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The curve of ion exchange ratio(%)-pH of the interaction between suspended particles with Cd(Ⅱ) in the Yellow River*

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Abstract—The curve of ion exchange ratio(%)-pH of the interaction between suspended particles with Cd(II) in the Yellow River was studied. The effects of lysine on this curve have been also investigated. The results showed that (1) Cadmium in $Cd(OH)^+$ form in the suspended particles exchanges with the cations. The exchange ratio of Cd^{2+} is nearly at its greatest value in the range of pH (8.0—8.5) in natural aquatic system; (2) Ion exchange ratio decreases as the concentration of Cd^{2+} raises from 8.9×10^{-6} mol/L to $2\times8.9\times10^{-6}$mol/L; (3) At the lysine concentration of 6.8×10^{-6} mol/L, it can promote the ion exchange ratio; (4) Adsorption of the suspended particles to cadmium is weaker in seawater and Jin Sha River than in the Yellow River.

Keywords: liquid-solid interaction; cadmium; ion exchange technique; suspended particles; Yellow River.

1 Introduction

70%—80% heavy metals interact with the suspended particles in a natural aquatic system, including many coordination reactions and liquid-solid interface processes. Regular interaction of elements and the suspended particles is a key to the controlling of movement and change of elements. So, the study of liquid-solid interaction and exploration of earth chemistry behavior of trace heavy metals in an aquatic system is an extremely important subject. This subject has been studying for a long time in the seawater, not only having had many reportage of experiment, but used theory of chemical adsorption, theory of surface complication and theory of interfacial stepwise ion/coordination particle exchange separately to expounded the curve of ion exchange ratio(%)-pH

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by quantitative formulas. Silt density of the Yellow River rank first in the world, and larger suspended particles than 140 mesh are over 80%. However, the study in the Yellow River has not been reported.

The pH is primary factor to effect liquid-solid interaction in a natural aquatic and this relationship has been quantitatively expounded by the curve of ion exchange ratio(%)-pH.

$$K = \frac{(RA)(B)^m}{(A)(RBm)}, \tag{1}$$

$$D = \frac{(RA)}{(A)}, \tag{2}$$

$$E\% = 100(RA)/[(A) + (RA)]C/C_0 \times 100. \tag{3}$$

Where K is the equilibrium constant, B is the ligand to be replaced on the suspended particles R, m is the number of ligand replaced by the metal ion A. D is the distribution, E (%) is the percentage of ion exchange, among C_0 and C are initial concentration of trace metal and equilibrium concentration. If the cation ion exchange reaction is being get, thus

$$\text{pH (range of cation ion exchange)} = -\frac{1}{m}\{\log[K(RBm) \pm 2]\}. \tag{4}$$

$$K = K_{(RA)}/K_{(RBm)}. \tag{5}$$

If the organic acid is added, K_{RA} in the above formula is direct ratio to the combined constant K_{OA}, between the organic acid and A, where (RBm) is direct radio to the concentration(OBm) of the organic acid, and the proportion constants are a_1 and a_2, respectively. Therefore, the Formula(4) may be extended to the Formula(6).

$$\text{pH} = \text{(range of cation ion exchange)} = -\frac{1}{m}\left\{\log\left[\frac{a_1 \cdot K_{OA} \cdot a_{2(OBm)}}{K_{RBm}} \pm 2\right]\right\}. \tag{6}$$

2 Materials and methods

Exchange reagent is some suspended particles unpolluted in the Yellow River in this experiment. It is from Lamawan, Qingshui River, Inner Mongolia. They were purified by the removal of trace heavy metals and organic(Zhang, 1985) and were transformed into sodium ones. The purifiedly suspended particles were analysed by X-ray diffraction, infrared radiation, and all analysis and so on. The results obtained are satisfactory.

Instruments and apparatus: Model Z-8000 polarized zeeman atomic absorption spectrophotometer(Japan); model 720 pH meter(USA); model SHA-B constant temperature Shaker (China).

