Sorption of Copper and Zinc by Humic Acids from Model Solutions

A. D. BUDAEVA, E. V. ZOLTOEV, G. I. KHANTURGAEVA and B. S. ZHAMBALOVA

Baikal Institute of Nature Management, Siberian Branch of the Russian Academy of Sciences, Ul. Sakhyanovoy 6, Ulan Ude 670047 (Russia)

E-mail: *ezol@binm.bsc.buryatia.ru*

Abstract

Sorption of Cu^{2+} and Zn^{2+} cations from model solutions by humic acids that were extracted from oxidized brown coals of Gusinoozyerskoye deposit has been investigated. An effect of pH value on the extraction of Cu^{2+} ions has been considered; sorption isotherms of Cu^{2+} and Zn^{2+} ions have been plotted. Maximum sorption exchange capacities of humic acids have been calculated on the basis of the Langmuir isotherm equation.

Keywords: humic acids, absorbent carbon, sorption, Langmuir isotherms

INTRODUCTION

Humic acids (HA) are multifunctional high-molecular compounds of high reactivity that is determined by carboxylic, hydroxyl, amine, carbonyl groups present in their structure. These compounds are capable to form stable complexes with ions of heavy metals (HM) and consequently they can be used to extract HM from sewage of galvanic and metallurgical manufactures. Great attention is given in recent years to the problem of complex formation of HA with ions of metals, since many biological, biochemical, and geochemical processes involve HAs due to their interaction with mineral elements [1].

The purpose of this paper is to study interaction of HA with HM ions under various conditions using ions of copper and zinc as an example.

EXPERIMENTAL

Medical absorbent carbon (AC) (MEDISORB Co., Perm) and HAs that were extracted from oxidized brown coals of Gusinoozyersk deposit (Buryatia) by water solutions of sodium hydroxide have been used as subjects of the research. The yield of HAs from oxidized brown coals comprises 80 % (in terms of coal organic matter, COM), ash content 3.0 %; the combined quantity of phenolic hydroxyls and carboxylic groups does not exceed 7.7 meq/g, that of carboxylic groups does not exceed 2.8 meq/g. According to data of work [2], HA are characterized by the following elemental composition, % in terms of COM: C 50.5, H 3.5, N 1.9, O 43.1, S 1.0. Table 1 gives some basic characteristics of HA and AC.

Solutions that were prepared around salts of associated metals ($CuSO_4 \cdot 5H_2O$ and $Zn(CH_3COO)_2 \cdot 2H_2O$) with the concentration of 100 mg/L (recalculated in terms of metal) as well as solid preparations of HA and AC with the particle size of <0.2 mm were used to research the interaction of copper and zinc ions with HA and AC. Concentration of Cu^{2+} ions in equilibrium solution after shaking with a sorbent and after filtration was determined by photocolorimetry of copper complexes with sodium diethyldithiocarbamate at the wavelength of 430–440 nm, and concentration of zinc ions was determined by photocolorimetry of zinc complexes with rhodamine C at the wavelength

TABLE 1

Characteristics of humic acids (HA) and absorbent carbon (AC)

Sorbent	Ash content, %	Adsorption activity	
		Benzene, cm^3/g	Methylene blue, mg/g
HA	3.0	0.01	37
AC	1.3	0.33	>100

of 610−650 nm [3]. The acidity of solutions was adjusted by adding a certain quantity of H_2SO_4 acid (0.05 and 0.5 mol/L) or NaOH alkali (0.01 mol/L) into the solution of the metal salt. The quantity of trapped ions of metals matches the difference between their initial concentration and the concentration upon the separation of the sorbent. Sorption was conducted under static conditions by shaking the solutions of metal salts with the being investigated sorbents over the course of a certain time at the temperature 20 °C.

