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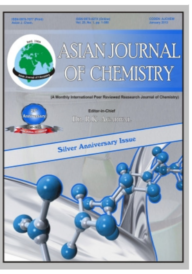

Preparation of Nano-Strontium Titanate Based on Glass Fiber Filter and Its Application in Speciation Analysis for Chromium

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Nano-strontium titanate based on glass fiber filter was successfully prepared by sol-gel method and characterized using XRD and SEM. Its application in speciation of Cr(III) and Cr(VI) from water was studied. Adsorption and elution were investigated under different conditions. The results showed that the nano-strontium titanate could crystal based on glass fiber, gaining a new block adsorbent like a leaf. At normal temperature, the adsorbent had strong adsorption capacity for Cr(III) and Cr(VI) in water, but two forms of chromium show different adsorption capacities at different pH values, that is, Cr (III) selectively retained at pH 7-14, but Cr(VI) can't be adsorbed. Whereas Cr(VI) retained at pH 1-3, but Cr(III) can't be adsorbed. Hence complete separation of the two forms of chromium is possible. Retained Cr(III) and Cr(VI) were eluted with 1 mol/L HCl and 2 mol/L NaOH, respectively. Based on these, a simple and sensitive method for the speciation, separation and preconcentration of Cr(VI) and Cr(III) in environmental water was developed. The method was applied for the speciation of chromium in environmental water samples and measured by atomic absorption spectroscopy.

Key Words: Nano-strontium titanate, Glass fiber filter, Speciation analysis, Chromium, Separation, Preconcentration.

INTRODUCTION

In recent years, the field of nano-materials has had the attention, imagination and close scrutiny of scientists and engineers[1]. One of its most interesting properties is that most of the atoms are on the surface of the nanoparticle. The unsaturated surface atoms can bind with other atoms that possess strong chemical activity and produce high adsorption capacity. Vassileva *et al.*[2,3] investigated the surface chemistry of high surface area oxides, *e.g.*, TiO_2, CeO_2 and ZnO and found that these materials have a very high adsorption capacity towards metal ions and give promising results when used for trace elements preconcentration and analyses. Studies have only recently used nano-barium strontium titanate and nano-calcium titanate powders in the adsorption of heavy metals in water[4-9] and the results indicated that nano-barium strontium titanate and nano-calcium titanate powders have higher adsorption capacity, but the nano- strontium titanate has not been studied. However, the nano-particles are so small that, when used in adsorption of metal ions, it was easy to coacervate and lose activity and are difficult to recover. Fixing nanometer powder onto different substrates corrects these problems[10-13]. Strontium titanate based on glass fiber filter has not been studied.

It is well known that the chromium metal and its compound are widely used in anodizing operation in the surface industry, chrome plating, leather tanning and various other industrial applications[14]. Chromium exists in the environment as chromium(III) and chromium(VI) oxidation states. The physiological effects of chromium on the biological system depend upon its oxidation state. Cr(III) may be considered as an essential trace element for the proper functioning of living organisms, on the contrary Cr(VI) can be toxic and has an adverse impact on the liver, lung and kidney[15]. For this reason, precise and accurate determination of both species in environmental samples is essential. The methods for determination and speciation of chromium(III) and chromium(VI) species mainly selective techniques are solid phase extraction followed by instrumental analysis[16,17]. In this work, a new method using strontium titanate based on glass fiber filter as sorbent has been developed for the separation and preconcentration of Cr(III) and Cr(VI) in water.

EXPERIMENTAL

X-ray diffraction on the sorbents were performed using an X' Pert Pro X-ray diffractometer (PANalytical B.V., Netherlands) and images of the glass fiber filter and strontium titanate based on glass fiber filter (GFST) were taken using an S-3400N scanning electronic microscope (Hitachi Japan). The parameters for all machines were adjusted according to the manufacturer's recommendations.

TABLE-1
FAAS OPERATING CONDITIONS

Element	Wave length (nm)	Spectral band width (nm)	Lamp current (mA)	Burner height (mm)	Acetylene gas consumption (mL/min)	Air consumption (mL/min)
Chromium	391.1	0.4	12	5.0	1250	5000

The concentration of chromium was determined using a WYX-9003A atomic absorption spectrometer (Shenyang Yi Tong Analytical Instrument Co. Ltd.), equipped with hollow cathode lamps for chromium and the operating conditions were summarized in Table-1.

The pH values were measured with a PHS-3C acidometer (Shanghai REX Instrument Factory, Shanghai, China) supplied with a combined electrode. The reagents, $Sr(NO_3)_2$ and citric acid, were analytical grade. Tetrabutyl titanate was chemically pure. Glass fiber filter was special for determination of TSP/IP by gravimetric method in environmental monitoring (Shi Jia Zhuang Lage Sci and Development Co. Ltd.).

