New Adsorbents from Ti(OPr^{n})_{4} by the Sol-Gel Process: Synthesis, Characterization and Application for Removing Some Heavy Metal Ions from Aqueous Solution

FUNDA SAYILKAN

HİKMET SAYILKAN

SEMA ERDEMOĞLU

ŞADİYE ŞENER

MURAT AKARSU

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Funda SAYILKAN,* **Hikmet SAYILKAN**
Department of Science, Faculty of Education, İnönü University,
44069, Malatya-TURKEY
e-mail: hsayilkan@inonu.edu.tr
Sema ERDEMOĞLU, Şadiye ŞENER
Department of Chemistry, Faculty of Arts and Sciences, İnönü University,
44069, Malatya-TURKEY
Murat AKARSU
Institut für Neue Materialien, D-66123, Saarbrücken-GERMANY

New adsorbents were synthesized by the sol-gel process from the product of a hydrolysis reaction and its coated form of titanium(IV)-n-propoxide for removing some heavy metal ions from aqueous solution. Titanium(IV)-n-propoxide was uncatalyst hydrolyzed with different amounts of water at room temperature and was found to react in a 1:1.6 ratio (mole of Ti:mole of H_2O). It was found that the condensation following the hydrolysis reaction was alcohol condensation. The hydrolysis-condensation product was characterized in detail by GC, Karl-Fischer coulometric titrator, NIR-spectroscopy, FT-IR spectroscopy, TG-DTA and elemental analysis. The hydrolysis-condensation product of titanium(IV)-n-propoxide was calcinated at 900 °C after drying at 100 °C and some of this product was coated with hydrolyzed NH_2-functional silanes [3-(2-aminoethylamino)ethylamino)propyl-trimethoxy silane] (Amino-1), and [3-(2-aminoethylamino)propylmethyldimetoxysilane] (Amino-2), separately. Adsorption capacities of uncoated and NH_2-functional silane coated hydrolysis-condensation products for Fe^{3+}, Cu^{2+} and Pb^{2+} ions in aqueous solution were investigated by FAAS. It was observed that the extent of adsorption was influenced significantly by the type and concentrations of coating materials, e.g., Amino-1 coated adsorbent prepared in methyl alcohol as 50% (w/w) and 100% (without methyl alcohol) adsorbed 90.67% and 100% of Fe^{3+}, respectively, while the uncoated form adsorbed only 5%. The adsorption isotherm was determined and the data were analyzed according to the Freundlich model.

Key Words: Sol-gel process, adsorption, adsorbent, waste water, heavy metals, coating.

*Corresponding author

Introduction

The release of heavy metals into our environment is still widespread. In certain areas of the world it is even increasing. The pollution of water resources due to the disposal of heavy metals has been an increasing worldwide concern for the last few decades. The most common metals found in wastewater that are significantly toxic to human beings (causing genetic mutations and cancer) and the ecological environment, include copper, cadmium, lead and mercury[1,2]. Numerous adsorbents of different forms have been utilized in chemical techniques for the removal of toxic substances from industrial wastewater[3−9]. Some of the major drawbacks in the use of these adsorbents are a) the high cost of the material, b) failure in adsorption of a range of metal ions simultaneously, and c) necessity of activating metal ion adsorbents with different acids or bases before use. For example, in the preparation of adsorbents derived from apricot seed hulls[5] the drawbacks are that the activation experiments are too lengthy and this in turn gives rise to product losses. Although plenty of research is available in this field, there seems to be no method developed for use in industry yet. A recent survey of the literature revealed that adsorbents of MO_x structure, synthesized by the sol-gel process, have not been utilized in the removal of important environmental pollutants. The synthesis and application of this type of adsorbent was studied for the first time by us[10].

Metal alkoxides are widely used for preparing new high-technology materials[10−13]. By the appropriate selection of metal alkoxides, a molecular oxide network can be obtained through appropriate inorganic polymerizations. By controlling the whole process accurately and characterizing all the chemical species formed throughout the reactions, high-tech materials with the desired properties can be synthesized. The process used for preparing these materials is called the sol-gel process. In this process, a solution of molecular precursors (mainly metal alkoxides or organically modified metal alkoxides) is converted by a chemical reaction into a sol or a gel that on drying and densification gives a solid material. The hydrolysis and condensation of metal alkoxides lead to oxopolymers, which transform into an oxide network upon calcination. The product that occurs after calcinating is TiO_2. It is well known that TiO_2 has been used as a photocatalyst for the photodegradation of phenolic compounds and organic dyes since 1970[14−18]. However, TiO_2 has not been used as an adsorbent for removing heavy metals from aqueous solution.

