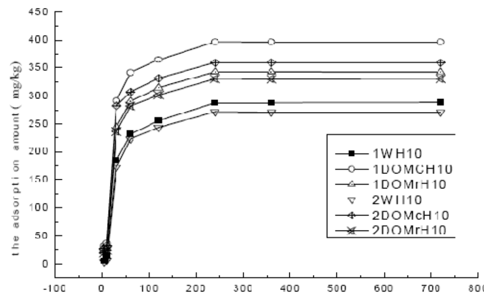

Figure 1 : Hg adsorption amount capacity with the change of time in the lower Hg content

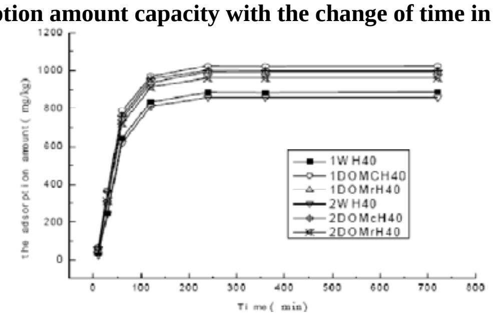

Figure 2 : Hg adsorption amount capacity with the change of time in the higher Hg content

In this study, the two kinds of DOM prepared from aquatic ecosystem all promoted the Hg adsorption to sediment, which can increase the accumulation and enrichment of Hg in the sediment along with the augment of self-purification ability for Hg in the overly water. However, Hg adsorbed onto sediment could release back to the overly water body under suitable conditions, resulting in the sediment being both of sink and source for Hg. It will contribute to Hg ecological risk to organism in the aquatic ecosystems.

Previous studies about the effect of DOM on heavy metal (Cd^{2+} and Hg^{2+}) adsorption onto soil/sediment showed that DOM had a promoting or inhibiting influence (TABLE 3), which may be associated with source, composition and properties of DOM and the different properties of the tested materials. The pH value of those DOM prepared from terrestrial waste all present as acid, except for pig manure and heap corruption sludge. Those acidic DOM had the stimulative effect on Cd^{2+} adsorption onto acidic soil and suppressive influence to neutral and alkaline soil, which resulted from the change pH value of soil solution caused by acid-alkali buffer action of DOM. However, the terrestrial acidic DOM had the prohibitive action on all the kinds of soil, including acidic, neutral, and alkaline soil, with the consequence of the different adsorption course to the two kinds of heavy metal in the tested materials. In this experiment, the pH value of two types of DOM prepared from organisms in aquatic ecosystems is all present as alkalinity, as with DOM from garbage leachate, had the stimulative effect to heavy metal adsorption onto alkaline soil/sediment. And it could be concerned with the pH value increase of soil or sediment resulted form the addition of DOM, which accompanied with the increase of heavy metal adsorption[14]. Thus, pH is an important factor influencing heavy metal adsorption onto soil/sediment[15,16]. In this experiment, DOMc prepared from *Ruditapes philippinarum* had a more strong promotion action to Hg adsorption onto sediment than that by DOMr from *Phragmites communis*, and the fact could be concerned with ingredient of mucus secretion from *Ruditapes philippinarum*, which would result in the immobilization of Hg into sediment. The molecular size and molecular structure of DOM all impact Hg fixation in sediment, which is even more than that of pH value under certain condition[3,4]. However, its influence mechanism remains unclear.

TABLE 3 : The effect of terrestrial DOM to heavy metal adsorption onto soil/sediment

Type of DOM	pH of DOM	Type of soil/sediment	pH of soil/sediment	Type of ion	Effect	Reference

Sludge	—	Acidic soil	4.02-6.44	Cd^{2+}	Promotion	[8]
		Neutral/ Alkaline soil	6.74-8.07	Cd^{2+}	Inhibition	
Manure, sludge, straw	5.75-7.20	Acidic soil	4.02	Cd^{2+}	Promotion	[9]
		Neutral/ Alkaline soil	6.74-8.00	Cd^{2+}	Inhibition	
Sediment, rice straw	6.73-7.47	soil	5.85-7.95	Cd^{2+}	Inhibition	[10]
Manure	8.19	Acidic soil	4.49	Cd^{2+}	Promotion	[11]
		Neutral soil	6.55	Cd^{2+} (Low content)	Inhibition	
		Neutral soil	6.55	Cd^{2+} (high content)	Promotion	
Halm	6.60	Acidic/ Neutral soil	4.49-6.55	Cd^{2+}	Inhibition	
Humus soil, halm, sludge	5.53-6.62	Acidic/ Neutral soil	5.31-7.05	Hg^{2+}	Inhibition	[12]
		Sediment from fish ponds	8.16	Hg^{2+}	Inhibition	
Garbage leachate	5.39-8.29	soil	4.53-8.25	Cd^{2+}, Pb^{2+}	Promotion	[13]

TABLE 4 : The fitting parameters of Kinetics adsorption of Hg in the sediment samples

Samples	Hg content	Chi^2/DoF	R^2	a	b	c
1#(CK)	10 mol/L	6.245	0.978	143.547	56.578	0.964
1#(DOM_c)	10 mol/L	3.267	0.982	156.256	60.053	0.969
1#(DOM_r)	10 mol/L	5.768	0.990	149.736	57.137	0.997
2#(CK)	10 mol/L	6.769	0.969	140.467	54.378	0.978
2#(DOM_c)	10 mol/L	3.647	0.984	155.954	58.239	0.968
2#(DOM_r)	10 mol/L	5.978	0.993	149.014	57.069	0.986
1#(CK)	40 mol/L	35.389	0.989	223.709	70.735	0.987
1#(DOM_c)	40 mol/L	28.381	0.985	274.235	78.782	0.990
1#(DOM_r)	40 mol/L	31.249	0.988	267.623	74.648	0.947
2#(CK)	40 mol/L	36.289	0.990	210.256	68.839	0.928
2#(DOM_c)	40 mol/L	29.103	0.995	269.647	75.163	0.975
2#(DOM_r)	40 mol/L	32.017	0.994	265.309	74.647	0.947

Factor affecting the Hg adsorption amount onto sediment

In the same processing, Hg adsorption quantity to 1# sample was higher than that in 2#, due to the high level of organic matter in 1# sample. Organic matter was one of the most important factors affecting adsorption of mercury ion in the sediments[17,18]. When the organic matter content increased by 1%, the fixed rate of metal ions can be increased by 30%, this was because in a certain range, the higher the content of organic matter in soil, the more heavy metal specific adsorption sites exist[19].

Fitting kinetic adsorption of Hg onto sediment was base on the equation of y = a-b*c^x, and the results (TABLE 4) showed that the fitting results got from this equation are perfect.

CONCLUSIONS

The addition of two kinds of DOM prepared from organisms in aquatic ecosystem increased the Hg adsorption rate and quantity onto sediment, and DOM from shellfish had a remarkably higher promotion action. The equation of y = a-b*c^x can better fit the kinetic adsorption process of Hg onto sediment in all the treatment. Organic matter was the important factors influencing Hg adsorption ability to sediment, and the sediment sample with high value of organic matter had the higher Hg adsorption quantity. Moreover, the addition of DOM prepared from the organisms living in the aquatic ecosystem could increase the Hg adsorption amount onto sediment, and DOM from *Ruditapes philippinarum* had the higher promoting effect than that from *Phragmites communis*.

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