The reagents, $Cr(NO_3)_3$ was guarantee reagent, HCl and NaOH was Analytical reagent, $K_2Cr_2O_7$ was primary reagent. Stock standard solutions of Cr(III) and Cr(VI) were prepared by dissolving appropriate amount of $Cr(NO_3)_3$ in 0.5 mol/L HCl and $K_2Cr_2O_7$ in distilled water. The water in this study was distilled water.

Preparation of the nano-strontium titanate based on glass fiber filter (GFST): Strontium titanate sol was synthesized by the citrate precursor method. For the preparation of the precursor solution, strontium nitrate, tetrabutyl titanate, citrate acid and ethylene glycol-1500 (EG-1500) were used as starting materials. First, a specific amount of tetrabutyl titanate was dissolved into ethanol. The mixture was stirred until it became transparent and yellow. Subsequently, citric acid were direct added to this solution on a magnetic stirrer and a clear solution was obtained. Then, strontium nitrate and EG-1500 solutions were added to this solution. The mixture was stirred continuously until it became a clear solution, pale brown in colour. Then, ammonium hydroxide solution was added to the precursor solution to adjust the pH value of 3.

The glass fiber filter calcined at 500 ºC for 1 h and was cooled to room temperature in a desiccator. It was immersed in the prepared strontium titanate sol for 15 min and then taken out and put in drying oven for drying at 105 ºC. This process was repeated three times. The dried glass fiber filter was burned at 500 ºC for 6 h under air atmosphere. Subsequently, it was cooled to room temperature in a desiccator. Nano-strontium titanate based on glass fiber filter (GFST) was immersed in 1 mol/L HNO_3 for 20 min. After washing to neutral with water, it was dried at 105 ºC and stored in a desiccator.

General separation and preconcentration procedure: A specific amount of Cr(III) and/or Cr(VI) solution were placed into 150 mL calibrated mark Erlenmeyer flasks with plug. Solutions were adjusted to a pH 13 in the case of preconcentration of Cr(III) in the mark Erlenmeyer flask 1 and to pH 1 in the case of preconcentration of Cr(VI) in the mark Erlenmeyer flask 2. The preconcentration of investigated species was then performed simultaneously. After dilution to the mark of 50 with water, 0.1 g of GFST was added. Covered with a plug, shaken for 10 min in a bath shaker (200 r/min). Then the supernatant fluid was poured out. Retained Cr(III) and Cr(VI) were desorbed with 5 mL of 1 mol/L HCl and 2 mol/L NaOH, respectively. Eluted samples were analyzed with flame atomic absorption spectrometry, the adsorption and preconcentration capacity was calculated.

RESULTS AND DISCUSSION

The X-ray diffraction patterns for glass fiber filter and GFST are shown in Fig. 1. It can be seen that the glass fiber filter was noncrystal (line 1), the sharps on the line 2 at 32.44, 39.98, 46.52, 57.82 and 67.84 can be attributed to strontium titanate. It can be concluded that strontium titanate loaded on the glass fiber filter had a perovskite structure. According the Scherrer equation, the average particle diameter of strontium titanate loaded on the glass fiber filter can be calculated[4] and about 24 nm.

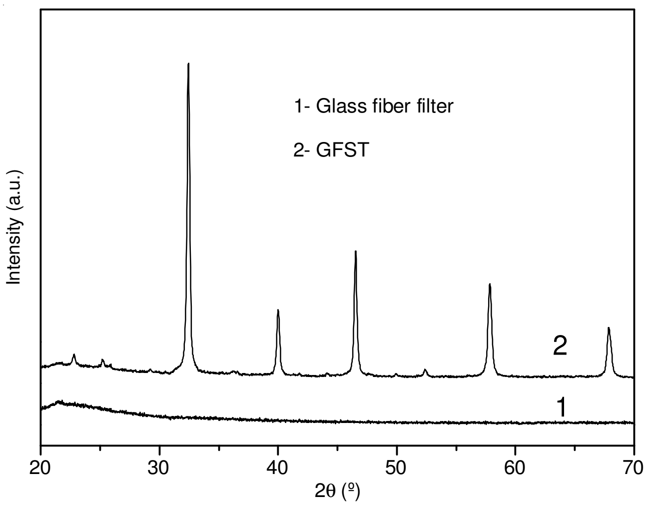

Fig. 1. XRD patterns of glass fiber filter and GFST

The SEM images of the glass fiber filter and GFST are shown in Fig. 2. The SEM images confirm that strontium titanate is shown on the surface of glass fiber. The strontium titanate could crystal based on glass fiber, gaining a new block adsorbent like a leaf.