Natural Yellow River water samples were collected from Lamawan, Qingshui River, Inner Mongolia. All the reagents are A. P. grade or are better than them.

The experiment has used ion exchange technique. The concentration of cadmium is analyzed by atomic absorption spectrophotometer.

One hundred mg of suspended particles and about 100ml natural Yellow River water were put into 100 ml breakers. The pH value of the solutions was adjusted by HCl or NaOH to produce equally-spaced pH values in the range of 3 to 12. The final solution has a metal concentration of 8.9×10^{-6} mol/L. After having been shaken in a constant temperature bath for two hours, the solutions were filtered and their pH values were measured. The solids were washed by some distilled water, followed by 10% HCl to release the trace cadmium on the surface of the suspended particles. Finally, the trace cadmium in the Yellow River water and the HCl solutions were analyzed.

3 Results and discussion

Relations of the ion exchange ratio(%)-pH of the Cd-suspended particles system in the absence and presence of lysine are shown in Fig. 1 and Fig. 2, respectively.

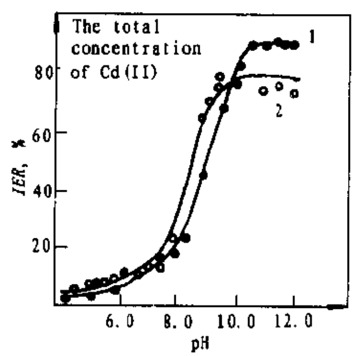

Fig. 1 The relationship between ion exchange ratio(%)-pH of the suspended particles and cadmium in the Yellow River(transform sand)
1: 8.9×10^{-6}mol/L; 2: $2\times8.9\times10^{-6}$mol/L

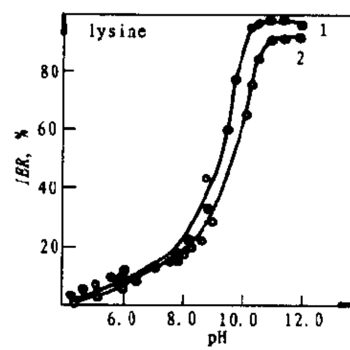

Fig. 2 Effect of lysine on the curves of IER (%)-pH (transform sand)
1: 6.8×10^{-6}mol/L; 2: 0

All curves in Fig 1 and Fig. 2 take the shape of S, which means that interaction between the suspended particles and heavy metals in the Yellow River is cation exchange reaction. So, from Formula (4) and Fig. 1 we can obtain pH = 4, $m=1$.

The experiment of ion exchange ratio(%)-pH showed that cation exchange reaction of cadmium as positive ion with suspended articles in the Yellow River is in exact agreement with cadmium of $Cd(OH)^{+}$ and $CdCO_3$ in river (Zhang, 1985). When the concentration of Cd^{2+} raises from 8.9×10^{-6} mol/L to $2\times8.9\times10^{-6}$mol/L, the maximum ion exchange ratio decreases from 90% to 76% in Fig. 1, which is all the same as Zhang(Zhang, 1985). When the points of two curves are less than 8.9 in pH, pH of filtrate will increase after the reaction, which shows that OH^{-} has been exchanged. When pH is greater than 8.9, pH of filtrate will decrease after the reaction, which shows that H^{+} has been exchanged.

At the lysine concentration of 6.8×10^{-6} mol/L, the following formula can express interaction of cadmium with suspended particles in the Yellow River:

$$\text{R-O-(org)Na} + \text{Cd(OH)}^{+} = \text{R-O-(Org)-Cd-OH} + \text{Na}^{+}.$$

Fig. 2 shows that maximum ion exchange ratio increases from 90% to 96% under the condition of the finite amount if ion exchange reagent after entering lysine, which shows that lysine can promote the ion exchange ratio. We can conclude that $\log K_{(Cd\text{-}OR)} = 1.89$ (pH = 8) and $\log K_{(Cd\text{-}OR)} = 5.25$(pH = 11) on cadmium coordinating with suspended particles. And it has been determined that $\log K_{(Cd\text{-}OR)} = 8.27$ of cadmium coordination reaction in existence of lysine in the Yellow River. So, $\log K_{(Cd-L)}$ is larger, which shows that it has formed a more steady triatic complex of "solid particles-organics-metal". Hence, it can promote the exchange reaction.

