Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Erdemoğlu, S. , Sayılkan, F. , Emre, F. B. , Akarsu, M. , Şener, Ş. and Sayılkan, H.(2005) 'Removal of Inorganic-Organic Bound Cu(II) from Different Aqueous Solutions by New Adsorbents Synthesized by Sol-Gel Process', Separation Science and Technology, 39: 6, 1385 — 1405

To link to this Article: DOI: 10.1081/SS-120030489

URL: http://dx.doi.org/10.1081/SS-120030489

SEPARATION SCIENCE AND TECHNOLOGY
Vol. 39, No. 6, pp. 1385–1405, 2004

Removal of Inorganic–Organic Bound Cu(II) from Different Aqueous Solutions by New Adsorbents Synthesized by Sol–Gel Process

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ABSTRACT

Hydrolysis product of alcohol modified titanium(IV)-*n*-propoxide and its coated form were prepared as new and regenerable adsorbents for adsorbing and removing Cu(II) ions from its different aqueous solutions. The hydrolysis and alcoholysis products and adsorbents were characterized using GC, ^{1}H-NMR, FT-IR, SEM, and TG-DTA analysis. It was found that Cu(II) ion adsorption rather increased when hydrolysis product of alcohol modified titanium(IV)-*n*-propoxide was coated with prehydrolyzed 3-mercaptopropyltrimethoxy silane in *n*-propanol and this coated

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DOI: 10.1081/SS-120030489 0149-6395 (Print); 1520-5754 (Online)

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material was used as adsorbent. Depending on the results of experiments performed at optimum conditions of initial Cu(II) concentration, amount of adsorbent, contact time, and pH, maximum adsorption of Cu(II), i.e., >98% has been achieved under the non-competitive conditions, while almost 60% is achieved under the competitive conditions of Pb(II), Zn(II), Fe(III), and alkali and earth alkali metals. It was also concluded that Cu(II) adsorption efficiency is not affected from the media containing acetate, tannic acid, or Turkish Blue dye. The adsorbent was easily regenerated with 5 N HNO_3 solution and used over and over again for the adsorption of Cu(II) ions.

Key Words: Waste water; Cu(II); Adsorption; Adsorbent; Sol–gel process; Coating.

INTRODUCTION

Many toxic heavy metals have been discharged to the environment as industrial wastes, causing serious soil, and water pollution. These metals are released into the environment in a number of different ways: coal combustion sewage wastewater, automobile emissions, battery industry, mining activities, and the utilization of fossil fuels is just few examples.[1] The pollution of water resources due to the disposal of heavy metals has been increasing worldwide concern for the last few decades.[2,3] It is well known that some metals can have poisonous or otherwise harmful effects on many of life forms. Heavy metals such as lead, mercury, copper, arsenic, zinc, and cadmium are highly toxic when absorbed into the body. They can cause accumulative poisoning cancer, brain, damage etc. Since they are metabolic poisons and enzyme inhibitors, they can cause mental retardation and semipermanent brain damage in young children. Since copper is also a widely used metal in our daily life, there are many actual or potential sources of copper pollution. Copper may be found as a contaminant in food, especially shellfish, liver, mushrooms, nuts, and chocolate. Briefly, any processing or container using copper material may contaminate the product such as, food, water, or drink. Copper is essential to human life and health but like all heavy metal is potentially toxic as well. For example, continued inhalation of copper-containing sprays is linked with an increase in lung cancer among exposed workers.[3]

The removal of heavy metals is thus very important in environmental remediation and clean up. Various physicochemical and biological methods have been studied for metal removal.[4] A number of traditional treatment techniques include precipitation-neutralization, ultra-filtration reverse osmosis, electrodeposition, solvent extraction, froth flotation, cementation, filtration, and evaporation. Adsorption on solid matrices is also reported to be a potential method for heavy metal removal. A variety of solid sorbents such as activated carbon, metal oxides, minerals, ion exchange, chelating resins, and selective ion exchange method have been used for removal of metal ions.[5–7] Banat et al. used chemical and physical activation of natural bentonite for the removal of heavy metal ions from aqueous solution.[8] In addition, natural occurring material as chitin and chitosan were investigated for removal of copper.[9] Rao et al. examined the performance of low-cost adsorbents as baggase and fly ash for the removal of copper and lead from aqueous solution.[10] However, these traditional sorbents have some common limitations such as low binding strength and selectivity and low resistance to chemicals, heat treatment, and radiation. To overcome the above limitations many new sorbents have been developed.[11–15]

Sol–gel process is an important and attractive technique applied not only for separation, pre-concentration, and purification processes but also for manufacturing the high-tech materials such as ceramics, inorganic–organic polymers, coating materials, ion sensors or adsorbents. Metal oxides prepared via sol–gel process exhibit high or low surface areas and hence they have an advantage over conventional materials for these potential applications. The sol–gel process is based on the hydrolysis and condensation of molecular precursors such as metal alkoxides. The hydrolysis and condensation of metal alkoxides lead to the formation of oxopolymers. The hydrolysis reactions of metal alkoxides can be controlled via the chemical modification with complexing ligands such as organic acids, β-diketonates or specific alcohols as 2-buthoxyethanol or 2-ethoxyethanol.[16]

The author's some previous works were on the synthesis of new adsorbents by means of hydrolysis–condensation reaction of β-diketonate, methacrylate modified and unmodified metal alkoxides.[17–19] Depending on the extensive literature survey, adsorbents prepared from the hydrolysis product of alcohol modified titanium(IV)-*n*-propoxide [$Ti(OPr^n)_4$] have not been studied previously for adsorbing Cu(II) ion from aqueous solution. In this present work, it was aimed to synthesize a new adsorbent by using hydrolysis reaction of 2-(2-buthoxyethoxy) ethanol (BEE) modified $Ti(OPr^n)_4$, and to study the adsorption of Cu(II) ions existing in different media onto this novel powder coated with prehydrolyzed 3-mercaptopropyltrimethoxy silane by means of sol–gel process.

