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Heavy metals in water bodies purified by suspended substrate of rivers

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Abstract: The equations, which are used to describe the relationships of adsorption quantity (s), adsorption percent (P_a), aqueous equilibrium concentration(c) of heavy metal on river suspended substrates and the ratio of adsorbent to water(j), are developed when heavy metal adsorption on river suspended substrate satisfies with linear adsorption equation. The results, according to the simulation from heavy metal adsorption on suspended substrates of several main Chinese rivers from a previous research report, indicated that these developed equations could describe the linear adsorption processes in practice very well, meanwhile, the adsorption equilibrium constant of adsorbent for heavy metal was an intensity factor regardless of ratio of suspended substrates to water but strongly depended on media's pH. Furthermore, the suspended substrates of Yellow River gave stronger purification ability for Pb than for Cd and Cu. When Cd was purified by different river suspended substrates, it exhibited that the order of their purification ability for Cd was that of Songhuajiang River > Zhujiang Pearl River > Yellow River, which was consistent with their contents of cation exchange capacity(CEC). In addition, we estimated and compared the purification ability of river suspended substrates for cadmium, and the resulting purification percent was 37.64%, 64.58% and 50.98% for Songhuajiang River, Yangtze River and Zhujiang River, respectively.

Keywords: heavy metal; suspended substrate; purification

Introduction

Heavy metals in water bodies are significantly different from organic pollutants that can be microbiologically degraded or decomposed. Generally, they are purified through their adsorption onto suspended substrates in rivers. Adsorption of heavy metals on river suspended substrates in certain extend reduces the toxicity of heavy metals, and thus acts as an efficient means to purify the polluted rivers (Gardiner, 1974). The characteristics and content of suspended substrates play important roles in distribution of heavy metals between water and suspended substrates of rivers. Season's change usually results in significant variation in content of suspended substrates(Wang, 1983; Jin, 1984). Meanwhile, suspended substrates coming from different rivers will include various physical and chemical characteristics, for example, they may possess diverse mineral compost. So, it will be difficult to compare and predict the purification ability of suspended substrates among of different rivers for heavy metals.

Usually, concentration of heavy metal in rivers is rather low, so, its adsorption process on suspended substrates of rivers can be simply described using linear adsorption equation. Adsorption equilibrium constant in this adsorption equation reflects purification ability of suspended substrates for heavy metals (Huang, 1977). However, it is still unclear if contents of suspended substrate influence adsorption equilibrium constants of adsorbent. How is the relationship of adsorption quantity and contents of adsorbent?

Here, we developed equations, which could be used to well describe the relationship of adsorption quantity, adsorption percent, aqueous equilibrium concentration of heavy metal on suspended substrates and the ratio of adsorbent and water. Meanwhile, previous experimental results about purification of river suspended substrates for heavy metals were used to simulate and evaluate the proposed equations. This study will be undoubtedly significative for predicting and evaluating purification processes of suspended substrates of rivers for heavy metals.

1 Theory

Adsorption equilibrium constants, as an important index, reflect combined effect of environmental

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factors including adsorbent's characteristic, media's pH and temperature, etc. on adsorption of heavy metals. As mentioned above, concentration of heavy metals in rivers is often low, and its adsorption on river suspended substrates can be simply described as a linear adsorption one. So, it can be written as

$$s = kc. \quad (1)$$

Here, s is the adsorption quantity(mg/g), k is the adsorption equilibrium constant (L/g), and c is the aqueous equilibrium concentration of heavy metal (mg/L).

Because adsorption quantity can also be expressed as

$$s = (c^0 - c)v/w = (c^0 - c)/j, \quad (2)$$

where, j represents the ratio of suspended substrates to water. So, Equation (1) can be further written as

$$(c^0 - c)/j = kc. \quad (3)$$

Equation (3) can be rewritten as

$$c^0/c = kj + 1, \quad (4)$$

or, if P_a was defined as

$$P_a = 100(c^0 - c)/c^0. \quad (5)$$

So, Equation (3) can be expressed as

$$P_a/j = k(100 - P_a), \quad (6)$$

and

$$100/P_a = 1/(kj) + 1. \quad (7)$$

Furthermore, if Equation (3) was used to describe the relationship of adsorption quantity and adsorption equilibrium constant, s can be further written as

