Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2013, 5(12):135-140

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Natural biological membrane to the accumulation of mercury in water of the Yellow river water effect research

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ABSTRACT

Being researched the effect of accumulation of mercury element, under different conditions such as different sampling points, different depth, different incubation time and different temperature etc., which was adsorbed by biofilm which was cultivated in the water of Yellow River. Meanwhile, analyzing the state of existence of mercury. The results show, biofilm has good function on mercury adsorption, and the longer the cultivation of biofilm, the better the adsorption ability. When PH=6，25-30°C，4h, the adsorption ability get the peak.

Key words: The Yellow River water; Biological membrane; Mercury; Adsorption; Accumulation effect.

INTRODUCTION

Hg is a kind of strong toxic metal elements, its toxicity to damage the intracellular enzyme system protein sulfhydryl group, damage to animal and human body's nervous system. Mercury (Hg) of environment is a kind of non-biodegradable toxic element, has many characteristics, such as high toxicity, persistence and mobility, it as an important part of persistent toxic pollutants has been more and more caught the attention of the scholars at home and abroad[1-2].

Biofilm of natural water body widely exist on surface of all kinds of rocks and surface sediment in rivers, lakes, wetlands, and it is composed of different kinds of microorganisms on earth. In the natural water environment, Solid surface of biofilm is the main mode for microbial life. Usually Mineral particles covered with organic shell [3-4], which will be strongly changed the adsorption behavior of mineral particles, the surface adsorption in water pollutants migration and transformation process plays a decisive role. The water of this experiment come from the Yellow River basin, using the biofilm is cultivated in the water body of Yellow River to adsorb mercury and analyzing its accumulation effect.

EXPERIMENT SECTION

1.1 The instruments

AMA 2542Automatic solid/ liquid Hg Analyzer (Milestone ,Italy)；
SHA – C reciprocating type water bath oscillator;
PHS - 25 type pH meter; Ultrapure water system.

1.2 Biofilm samples collection and develop

1.2.1The cultivation of the biofilm accumulation experiments

Using rough surface of pieces of glass to obtain samples of biofilm. Firstly, washing it thoroughly by detergent ,Secondly, cleaning it again with deionized water, and then put them into the V (H_2O) : V (HNO_3) = 6:1 solution in soaking treatment for 24 h. Tied three groups of two pieces of glass on both ends of 1 m long nylon rope as biofilm carrier which are fixed in the Hua Yuan Kou Yellow River, Huang Zhuang and GangLi reservoirs below the surface in 20 cm depth respectively, cultivated in different time, to obtain biofilm from surface and 1 m deep

water. Then, transferring the biofilm cultivated in a certain time to the laboratory to analysis.

1.2.2 The cultivation of the biological membrane adsorption experiments
Selection of water Hua Yuan Kou section of Yellow River as biofilm water laboratory training. At room temperature (25±1□), atmospheric pressure condition, the river water bearing installed respectively in two glass containers, will be cleaned multichip glass fixed in the four biofilm training device, and then respectively every 2 biofilm training device level below the surface in the same water samples of glass containers, about 30 cm. At the same time, in order to make sure the slides on the adhesion on the same traits of biofilm.Training process, the amount of aeration on a daily basis, in order to increase the dissolved oxygen in the water.At the same time, the determination of water temperature changes.

1.3 The sample testing
The determination of total mercury: total Hg in the sample is completed automatically by the AMA 2542 automatic solid/liquid Hg Analyzer (Milestone, Italy).

Mercury form detected: the continuous chemical extraction[5], in turn, extracting samples can exchange state, carbonate state, iron and manganese oxides combination state, organic combination of state and residual state of mercury.

Determination of organic matter: according to the literature 6 determination of TOC, organic matter (g/kg) = organic carbon by 1.724 g/kg [6].