EXPERIMENTAL

Apparatus

n-Propanol liberated by the reaction occurred between $Ti(OPr^n)_4$ and BEE was determined by Perichrom Peri 2000 Model GC, using calibration curves, where internal standard technique was used and *n*-hexane was chosen as the standard. ^{1}H-NMR spectra was recorded on a 60 MHz Perkin Elmer Spectrometer in $CDCl_3$. Infrared spectra of the solid products were recorded by using KBr pellets with a Perkin Elmer 283 Model FT-IR Spectrophotometer. Hydrolysis reaction of 3-mercaptopropyltrimethoxy silane (SH–Si) was tested by Mettler 2200 Model Karl-Fischer Coulometric titrator. Thermal analysis of adsorbent powders was made by Setaram TG-DTA A24 Model thermal analyser. The surface morphology of the adsorbents was investigated by Jeol JSM 6400F Model scanning electron microscopy.

In order to determine Cu(II) ion concentration of all aqueous solutions treated during the study, Philips PU9100X Model flame atomic absorption spectrometer (FAAS) using air acetylene flame was used. Wavelength 324.8 and 0.5 nm slith width were chosen for Cu(II) ion detection. Hallow cathode lamp current was 5 mA. All measurements with FAAS were repeated five times and no result was accepted if standard deviation was greater than 0.1 mg L^{-1}. The pH measurements were made on Jenway 3010 Digital Ion Analyser combined with Crison model pH electrode.

Chemicals

Titanium(IV)-*n*-propoxide (Fluka) was used as precursor for adsorbent powder synthesis and BEE (Aldrich) was used as a modifier for $Ti(OPr^n)_4$. 3-mercaptopropyltrimethoxy silane (SH–Si) (Aldrich) was used as coating material for adsorbent surface. *n*-Hexane and *n*-propanol purchased from Merck was used as solvent after drying over the molecular sieves (Fluka, Germany, 3ÅXL8). Cu(II) solution of 1000 mg L^{-1} was prepared from $Cu(NO_3)_2$ (Fischer Scientific) and this stock solution was used for copper ion source during the adsorption experiments. All acids and bases obtained from Merck were analytical grade. Distilled water obtained from Milli-Q System (Millipore) was used during the experimental studies. The pH meter was standardized using buffer solution (Merck) with pH values 7 and 4.

Material Synthesis and Preparation of Adsorbents

Alcoholysis Reaction of $Ti(OPr^n)_4$ with BEE

$Ti(OPr^n)_4$ of 0.23 mol was dissolved in 10 g *n*-hexane via stirring until a homogeneous and dark yellow solution occurred. BEE of 0.92 mol was added drop by drop to the solution allowing to react for 3–4 hr at ambient temperature where the solvent and the liberated *n*-propanol were removed under vacuum condition, until a light yellow colored viscous liquid was obtained. The liberated *n*-propanol was measured by GC and the alcoholysis product was characterized by using ^{1}H-NMR spectrophotometer.

Hydrolysis Reaction of BEE Modified $Ti(OPr^n)_4$

After dissolving BEE modified $Ti(OPr^n)_4$ in *n*-hexane, uncatalyzed hydrolysis of this solution was carried out by adding drop by drop 4 mol of distilled water per mole of $Ti(OPr^n)_4$. Reaction appeared to be more exothermic as the amount of water increased. Viscous solution turned to a gel form during the reaction. The gel was dried at ambient temperature for a day, then dried again in a vacuum steriliser at 100°C for 2 hr. At this temperature, the gel slowly turned to a yellow colored powder.

Preparation of Surface Coating Solution: Hydrolysis of SH–Si

SH–Si was hydrolyzed just by adding 1–3 mol of distilled water per mole of SH–Si, without any solvent and catalyst. The mixture was stirred at ambient temperature until a clear and homogeneous solution formed. The alcohol formed between hydroxyl group of water and methoxy group of SH–Si was removed by applying vacuum. The percentage of unreacted water was measured by the Karl-Fischer Coulometric titrator. The liquid product was very viscous and colorless. The product was diluted with *n*-propanol at 50% (w/w) ratio and this diluted solution was used as coating solution.

Preparation of Coated and Uncoated Adsorbents

Powders obtained by the hydrolysis product of BEE modified $Ti(OPr^n)_4$ was divided into two portions, after heating at 100°C. One portion was named as uncoated adsorbent. The other portion was dipped into the coating solution and the mixture was stirred for 2 hr at ambient temperature. Solid phase was then filtered and dried in a vacuum steriliser for 2 hr at 120°C. Thus, surface coated adsorbent was obtained. Mercapto groups in the coated adsorbent were characterized using FT-IR spectrometer. Both the uncoated and coated adsorbent powder was examined by means of Cu(II) adsorption tests, without any further treatment. The procedure for the preparation of adsorbents is summarized in Fig. 1.

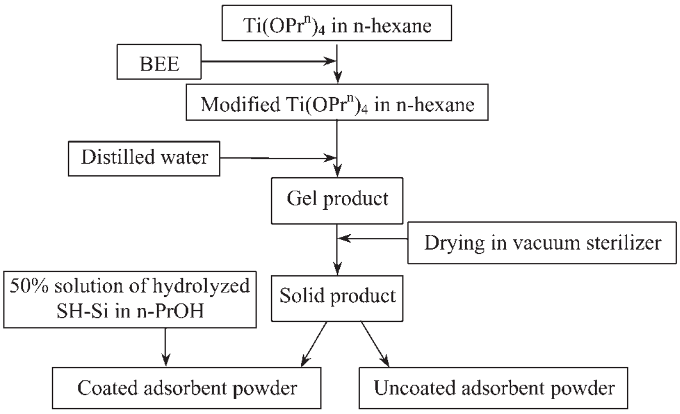


Figure 1. The procedure for the preparation of uncoated and SH–Si coated adsorbent powder.