RESULTS AND DISCUSSION

Efficiency of sorption is governed by kinetics of the process. A kinetic curve i.e. the variation of the extraction degree of ions from the solution with time was generated as the main kinetic dependence. Figure 1 gives kinetic curves of sorption of copper (II) ions. It is evident that the steady-state equilibrium in the distribution of Cu^{2+} ions between the sorbents and the solution is reached upon 2−3 h.
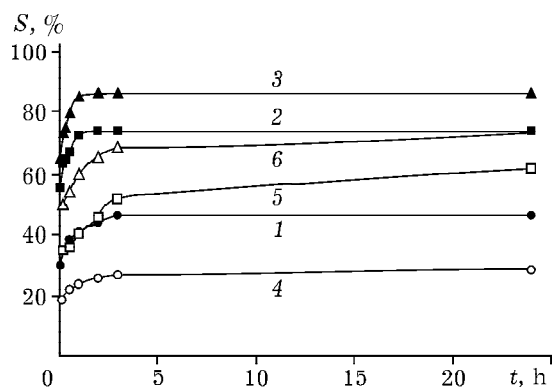
Sewage differs not only in composition, but also in acidity; therefore, it is necessary to recognize the influence of pH value upon sorption of HM ions. Studying the reaction of the medium on sorption of Cu^{2+} ions was conducted in the pH interval 1.0−5.0 with varying weighted samples of sorbent (1, 2, 3, and 5 g per 1 L of solution for purification). The analysis of curves of the dependence $S = f(pH)$ (Fig. 2) suggests that the greatest efficiency of sorption of copper ions under conditions of the investigation is observed in the pH interval of 3.0−5.0 for HA and 4.0−5.0 for AC. With increasing acidity of the solution to reach the pH of 1.0−2.0, extraction degree of copper ions by HA tapers off from 46 to 2−11 % with the consumption of sorbent $P = 1$ g/L, and sorptive capacity (Γ) decreases 4−23 times; when $P = 2$ g/L, the extraction degree decreases from 61 to 10−34 %, the Γ magnitude decreases 1.8−5 times; when $P = 3$ g/L, these indices decrease from 73 to 14−45 % and 1.6−5 times, respectively; when $P = 5$ g/L, the extraction degree of copper ions by HA tapers off from 86 to
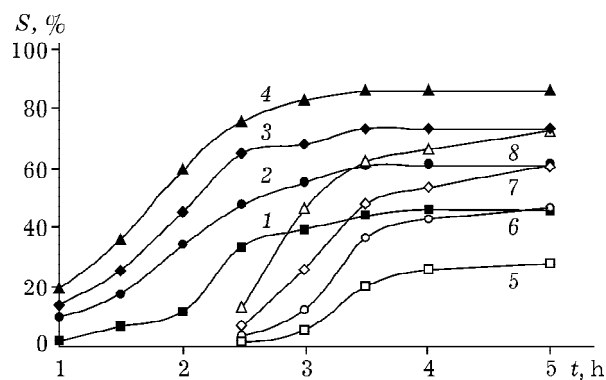

Fig. 1. Kinetic curves of sorptions of Cu^{2+} ions by humic acids (HA) (*1−3*) and by absorbent carbon (AC) (*4−6*). Ion concentration of Cu^{2+} is 100 mg/L, pH 4.0 for HA and 5.0 for AC, temperature of 20 °C; consumption of sorbent, g/L: 1 (*1, 4*), 3 (*2, 5*), 5 (*3, 6*); *S* is extraction degree of ions from solution.

Fig. 2. Extraction degree of Cu^{2+} ions by HA (*1−4*) and AC (*5−8*) *vs.* pH of the solution. Duration of sorption is 24 h, initial concentration of Cu^{2+} 100 mg/L; consumption of sorbent (*P*), g/L: 1 (*1, 5*), 2 (*2, 6*), 3 (*3, 7*), 5 (*4, 8*).

19−60 %, and sorptive capacity decreases by the factor of 1.5−4.5.

No absorption of Cu^{2+} ions by absorbent carbon occurs in highly acid solutions (pH 1.0−2.0). Extraction degree of Cu^{2+} by absorbent carbon decreases from 28 to 1−5 % as pH increases to 2.5−3.0 at $P = 1$ g/L, sorptive capacity Γ declines 5−24 times; when $P = 2$ g/L, the extraction degree drops down from 47 to 3.5−12 %, and the Γ magnitude drops down 4−13 times; when $P = 3$ g/L, these parameters decrease from 61 to 7−26 % and 2−9 times, respectively; when $P = 5$ g/L, the extraction degree drops down from 73 to 13−47 %, and the Γ magnitude decreases 1.5−5.5 times. Extraction degree of Cu^{2+} ions regularly increases with the increasing quantity of sorbent. A decrease of the extraction degree in acidic region (pH < 3.0−3.5) is caused by slight dissociation of carboxylic groups of sorbents.

