Study on the adsorption behavior of Co(II), Pb(II) on modified sodium trititanate whisker and its application to wastewater

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Abstract—The modification of sodium trititanate whisker surface was performed by means of impregnation procedure to fabricate the modified sodium trititanate whisker, which was characterized by scanning electron microscopy(SEM) and infrared spectroscopy(IR). Its adsorptive performance for Co(II), Pb(II) in a static system was investigated by inductively coupled plasma atomic emission spectrometry(ICP-AES). The main factors affecting adsorption and desorption of Co(II), Pb(II), the adsorptive capacity of Co(II), Pb(II) in optimal condition and adsorption isotherm and the influence of coexistent ions were examined. The comparative test for selectivity was done. The adsorptive rate for Co(II) and Pb(II) on 0.2500 g of modified sodium trititanate whisker at PH 5.0 was the best. Co(II), Pb(II) adsorbed on the modified sodium trititanate whisker could be eluted with 10 mL of 3.0 mol/L HCl. The adsorptive performance of modified sodium trititanate whisker was better than that of unmodified sodium trititanate whisker. The sorbent has been applied to the enrichment and separation of Co(II), Pb(II) in water sample to determine Co(II), Pb(II).

Keywords—modified sodium trititanate whisker; inductively coupled plasma atomic emission spectrometry(ICP-AES); Co(II), Pb(II); adsorption

I. INTRODUCTION

Lead and cobalt ions are used widely in modern industrial production and can cause much toxicity to organisms, which are one of heavy metal elements that cause environmental pollution. Excessive lead ions entering human body can cause acute poisonous symptoms and affect the nerve system and digestive system, and cause anemia[1]. As the content of lead and cobalt ions in natural waters is normally at the low level, and thus ICP-AES technique is not capable of detecting them in water. As a result, pre-concentration and separation are required. In recent years, the methods widely used to determine micro and trace amount lead components are mainly involved in: ion exchange[2], solid-phase micro extraction [3], solid-phase extraction [4-5] and so on. Attention has been paid to solid-phase extraction in the sense that it operates simply and the speed of analysis is fast, concentration multiple is high, it can unify many kinds of different examinations methods.

Sodium trititanate whisker with larger specific surface area, is fascinating new enrichment material, in the sense that it has special laminated structure[6-7]. The inter laminar space is rather large, Most important, there are plenty of Na+ ions which are prone to be exchanged by heavy metal ions. But the adsorptivity and selectivity of sodium trititanate whisker for molybdenum ions are not very satisfactory, thus its surface needs modifying.

In this paper, modified sodium trititanate whisker was prepared by using impregnation method. The adsorption properties of the sorbent to Co(II), Pb(II) in static system, main factors of having an effect on adsorption and desorption, adsorption isotherms and influence of common existence ions on the determination of Co(II), Pb(II) were investigated by ICP-AES. The selection experiment of the sorbent was also done. It had been applied to the determination of Co(II), Pb(II) in environmental water samples.

II. EXPERIMENTAL

A. Main apparatus

A VISTA MPS inductively coupled plasma atomic emission spectrometer (purchased from Varian, Inc, USA) was used for the determination of the studied ions. The pH values were measured with the PHS-3C Precision pH/mV Meter (Shanghai LIDA Instrument Factory, Shanghai, China) supplied with a combined electrode.

The main operation conditions of ICP-AES: Incident power, 1.00 kW; Carrier gas (Ar) flow rate, 15.0 L/min; Auxiliary gas (Ar) flow rate, 1.50 L/min; Atomization gas, 200 kPa; Pump-velocity, 15 r/min; Wavelength, Mo 202.032 nm.

B. Main reagents

Standard stock solution of Co(II) (1.0 g/L) was prepared by dissolving Co(NO3)2·6H2O of analytical purity in nitric acid(1+49), and diluting the solution to 250 mL with nitric acid(1+49); Standard stock solution of Pb(II) (1.0 g/L) was prepared by dissolving Pb(NO3)2 of analytical purity in nitric acid(1+49), and diluting the solution to 250 mL with nitric acid(1+49); Standard working solutions of Co(II) and Pb(II) were prepared by appropriate dilution with nitric acid(1+49) from the stock solution of Co(II) and Pb(II), immediately prior using, and the concentrations were as follows: 0.5, 1.0, 3.0, 5.0, 8.0, 10.0, 12.0 mg/L. The foreign ions solutions (1.0 g/L) were prepared by conventional methods; Sodium trititanate whisker (<200 mesh) was purchased from Shanghai Jingxu Composite manufacturing co., LTD.

Analytical grade chemical reagents were used throughout as well as doubly distilled water.
C. Experimental method

1) Preparation of modified sodium trititanate whisker

Activated: Prior to use, the material was dispersed in 3.0 mol/L of HNO₃ being further marinated for 24 h at room temperature. Afterwards, the material was washed with water until remove the excessive acid, then filtrated and dried at 105 °C, wetted and then sifted out by 100 sifters.