Adsorption Experiments

Cu(II) ion adsorption from the single metal aqueous solutions was investigated by batch and column methods by means of adsorption–equilibrium experiments. The effects of initial metal concentration, pH, amount of adsorbent, and contact time on the adsorption efficiency were studied. The effect of various cations and various media on the adsorption of Cu(II) onto adsorbents were also tested.

Ten milliliter of aqueous copper solution with known concentration (in the range of 10–50 mg L^{-1}) and pH (in the range of 2–6) was poured directly into 50 mL beaker and equilibrated using a magnetic stirrer. The pH of the initial solution was adjusted to the pH value using NaOH and HCl at room temperature. Known amount of either uncoated or coated adsorbent (in the range of 0.25–1.00 g) was added into the beaker and then content of the beaker was stirred magnetically for a given time in the range of 5–50 min. After filtration using a 0.2 μm microfilter, the concentration of Cu(II) in the aqueous phase was analyzed using FAAS. The amount of adsorption was calculated based on the difference of Cu(II) concentration in the aqueous phase before and after adsorption according to

$$\text{Adsorption, } \% = \frac{C_0 - C_e}{C_0} \times 100 \qquad (1)$$

where C_0 is the initial Cu(II) concentration (mg L^{-1}), C_e is the final or equilibrium Cu(II) concentration (mg L^{-1}).

The adsorption capacity was calculated according to

$$\text{Adsorption capacity } (Q),\ \text{mg g}^{-1} = \frac{(C_0 - C_e)V}{W} \tag{2}$$

where Q is the amount of Cu(II) adsorbed onto unit amount of adsorbent (mg g^{-1}), V is the volume of Cu(II) solution (L), and W is the weight of the adsorbent (g).

Adsorption studies in the column method was conducted using a 5 cm × 10 mm ID glass column packed with 1.0 g of coated adsorbent, and connected with a pump at room temperature. The content of column was first washed with distilled water. Then, 10 mL of 10 mg L^{-1} copper solution was allowed to pass through the column at a flow rate of 0.2 mL min^{-1}, after adjusting its pH to optimum pH value (pH 2–5). The concentration of Cu(II) in the aqueous phase was analyzed using FAAS.

For desorption studies in the batch technique, 1.0 g of coated adsorbent was loaded with Cu(II) using 10 mL of 10 mg L^{-1} Cu(II) solution at optimum pH and optimum contact time (40 min). Cu(II) loaded adsorbent was collected, and gently washed with distilled water to remove any unadsorbed Cu(II) ion. After filtration, the amount of adsorbed Cu(II) onto adsorbent was determined by FAAS. Loaded adsorbent was magnetically agitated for 40 min with 10 mL of various concentrations of HCl or HNO_3. The amount of desorbed Cu(II) in the filtrated solution was determined as defined before. The same adsorbent was rinsed with deionized water for five times and then used for the adsorption of 10 mg L^{-1} copper. This procedure was repeated for five cycles.

The desorption of 10 mg L^{-1} of copper retained in the column was also carried out by allowing 10 mL of 5 N HNO_3 solution to pass through the column at a flow rate of 0.2 mL min^{-1}, which was loaded with 1.0 g of the adsorbent. The Cu(II) concentration in the solution obtained after the desorption with 10 mL of 5 N HNO_3 was analyzed by FAAS. After the regeneration, the column was rinsed with deionized water for five times. Then, 10 mL of 10 mg L^{-1} copper solution was again passed through the column at the flow rate of 0.2 mL min^{-1} for the adsorption of copper in the column. This procedure was repeated for five cycles.

Desorption of copper was calculated by using the equation given below,

$$\text{Desorption ratio, } \% = \frac{C_D}{C_0 - C_e} \times 100 \tag{3}$$

where C_D is the concentration of Cu(II) desorbed to elution medium (mg L^{-1}), C_0 is the initial Cu(II) concentration (mg L^{-1}) before adsorption, C_e is the final or equilibrium Cu(II) concentration after adsorption (mg L^{-1}).

RESULTS AND DISCUSSION

Characterization of Adsorbent

According to the GC measurements, maximum amounts of liberated alcohol in the alcoholysis reaction was found as 4 mol of *n*-propanol per mole of $Ti(OPr^n)_4$. This result is consistent with the NMR results. Therefore, the reaction stoichiometry can be given as

$$Ti(OPr^n)_4 + 4BEE \longrightarrow Ti(BEE)_4 + 4PrOH^n \qquad (4)$$

During the hydrolysis reactions of metal alkoxides, by release of either water or alcohol, condensation proceeds rapidly as soon as hydrolysis occurs. In these experiments, BEE and hydroxyl groups bonded to the Ti atom in the hydrolysis product of $Ti(BEE)_4$ were also detected in the FT-IR spectrum. Namely, the alkoxide groups of the alcoholysis product do not fully remove with hydroxyl groups of water. According to the results of FT-IR spectrum, hydrolysis–condensation reaction of $Ti(BEE)_4$ can be suggested as follows:

$$Ti(BEE)_4 + XH_2O \xrightarrow{\text{Hydrolysis}} Ti(BEE)_{4-x}(OH)_x + Xn - PrOH \qquad (5)$$

$$Ti(BEE)_{4-x}(OH)_x \xrightarrow{\text{Condensation}} Ti(BEE)_{(4-x)-y}(O)_y + yn - PrOH \qquad (6)$$

where $x < 4$ and $y < x$.[17,19]

In the FT-IR spectrum of this hydrolyzed product dried at 100°C, the bands situated at 2959, 2936, and 2873 cm^{-1}, correspond to, C–H and $-CH_2-$ stretching of aliphatic $-CH_2-$ and $-CH_3-$ groups. C–H bending vibrations of such groups can be observed in the 1360–1468 cm^{-1} spectral region. Ti–O–Ti, Ti–O and Ti(O–C) vibrations were observed at 624, 949, and 1132 cm^{-1}, respectively. These vibrations show that, a complete hydrolysis does not occur. A broad band between 3130 and 3500 cm^{-1} corresponds to the O–H stretching mode of Ti–OH. The O–H bending vibration was observed as a weak band close to 1658 cm^{-1}.