This study was performed to find out whether coated/uncoated TiO_2 can be used as adsorbents to remove Fe^{3+}, Pb^{2+} and Cu^{2+} ions from aqueous solution. In the first part of this investigation, titanium(IV)-n-propoxide was hydrolyzed and then the product was dried at 100 °C and calcinated at 900 °C. In the second part, several coated adsorbents were prepared by treating the powders with 2 different NH_2-functional silanes, each in 1%, 50% and 100% (w/w) solutions in methanol. These products were characterized by FT-IR spectra and BET measurements. In the third part, the adsorption of some heavy metal ions by both coated and uncoated powders was investigated. The results showed that the surface coated adsorbents can effectively eliminate Fe^{3+} and Pb^{2+} ions from aqueous solution. Our approach is likely to be applied succesfully for a range of inorganic-organic contaminants.

Methods

Chemicals

Titanium(IV)-n-propoxide (Fluka), 3-(2-aminoethylamino)-ethylamino)propyltrimethoxysilane and 3-(2-aminoethyl-amino)propylmethyldimethoxysilane (Aldrich) referred to hereafter as Ti(OPr^n)$_4$, Amino-1 and Amino-2,

respectively, were used as starting precursors for obtaining adsorbent and coating materials, respectively, and were used as received. Analytical grade nitrate salts of Fe(III), Pb(II) and Cu(II) were supplied by Merck. Metal stock solutions were prepared as 1000 mg/L. Methyl ethyl ketone (MEK) (Merck) and methyl alcohol (Merck) were used as solvents and were stored over molecular sieves (Fluka, 3ÅXL8) for a day before use.

Moisture contents, 0.0011% in MEK and 0.0021% in methyl alcohol, were detected by a Karl-Fischer coulometric titrator.

Apparatus

The total amount of n-propanol formed in the hydrolysis and subsequent condensation reaction between $Ti(OPr^n)_4$ and water was determined by Perichrom Peri-2000 Model GC, using a calibration curve. The internal technique was used and MEK was chosen as the standard. The extent of the hydrolysis was measured using a Nicolet 66 SXR Model Differential NIR-spectrometer. The infrared spectrum of the surface coating solution was obtained with a Perkin Elmer 283 model FT-IR spectrophotometer using CaF_2 disks. The infrared spectra of dried, calcinated and coated powders were obtained by FT-IR spectrophotometer using KBr pellets. The percentage of unreacted water was measured by Mettler DL18 model Karl-Fischer coulometric titrator. The hydrolysis-condensation product was separated from the aqueous part in a vacuum. Elemental and TG-DTA analyses were carried out on the water-free sample by Perkin Elmer 5500 model element analyzer and Setaram A24 model thermal analyzer, respectively. Several surface characteristics of coated and uncoated adsorbents were estimated by analysis of adsorption/desorption data, using a Micrometics ASAP 2000 BET analyzer. BET surface area was calculated using the many points method, but pore distribution was calculated according to the method of Barret-Jayner-Halenda (BJH)[19]. A Philips PU9100X model flame atomic absorption spectrophotometer operating with air-acetylene fuel was used to determine Cu^{2+}, Fe^{3+} and Pb^{2+} concentrations in solutions treated during the study. Wavelengths were 324.5 nm, 217 nm and 248.3 nm for Cu, Pb and Fe, respectively. Slit width was 0.5 nm for all the elements and the hollow cathode lamp current was 5 mA.

Procedure

Hydrolysis of $Ti(OPr^n)_4$

$Ti(OPr^n)_4$ (0.001 mole) was hydrolyzed with various quantities of water [1-4 moles per mole of $Ti(OPr^n)_4$] in MEK (12 g) without using any catalyst. In the hydrolysis reaction, water was added drop by drop. After adding water, the reaction mixture was stirred for 30 min at ambient temperature. A colloidal mixture was formed as soon as water was added, and the product changed into a gel as the reaction proceeded. The reaction appeared to be more exothermic as the amount of water increased. On removal of the solvent and the liberated alcohol under vacuum, a water-free gel product was obtained. The gel was dried at ambient temperature for a day, and then dried again in a vacuum sterilizer at 100 °C for 1 h. At this temperature, the gel slowly became a colorless powder.

Preparation of surface coating materials: Hydrolysis of Amino-1 and Amino-2

Amino functional silanes (Amino-1 and Amino-2) were hydrolyzed separately without solvent and catalyst by adding 3 moles of water per mole of silane. The mixtures were stirred until they formed a clear and

homogeneous solution at ambient temperature. Alcohol formed between the hydroxyl group of water and methoxy groups of silanes was removed under vacuum. The products thus obtained were very viscous liquids. Then 1%, 50% and 100% (without methanol) of solutions (w/w) of these products were prepared with diluted methanol and used as coating solutions. These products were characterized by FT-IR spectra.