Modified: The modified sodium trititanate whisker was prepared by using impregnation method in 0.01 and 0.05 mol/L of ethanol solution of 8-hydroxyquinoline for 24 and 48 h, respectively, and then washed with water until remove the excessive acid, filtrated and dried at 50~60 °C, wetted and stored until use.

2) Adsorption experiment

A portion of sample solution containing the investigated ions was transferred to a 50 mL colorimetric cylinder. The pH value was adjusted to 5.0 with diluted HCl and/or NaOH, and the final volume was diluted to 50 mL. Then, 0.2500 g modified sodium trititanate whisker was added, and the solution was stirred vigorously for 5 min and placed for 2 h to facilitate adsorption of Co(II) and Pb(II) ions onto the sorbent, and then centrifugated. After centrifugation, the concentrations of the unadsorbed ions in the liquid phase were determined directly by ICP-AES.

3) Elution experiment

A portion of sample solution containing Co(II) and Pb(II) ions was transferred to a 50 mL colorimetric cylinder. The adsorption experiment was carried out at the optimum conditions, and then centrifuged. After centrifugation, the amounts of the adsorbed ions were eluted with 10 mL of 3.0 mol/L of HCl, and the solution was stirred vigorously for 7 min and placed for 12 h, at last the amounts of the adsorbed ions were measured by ICP-AES.

III. RESULTS AND DISCUSSION

A. Selection of sorbent

25 μg of Co(II) and Pb(II) ions were transferred to a series of 50 mL colorimetric cylinders, respectively. The pH was adjusted to 5.0 with diluted HCl and/or NaOH, and the final volume was diluted with water. Then, 0.2500 g of sodium trititanate whisker modified by the above four different ways was added, respectively, and the solution was stirred vigorously for 5 min and placed for 2 h, and then centrifuged. After centrifugation, the concentrations of the unadsorbed ions in the liquid phase were determined directly by ICP-AES. It could be shown that the adsorption rate of sodium trititanate whisker modified by 0.05 mol/L of ethanol solution of 8-hydroxyquinoline for 24 for Co(II) and Pb(II) ions was highest, so it was selected as sorbent.

B. Characterization of modified sodium trititanate whisker

1) Analysis of scanning electron microscopy

Sodium trititanate whisker and modified sodium trititanate whisker were shown in Fig.1, Fig.2. It could be seen that the particles of modified sodium trititanate whisker were even, so the ratio surface areas were much larger.

2) Analysis of IR spectra

Sodium trititanate whisker and modified sodium trititanate whisker were shown in 1, 2. in the Fig.3. By analysis of IR spectrums, it was shown that characteristic peaks of infrared absorption corresponded to absorption peaks of benzene skeleton, carbon-hydrogen bond of benzene skeleton and carbon-nitrogen bond in 2, respectively, so it was proved that 8-hydroxyquinoline had been loaded on the sodium trititanate whisker.

C. Adsorption experiment

1) Influence of pH on adsorption

According to references [8], pH plays a very important role with respect to the adsorption of sorbent for metal ions. The surface potential of modified sodium trititanate whisker is determined by H⁺ and OH⁻, surface of modified sodium trititanate whisker can integrate OH⁻ of H₂O and thus the surface with negative charges is prone to adsorption to cation(metal ions), when pH is high. On the contrary, the
surface with positive charges is prone to adsorption to anions. During the experiments, 25 μg Co(II) and Pb(II) ions were transferred to a 50 mL colorimetric cylinder, and the mass of sorbent was 0.2500 g. The influence of pH on the adsorption of Co(II) and Pb(II) ions were investigated. The results were shown in Fig.4. It can be seen that the adsorption rate of modified sodium trititanate whisker to Co(II) and Pb(II) ions were above 95% when pH was set at 5.0, and consequently, the optimal pH was set at pH 5.0.

![Fig.4 Effect of pH on the adsorption rate](image)

2) Influence of dosage of sorbent

In order to get the acceptable dosage of sorbent for the adsorption of Co(II) and Pb(II) ions, the experiment was carried out at pH 5.0, the results were shown in Fig.5. The results were shown that when its dosage was over 0.10 g, its adsorption rate can be over 97%. Taking one thing with another, the optimum dosage of sorbent was 0.2500 g.

![Fig.5 Influence of amount of sorbent on adsorption rate](image)

3) Influence of oscillation time and quiescent time on adsorption

The influences of different oscillation and quiescent time on the adsorption of Co(II) and Pb(II) ions were separately inspected. As was shown from the results, when the oscillation time surpassed 5 min, and quiescent time 2 h, the adsorption rate of modified sodium trititanate whisker to Co(II) and Pb(II) can be above 98.5%, it were indicated that Co(II) and Pb(II) ions could be adsorbed quantitatively and fast.

D. Desorption experiment

1) Selection of eluent

As is shown from Fig.4 that the adsorption of Co(II) and Pb(II) ions is ideal at high pH, so Co(II) and Pb(II) ions may be easily desorbed on this condition. In the light of the proposed experimental technique, several kinds of acid system were studied for desorption of adsorbed ions. The results obtained indicated that the desorption rate of HCl for Co(II) and Pb(II) were the highest and above 90%, followed by HNO₃, H₂SO₄ worst, thus HCl was selected for eluent. Co(II) and Pb(II) ions were eluted completely by 10 mL 0.5 mol/L of HCl solution was selected for the further experiments.