Depending on the results obtained by the Karl-Fischer titration, in the uncatalyzed hydrolysis reaction of SH–Si, 1.50 mol of water was used per mole of SH–Si. After diluting with *n*-propanol to prepare 50% (w/w) solution of SH–Si, this dilute solution was used as coating material. The hydrolysis reaction of SH–Si can be written as follows:

$$\begin{aligned} &R - Si(OCH_3)_3 + 3/2H_2O \\ &\quad \longrightarrow R - Si(OCH_3)_{3/2} + 3/2CH_3OH \quad (R \text{ is } SH - (CH_2)_{3}\text{-}) \end{aligned} \qquad (7)$$

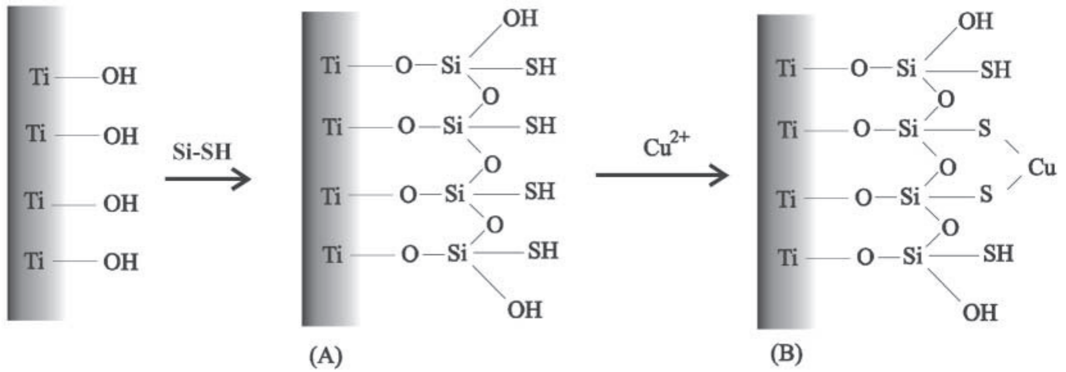
The second portion of the hydrolysis product of $Ti(BEE)_4$, dried at 100°C, was treated with the prehydrolyzed SH–Si coating solution. By adding the adsorbent into the coating solution prehydrolyzed SH–Si was transferred to the adsorbent surface as a coating. During this procedure, siloxane-bonds are formed by the condensation of hydroxyl groups as well as methoxy groups.

FT-IR measurements were also performed to find out whether the surface was coated or not. In the FT-IR spectrum of coated adsorbent, there is a small band at 2574 cm^{-1} corresponding to the characteristic S–H stretching. The absorption bands at 2960, 2936, and 2871 cm^{-1} are assigned $-CH_2-$ and C–H stretching of aliphatic $-CH_2$ and CH_3 groups, respectively. C–H bending vibration was observed in the 1360–468 cm^{-1} spectral region. Ti(O–C) and Ti(C–O) vibrations were also observed at 1128 and 1260 cm^{-1}, respectively. The bands at 708 and 805 cm^{-1} are assigned to symmetric and asymmetric Si–O stretching vibrations. Si(C–O) stretching was observed at 981 cm^{-1}. The peak observed at 627 cm^{-1} was assigned to Si–O–Ti vibration. A band at 926 cm^{-1} corresponds to non-bridging Si–OH stretching. A broad band between 3134 and 3672 cm^{-1} corresponds to the O–H stretching mode. The O–H bending vibration was observed as a weak band close to 1660 cm^{-1}.

These results showed that the surface of adsorbent was coated with the prehydrolyzed SH–Si. The coating material may be bonded to TiO_2 surface by the hydrogen bonds/or van der Walls interaction. The bonding reaction between TiO_2 surface and the coating material may be suggested as given in Fig. 2(A).

Thermal analysis of the coated adsorbent showed weight losses in three steps. The powder loses approximately 8% of its original weight by heating from 17.50°C to 124°C. This weight loss was accompanied by an endothermic peak in DTA curve, indicating that the weight loss primarily is due to the elimination of physically adsorbed water or solvent. The distinct exothermic peak in DTA curve between 238°C and 294°C with approximately 32% weight loss in TGA curve was attributed to combustion of carboneous materials that remained on the surface of adsorbent powder and coating material. The exothermic peak around 650°C in DTA curve with about 14% weight loss can be ascribed as degradation and dehydroxylation of groups onto surface of adsorbent and coating material. A total weight loss was determined as 54%. There was no significant weight change above 650°C.

SEM images given in Fig. 3 were taken to observe the surface morphology of the uncoated adsorbent powder, dried at 100°C [Fig. 3(A)], calcined at 900°C [Fig. 3(B)] and coated adsorbent powder [Fig. 3(C)]. While the surface of the coated adsorbent has a smooth surface, dried and uncoated powder has a very rough surface. The particle sizes of the adsorbent powders are very high as 20 nm may be due to the aggregation. According to this result, the surface areas of these powders are nearly zero in BET analysis. This result is confirmed by BET analysis.



Si-SH: OH(CH2)3Si-(OCH3)2-SH

Figure 2. The bonding reaction between TiO_2-surface and the coating material (A) and adsorption mechanism of Cu(II) ions on SH–Si coated adsorbent (B).