$$s = kc = k(c^0 - sw/v) = k(c^0 - sj). \quad (8)$$

Then, the following equation was successfully obtained as

$$c^0/s = 1/k + j. \quad (9)$$

Among of these developed equations, equation (4), (7) and (9) represented the relationship of aqueous equilibrium concentration, adsorption percent, adsorption quantity and the ratio of adsorbent and water, respectively. According to equations (4), (7) and (9), it is easy to conclude that aqueous equilibrium concentration of heavy metal decrease and its adsorption percent increase with the increase of the ratio of adsorbent to water, assuming adsorption equilibrium constant independent of ratio of suspended substrate to liquid. Previously, it has been reported that such phenomenon was observed and named as "effects of mud and sand". From Equation (9), it is very easy to understand this phenomenon. Furthermore, it will be possible to calculate adsorption equilibrium constant from the simulation of adsorption quantity of heavy metals in different ratio of adsorbent and water according to above equation (Gao, 1983). This resulting data will be more valuable than that from simple mathematics average at individual ratio of solid to liquid(Chen, 1995).

Usually, relationship of adsorption equilibrium constants and media's pH can be simulated using linear correlation equation(Institute of Soil Science, CAS, 1978) as

$$\log(k) = a\,\mathrm{pH} + b. \quad (10)$$

So, we can obtain adsorption equilibrium constant with Equation (10) at different pH, which will be further used to estimate purification ability of suspended substrates coming from different rivers for heavy metals.

2 Experimental

Cd adsorption by yellow brown soil in different ratio of soil to water was performed. Ratio of soil to water was 2.0, 4.0, 6.0, 8.0, 10.0, 15.0, 20.0, 30.0, 50.0, 75.0, 100.0 and 150.0 g/L, respectively, and the total volume was 50 ml containing 0.01 mol/L $CaCl_2$ with initial Cd concentration of 1.142 mg/L. Cd equilibrium was obtained by shaking these solutions in a horizon-direction shaker for 2h, and then centrifuged for 10 min at 4000 r/min. The concentration of Cd in the extract was determined using

Hitachi 180-80 Atomic Absorption Spectroscopy. Cd adsorption amount by soil was calculated from the difference between the amount added and the amount remaining in the solution.

3 Results and discussion

3.1 Adsorption equilibrium constant by simulating adsorption quantity and content of suspended substrates of rivers

Adsorption quantity changes with content of suspended substrate in equilibrium media. According to Equation (9), it can be obtained that relationship of c_0/s and j will be linear if adsorption equilibrium constant is independent of concentration of suspended substrates. In contrast, the linear simulation can not be obtained if adsorption equilibrium constant varies with content of suspended substrates.

Fig. 1(a), (b) and (c) are three linear simulation curves from adsorption of Cu, Pb and Cd, respectively, on suspended substrates of Yellow River, in which the original data came from Chen's previous experimental results(Chen, 1995). Undoubtedly, all of curves are linear with good correlation, meanwhile, the slope of 1.0 well agrees with the theoretical value.

The simulation results for Cu, Pb and Cd are shown as equations (11), (12) and (13), respectively.

(a): $c_0/s = j + 2.37 \quad (r^2 = 0.9992,\ p < 0.001,\ n = 5)$, (11)

(b): $c_0/s = j + 0.19 \quad (r^2 = 0.9996,\ p < 0.001,\ n = 5)$, (12)

(c): $c_0/s = j + 1.91 \quad (r^2 = 0.9844,\ p < 0.001, n = 6)$. (13)

According to the intercept, adsorption equilibrium constant (k) of suspended substrates of Yellow River for Cu, Pb and Cd is 0.422, 5.376 and 0.524, respectively. Therefore, suspended substrates of Yellow River give a high purification ability for Pb than for Cd and Cu. In other hand, Pb has larger hydrated radii than Cd and Cu (Chen, 1995). So, it also suggests that this method is valid to evaluate adsorption process of heavy metals on suspended substrate of rivers.