2) Effect of heater temperature on recovery

Although the recoveries of HCl of both kinds for Co(II) and Pb(II) ions were highest, the recovery were not ideal. So the influence of heater temperatures on recovery of Co(II) and Pb(II) ions were taken into account. The results were given as follows: Co(II) and Pb(II) ions were hard to be eluted at the room temperature, due to the positive effect of the temperature, moreover, the recovery had reached above 90% at 100°C, and thus 100°C was chosen for subsequent procedure.

3) Influence of HCl on recovery

Subsequently, the influence of various concentrations of HCl for desorption of adsorbed ions were studied at 100°C. The results obtained can be seen that 10 mL 3.0 mol/L of HCl was sufficient for complete elution. Consequently, it was selected for the further experiments.

<table>
<thead>
<tr>
<th>HCl(mol/L)</th>
<th>Co(II)</th>
<th>Pb(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>93.6</td>
<td>6.8</td>
</tr>
<tr>
<td>1.0</td>
<td>97.9</td>
<td>85.5</td>
</tr>
<tr>
<td>3.0</td>
<td>100.2</td>
<td>95.2</td>
</tr>
<tr>
<td>5.0</td>
<td>99.7</td>
<td>99.6</td>
</tr>
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</table>

E. Adsorption isotherm

The above experiments were carried out using relatively low concentrations of Co(II) and Pb(II) ions. In order to obtain information about the coverage of Co(II) and Pb(II) ions taken up on modified sodium trititanate whisker, the relationship was inspected between concentrations of Co(II) and Pb(II) ions and adsorption capacity, the experiment was carried out when pH was at 5.0 and dosage of modified sodium trititanate whisker was 50 μg, the results were shown in Fig.6. It can be seen that the amount adsorbed increased with increase in metal ions concentration. Although adsorption capacity has not yet reached saturation in the experiment, adsorption capacity of the modified sodium trititanate whisker for Co(II) and Pb(II) is satisfying.
F. Selectivity experiment

250 μg of Pb(II), Mn(II), Cr(III), Co(II) and Cu(II) ions were added to a 50 mL of colorimetric cylinder, and pH was adjusted to 5.0, then diluted with water. Afterwards, 0.100 0 g unmodified and modified sodium trititanate whisker were added, and the solution was stirred vigorously for 5 min and placed for 2 h, and then centrifuged. After centrifugation, the concentrations of the unabsorbed ions in the liquid phase were determined directly by ICP-AES. It could be seen from Table 2 that the adsorption rate of modified sodium trititanate whisker for most metal ions except Co(II) and Pb(II) were lower than that of unmodified sodium trititanate whisker, and it proved that the selection was better after modified.

<table>
<thead>
<tr>
<th>Ions</th>
<th>Mn(II)</th>
<th>Co(II)</th>
<th>Cr(III)</th>
<th>Cu(II)</th>
<th>Pb(II)</th>
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<tbody>
<tr>
<td>Adsorption rate of modified(%)</td>
<td>21.3</td>
<td>89.9</td>
<td>17.6</td>
<td>24.0</td>
<td>94.3</td>
</tr>
<tr>
<td>Adsorption rate of Unmodified(%)</td>
<td>23.5</td>
<td>75.0</td>
<td>21.3</td>
<td>24.1</td>
<td>85.6</td>
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IV. APPLICATION IN ICP-AES ANALYSIS

A. Detection limit and precision

According to the definition of IUPAC, the detection limit (3σ) of this method for Co(II) and Pb(II) were 0.00049 mg/L and 0.00037 mg/L, respectively; and the relative standard deviation was 1.6% and 1.4% for 0.5 mg/L Co(II) and Pb(II) (n=9), respectively.

B. Water sample determination

A portion of river and well water samples were transferred to a series of 50 mL of volumetric flasks, pH was adjusted to 5.0, accordance with the proposed method, adsorption and desorption of Co(II) and Pb(II) ions were examined, the concentration of Co(II) and Pb(II) ions in the eluent were determined directly by ICP-AES, together with the blank and standard addition experiment, The results were shown in Table 3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Element</th>
<th>Added(µg)</th>
<th>Recovered(µg)</th>
<th>Recovery(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Well water</td>
<td>Pb</td>
<td>0.0100</td>
<td>0.0101</td>
<td>101.6</td>
</tr>
<tr>
<td></td>
<td>Co</td>
<td>0.0100</td>
<td>0.0094</td>
<td>93.3</td>
</tr>
<tr>
<td>Yudai river water</td>
<td>Pb</td>
<td>0.0100</td>
<td>0.0096</td>
<td>96.1</td>
</tr>
<tr>
<td></td>
<td>Co</td>
<td>0.0100</td>
<td>0.0092</td>
<td>91.5</td>
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</table>

REFERENCES