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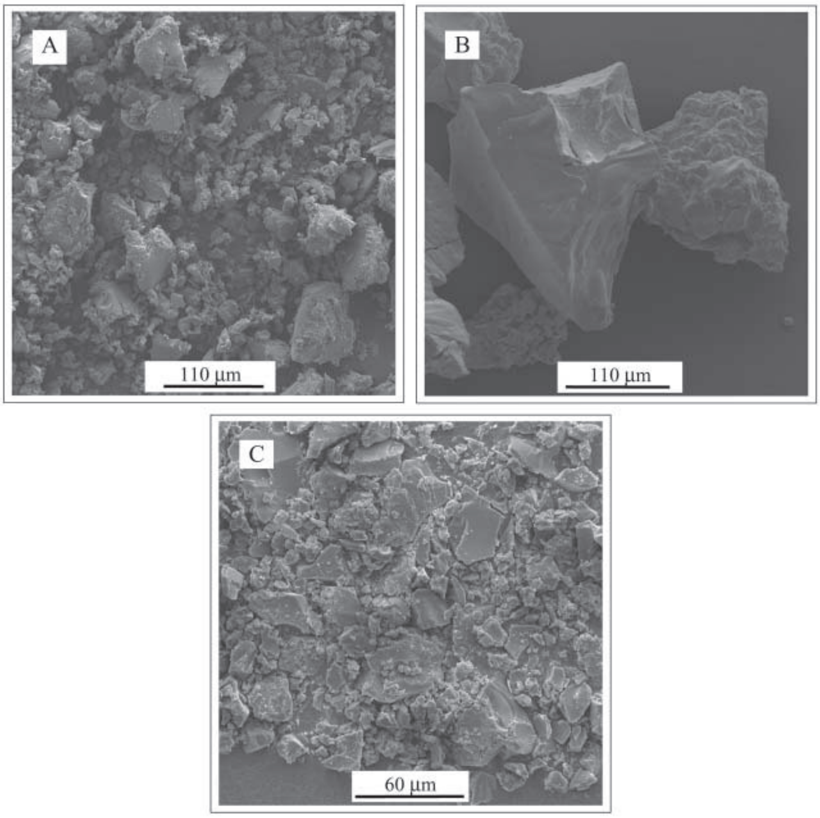

Figure 3. Scanning electron micrographs of (A) uncoated adsorbent (dried at 100°C) magnified 250 times, (B) calcined adsorbent (at 900°C) magnified 250 times, (C) SH–Si coated adsorbent magnified 500 times.

Adsorption of Cu(II)

Adsorption of Cu(II) onto uncoated and SH–Si coated adsorbent was systematically investigated by parameters such as initial concentration of Cu(II) ion in solution, amount of adsorbent, pH, and contact time, where single solution of Cu(II) ion was used. Preliminary studies performed to observe the adsorption capacities of uncoated and coated adsorbents showed that the maximum adsorption ratio of uncoated adsorbent was as low as 35% compared to coated adsorbent. Therefore, it was aimed to optimize only the adsorption conditions for SH–Si coated adsorbent. After the optimization study, adsorption capacity of the coated adsorbent, and the effects of various cations and various aqueous solutions in which Cu(II) ions exist on the adsorption of Cu(II) ion were also examined.

The Effect of Process Parameters

Figure 4(A) shows the effect of amount of adsorbent. As the optimum amount of adsorbent, 0.5 g was found to be sufficient to reach the equilibrium for 20 mg L^{-1} of Cu(II) solutions. There was no significant change after using 0.5 g of adsorbent.

Figure 4(B) shows the effect of the initial Cu(II) ion concentration (in the range of 10–50 mg L^{-1}) on the adsorption of Cu(II) by coated adsorbent. Adsorption of Cu(II) was very high at the beginning amounts of the adsorbent and equilibrium level was very slowly and gradually reached. Adsorption is slowly decreased after 20 mg L^{-1} of Cu(II). As reported in the literature, copper concentrations higher than 50–100 mg/L^{-1} can be easily decreased by means of electrochemical treatment, reverse osmosis, or chemical treatment of the wastewater. Nevertheless, application of these methods becomes costly at lower concentrations.[20] Therefore, removal of 20–30 mg L^{-1} Cu(II) by adsorbing onto SH–Si coated adsorbent is very satisfactory for Cu(II) removal from wastewaters, and 20 mg L^{-1} of Cu(II) solutions were chosen optimum and this value was used to optimize the other conditions.

Heavy metal adsorption is a pH dependent process. In the absence of complexing agents, hydrolysis and precipitation of the metal ions are affected by the concentration and formation of soluble metal species. Precipitation of Cu(II) ions occur after pH 6, which also depends on the concentration of metal ions in the medium. The degree of metal sorption at different pH values was determined by batch equilibration technique. The pH of 20 mg L^{-1} Cu(II) solution was adjusted by adding HCl or NaOH. The optimum pH for the adsorption of Cu(II) is shown in Fig. 4(C). The maximum adsorption was achieved, i.e. 100%, when solution pH is 1–5. It was observed that adsorption slightly decreases because of slow precipitation of Cu(II) from solution after pH 6.

The dependence of adsorption on contact time was examined from 5 to 60 min. As can be observed from Fig. 4(D), maximum adsorption of Cu(II) ions have been achieved almost at 40 min, implying that equilibrium has been reached. Therefore, contact time was chosen as 40 min from now on for all the experiments. It should be noted that in such an adsorption process, there are several parameters determining the adsorption rate, such as sorbent structural properties (e.g., size, porosity, topography, and surface area), amount of sorbent, metal ion properties (e.g., hydrated ionic radius), initial concentration of metal ions, chelate-formation rate, and of course, existence