1.4 Adsorption experiments
We allocate 0.1mg/L $HgCl_2$ solution with different pH, different concentrations of Na^+ using deionized water, move 20ml the adsorption solution in inner diameter is 100mm glass in a petri dish. After washing pieces of glass with biofilm with deionized water , we put the glass in different adsorption solution, set the temperature, pH value and time, and begin the adsorption experiments in a water bath oscillator. After the adsorption equilibrium, AMA254 mercury measurement instrument has been applied to the determination of mercury content in solution after adsorption, calculate according to the mercury concentration in the solution change before and after adsorption adsorption capacity and removal rate:

$$q = (Co - Ce)\ V/W \quad (1)$$
$$E = (C0 - Ce) / C0 \times 100\ \% \quad (2)$$

q —Unit mass adsorption capacity, ug/ g ;
Co —Mercury starting mass concentration ;mg/ L
Ce —After adsorption residual mass concentration of mercury ; mg/ L
V —Solution volume ; L
W —Quality of biofilm ;g

RESULTS AND DISCUSSION

2.1 Organic matter content in the biofilm
Table 1 shows TOC in the Yellow River autumn biofilm mass fraction. The data can be seen that ,there are high content of TOC in biofilm contains generally, and large amounts of organic matter in them. Organic matter is mainly composed of humic acid and microbes ,can also interact with organic matter. Therefore a biofilm of mercury and other heavy metal pollutants in the water of the organic matter enrichment, migration, transformation has great influence.

Tab. 1 The content of TOC in biological membrane(*n* = 3) / %

The sampling point	HuaYuanKou	Huang Zhuang	GangLi reservoirs
The surface layer	11.56±0.05	8.84±0.04	14.50±0.05
1m depth	10.75±0.04	7.65±0.03	8.76±0.05

2.2 Mercury in biological membrane forms
Table 2 shows the biofilm samples through multi-step chemical extraction of five kinds of forms of mercury content. As can be seen from table 2, residue, can exchange and organic combination states of mercury content is higher in biofilm samples, carbonate combined with iron and manganese oxide combination states of mercury content is relatively small. In various forms of mercury, only residual state for creatures cannot use state, as shown in table 2 after the role of water biological membrane, mercury most with residue accumulation, reduce the toxicity of

mercury to the environment.

Tab. 2 Ratio of different forms of mercury content in the biofilm of the Yellow River section water

The sampling point	Can exchange state mercury	Carbonate combination state	Manganese oxide of iron	Combined with the state	Residual mercury
HuaYuanKou	21.40	23.62	10.85	29.40	14.73
Huang Zhuang	9.17	6.85	3.26	27.85	52.87
GangLi reservoirs	16.17	3.89	2.89	29.86	47.19
The average	15.58	11.45	5.67	29.03	38.26

2.3 The influence factors of biofilm on the mercury accumulation

2.3.1 Water depth impact on biofilm total mercury content

Figure1 Shown the mercury content in three different sampling points of surface and 1 m water depth in the biofilm, 1 m deep water biofilm were greater than the surface of the mercury content of mercury content in the biofilm. The mercury levels in 1 m deep water is 1.7 times in the surface layer of biofilm at the GangLi reservoirs sample point. The water depth is different, different nutrition in biological membrane micro ecosystem structure, the mercury accumulation ability is different also.

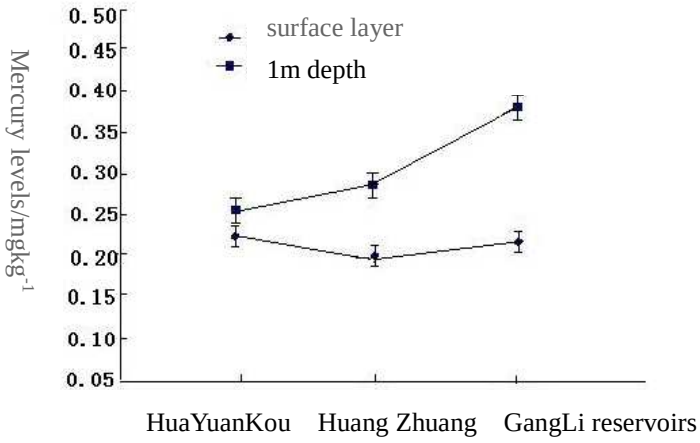

Fig. 1 Mercury content in different depth of biofilm

2.3.2 Incubation time effect on the biofilm total mercury content

Figure 2 shows the total mercury content in the biofilm after growth 30 d, 60 d, 90 d .As can be seen from the figure 2, with the increase of growth days, the total mercury content in biofilm also will increase.1 m deep water biofilm were greater than the surface of the mercury content of mercury content in biofilm; Each sample point foster 60 d the total mercury content in the biofilm were 1.25 times more than the train 30 d, but cultivate 90 d after the total mercury content in the biofilm rose by an average of 1.7 times than the cultivation of 60 d.