Maximum sorptive capacities can be attained at the pH 3.5 for HA (46.5 mg/g) and at the pH 5.0 for AC (28.5 mg/g). In the range of pH values 1.0−2.0, the minimal sorptive capacity of HA is evidenced at $P = 1$ g/L, the maximum one − at $P = 2$ g/L; a decrease of Γ magnitude occurs with further increase in the quantity of sorbent. When pH is 2.5−5.0, sorptive capacity of HA for Cu^{2+} ions tends to decrease with an increased quantity of sorbent (Table 2).

Sorptive capacity of AC for Cu^{2+} increases with the increased quantity of sorbent over the pH region of 2.5−3.0, and it decreases at pH 3.5−5.0.
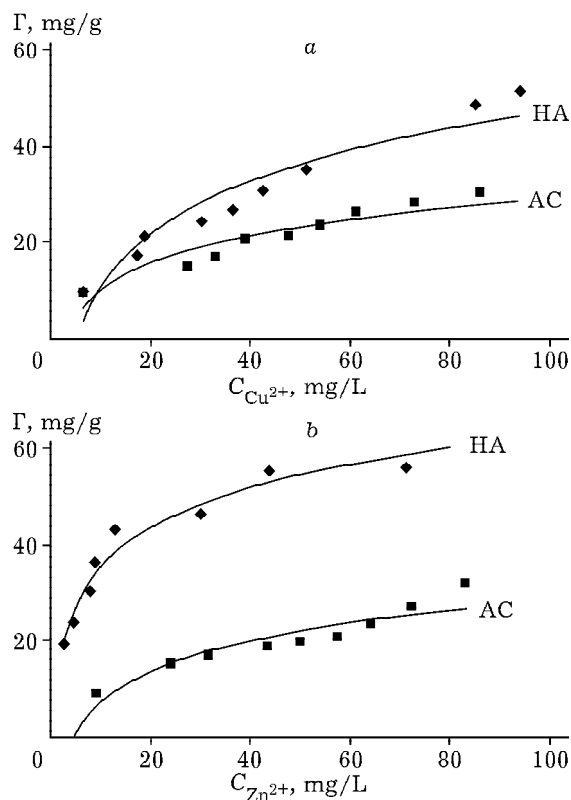
Fig. 3. Sorption isotherms of Cu^{2+} (a) and Zn^{2+} (b) by humic acids and absorbent carbon. Conditions of sorption: initial concentration of metal is 100 mg/L; pH 4.0 for HA and 5.0 for AC (a), pH 5.0 (b); duration of sorption is 24 h, temperature is 20 °C; Γ is sorptive capacity, C is equilibrium concentration.

It is found that the competitive effect of H^+ ions on sorptive capacity in acidic region (pH 1.0−2.0 for HA and pH 2.5−3.0 for AC) shows a rise with a decrease in the consumption of sorbent.

TABLE 2

Influence of pH on sorptive capacity of HA and AC (initial concentration of Cu^{2+} is 100 mg/L, duration of sorption is 24 h)

pH	Sorptive capacity, mg/g							
	HA				AC			
	P, g/L							
	1	2	3	5	1	2	3	5
1.0	1.9	4.9	4.7	3.9	0	0	0	0
1.5	6.8	8.9	8.6	7.3	0	0	0	0
2.0	11.6	17.4	15.3	12.1	0	0	0	0
2.5	34.1	24.1	22.0	15.4	1.2	1.8	2.3	2.7
3.0	40.4	28.1	23.1	16.7	5.5	6.1	8.8	9.5
3.5	44.7	31.0	24.8	17.4	20.9	18.7	16.3	12.7
4.0	46.5	31.0	24.8	17.4	25.8	22.0	18.0	13.5
5.0	46.5	31.0	24.8	17.4	28.5	23.7	20.7	14.8

From sorption isotherms of Cu^{2+} and Zn^{2+} ions from water solutions of HA and AC that are given in Fig. 3, it will be obvious that HAs are more effective by comparison to AC. Maximum sorptive capacities of HA for Cu^{2+} and Zn^{2+} ions are rather close and they comprise 52 and 56 mg/g, respectively. These parameters of AC comprise 30.6 and 32 mg/g, respectively.