Preparation of Adsorbents

Metal-organic adsorbents were obtained by the hydrolysis-condensation product of $Ti(OPr^n)_4$. This product was dried in a vacuum sterilizer at 100 °C and then ground to a fine powder in a grinder. The powdered material was divided into 3 portions. The first portion was calcinated at 900 °C in a muffle furnace for 60 min, and then used without any treatment for metal ion adsorption. The second and third portions were dipped into coating solutions (Amino-1 and Amino-2) prepared in methanol as 1%, 50% and 100% (without methanol), respectively, and the mixtures were stirred for 60 min at ambient temperature. Then they were filtered and dried in a vacuum sterilizer for 90 min at 120 °C. Thus, surface coated and uncoated adsorbents were obtained. Amino groups on the coated adsorbent surface were characterized by FT-IR spectrum. The procedure for the preparation of coated and uncoated adsorbent powders is shown in Figure 1.
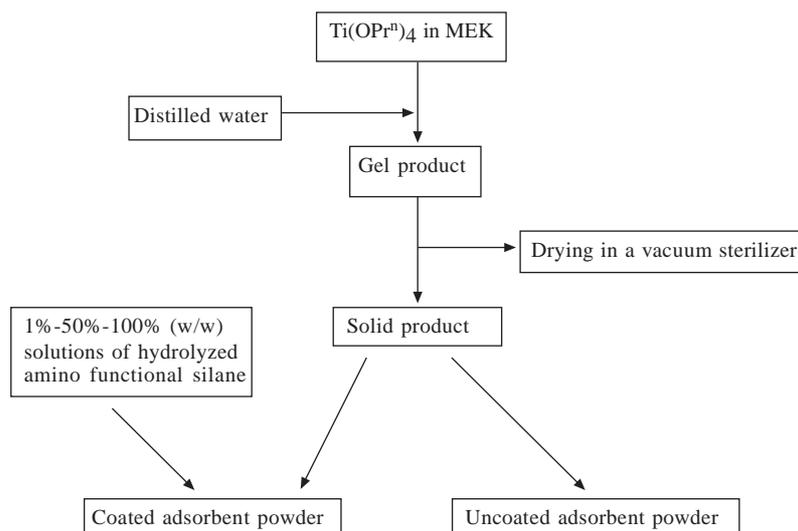
Figure 1. The procedure for the preparation of coated and uncoated adsorbent powders.

Adsorption experiments

Adsorption tests were performed by applying the batch technique at solution pH. Aqueous solutions of Fe^{3+}, Cu^{2+} and Pb^{2+} nitrates were prepared at concentrations of 11.8 mg/L, 4 mg/L and 7.5 mg/L, respectively. Then 15 mL of each solution were treated with 0.4 g of adsorbent (uncoated or coated) at room temperature. Stirring was performed magnetically and stirring time was 40 min, since it was determined that there was no significant change in the amount of adsorption after that time. After ordinary filtration, the filtrates were passed through 0.2 μm microfilters and the concentration of each metal ion in the supernatant was determined by FAAS. The effect of the initial concentration of Fe^{3+} was examined in the range 2.5-20 mg/L for 0.4 g of Amino-2 coated adsorbent at solution pH (pH 4) and room temperature for a 40 min contact time. According to preliminary studies, Fe^{3+} was adsorbed on Amino-2 coated adsorbent in the maximum

ratio. Therefore, the desorption of Fe^{3+} on the surface of Amino-2 coated adsorbent was examined. The adsorbent was treated with 3 N HNO_3 solution for 40 min. After filtration, the Fe^{3+} ion concentration in filtrate was measured. The regenerated adsorbent was dried in a vacuum sterilizer at 80-90 °C, and reused for adsorption of Fe^{3+}. The adsorption-desorption cycles were repeated 3 times using the same adsorbent.

Results and Discussion

Hydrolysis of $Ti(OPr^n)_4$

According to the Karl-Fischer titration results, for a complete hydrolysis of titanium(IV)-n-propoxide, 1.6 moles of water was required. This result was also confirmed by differential NIR-spectroscopy measurements, in which the area under the free H_2O peak (5212-5275 cm^{-1}) was calculated. According to the data from the Karl-Fischer titrations and NIR-spectroscopy, the hydrolysis reaction of $Ti(OPr^n)_4$ proceeds in the form

$$Ti(OPr^n)_4 + 1.6H_2O \longrightarrow Ti(OPr^n)_{2.4}(OH)_{1.6} + 1.6PrOH^n$$

where OPr^n is CH_3-CH_2-CH_2-O-

In order to find the extent of the condensation reaction after the hydrolysis reaction, the amount of total n-propanol formed must be measured. It was found by gas chromatography that the total amount of n-propanol formed in the reactions was 2.9 moles. The molar amount of water used for hydrolysis reaction is lower than the molar amount of the total liberated alcohol. This result clearly shows that alcohol condensation occurs between hydroxyl and propoxide groups that are bonded to Ti. The actual stoichiometry of the condensation reaction is

$$Ti(OPr^n)_{2.4}(OH)_{1.6} \longrightarrow Ti(OPr^n)_{1.1}(OH)_{0.3}(O)_{1.3} + 1.3PrOH^n$$

It is observed that the amount of alcohol in the condensation reaction is lower than that formed in the hydrolysis reaction. This behavior can be reasoned as follows: the amount of alcoholate bonded to the metal before hydrolysis is greater than that of the hydrolysis product. It is probable that the alcohol released on hydrolysis can form hydrogen bonds with the hydroxide group on the metal and this makes condensation difficult.