Influence of pH on adsorption of Cr(III) and Cr(VI): Differences between sorption capacities of Cr(III) and Cr(VI) on the GFST surface provide the main reason for their selective preconcentration on the surface. Results concerning the effect of pH on the adsorption are presented in Fig. 3 and it is apparent that pH > 7 is appropriate for the adsorption of Cr(III) on GFST. The quantitative recovery of Cr(VI) is obtained at pH values ≤ 3. Depending on the pH, GFST can then selectively adsorb Cr(III) or Cr(VI), this makes GFST a very promising solid phase extractant in the separation of Cr(III) and Cr(VI).

Effect of contact time: At room temperature, the adsorption capacities for Cr(III) and Cr(VI) were determined with different shaking times (Fig. 4). The results indicate that the adsorption capacity increased with an increase in shaking time

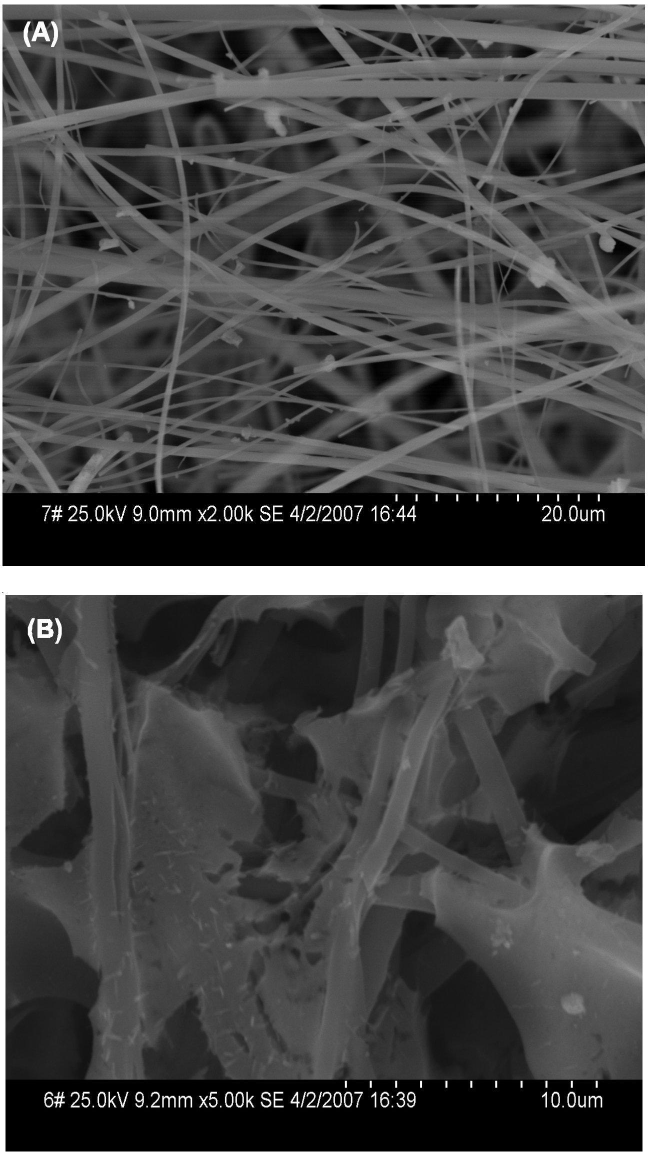

Fig. 2. (A) SEM images of glass fiber filter; (B) SEM images of GFST

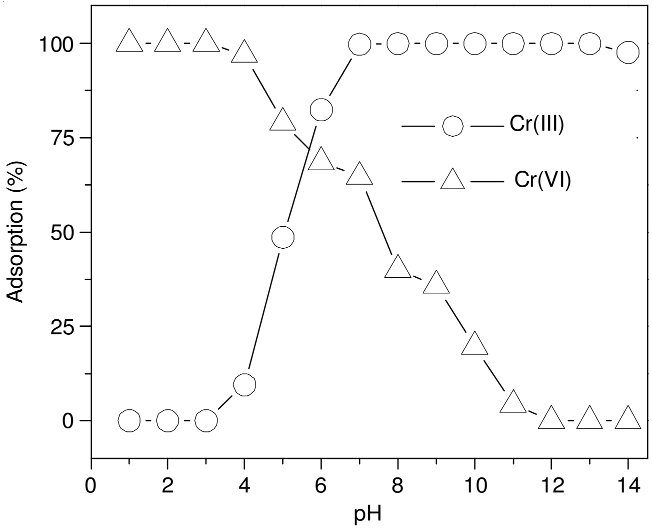

Fig. 3. Effect of pH on the adsorption

and reached equilibrium at 10 min. Therefore, the shaking time was 10 min in this study.