With the different time of cultivating, is not the same as the biofilm's stage of development, the different stages of biofilm of mercury enrichment effect is different also, to cultivate the longer, the higher the mercury levels in the biofilm.

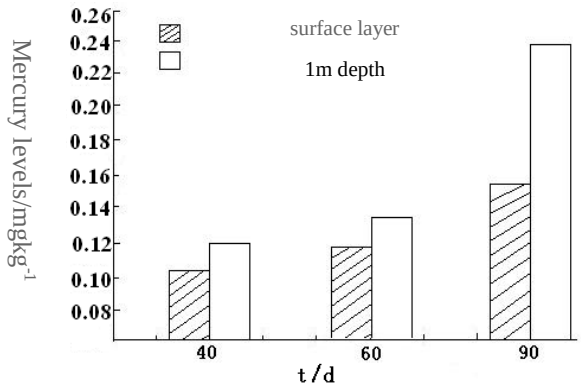

Fig. 2 Different growth days of mercury content in the biofilm

2.3.3 Different temperature on the influence of the total mercury content in the biofilm

Figure 3 shows the total mercury content in the biofilm in the summer, autumn and winter. The biofilm in the total mercury content reached the highest in the summer, winter minimum from the figure 3. Each sample point total mercury content in the biofilm in summer significantly higher than other seasons; Among them, the hillock reservoir sampling point in the summer the total mercury content in the biofilm is 6.8 times, winter Huang Zhuang sample point was 4.2 times than that in winter, summer xingshugang reservoirs in the sample point was 3.8 times of winter in summer.

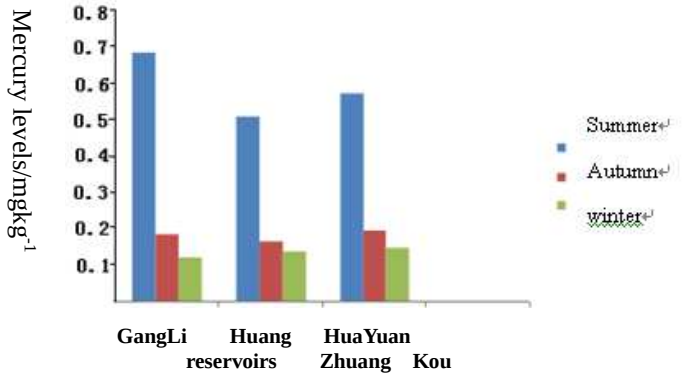

Fig. 3 Different season total mercury in biofilm

Temperature can provide energy for biofilm adsorption, temperature is high in the summer, so there are the more the energy provided, the elemental mercury levels in the biofilm is the higher; the temperature is very low in the Winter,it can provides limited energy, elemental mercury levels in the biofilm is the lowest.

2.3.4 Different sampling sites of elemental mercury content in the biofilm

Mercury in biological membrane at different sampling element is shown in figure 1 and figure 3. As can be seen from the figure 1,sample point of mercury content in biofilm in 1 m deep water up to 0.39 mg·kg^{-1} at GangLi reservoirs, the surface of biofilm mercury levels compared with other sampling points is higher also, 0.22 mg·kg^{-1}, it can be seen from the figure 3, hillock reservoir sampling point mercury levels up to 0.68 mg·kg^{-1} in the summer, the winter is the lowest 0.11 mg·kg^{-1}.

2.4 Biofilm research on mercury adsorption conditions

2.4.1 The effects of adsorption time

Figure 4 shows Biofilm on 1 mg. L^{-1} Hg^{2+} adsorption time curve in the pH = 6, the temperature is 25 □, C (Na^{+}) = 0.1mol. l^{-1} . The adsorption of Hg^{2+} time curve as shown in figure 4, you can see a biofilm on mercury adsorption reached 85% in 0.5 h, 4 h after adsorption, was 90%, and the basic flat, then illustrate the adsorption equilibrium, after adsorption experiments, choose 4 h as adsorption equilibrium time.