In the FT-IR spectrum of this hydrolysis-condensation product dried at 100 ^oC, the bands at 2975 and 2896 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 1372-1470 cm^{-1} spectral region. Ti-O and Ti(O-C) vibrations were observed at 970 and 1085 cm^{-1}, respectively. These vibrations show that a complete hydrolysis does not occur. Namely, the alkoxide groups bonded to the Ti atom are not fully removed by the hydroxyl groups of water. A broad band between 3110 and 3500 cm^{-1} corresponds to the O-H stretching mode of Ti-OH. An O-H bending vibration was observed at 1655 cm^{-1}.

In the FT-IR spectrum of powder calcinated at 900 °C, O-H and C-H stretching and bending vibrations were not observed. This result suggests that the calcinated powder of the hydrolyzed-condensated product is formed in a great amount as TiO_2. A Ti-O-Ti vibration was also observed at approximately 620 cm^{-1}. A broad band occurred between 1190 and 1375 cm^{-1}, corresponding to the Ti(O-C) vibration. The groups of Ti-O and Ti-O-C can form a connected network between TiO_2 particles.

Thermogravimetric analysis (TGA) of the gel powder dried at 100 °C showed weight losses in 2 steps. This product lost about 10% and 18.98% of its original weight at 200 °C and 405 °C, respectively. Thus,

the total weight loss was 28.98%, corresponding to 71.02% TiO$_2$ and 42.57% Ti. There was no significant weight change above 430 °C. In the elemental analysis of this product, the quantities of TiO$_2$ and Ti were 69.64% and 41.75%, respectively. The weight loss (8.58%) in the first stage corresponds to the elimination of physically adsorbed water or solvent. This weight loss was accompanied by an exothermic peak at around 275 °C in the differential thermal analysis (DTA) curve. The exothermic peak around 400-410 °C in the DTA curve with a weight loss of about 20.48% can be attributed to combustion of carboneous materials bonded to the Ti atom.

According to the thermogravimetric analysis, the maximum weight loss of calcinated gel powder was 1%. This result corresponds to 99% for TiO$_2$. The DTA shows one endothermic phenomenon at around 140 and 260 °C, which can be ascribed to the removal of water bonded to the Ti atom. In the DTA curves, the phase transitions of the hydrolysis-condensation product were examined. It was observed that the hydrolysis-condensation product is amorphous at room temperature and 300 °C. This amorphous structure transforms into anatase/brookite form during the calcination at around 300-600 °C. In the DTA curve, a small exothermic peak at 760 °C shows the phase transformation between anatase and rutile.
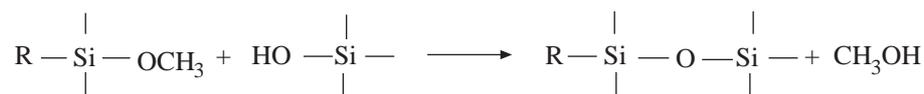
Hydrolysis of amino functional silanes

In the FT-IR spectrum of hydrolyzed Amino-2, the bands situated at 2940, 2897 and 2832 cm^{-1} correspond to –CH$_2$- and C-H stretching of aliphatic –CH$_2$ and CH$_3$ groups, respectively. A C-H bending vibration was observed at 1240 cm^{-1}. The bands at 764 and 800 cm^{-1} are assigned, respectively, to symetric and asymetric Si-O stretching vibrations. A band at 908 cm^{-1} corresponds to nonbridging Si-OH stretching. Si-(O-CH$_3$) stretching was observed at 1260 cm^{-1}. A broad band between 3130 and 3530 cm^{-1} corresponds to the O-H stretching mode. The O-H bending vibration was observed as a weak band close to 1670 cm^{-1}. A band at 1610 cm^{-1} is assigned -C-NH-C- bending vibration. A C-N vibration and N-H bending vibrations were observed at 1260 and 1190 cm^{-1}, respectively.

