

Synthesis of New Adsorbent as Metal Ion Capture Material

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To improve the adsorption ability of metal ions, new adsorbents were synthesized with the β -diketones carried on the octadecyl-group bonded to the silica gel. The β -diketones such as benzoyltrifluoroacetone (BFA), dibenzoylmethane (DBM) and thienoyltrifluoroacetone (TTA) were used as the metal ion adsorption reagents. The properties of those three adsorbents were evaluated by adsorption ability of copper (II) ion from aqueous solution. It was found that copper (II) ion was adsorbed to the adsorbents in the order of BFA > TTA > DBM. This new method has an advantage that the water-insoluble chelate reagent can be used to remove the metal ions from aqueous solution without using organic solvents. It is indicated that these adsorbents are effective as the metal ion capture materials.

Key words : adsorbent , copper (II) ion, β -diketone, octadecyl-group bonded silica gel, aqueous solution.

Introduction

The solvent extraction technique is one of the effective methods to remove toxic metal ions [1]. To improve the extractability for metal ions, the silica gel, which bonded with an octadecyl-group, was added to the normal solvent extraction system [2]. This solvent extraction technique has two reaction stages. In the first reaction, the metal ions in an aqueous phase were combined to the chelate reagent, and were extracted into an organic phase. After that reaction, the metal chelate in the organic phase was moved to the gel phase. By this second reaction, the extractability is improved in comparison with normal solvent extraction system. More convenient system was used for further application work which does not use an organic phase to simplify the capture system for toxic metal ions. The reason why

an organic phase was needed in the previous work is; an octadecyl-group bonded silica gel particle was aggregated on the aqueous phase if the gel was used without the organic phase, and the extraction reaction was incomplete. The new silica gel, which was bonded on octadecyl-group (C18), was synthesized to prevent the aggregation in the aqueous solution. The particle size has been improved greater than that used before. And the chelate reagent was carried on C18 by hydrophobic interaction to synthesize a metal capture material. This new C18, which carried chelate reagent, was dispersed in the aqueous solution. Without using the organic phase, the metal ion in aqueous solution was adsorbed on new C18 adsorbent.

In this study, the new adsorbents were synthesized. They carry the chelate reagents such as β -diketones

(benzoyltrifluoroacetone (BFA), dibenzoylmethane (DBM) and thienoyltrifluoroacetone (TTA)) onto C18 which were abbreviated BFA-, DBM- and TTA-C18 respectively. They were evaluated in terms of adsorption ability of copper (II) ion from aqueous solution.

Experimental

Reagents

The silica gel (particle size 1.0-2.0 mm) was obtained from Wako Pure Chemical Industries. An n-octadecyltrichlorosilane was obtained from Tokyo Kasei. A toluene from Wako Pure Chemical Industries was dehydrated with activated molecular sieves (3A 1/16). Three kinds of β -diketones (BFA, DBM and TTA) shown in Fig. 1 were obtained from Dojindo Laboratory. All of the reagents were analytical grade and used without further purification. Deionized water was prepared by Milli-Q Gradient A10 MILLIPORE and used throughout.

Apparatus

A VARIAN VISTA-PRO inductively coupled plasma atomic emission spectrometry (ICP-AES) was used for the determination of concentration of copper (II) ion. The pH value of the aqueous solution was measured by HORIBA F-21 equipped with glass electrode.

Preparation of C18

The silica gel was crushed and sieved through a stainless steel sieve (0.50-1.0 mm). It was washed with 0.1 mol dm^{-3} hydrochloric acid for 2 hours or more, washed with water and dried at 403 K for 1 day.

100 g of the silica gel was refluxed at 423 K for 4 hours after it was mixed with 1000 cm^3 of unhydrate toluene and 100 g of n-octadecyltrichlorosilane. And then 300 cm^3 of methanol was added and refluxed at 373 K for 3 hours. It was cooled to room temperature and washed several times with toluene and methanol.

After filtration, it was dried at room temperature in vacuum.

Preparation of adsorbents

50 cm^3 of toluene containing 0.5 mol dm^{-3} of BFA, DBM or TTA were added to 10 g of C18. After standing for 24 hours at 277 K, it was filtered, washed with water and dried at room temperature in vacuum. These synthesized adsorbents were stored in a brown bottle at 277 K.

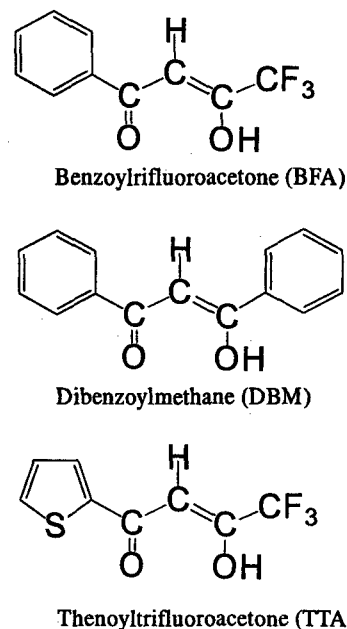


Fig.1 Structure of β -diketones.