When the initial concentration of Cd^{2+} exceeded 4.89×10^{-6} mol/L, chemical precipitation will be produced in a natural aquatic system. When pH of a river is lower, the concentration of Cd^{2+} is decreasing since adsorption of the suspended particles to cadmium played a leading role in an aquatic system. The adsorption will increase as pH raises, and there is greatest value in critical pH value (pH = 8.05. $[Cd^{2+}] = 2 \times 8.9 \times 10^{-6}$ mol/L). Exceeding the value, hydrolyzation and precipitation of metallic ion will take the guiding position. The experiment has demonstrated that the adsorption and chemical precipitation exist simultaneously. Both are the important processes in the transformation of heavy metals from aqueous phase into solid one.

Effect of ionic strength, temperature and exchange reagents to E(%): Fig. 3 shows that the curves of E(%)-pH are all S-shaped in seawater($I = 0.7$, $T = 25$℃) and the Yellow River ($I = 0.2$, $T = 15$℃). The ion exchange ratio is larger in the Yellow River, which shows that they have produced the competitive interaction in the adsorption of many positive and negative ions to Cd^{2+} on the surface of trace particles, as the ionic strength of seawater is larger. Besides, illite is between 40—80 mesh, the suspended particles in the Yellow River is between 120—140 mesh. As size is growing, surface will decrease, and ion exchange will cut down.

Fig. 4 is clear that the maximum adsorption is 2 mg/g in the Jin Sha River($I = 10^{-3}$, fresh water, $T = 15$℃, pH = 9). This shows that the adsorption of solid particles to cadmium is weaker than the Yellow River. The concentration of Cd(II) is the same in two media, the former size of exchange reagent is smaller than 50 mesh, and it is 0.1 g/L. This is a primary factor for smaller adsorption.

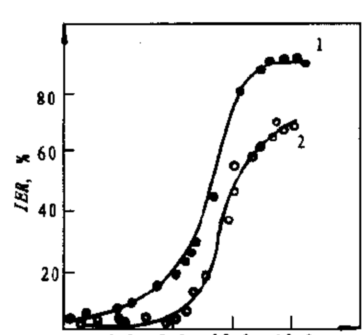

Fig. 3 The curves of E(%)-pH of the suspended particles with cadmium in different medium
1. River; 2. Sediment

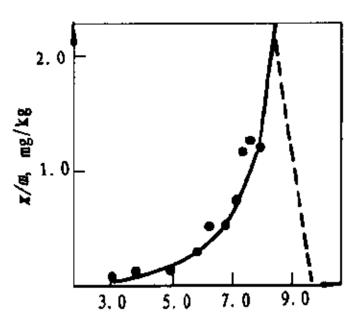

Fig. 4 pH effect of the sorption of cadmium on particles in the Jin Sha River

4 Conclusions

In brief, ion exchange ratio(%) of suspended particles to cadmium in the Yellow River is greater than seawater and the Jin Sha River. The changing range of pH is similar to $pH_{(range\ of\ ion\ exchange)} = 4$. The curves of ion exchange ratio(%)-pH showed that pH of a river is a primary factor for controlling heavy metal movement and transformation. pH in the Yellow River is between 8.0—8.5 all the year round, and it is a buffer system of heavy carbonate. Under pH of natural aquatic system, ion exchange ratio of cadmium is in the leaping area, which shows that the adsorption is the better for the suspended particles to cadmium. And the ability is a major factor of self-purification in the Yellow River.

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