Preparation of Adsorbents

After coating the adsorbent surfaces with the prehydrolyzed amino functional silanes, the powders were dried in a vacuum sterilizer for 90 min at 120 °C. Thus, the prehydrolyzed amino functional silanes were transferred to an adsorbent surface as a coating by curing at 120 °C. During this procedure, siloxane bonds are formed by the condensation of hydroxyl groups as well as methoxy groups, as shown in the following:

$$R-\underset{|}{\overset{|}{Si}}-OH \ + \ HO-\underset{|}{\overset{|}{Si}}- \ \longrightarrow \ R-\underset{|}{\overset{|}{Si}}-O-\underset{|}{\overset{|}{Si}}- \ + \ H_2O$$

and/or

$$R-\underset{|}{\overset{|}{Si}}-OCH_3 \ + \ HO-\underset{|}{\overset{|}{Si}}- \ \longrightarrow \ R-\underset{|}{\overset{|}{Si}}-O-\underset{|}{\overset{|}{Si}}- \ + \ CH_3OH$$

FT-IR measurements were also performed to find out whether the surface of the adsorbent was coated or not. In the FT-IR spectra of adsorbent powder calcinated at 900 °C coated with prehydrolyzed Amino-2 silane (50% , w/w), a broad band between 3200 and 3490 cm^{-1} corresponding to the O-H stretching mode

was not observed. The bands at 2932, 2874 and 2818 cm^{-1} correspond to the –CH$_2$- and C-H stretching of aliphatic –CH$_2$ and CH$_3$ groups, respectively. The bands at 760 and 798 cm^{-1} are assigned, respectively, to symmetrical and asymmetrical Si-O stretching vibrations. A band at 918 cm^{-1} corresponds to nonbridging Si-OH stretching. Si-(O-CH$_3$) stretching was observed at 1261 cm^{-1}. The O-H bending vibration was observed as a weak band close to 1662 cm^{-1}. A band at 1608 cm^{-1} is assigned to -C-NH-C- bending vibration. A C-N vibration and N-H bending vibration were observed in the1190 and 1105 cm^{-1} spectral regions, respectively. These results showed that the surface of TiO$_2$ based adsorbent powder was coated with the prehydrolyzed Amino-2. The hydrogen bonds occurred by the interaction between the hydroxyl groups of Amino-2 silane and the oxygen atom of TiO$_2$. The bonding reaction between the TiO$_2$ surface and the coating material may be suggested as shown in Figure 2.
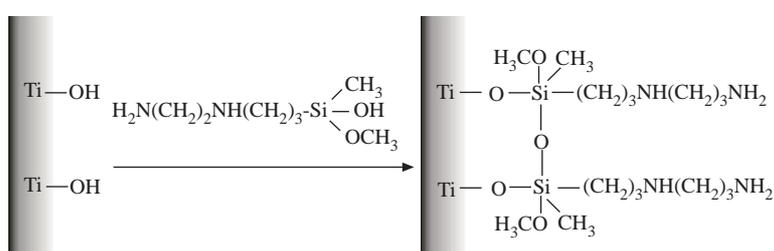
Figure 2. The bonding reaction between TiO$_2$ surface and the coating material.

The adsorbent powder coated with prehydrolyzed Amino-2 (50%, w/w) was distrupted untill 430 °C. According to the TG, the weight loss of this adsorbent was 3.84%, corresponding to 96.26% for TiO$_2$. In the DTA of this adsorbent, the endothermic peaks at 229 °C and 409 °C can be ascribed to the removal and combustion of water and organic groups. The phase transitions of this adsorbent were also examined from the DTA curves. In the DTA curves, 2 exothermic peaks at 496 and 569 °C show the phase transformation from the amorphous to anatase form.

Adsorption experiments

After adsorbing the Fe^{3+} (and Pb^{2+}) ion on the surface of Amino-2 silane (50%, w/w) coated adsorbent, adsorbent powder was filtered and dried in a vacuum sterilizer for 60 min at 80 °C and then FT-IR measurements were performed to find out whether the metal ion was adsorbed on the surface of coated adsorbent. In the FT-IR spectrum of this adsorbent, nearly all bands (vibration or bending) were observed as very small and weak bands compared to the spectrum of adsorbent powder calcinated at 900 °C and coated with prehydrolyzed Amino-2 silane. In the FT-IR spectra of this adsorbent, the very small and weak bands situated at 2942, 2939 and 2823 cm^{-1} correspond to –CH$_2$- and C-H stretching of aliphatic –CH$_2$ and CH$_3$ groups, respectively. A C-H bending vibration was observed as a fairly small band at 1220 cm^{-1}. The very weak bands at 763 and 816 cm^{-1} are assigned, respectively, to symmetrical and asymmetrical Si-O stretching vibrations. The bands 919 and 1260 cm^{-1} correspond to nonbridging Si-OH and Si-(O-CH$_3$) stretching. The O-H bending vibration was observed as a broad band close to 1660 cm^{-1}. The fairly small band at 1610 cm^{-1} is assigned to a -C-NH-C- bending vibration. The small bands observed in the 1099 and 1135 cm^{-1} spectral regions correspond to the C-N vibration and N-H bending vibrations, respectively. According to these results, the N atoms of surface coating material act as an electron pair donor and the

metal atom acts as an electron pair acceptor. N and metal atoms bond together by sharing the electron pair supplied by the N atom, which has base properties because of the unpaired electrons.