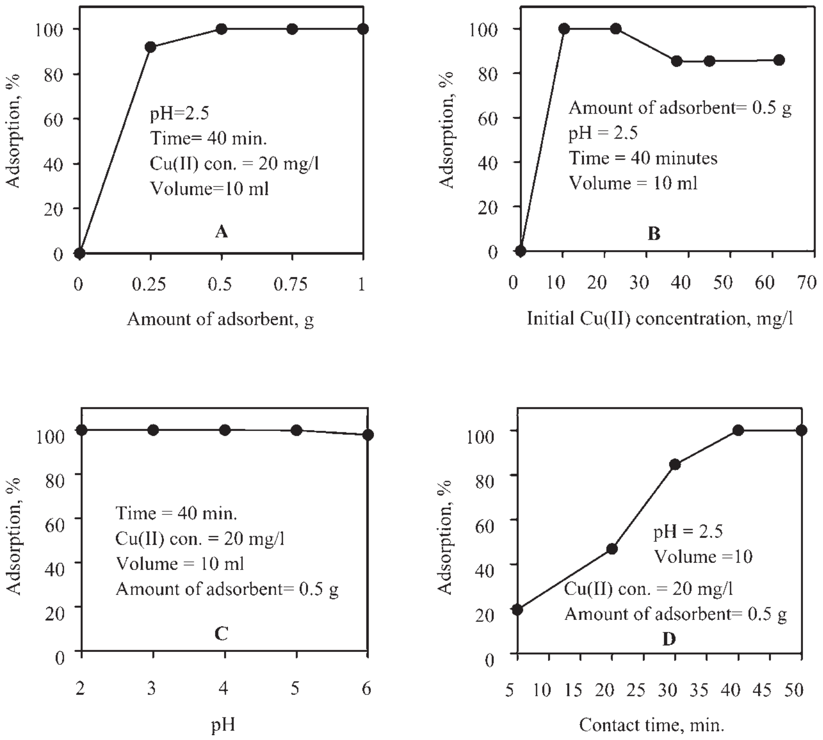

Figure 4. The graphs showing the effect of initial Cu(II) ion concentration (A), amount of adsorbent (B), pH of solution (C), and contact time (D) on the removal of Cu(II) ions by adsorbing onto SH–Si coated adsorbent.

of other ions which may compete with the ions of interest for the active adsorption sites. All this studies published in the literature has been carried out under different experimental conditions. Then, it is too difficult to compare the equilibrium adsorption times reported elsewhere. For example,[21] have investigated separation of cobalt, nickel, and copper ions with alamine liquid films and they reported that equilibrium was achieved in about 4–5 hr. In the literature, adsorption kinetics of heavy metal ions on various sorbent have shown a wide range of adsorption rates.[22,23] The maximum adsorption value, $>98\%$, was achieved at 40 min in our study, which seems to be very fast and satisfactory.

Equilibrium study for Cu(II) adsorption was carried out at room temperature (Fig. 5). Examination of Fig. 5 reveals that the adsorption sharply increases and adsorption capacity of SH–Si coated adsorbent increased as

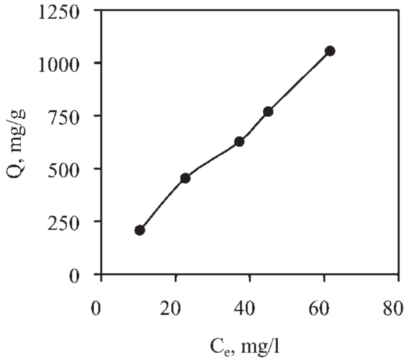

Figure 5. Equilibrium isotherm for the adsorption of Cu(II) onto SH–Si coated adsorbent.

the function of the initial concentration of Cu(II) ion within the aqueous medium.

Adsorption of Cu(II) Ions from Different Matrices

Effect of different matrices were also investigated for removal of Cu(II) ions from aqueous solution. Cu(II) solution of 20 mg L^{-1} prepared from copper acetate, 20 mg L^{-1} Cu(II) in 500 mg L^{-1} tannic acid solution and 20 mg L^{-1} Cu(II) in 50 mg L^{-1} Turkish Blue dye solution, and 20 mg L^{-1} Cu(II) solution consisting of 20 mg L^{-1} Na, K, Ca, Mg, Fe(III), and 15 mg L^{-1} Pb and 10 mg L^{-1} Zn, respectively, were treated with SH–Si coated adsorbent at optimum conditions obtained by the batch tests (i.e., pH 2–6, contact time 40 min 20 mg L^{-1} of Cu(II) concentration, 0.50 g of adsorbent and 10 mL solution volume). Table 1 briefly summarizes the results of experiments suggesting that adsorption of Cu(II) onto the coated adsorbent from waste waters containing mainly Na, K, Ca, Mg, Fe(III) and significantly Pb and Zn was highly favorable. It is also clear that adsorption proceeds, as the solution contains acetate ions, tannic acid, and a dye.

Desorption and Repeated Use

For regeneration of SH–Si coated adsorbent, 10 mL of HCl solution at different concentrations (0.1, 0.5, 1.0, 1.5, 2.0 N) was examined at the conditions of the adsorption experiments. After 40 min of stirring and filtration, Cu(II) concentration in elution solution was determined. It was observed that, when HCl solution was used for the desorption of Cu(II) from the

Table 1. Removal of 20 mg L^{-1} Cu(II) ion from different matrix solutions.

Medium in which copper exists	Adsorption (%)[a]
Solution prepared with $Cu(NO_3)_2 \cdot 4H_2O$	100 ± 0.9
Solution prepared with $Cu(acetate)_2$	100 ± 1.1
In 500 mg L^{-1} tannic acid solution	82.3 ± 1.5
In 50 mg L^{-1} Turkish Blue dye solution	80.2 ± 1.3
In solution containing, Na, K, Ca, Mg, Fe(III) (20 mg L^{-1} of each cation), 10 mg L^{-1} Cr, 5 mg L^{-1} Mn, 15 mg L^{-1} Pb, 10 mg L^{-1} Zn	59.6 ± 1.8

[a] $n = 5$.

adsorbent which sorbed 5 mg L^{-1} copper was not higher than 35%, even after 60 min of stirring. Therefore, 10 mL of 5 N HNO_3 solution was tried to desorp Cu(II) from 1.0 g of adsorbent which sorbed 10 mg L^{-1} copper. After 40 min of stirring and filtration, Cu(II) concentration in elution solution was determined. After desorption, the adsorbent was rinsed with distilled water for several times and was used again for adsorption route. This procedure was repeated three times for either batch or column method. The results of cycle tests were presented in Table 2. It was shown that, rather than batch method, column tests gave better results revealing that adsorption of Cu(II) have not decreased even after five times of regeneration.

If the desorption tests results determined from the batch and column technique were compared, it is not a surprise to achieve higher desorption ratios in the column. The reason for this can be explained that when the flow rate is adjusted to 0.2 mL min^{-1}, 10 mL of 5 N HNO_3 solution can

Table 2. Comparison of the results for the adsorption–desorption cycle tests for 10 mg L^{-1} of Cu(II) at batch and column method.

