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Research Article

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Influence of dissolved organic matters prepared from organisms in aquatic ecosystem on mercury adsorption in sediment

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ABSTRACT

Two kinds of dissolved organica matter (DOMc and DOMr) prepared from Ruditapes philippinarum and Phragmites communis, which are the common species in aquatic ecosystems, were used to study the characteristic of mercury (Hg) adsorption onto sediment collected from Jiaozhou bay. The results exhibited that Langmuir equation and Freundlich equation both better fitted to the Hg isothermal adsorption process onto sediment in all treatments. The addition of the two kinds of DOM had the obvious stimulative action to Hg adsorption onto sediment compared with that in the control groups. Moreover, DOMc had a slightly higher promotion action at Hg adsorption to sediment than that by DOMr. Compared with the control groups, the maximum of adsorption in two samples were elevated by 116% and 117% in DOMc treatment, and 110% and 109% in DOMr treatment, respectively. And then, the organic matter and pH were the important factors influencing Hg adsorption ability to sediment. In general, the organism in aquatic ecosystem could increase Hg adsorption quantity into sediment by the action of their DOM, with the result of the decrease of biological effectiveness of Hg. And this increased the amount of Hg in sediment to a certain extent, which increased the Hg risk in the water body.

Keywords: mercury; DOM; aquatic ecosystem; adsorption; 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]. 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 clarify 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.

EXPERIMENTAL SECTION

1.1 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

	Hg (mg/kg)	pH	Organic matter (g/kg)	CEC/ [c mol(+)/]	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	0.090	3.74	0.104	12%	43%	24%	21%
$2^{\#}$	0.053	7.31	6.18	0.050	1.19	0.127	21%	37%	27%	15%

1.2 Preparation for DOM used in this experiment1

DOM_c was prepared from *Ruditapes philippinarum* based on the method used by Barricuso [6]. *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_K	0.003	1.56	2.98	8.47

1.3 Isothermal adsorption test

Interrupted batch method was used in this experiment. The initial Hg concentrations were set as 1.0, 2.0, 5.0, 10.0, 20.0, 30.0, 40.0, 60.0 mg/L. 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 in the station of vibration for 4 hours, and then, the supernatant was detected for their Hg content after centrifugation for 5 minutes.

1.4 The effect of pH to Hg adsorption in sediment

The background Hg concentrations was set as 10.0 mg/L, with the background ion level and ratio of solid/liquid in keeping with the first experiment. The application of 1 mol/L NaOH solution and HCl was to adjust the value of initial pH as 1.00、3.00、5.00、7.00、9.00、11.00、13.00 and the following steps were same as that mentioned above.

1.5 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. 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.

RESULTS AND DISCUSSION

2.1 Effect of DOM to isothermal adsorption characteristics of Hg in sediments

Fig.1 showed that velocity of Hg adsorption to sediment increased with enlargement of Hg concentrations in solution, 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 117% and 109% compared with CK, respectively. And to 2#, the data was 116% and 110%, respectively.

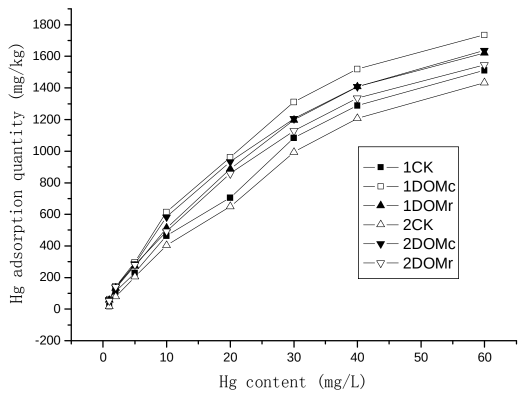

Fig. 1 Adsorption isotherms curve of Hg in the two sediment samples

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 [12]. Thus, pH is an important factor influencing heavy metal adsorption onto soil/sediment [13-15]. 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]. And then, 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	[7]
		Neutral/ Alkaline soil	6.74-8.07	Cd^{2+}	Inhibition	
Manure, sludge, straw	5.75-7.20	Acidic soil	4.02	Cd^{2+}	Promotion	[8]
		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	[9]
Manure	8.19	Acidic soil	4.49	Cd^{2+}	Promotion	[10]
		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	[11]
		Sediment from fish ponds	8.16	Hg^{2+}	Inhibition	

Fitting isothermal adsorption of Hg onto sediment was base on two equations, including Langmuir equation and Freundlich equation, and the results (table 4) showed that the fitting results got from these two equations are perfect. From the result derived from Langmiur equation, a conclusion about Hg adsorption quantity onto sediments can be got, namely, DOM_c>DOM_k>CK. In Freundlich equation, n means a coefficient of adsorption capacity and intensity of heavy to soil/sediment, which represent the strong heavy metal adsorption to sediment with its high value.

Table 4 The fitting parameters of isothermal adsorption of Hg in the sediment samples

Sediment sample	Type of process	Langmuir equation G=alogC+b			Freundlic equation G=alogC+b		
		G_m	K_1	R^2	K_2	n	R^2
1#	CK	1511	2.845	0.997**	26.8	1.638	0.992**
	DOM_c	1736	3.241	0.991**	34.5	2.246	0.986**
	DOM_k	1621	3.087	0.999**	30.5	2.018	0.995**
2#	CK	1432	2.25	0.998**	36.8	1.479	0.987**
	DOM_c	1637	3.188	0.999**	42.3	2.186	0.994**
	DOM_k	1546	2.976	0.999**	39.8	1.879	0.991**

*Note: *p<0.05 Significant level, **p<0.01 remarkably significant level*

2.2 Effect of DOM to the characteristics of Hg adsorption in sediments by different pH value

With increase of pH value, the Hg adsorption rate increased quickly, reached the maximum adsorption quantity at pH value of 9, and then decreased according to increase of pH, in all the situations (Fig. 2). pH value of the solution system is one of the main factors affecting the adsorption of metal ions in the solid phase, and pH control surface charge properties in soil/sediment, specific Hg adsorption to iron and manganese oxides, the combination of Hg and humus [16]. In the range of lower pH value, the more $Hg(OH)_2$ appeared with the increase of pH level, which led to the increase of Hg adsorption quantity. However, the increase of Hg(OH)Cl caused by rise of pH value resulted in the decrease of adsorption quantity [17]. 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 [18, 19]. 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 [20].

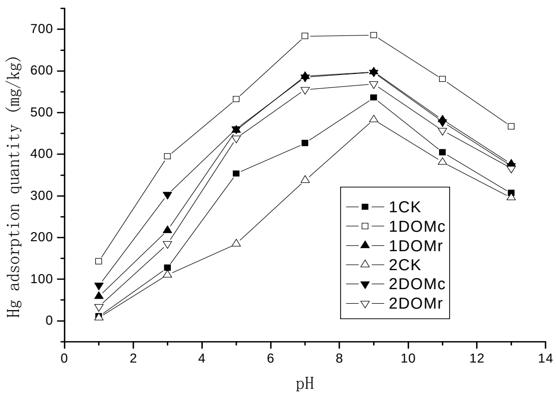

Fig. 2 The influence of pH on Hg adsorption in sediment samples

CONCLUSION

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 Langmuir and Freundlich equation can better fit the isothermal adsorption process of Hg onto sediment in the different DOM treatment. Organic matter and pH were the important factors influencing Hg adsorption ability to sediment. The sediment sample with high value of organic matter had the higher Hg adsorption quantity, and the sediment samples had the highest Hg adsorption quantity at the point of pH value being 9 under the condition of all treatment.

Acknowledgments

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