BET surface areas, micropore volumes and the percentages of metal ion adsorption by coated and uncoated adsorbents are shown in Table 1.

Table 1. Some surface characteristics and percentages of metal ions* adsorption results of uncoated and coated adsorbents.

	Cu^{2+}	Fe^{3+}	Pb^{2+}	Sa	Vm
Uncoated adsorbent	4	5	4.5	183.04	0.145
Amino-1 coated adsorbent					
a	22.50	12.71	21.00	140.99	0.144
b	15.00	90.67	98.30	4.63	0.133
c	2.50	100.00	98.30	1.96	0.090
Amino-2 coated adsorbent					
a	25.00	23.71	38.60	170.81	0.101
b	40.00	100.00	84.21	16.36	0.088
c	55.00	100.00	87.71	1.73	0.080

Sa-BET surface area, m^2/g; Vm-micropore volume, mL/g.
*Start concentrations of metal ions solutions are 4 mg/L; 11.8 mg/L and 5.7 mg/L, respectively.
a: 1% (w/w) solution of Amino-1 (and Amino-2) functional silane in methanol.
b: 50% (w/w) solution of Amino-1 (and Amino-2) functional silane in methanol.
c: 100% (w/w) solution of Amino-1 (and Amino-2) functional silane in methanol.

Both the BET surface area and micropore volume of the treated adsorbents were reduced significantly as the coating materials concentrations increased. This is due to the coating materials settling into/onto the pores and surfaces of the adsorbents. The difference in these characteristics is not significantly increased between uncoated adsorbent and adsorbent coated with the lower concentration (1%, w/w) of the coating material. However, the amount of adsorbate is very significantly different. Although the surface areas of coated adsorbents are smaller than those of uncoated adsorbents, metal ions, especially Fe^{3+} and Pb^{2+}, can be adsorbed by coated adsorbents more tightly because the functional group of the coating material is strongly metallophilic, which has hard acid properties. Thus, these types of adsorbents are potential adsorbers of heavy metal pollutants. It is well known that the adsorption capacities of adsorbents are influenced by the surface area and total pore diameter of the adsorbent, and adsorbate size and acidity, the type and concentration of the coating material, and the hard or soft acid/base properties of functional groups and metal ions. Table 1 shows that the adsorption of Cu^{2+}, Fe^{3+} and Pb^{2+} ions on the surface of the different adsorbents is different. For example, while Fe^{3+} and Pb^{2+} ions are adsorbed on the coated adsorbent surface at the maximum ratio, the Cu^{2+} ion is adsorbed at a lower ratio. It is seen that the functional groups on the surfaces of the adsorbents are available for interaction with heavy metal ions. A strong dipol-dipol interaction between the functional group and metal ion is important. The classification of the acid properties of metal ions used in our experiments should be written as follows:

Fe^{3+} is hard acid, Pb^{2+} is borderline acid, and Cu^{2+} is soft acid.

It is known that the R-NH$_2$ group is hard base and the Fe^{3+} ion is hard acid. Therefore, the superior adsorption of the Fe^{3+} ion on NH$_2$-coated adsorbent is not surprising since this ion has the same properties as the NH$_2$ group used as base. The Cu^{2+} ion was generally adsorbed at the minimum ratio by the amino

functional silane coated adsorbent surface because of a soft acid-hard base weak interaction. Cu^{2+} adsorption was decreased by the increase in the ratio of coating from 1% to 100% with Amino-1, while the adsorption of Cu^{2+} increased with an increase in the ratio of coating with Amino-2. This behavior can be reasoned as follows: Amino-1 contains more amino groups ($-NH_2$ or $-NH-$) than Amino-2. Furthermore, Amino-2 has more alkyl groups than Amino-1 not bonded to amino groups. The alkyl group is a soft base. Thus, Amino-2 is a softer base than Amino-1, which makes the interaction of Cu^{2+} with Amino-2 stronger.

Isotherm studies were performed with a constant amount of Amino-2 coated adsorbent and varying initial concentrations of Fe^{3+} in the range 2.5-20 mg/L, at room temperature and pH 4. The amount of adsorption was calculated using the formula based on the difference in Fe^{3+} concentration in aqueous solution before and after the adsorption process, according to

$$q_e = \frac{(C_o - C_e)V}{W} \tag{1}$$

where q_e is the adsorption capacity or amount of Fe^{3+} adsorbed on the unit amount of adsorbent (mg/g), C_o is the initial Fe^{3+} concentration (mg/L), C_e is the final or equilibrium Fe^{3+} concentration (mg/L), V is the volume of the solution (L) and W is the weight of the adsorbent added to the adsorption medium.