Table 1 Relationship of c_0/s and j for Cd adsorption on Songhuajiang River, Yellow River and Zhujiang River

	Songhuajiang River	Yellow River	Zhujiang River
Simulation equation	$c_0/s = j + 0.332$	$c_0/s = j + 1.91$	$c_0/s = j + 0.936$
Correlation coefficient, r^2	0.9978	0.984	0.9765
Equilibrium constant	3.01	0.53	1.07

Although adsorption equilibrium constant of river suspended substrate exhibits as distinct parameter regardless of its content, it will be significantly different when they come from different sources. Here, relationships of c_0/s and j for Cd adsorption on Songhuajiang River, Yellow River and Zhujiang River were obtained as Table 1.

Table 1 shows that adsorption ability of suspended substrates of rivers for Cd appeared obvious difference when they came from different sources. Among of them, the order of relative purification ability by suspended substrates of rivers for Cd is Songhuajiang River > Zhujiang River > Yellow River. In view of the content and constitutes of clay minerals included in suspended substrates, percent of montmorillonite and illite is 85%, 30% and 56% in the suspended substrates of Songhuajiang River, Zhujiang River and Yellow River, respectively. So, the adsorption quantity for Cd on suspended substrate of Songhuajiang River should greater than that of Yellow River and then Zhujiang River.. However, content of CEC of Zhujiang River (175.2 mmol/kg) is bigger than that of Yellow River (82.7 mmol/kg). Meanwhile, suspended substrates of Zhujiang River include large numbers of metal oxides that will significantly increase its specific adsorption for heavy metals.

Fig. 1(d) showed plot of c_0/s of Cd adsorption in YB soil to j in a wide range of soil to water ratio. It is obvious that this plot gave a satisfying linear simulation [$c_0/s = j + 21.68$, $r^2 = 0.9984$, $p < 0.001$, $n = 12$). So, it suggested that our proposed equation be not only used to simulate the adsorption process of Cd in sediments but also in soils.

3.2 Effect of pH on adsorption of heavy metal on suspended substrate of rivers

Adsorption of heavy metal on adsorbent strongly depended on media's pH. Usually, adsorption quantity reduces with pH's decrease, which is mainly due to decrease of surface negative charge of adsorbent in low pH media. Logarithm equation was usually used to simulate relationship of adsorption equilibrium constant and pH(9).

Fig. 2 (a), (b) and (c) were obtained by simulating adsorption equilibrium constants of suspended substrates coming from different rivers for Cd adsorption and pH using Equation (10). It can be found that the relationship of log(k) and pH is linear and they can be expressed as equations(14), (15) and (16) for Cd adsorption on suspended substrates of Songhuajiang River (a), Yangtze. River (b) and Zhujiang River (c), respectively.

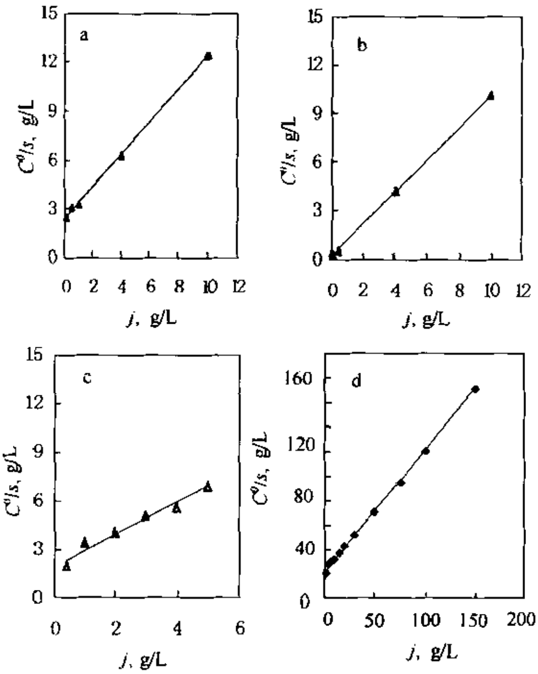

Fig. 1 Simulation curves of c_0/s vs j for adsorption of Cu (a), Pb(b) and Cd(c) by the suspended substrates of Yellow River, d is the plot of c_0/s vs j for Cd adsorption in yellow brown soil