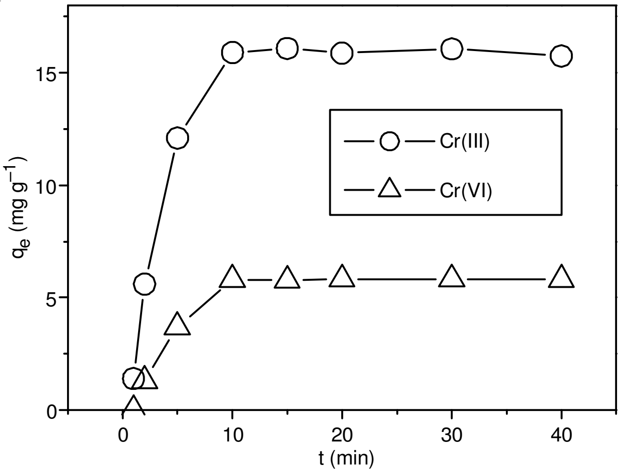

Fig. 4. Effect of contact time on adsorption

Adsorption capacity: According to Fig. 4, at room temperature, the static adsorption capacities of GFST to Cr(III) and Cr(VI) were 16.08 mg/g and 5.86 mg/g, respectively.

Elution conditions: Fig. 3 shows that the adsorption of Cr(III) at pH = 3 and Cr(VI) at pH = 12, could be negligible. So, after the Cr(III) and Cr(VI) were adsorbed under the optimized adsorption conditions. Elution of Cr(III) and Cr(VI) from GFST surface, by HCl and NaOH, respectively, at different concentrations and volumes was investigated. Recovery was quantitative (> 95 %) with 5 mL 1 mol/L HCl and 2 mol/L NaOH for Cr(III) and Cr(VI), respectively.

After elution, the GFST was dried and reused 10 times. Its adsorption performance did not decrease, indicating that this adsorption agent was very stable.

Effect of coexisting ions: The influences of possible matrix ions in the environmental samples and some transition metals were also examined. So various interfering ions were added into 50 mL volumetric flask containing 0.25 μg of Cr(VI) and Cr(III). The recovery of heavy metal ions were determined according to experimental method with the error controlled within ± 5 %. The results showed that in the presence of 1000 mg/L Na^+, K^+, NO_3^-; 500 mg/L Mg^{2+}, Ca^{2+}, Mn(VII), SO_4^{2-}; 200 mg/L Mn(II), Zn^{2+}, 50 mg/L Al^{3+}, Pb^{2+}, Cd^{2+},Cu^{2+}, Co^{2+} and Fe^{3+}. The recoveries of the Cr(VI) and Cr(III) were still above 95 %. It can be seen that the presence of major ions had no obvious influence on the recovery under the selected conditions.

Application to the real samples: The proposed method was applied to the separation, preconcentration and determination of Cr(III) and Cr(VI) in a natural river water sample (Hun-he river, Shenyang, China) and a lake water sample (Nan-hu lake, Shenyang, China) and a tap water sample collected from the water supply of Shenyang city. The river water and lake water samples were filtered through a 0.22 μm membrane filter and analyzed immediately. The analytical results and the associated recovery are given in Table-2. The recoveries were 95.0-101.0 % for Cr(III) and 94.0-98.5 % for Cr(VI), which are excellent for trace analysis.

Conclusion

Nano-strontium titanate based on glass fiber filter (GFST) was successfully prepared and the new block adsorbent like a leaf was used for separation and preconcentration of Cr(III)

TABLE-2
RESULTS FOR THE DETERMINATION OF Cr(III) AND Cr(VI) IN THE WATER SAMPLES

Samples	Found (mg/L)		Added (mg/L)		Recovered (mg/L)		Recovery percentage (%)	
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)
Tap water	0.0126	0	0.0100	0.0100	0.0222	0.0094	96.0	94.0
		0	0.0200	0.0200	0.0328	0.0189	101.0	94.5
		0	0.0500	0.0500	0.0604	0.0482	95.6	96.4
River water	0.0235	0.0115	0.0100	0.0100	0.0330	0.0210	95.0	95.0
		0.0115	0.0200	0.0200	0.0431	0.0312	98.0	98.5
		0.0115	0.0500	0.0500	0.0717	0.0604	96.4	97.8
Lake water	0.1743	0.0213	0.1000	0.0100	0.2732	0.0309	98.9	96.0
		0.0213	0.2000	0.0200	0.3681	0.0406	96.9	96.5
		0.0213	0.5000	0.0500	0.6716	0.0691	99.46	95.6

and Cr(VI). Two forms of chromium showed different exchange capacities at different pH values, *viz.* Cr (III) selectively retained at pH 7-14, whereas Cr (VI) retained at pH 1-3. Hence complete separation of the two forms of chromium was possible. Retained species were eluted with 5mL of 1 mol/L HCl and 2 mol/L NaOH. The method has been applied to the preconcentration and separation for flame atomic absorption spectrometric determinations of Cr(III) and Cr(VI) in surface water and tap water samples with satisfied results.

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