The adsorption of Fe^{3+} on Amino-2 coated adsorbent was systematically studied by investigating the constant parameters as described above and different initial concentrations of Fe^{3+} to optimize the adsorption isotherm test. Depending on the initial concentrations, the percentages of adsorption of Fe^{3+} for Amino-2 coated adsorbent are presented in Figure 3.
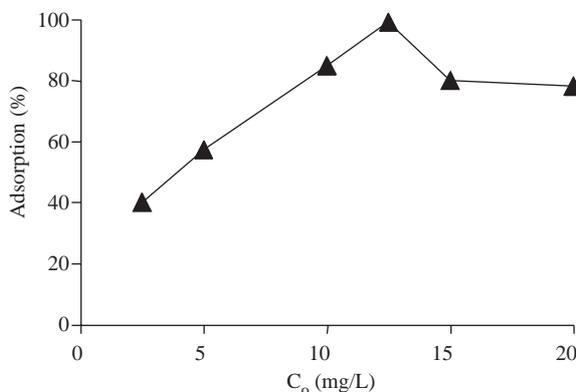

Figure 3. The effect of initial concentration on the adsorption percentages of Fe^{3+}.

The adsorption isotherm deals with the equilibrium of the metal ions between the aqueous solution and the solid phase. An equilibrium study was performed with different initial concentrations of Fe^{3+}. Other parameters such as pH, contact time, temperature and amount of adsorbent were kept constant. To arrive at the adsorption capacity at the adsorbent surface, the equilibrium adsorption isotherm data were analyzed using the Freundlich isotherm. This isotherm is given by the equation[20]

$$\ln q_e = \ln K_F + a \ln C_e \tag{2}$$

where q_e is the amount of Fe^{3+} adsorbed per unit weight of adsorbent (mg/g), C_e is the final or equilibrium Fe^{3+} (mg/L), a is the Freundlich constant and K_F is the adsorption coefficient. The values of the Freundlich

constants K_F and a were calculated from the intercept, and the slope of the linear plots of lnq_e versus $lnCe$, prepared using the values of q_e and C_e, obtained from the experimental adsorption data determined in solutions of different initial Fe^{3+} concentrations in solution using constant parameters is given in Figure 4
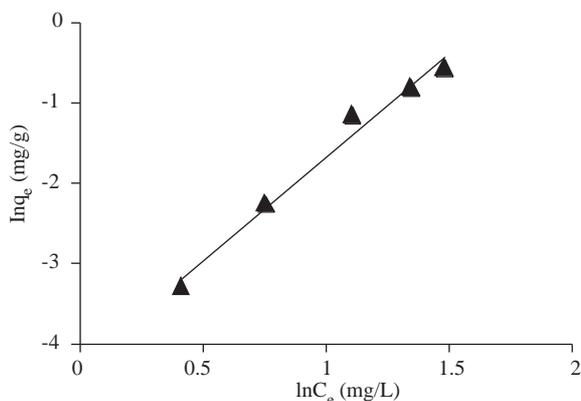
Figure 4. Freundlich isotherm for adsorption of Fe^{3+} on Amino-2 coated adsorbent.

The Freundlich constants K_F and a and correlation coefficient (r^2) for Fe^{3+} are presented in Table 2.

Table 2. Freundlich constants and correlation coefficient for the adsorption of Fe^{3+} on Amino-2 coated adsorbent.

Adsorbed	K_F	a	r^2
Fe^{3+}	0.0147	2.58	0.9825

The Freundlich constant a is a measure of the deviation from the adsorption linearity. If a is equal to unity the adsorption is proved to be linear, which means that adsorption sites are homogeneous or these sites of the adsorbent are not in limiting quantity and are not modified by the adsorption process itself. If a is less than unity, it implies that increased adsorption modifies the adsorbent, giving rise to increases in adsorption capacity, such as forming new adsorption sites on the adsorbent surface. If a is greater than unity the adsorption bond becomes weak, and the q_e changes significantly with small changes in C_e. It is clear that physical adsorption occurs between the Fe^{3+} ion and the adsorbent surface, which results in a high adsorption capacity for the adsorbent.

Table 3 gives the adsorption and desorption values of Fe^{3+} after 3 cycles. Fe^{3+} adsorption on the regenerated adsorbent is decreased after desorbing cycles. Nevertheless, a relatively high amount of metal ion was adsorbed.

Table 3. The adsorption results for Fe^{3+} before and after regeneration.