	Batch method		Column method	
Cycle No	Adsorption (%)[a]	Desorption (%)[a]	Adsorption (%)[a]	Desorption (%)[a]
1	100 ± 0.7	2.75 ± 0.9	96.0 ± 1.7	94.0 ± 2.3
2	97.0 ± 1.4	78.0 ± 2.0	96.0 ± 1.9	96.0 ± 1.8
3	100 ± 2.1	50.0 ± 3.2	100 ± 1.7	85.0 ± 2.7
4	96.0 ± 4.6	47.0 ± 7.8	98.0 ± 2.3	80.0 ± 1.4
5	95.0 ± 5.3	45.0 ± 9.2	96.0 ± 1.8	78.0 ± 2.9

[a] $n = 3$.

fully pass through the column in 50 min. Therefore, the contact time is not lower than that applied in the batch technique (40 min). In addition, the copper released from the surface by the regeneration with 5 N HNO_3 solution may retain again, since magnetic agitation was applied without shaking. Therefore, the adsorption and desorption in the batch technique seems to be achieved randomly, however there is no any mechanical destroy in the column method. As seen from the Table 2, the standard deviations for the results determined in column method are lower and consistent than those in the batch method.

Adsorption Mechanism

Figure 6 shows the FT-IR spectra of 50% (w/w) solution of prehydrolyzed SH–Si in *n*-propanol (A), hydrolyzed and dried product of $Ti(BEE)_4$ (B), coated product of the hydrolyzed-dried of $Ti(BEE)_4$ (C), 10 mg L^{-1} of Cu(II) adsorbed coated adsorbent (D), and regenerated adsorbent with 5 N HNO_3 solution (E) recorded in the range of 2000–2800 cm^{-1}. In the spectrum (A), the characteristic band of SH-group was observed as small and broad band at 2570 cm^{-1}, while the same band is not appeared in spectrum (B). After adsorbing of the Cu(II) ion onto adsorbent, the shift and intensity of the S-H stretching band is very decreased (spectrum D), when compared with the band in spectrum (C). Depending on the spectrum (D), it can be said that some of the free-SH groups are remained on the adsorbent surface

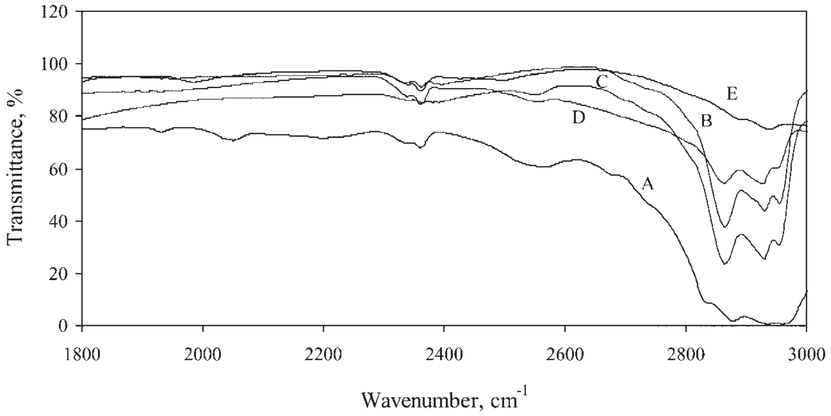

Figure 6. FT-IR spectra of prehydrolyzed SH–Si (A), hydrolyzed and dried product of $Ti(BEE)_4$ (B), coated product of the hydrolyzed-dried of $Ti(BEE)_4$ (C), Cu(II) ion adsorbed coated powder (D), and adsorbent regenerated with 5 N HNO_3 solution (E).

and these groups are not interacted with Cu(II) ions. After regenerating of adsorbent with 5 N HNO_3 solution, the characteristic band of SH− was also observed at 2568 cm^{-1}. This means that the coating material is still standing on the adsorbent surface and is not degraded. According to these results, the adsorption reaction of Cu(II) ion may be represented as shown in Fig. 2(B).

Figure 7 shows the SEM images taken to observe the surface morphology of the adsorbent treated after adsorbing of the Cu(II) ion (A), after desorbing Cu(II) ion with HNO_3 solution (B) and after adsorbing of Cu(II) ion bonded to organic dye molecules during the study. As Fig. 7(A) is compared with Fig. 3(C), it seems that there is no any degradation and roughness on the

