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Adsorption Behavior of Divalent Metal Ions with β -diketone Retained on Octadecyl Silica Gel

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Abstract

This investigation looked at the separation of divalent metal ions, such as Cu(II), Cd(II) and Pb(II), in an aqueous solution. The adsorbents were synthesized with β -diketones, such as 4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (TTA) or 4,4,4-trifluoro-1-phenyl-1,3-butanedione (BFA), retained on the octadecylsilica (C18). The reaction ability of these adsorbents (TTA-, BFA-C18) was evaluated by adsorption reaction behavior. It was found that the metal ions examined here were adsorbed both on TTA-C18 and BFA-C18 at pH 1.5-6.0 and the selectivity series was found in the order $\text{Cu}^{2+} > \text{Pb}^{2+} > \text{Cd}^{2+}$. These synthesized adsorbents have an advantage that the water-insoluble chelate reagents can be used without using organic solvents.

Key words: adsorbent, β -diketone, Cu(II), Cd(II), Pb(II)

1 Introduction

Cadmium and lead, both of which have been reported to be terribly toxic to animals and human beings, are frequently encountered together in fine-chemical process or battery industry wastewater. A solvent extraction using β -diketone such as 4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (TTA : Fig.1) is known to be one of the most effective methods for removal the toxic metal ions.[1] However, separation among similar structural metal ions is difficult in a batch processing. We have developed a new solvent extraction method to efficiently remove metal ions using an octadecylsilica (C18).[2] This method showed an increase in the extraction ability of the metal ions compared with the normal solvent extraction method.[3] A system developed do not need organic solvent by retaining the β -diketone directly onto C18. It was reported that the synthesized material has adsorption ability of divalent transition metal ions, and the adsorption selectivity series was $\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} \geq \text{Zn}^{2+} > \text{Mn}^{2+}$. [4] In this study, the TTA and 4,4,4-trifluoro-1-phenyl-1,3- butanedione (BFA : Fig.1) as β -diketone chelating agent were

retained onto C18. They were abbreviated as TTA-C18 and BFA-C18. These adsorbents were applied to adsorb divalent toxic heavy metal ions, Cu^{2+} , Cd^{2+} and Pb^{2+} , from an aqueous solution. The results are reported with the quantitative analysis of adsorption behavior for the metal ions using TTA-C18 and BFA-C18.

Fig. 1 Structure of 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (TTA) and 4,4,4-trifluoro-1-(2-phenyl)-1,3-butanedione(BFA).

2 Experimental

2.1 Reagents and Apparatus

The silica gel (Wako Pure Chemical Industries, 1 - 2 mm particle size) was crushed and sieved to a size of 0.50 - 1.0 mm. TTA and BFA were purchased from Dojindo Laboratories. All other reagents were analytical grade. Deionized water was prepared by Milli-Q Gradient A10 (MILLIPORE) and used throughout.

An inductively coupled argon-plasma atomic emission spectrometry (ICP-AES, VARIAN VISTA-PRO) was used to determine metal ion concentration in aqueous solution. The pH values of aqueous solutions were measured by a pH meter (HORIBA F-21) equipped with a glass electrode.

2.2 Preparation of TTA-C18 and BFA-C18

C18 was synthesized according to a published method.[5] In order to synthesize the TTA-C18 and BFA-C18, 50 cm³ of toluene containing 0.5 mol dm⁻³ TTA or BFA was added to 10 g of C18. After standing for 24 hours at 277 K, the mixed solution was filtrated, washed with deionized water and dried at room temperature under vacuum.

2.3 Adsorption Reaction

Aqueous solutions were prepared containing 1.0×10^{-4} mol dm⁻³ metal ions (Cu^{2+} , Cd^{2+} or Pb^{2+}), 0.1 mol dm⁻³ sodium perchlorate and 2.0×10^{-2} mol dm⁻³ of buffer agent (chloroacetic acid or acetic acid). A 20 cm³ aliquot of each solution, along with 0.3 g of TTA-C18 or BFA-C18, was put into a 50 cm³ stoppered glass tube. The tubes were shaken a few times each day to reach reaction equilibrium (within 36 hours) at 298 K. After the reaction was complete, the mixed solutions were filtered. The concentration of metal ions in the aqueous solutions was determined by ICP-AES and the pH value was measured.

3 Results and discussion

3.1 Characterization of Material

The bonded Si-octadecyl group was confirmed by measuring FT-IR spectra of the synthesized C18. The amount of TTA or BFA retained on C18 was found to be 0.19 ± 0.01 mmol g⁻¹. (n=3) and 0.095 ± 0.008 mmol g⁻¹ (n=4), respectively. These values were measured by the flask combustion method.[6] Meanwhile, silica gel that had not bonded with an octadecyl group was not able to retain β -diketone.