Adsorption copper (II) ion

A 20 cm^3 portion of aqueous solution containing $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ copper (II) nitrate and $2.0 \times 10^{-2} \text{ mol dm}^{-3}$ buffer (chloroacetic acid or acetic acid) solution to control pH and 0.3 g of adsorbent (silica gel, C18, BFA-, DBM- or TTA-C18) were put into a 50 cm^3 stoppered glass tubes. The pH was adjusted with perchloric acid and sodium hydroxide. The ionic strength of the aqueous solution was controlled at 0.1 mol dm^{-3} with sodium perchlorate. The stoppered glass tubes were shaken 4 times a day to reach

adsorption equilibrium at 298 K. After the reaction, the mixed solution was filtered, the copper (II) ion concentration was determined by ICP-AES and the pH value of aqueous phase was measured.

Results and Discussion

Adsorption behavior of copper (II) ion

The relationship between the adsorption percentage of copper (II) ion and reaction time was shown in Fig.2. It shows that synthesized adsorbents have ability to adsorb copper (II) ion. BFA-, TTA-C18 reached adsorption equilibrium in about 12 hours, whereas DBM-C18 reached adsorption equilibrium in about 48 hours. All adsorption experiment described had been done at equilibrium state.

The relationship between adsorption percentage of copper (II) ion and pH in the aqueous solution was given in Fig. 3. It shows that the synthesized adsorbents can adsorb copper (II) from the aqueous solution quantitatively, whereas the silica gel and C18 can not adsorb copper (II) ion in this pH range. The adsorption percentage of copper (II) ion depended on pH, and copper (II) ion was adsorbed almost completely from aqueous solution at pH 3.5.

The half-adsorption pH values ($pH_{1/2}$) defined as pH at 50 % adsorption of copper (II) ion obtained in this study are listed in Table I. The small value of $pH_{1/2}$ indicates that the adsorbent has high adsorption ability of copper (II) ion. Consequently, the order of adsorption ability of copper (II) ion is BFA- > TTA- > DBM-C18. This order depends on the reactivity of copper (II) ion and β -diketone on C18. Generally, complex formation constant of chelate reagent increased with decreasing acid dissociation constant (pK_a). The values of acid dissociation constant of β -diketones are listed in Table II. The order of adsorption ability is in accordance with the

order of the pK_a values. The chelate reagent of small dissociation constant has high adsorption ability.

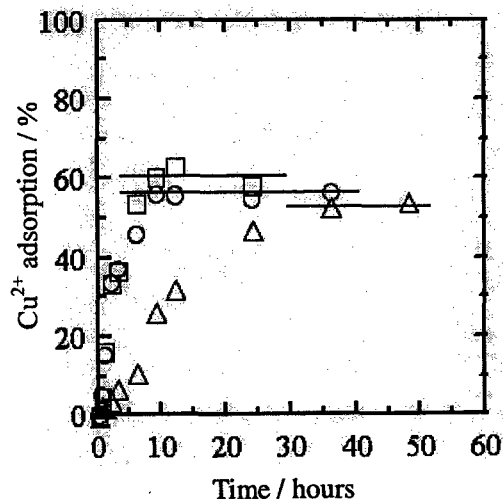


Fig.2 Effect of reaction time on adsorption of copper (II) ion.

- : BFA-C18 : pH 2.0
- △ : DBM-C18 : pH 2.8
- : TTA-C18 : pH 2.5

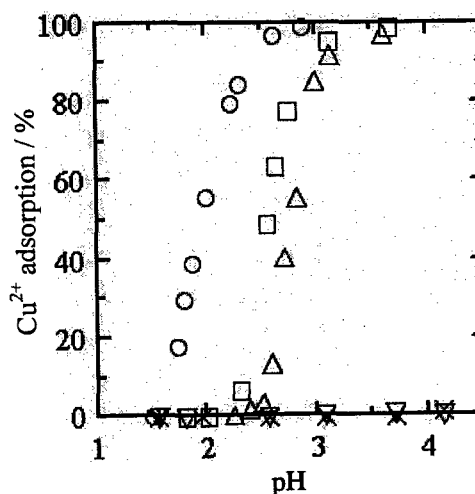


Fig.3 Effect of pH on adsorption of copper (II) ion.

- : BFA-C18 ; △ : DBM-C18 ; □ : TTA-C18
- × : C18 ; ▽ : Silica gel

Table I The half-adsorption values of pH.

	BFA-C18	DBM-C18	TTA-C18
pH _{1/2} value	2.0	2.8	2.5

Table II The acid dissociation constants (pK_a) of β -diketones.

	BFA	DBM	TTA
pK _a value	6.03*	9.35**	6.33*

* [3], ** [4]

Conclusion

In this study, the synthesized adsorbents were used to adsorb copper (II) ion, without aggregating the particle in the aqueous solution. Moreover, this method has an advantage because the water-insoluble chelate reagent such as β -diketone can be used to remove the metal ions in aqueous solution without using organic solvents. The adsorbents are expected to be new metal ion capture material.

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