Adsorption of Fe^{3+} (before desorption) (%)	Desorption of Fe^{3+} (after first cycle) (%)	Adsorption of Fe^{3+} (after first desorption) (%)	Desorption of Fe^{3+} (after second cycle) (%)	Adsorption of Fe^{3+} (after second desorption) (%)	Desorption of Fe^{3+} (after thirst cycle) (%)	Adsorption of Fe^{3+} (after thirst desorption) (%)
100	92	87	84	80	78	72

Conclusion

In this work the following were achieved:

a) The adsorption of heavy metal ions by coated and uncoated adsorbents was investigated. $Ti(OPr^n)_4$ was converted into a new adsorbent by hydrolysis-condensation with various quantities of water and without catalyst.

b) From the hydrolysis-condensation product of this alkoxide, adsorbents were prepared and tested for some heavy metal ions, which are well known contaminants in a wide variety of industrial wastewaters.

c) On the basis of the data, it is concluded that adsorbents prepared by the sol-gel process can be used to remove heavy metal ions from industrial wastewater efficiently. The method for preparing these adsorbents is simple, economical and fast and can be carried out at room temperature.

d) This work has also demonstrated that the adsorptive properties of the adsorbent could be improved by coating their surfaces. Although the surface areas of coated adsorbents are smaller than those of unmodified adsorbents, metal ions, especially Fe^{3+} and Pb^{2+}, can be adsorbed by coated adsorbents more strongly because the functional group of the coating material is strongly metallophilic due to its hard acid character.

e) Adsorption was strongly dependent on the initial concentration of solution. Generally, the capacity increased with increases in the initial concentrations of metal ions.

f) The Freundlich constant, a, was 2.58 for Fe^{3+}. It is observed that a is greater than unity. This shows that the adsorption bond becomes weak, and the q_e changes significantly with small changes in C_e. After the adsorption of Fe^{3+}, the adsorbent can be regenerated and reused.

g) Furthermore, the applicability of our adsorbents to the purification field brings an originality to our work.

References

1. M. Kumar, D.P.S. Rathore and A.K. Sing, **Talanta, 51**, 1187 (2000).

2. R.A. Gayer, "**Toxic Effect of Metals. Casaret and Doulls Toxicology, the Basic Science of Poisons**" 4th ed. Amdur, Douwl, Klaasen, Eds. Pergamon Press, New York, 1991.

3. V.K.Gupta, M. Gupta and S. Shanna, **Wat. Res. 35**, 1125 (2001).

4. S.H. Lin and R.S. Juang, **J. Hazard. Mater. B92,** 315 (2002).

5. H. Sayılkan and B. Çetinkaya, **Chim. Acta Turc. 19,** 257 (1991).

6. P.A. Brown, S.A. Gill and S.J. Allen, **Wat. Res. 34 (16),** 3907 (2000).

7. T. Vaughan, C.W. Seo and W.E. Marshall, **Bioresource Technol. 78,** 133 (2001).

8. E. Salinas, M. Elarzo de Orellano, I. Rezza, L. Martinez, E. Marchesvky and M. Sanz de Tosetti, **Bioresource Technol. 72,** 107 (2000).

9. W.E. Marshall, L.H. Wartelle, D.E. Boler, M.M. Johns and C.A. Toles, **Bioresource   Technol. 69,** 263 (1999).

10. H. Sayılkan, Ş. Şener, E. Şener and E. Arpaç, **J. Mater. Sci. 34,** 5325 (1999).

11. H. Sayılkan, E. Ekinci and E. Arpaç, **Turk. J. Chem. 17,** 196 (1993).

12. J. Gallardo, P. Galliano, R. Moreno and A. Duran, **J. Sol-gel Sci. Technol. 19,** 107 (2000).

13. K. Velez, J.F. Quinson and B. Fenet, **J. Sol-gel Sci. Technol. 16,** 201 (1999).

14. B. Tryba, A.W. Morawsky and M. Inagaki, **Appl. Catalysis B. Env. 1274,** 1 (2002).

15. I. Ilisz, A. Dombi, K. Mogroyosi, A. Farkas and I. Dekani, **Appl. Catalysis B. Env. 39,** 247 (2002).

16. W. Xiaohong, J. Zhaohua, L. Huiling, L. Xuandong and H. Xinguo, **Mater. Chem. Phys. 9722,** 1 (2002).

17. R.S. Sonawane, S.G. Hedge and M.K. Dongare, **Mater. Chem. Phys. 77,** 744 (2002).

18. Z. Sun, Y. Chen, Q. Ke, Y. Yang and J.Yuan, **J. Photochem. Photobiology A: Chem. 149,** 169 (2002).

19. E.P. Barret, L.G. Joyner and P.P. Halenda, **J. Am. Chem. Soc. 73,** 373 (1951).

20. F.A. Banat, B. Al-Bashir, S. Al-Asheh and O. Hayajneh, **Environ. Pollut. 107,** 391 (2000).