3.2 Analysis of Adsorption Behavior

Since the divalent metal ions such as Cu^{2+} , Cd^{2+} or Pb^{2+} were used for this study, the reaction between TTA-C18

or BFA-C18 and the metal ions can be expressed as

where HR and M^{2+} represents the TTA or BFA retained on C18 divalent heavy metal ion, respectively. The subscript “sol” denotes the species on the solid phase C18, “aq” denotes the species in the aqueous phase. The “ K ” is referred to as distribution constant and can be written as the following equation (2):

$$K = [MR_2]_{(sol)} [H^{+}]^2_{(aq)} / [M^{2+}]_{(aq)} [HR]^2_{(sol)}. \quad (2)$$

The equation (2) is made logarithmic as the following equation (3):

$$\log K = \log [MR_2]_{(sol)} / [M^{2+}]_{(aq)} + 2\log [H^{+}]_{(aq)} - 2\log [HR]_{(sol)}. \quad (3)$$

In addition, the distribution coefficients (K_d) can be calculated as follow:

$$K_d = \text{moles of metal ion per 1 g of TTA-C18 or BFA-C18} / \text{moles of metal ion per 1 cm}^3 \text{ of solution}. \quad (4)$$

The equation (4) can be expressed as the following equation (5):

$$K_d = [MR_2]_{(sol)} / [M^{2+}]_{(aq)}. \quad (5)$$

That is, we can get the following equation (6) from equation (3) and (4).

$$\log K_d = \log K + 2pH + 2\log [HR]_{(sol)} \quad (6)$$

Because “ K ” and “ $[HR]_{(sol)}$ ” are constant, it can be expected to get a slope +2 line when it shows the plots of $\log K_d$ versus pH.

Fig.2 shows the plots of $\log K_d$ versus pH of the aqueous solutions. The solid lines in the figure show those with slope +2. From this result, the reaction in our system can be well expressed by equation (1) for the divalent ions studied. On this reaction, two hydrogen ions were emitted to the aqueous solution when one metal ion, and two TTA and BFA molecules on the C18 formed a chelate complex. Accordingly, it was concluded that these metal ions were adsorbed on these materials by an ion-exchange reaction. This reaction is a competing reaction between the metal ion and H^{+} expressed with equation (1). Therefore, the results given by this system indicate that the reactivity is high in order of $Cu^{2+} > Pb^{2+} > Cd^{2+}$ from an acid side. This order is good agreement with solvent extraction method.[7] Therefore, it is thought that this reaction is

Fig.2 Distribution coefficient of divalent metal ions as a function of pH with TTA-C18 (closed symbols) and BFA-C18 (open symbols). Square symbols, Cu^{2+} ; Circle symbols, Cd^{2+} ; Triangle symbols, Pb^{2+} .

a chelating reaction as well as the solvent extraction system, and the reactivity is decided depending on the stability between metal ion and chelating reagent.[8]

In table 1, the pH values of the half-adsorption ($\text{pH}_{1/2}$) are given for the TTA-C18 and BFA-C18 systems. The "Difference" in table 1 is difference of the $\text{pH}_{1/2}$ values between the metal ions, and when the Difference value is greater, it is shown to separate easily by controlling pH of the aqueous solution containing metal ion. From the table 1, these materials have high mutual separation ability of the metal ions. Using BFA on this system, the metal ions could be adsorbed at high acid range than using TTA-C18 system.

The Difference values of this BFA-C18 system between Pb^{2+} - Cd^{2+} was 1.4 although that of the TTA-C18 system was 0.8. This result shows that BFA-C18 system has better mutual separation ability between Pb^{2+} - Cd^{2+} than that of the TTA-C18 system. In contrast, TTA-C18 is excellent in separation between Cu^{2+} - Pb^{2+} .

It was reported that the Cd^{2+} can be extracted only less than 50% by using nitrobenzene with TTA system.[7] Otherwise, in our systems can be adsorbed Cd^{2+} . When the selectivity between Cu^{2+} - Pb^{2+} of our system is compared with the solvent extraction system, our system has high separation ability because it is 2.6 in the solvent extraction system while the difference of $\text{pH}_{1/2}$ is 2.9 in our system. Thus, it can be said that chelating agent-retained onto C18 system improved the extraction ability and selectivity than the solvent extraction system.

Table 1 The values of $\text{pH}_{1/2}$ and difference between $\text{pH}_{1/2}$ of divalent heavy metal ions with TTA-C18 and BFA-C18.

Adsorbents		Cu^{2+}	Pb^{2+}	Cd^{2+}
TTA-C18	$\text{pH}_{1/2}$	2.5	5.4	6.2
	Difference	2.9	0.8	
BFA-C18	$\text{pH}_{1/2}$	2.0	4.4	5.8
	Difference	2.4	1.4	
SE ^{a)}	$\text{pH}_{1/2}$	2.8	5.4	— ^{b)}
	Difference	2.6		

a) SE shows solvent extraction system using nitrobenzene with TTA.[7]

b) Extraction ratio < 50%

Our system achieves the effect of β -diketone solvent extraction system by using this reported material that retaining β -diketone on C18. Moreover, this system has an advantage of a chelating agent that can be used effectively to separate and remove toxic heavy metal ions, such as Cu(II), Cd(II) and Pb(II), from an aqueous solution without organic solvents. It can be expected in a reduction of the amount of toxic organic solvent used.

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