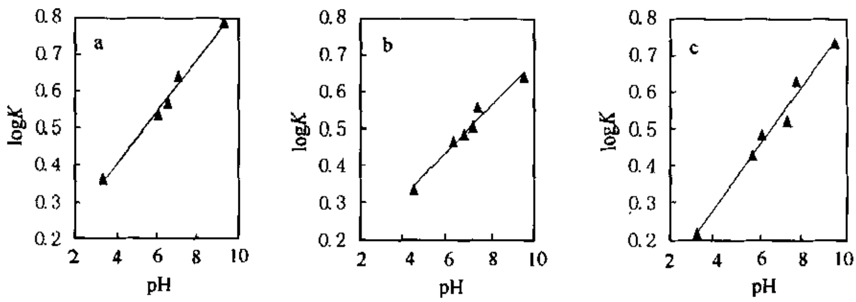

Fig.2 The simulation curves of log(k) vs pH for Cd adsorption by the suspended substrates of Songhuajiang (a), Yangtze River (b) and Zhujiang River (c), respectively.

(a) $\log k = 0.073\text{pH} + 0.103$ ($r^2 = 0.9891$, $p < 0.001$, $n = 5$), (14)

(b) $\log k = 0.061\text{pH} + 0.074$ ($r^2 = 0.9691$, $p < 0.001$, $n = 6$), (15)

(c) $\log k = 0.085\text{pH} - 0.059$ ($r^2 = 0.9790$, $p < 0.001$, $n = 6$). (16)

So, adsorption equilibrium constants with pH well satisfied with logarithm equation. Moreover, purification ability of suspended substrates for heavy metals can be further used to evaluate and estimate through the simulation from both of the dependence of adsorption quantity on pH and content of suspended substrates of rivers.

3.3 Estimation of purification process of suspended substrates of rivers for heavy metals

Three-dimensional graph by plotting c_0/s as a function of equilibrium constant and soil-to-liquid ratio can be obtained as Fig. 3 by least-square smoothing algorithm. c_0/s increases with increase of ratio of suspended substrate to liquid, and decreases with decrease of adsorption equilibrium constant. According to this plane, purification ability of suspended substrates of rivers for heavy metals can be obtained in different pH and content of suspended substrates of rivers (Wen, 1998; Allen, 1995).

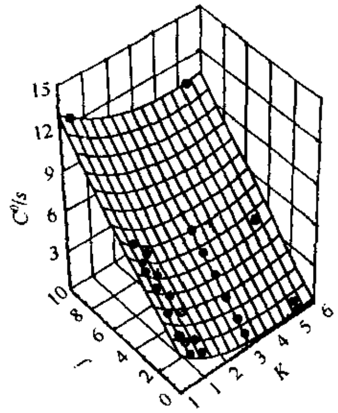

Fig.3 c^0/s as a function of equilibrium constant (k) and soil-to-liquid ratio (j). The graphic surface is obtained by least-square smoothing algorithm

In fact, the average pH are 6.6, 7.0 and 6.7 for Songhuajiang River, Yangtze River and Zhujiang River, respectively. So, it can be obtained that the k values of suspended substrates for Cd are 3.85, 3.17 and 3.24 correspondingly from equations (14), (15) and (16). In addition, the average contents of suspended substrates of rivers are 0.157, 0.575 and 0.321 g/L for Songhuajiang River, Yangtze River and Zhujiang River, respectively (Fang, 1988).

If these rivers was polluted by cadmium and assumed in the same original concentration, the purification percent is 37.64, 64.58 and 50.98 for Songhuajiang River, Yangtze River and Zhujiang River, respectively. This resulting data exhibited that the average purification abilities of suspended substrates of rivers for heavy metals were in the range of 30%—70%. Generally, content of suspended substrates of rivers is rather high during the plentiful rainfull. So, purification ability of suspended substrates of Yangtze River for heavy metal increased from 64.58% to 82.62% if the concentration of suspended substrates increased from 0.575 g/L to 1.5 g/L. It suggests that increasing the content of suspended substrates of rivers would significantly increase its ability to purify polluted rivers.

Importantly, the deduced equation can be further extended to other adsorption processes such as for organic pollutants on suspended substrates of rivers. Meanwhile, they can also be used to describe adsorption of heavy metals and organic pollutants on soil or clay minerals if these adsorption processes can satisfy with linear adsorption equation.

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