Experimental results of sorption of Cu^{2+} and Zn^{2+} ions *versus* equilibrium concentration of cations have been processed in terms of coordinates of Langmuir equation [4]:

$$\Gamma = \Gamma^* kC/(1 + kC)$$

where Γ^* is the maximum sorptive capacity of sorbent, mmol/g; k is the constant of adsorption equilibrium; C is equilibrium concentration of adsorbate, the mmol/dm^3. Magnitude Γ^* can be determined upon representing the expression in a linear form:

$$\frac{1}{\Gamma} = \frac{1}{\Gamma^*} + \frac{1}{\Gamma^* kC}$$

Dependences of a reciprocal sorption of Cu^{2+} ions on $1/C_{Cu}$ argument are described by the equations $y = 0.58x + 1.13$ with the approximation plausibility $R^2 = 0.98$ (HA); $y = 0.48x + 2.24$ with $R^2 = 0.89$ (AC); and for sorption of Zn^{2+} ions, $y = 0.10x + 1.11$ ($R^2 = 0.98$) (HA); $y = 0.76x + 2.07$ ($R^2 = 0.96$) (AC). The values of maximum exchange capacity that have been calculated from the approximation of linear Langmuir equation were equal to 56.2 and 28.4 mg/g for Cu^{2+} (HA and AC, respectively), and 58.9 and 31.6 mg/g for Zn^{2+} (HA and AC, respectively). The calculated values of maximum sorptive capacity agree well with the experimentally received values: Γ (Cu^{2+}) = 52.0 and 30.6 mg/g for HA and AC, respectively, Γ (Zn^{2+}) = 56.0 and 32.0 mg/g for HA and AC, respectively. Comparative analysis of experimental and calculated values of sorptive capacity testifies that a reliable determination of maximum sorptive capacity of HA for Cu^{2+} and Zn^{2+} ions is possible using Langmuir equation.

CONCLUSIONS

1. The influence of pH value on the extraction degree of Cu^{2+} ions and sorptive capacity of humic acids and medical absorbent carbon with various quantities of sorbent has been considered. It was found that the greatest efficiency of sorption of Cu^{2+} ions was observed in the pH interval of 3.0−5.0 for HA and the pH interval of 4.0−5.0 for AC. A decreased extraction degree of Cu^{2+} ions in acidic region (pH < 3.0−3.5) is caused by a slight dissociation of carboxylic groups of sorbents. In acidic region (pH 1.0−2.0), the minimal sorptive capacity of HA is evidenced at $P = 1$ g/L, and the maximum one − at $P = 2$ g/L. A decrease of Γ magnitude occurs during the further increase in the quantity of sorbent. In the region of pH values 2.5−5.0, sorptive capacity of HA for Cu^{2+} ions tends to decrease and the quantity of sorbent tends to increase. Sorptive capacity of AC for Cu^{2+} increases in the pH region of 2.5−3.0 with an increase in the quantity of sorbent, and it decreases at pH 3.5−5.0. The less is the consumption of sorbent, the stronger is the influence of the competition of H^+ ions on the sorptive capacity (pH 1.0−2.0 for HA and pH 2.5−3.0 for AC).

2. Analysis of sorption isotherms for Cu^{2+} and Zn^{2+} has demonstrated that HA are more effective by comparison to AC in the processes of extraction of divalent cations from model solutions. Sorptive capacities of HA for Cu^{2+} and Zn^{2+} ions are close and they comprise 52 and 56 mg/g; those of AC are 30.6 and 32 mg/g, respectively.

3. Maximum sorptive capacities of HA and AC have been calculated from approximation of a linear Langmuir equation: these values for Cu^{2+} were equal to 56.2 and 28.4 mg/g for HA and AC, respectively; the values for Zn^{2+} were 58.9 and 31.6 mg/g for HA and AC, respectively.

REFERENCES

1 D. S. Orlov, *Soros. Obraz. Zh.*, 2 (1997) 56.

2 B. Ts. Batuev, E. V. Zoltoev, N. V. Bodoev *et al.*, *Chem. Sustain. Dev.*, 13 (2005) 501.
URL: http://www.sibran.ru/English/CSDE.HTM

3 Yu. O. Lurie, A. I. Rybnikova, Khimicheskiy analiz proizvodstvennykh stochnykh vod, Khimiya, Moscow, 1966.

4 F. Daniels, R. A. Alberty, Physical Chemistry, 4th ed., John Wiley and Sons, NY, 1975.