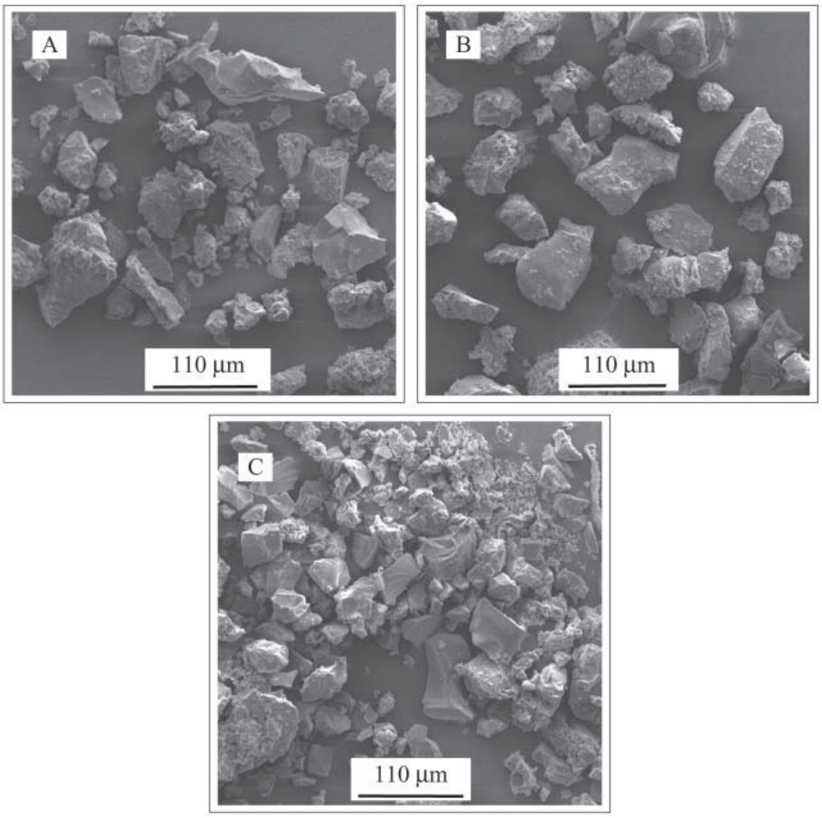

Figure 7. Scanning electron micrographs of SH−Si coated adsorbent, after the adsorption of Cu(II) (A), after the desorption of Cu(II) with 5 N HNO_3 solution (B), and after the adsorption of Cu(II) ion bonded to organic dye molecule (C). Magnification for each micrograph is 250 times.

adsorbent surface after adsorbing of Cu(II) ion. Furthermore, the surface coating material is still seen on the adsorbent surface. After the adsorption of Cu(II), SH− groups of coating material are also observed as small band at 2567 cm^{-1} as shown in Fig. 6(D). The results of regeneration experiments showed that the adsorbent surface is not broken by HNO_3 solution (Fig. (7B)). After desorbing of Cu(II) ion, SH− groups are also seen at 2565 cm^{-1} as small stretching band (Fig. 6(E)). After adsorbing of Cu(II) ion bonded to organic dye (Fig. 7(C)), it was determined that an insignificant part of the surface of adsorbent was spoiled, but the great amount of powder was not changed. This result is consistent with the FT-IR measurements. It was concluded that the adsorbent prepared by sol–gel process in this experiment can be regenerated and used repeatedly for the adsorption of Cu(II) ion existing in various aqueous solutions.

According to the results of the adsorption of Cu(II) ions from different matrices, it was found that the amount of Cu(II) ion adsorbed was 60%. It is seen that the coating material is very influential against to Cu(II) than the other ions. It is known that, the adsorption capacities of adsorbents were influenced with the surface area and total pore diameter of the adsorbent, adsorbent size and acidity, type and concentration of the coating material, the hard or soft acid–base properties of functional groups and metal ions. The amount of Cu(II) ion adsorbed onto the coated adsorbent was obtained at the maximum ratio at non-competitive condition than that at competitive condition. This result is due to the hard–soft acid–base properties of adsorbent and adsorbats. The classification of the acid properties of metal ions used in this study can be written as follows:

Na^+, K^+, Mg^{2+}, Ca^{2+}, Fe^{3+} (hard acids).

Zn^{2+}, Pb^{2+} (borderline acids).

Cu^{2+} (both borderline and soft acid).

It is known that the R–SH group is both borderline and soft base. Therefore, superior adsorption of Cu(II) ion onto SH–Si coated adsorbent is not surprising since this ion has the same properties with SH-group as a base. R–SH groups can also react with Zn(II) and Pb(II) ions, therefore the amount of Cu(II) ion adsorbed was found as low as 60% under the competitive conditions.

CONCLUSIONS

$Ti(OPr^n)_4$ was converted to a new product $[Ti(BEE)_4]$ by modification with 2-(2-butoxyetoxy) ethanol, in which the metal-oxygen bonds are quite strong and stable against the hydrolysis as demonstrated by FT-IR analysis. The hydrolysis–condensation product of Ti(BEE)$_4$ only dried at 100°C and that dried and coated with prehydrolyzed 3-mercaptopropyltrimetoxy silane were examined to be possible adsorbents for removal of Cu(II) from different aqueous solutions. The adsorption property of uncoated was very poor, i.e., 35%, compared to coated adsorbent which gave higher adsorption ratios greater than 98%. The optimization of adsorption parameters including initial Cu(II) concentration, amount of adsorbent, pH, and contact time were performed for coated adsorbent. The amount of Cu(II) adsorbed at non-competitive conditions was achieved at a maximum ratio depending on the hard acid-hard base or soft acid-soft base interactions between the functional group on the coating material and metal ion. Only the 60% of Cu(II) could be removed under the competition of Pb(II), Zn(II), Fe(III), Cr(III), Mn(II), Na, Ca, and Mg cations. It was also high however the Cu(II) solution was prepared from different copper salts such as Cu(NO$_3$)$_2$ and Cu(acetate)$_2$, and the Cu(II) solution contained different organic matrices such as tannic acid which has the properties similar with humic acid found abundantly in the waste waters and Turkish Blue dye molecules to simulate the textile industry waste waters. When the removal of copper from these different media were investigated, the average components that may found in the waste water from different sources were considered, since there are no average waste water high with copper(II). Nevertheless, the maximum copper concentration allowed by EPA in the primary drinking waters is 1.3 mg L^{-1}.

Adsorbed Cu(II) ions were desorbed up to 96% by using 5 N HNO$_3$ as the desorption agent where the column method was applied for the adsorption and desorption. Repeated adsorption–desorption processes showed that this novel prehydrolyzed SH-Si coated Ti(BEE)$_4$ based adsorbent is very suitable for Cu(II) ion removal from different aqueous solutions. It has been reported in the literature that there are some limitations for the adsorbents prepared by sol–gel process.[13,15] These reports imply that, sol–gel silica sorbent has two shortcomings, i.e., slow removal kinetics and small removal capacity, which can be attributed to the nature of entrapment method. However, the results of this study reveals that removal time for Cu(II) ions is very fast and the adsorption capacity linearly increases when the initial Cu(II) concentration is increased.

Consequently, it was concluded that SH–Si coated Ti(BEE)$_4$ powder may be chosen as an efficient adsorbent either for the removal of Cu(II) from environmental aqueous samples[24,25] or for the separation of trace Cu(II) from aqueous analytical solutions in which copper exists as a trace metal. It may be also possible to use this adsorbent for pre-concentration of copper for further analytical studies.

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Received April 2003
Revised July 2003

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