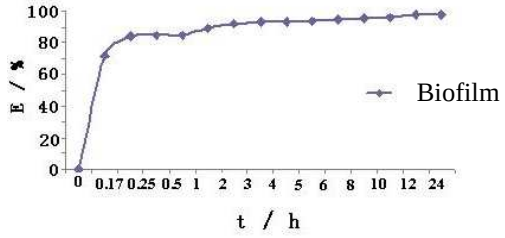

Fig. 4 The effects of adsorption time

2.4.2 The influence of pH value on adsorption

PH value on the absorption of mercury biofilm is shown in figure 3.PH value is the most important factor of influence on the effectiveness of heavy metal. With the increase of pH value, solution of $HgCl_2$ content is reduced, and Hg $(OH)_2$ content increased. Within the scope of the low pH value, hydroxyl form of mercury than chloride form more easily by adsorption, mercury adsorption is mainly affected by hydroxyl[7], the increase of pH, biological membrane adsorption amount of mercury also will increase, but, when pH values continue to rise, the Hg (OH) Cl activity than the Hg $(OH)_2$ high[8],so mercury adsorption quantity reduce instead. By the chart shows, in the pH = 6, the biofilm on the mercury adsorption quantity is at its maximum, so the pH = 6 is the optimal pH of biological membrane adsorption.

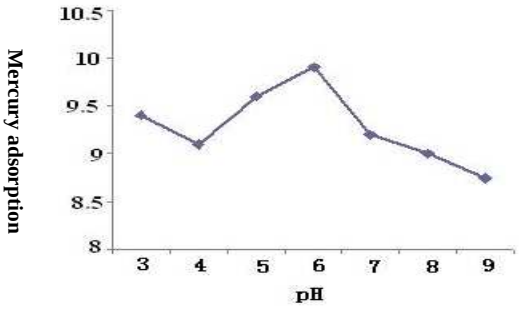

Fig. 5 PH value the relationship with the mercury adsorption curve

2.4.3 The influence of temperature on the adsorption

Figure 4 shows the influence of temperature on biological membrane absorption mercury. The results show that at a certain temperature range appropriately raise the temperature, is conducive to the growth of biofilm on the protozoa and adsorption; Adsorption process for absorption of heat, on the other hand, increasing the temperature activation ion in the solution by the increase in the number, the adsorption process of ion effective collision number increased, the adsorption rate is greater than the desorption rate, the overall performance for the adsorption quantity increases, when the temperature exceeds 30℃, the adsorption of leveling off, continue to heat up resolution rate is greater than the adsorption rate will lower the amount of adsorption, therefore, appropriate temperature of 25 to 30℃ for the adsorption of mercury

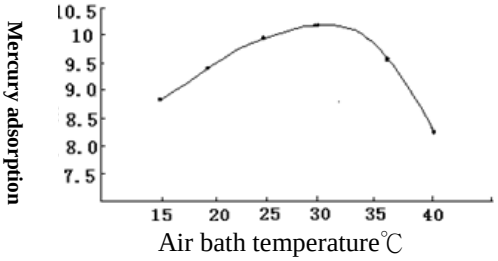

Fig. 6 temperature and the mercury adsorption curve

2.4.4 Adsorption model

Under the condition of 25 ℃, we put up 0.5, 1.0, 2.0, 3.0 mg. L^{-1} Hg^{2+} solution respectively, pH value is 6, oscillating it for 4 hours in the water under the action of biofilm and keep constant temperature, calculating the adsorption quantity, using the Langmuir and Freundlich adsorption isotherm adsorption of mercury for biofilm to fitting and thermodynamic data, the results are shown in table 3. The table shows that Langmuir equation is more suitable for describing the adsorption process of mercury in the biofilm.

Tab. 3 Biofilm Langmuir and Freundlich equation of adsorption isotherm parameters

Freundlich adsorption isotherm			Langmuir adsorption isotherm		
$\ln Q_e = \ln k_f + \frac{1}{n} \ln C_e$			$\frac{C_e}{Q_e} = \frac{1}{Q_m} C_e + \frac{1}{k_1 Q_m}$		
Kf/mg.g^{-1}	1/n	R^2	Qmax/mg.g^{-1}	K1/L.mg^{-1}	R^2
8.752	0.823	0.9713	65.36	0.0196	0.9946

K_f —empirical constant;
N—adsorption intensity;
C_e —liquid equilibrium concentration (mg/L);
Q_e—solute in the solid phase adsorption capacity (mg/g);
Q_m—he largest of solute in the solid phase adsorption capacity (mg/g)
K_1 —Adsorption constant

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