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Study on the Adsorption of Vanadium (V) with *Scenedesmus obliquus*

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Methods were examined for the separation and preconcentration of V (V) by living algae. The adsorption rate of V (V) was 43% in neutral medium and was above 60% when appropriate H_2SO_4 of Zn^{2+} solution was added. When H_2SO_4 and Zn^{2+} were added together, the adsorption rate of V (V) can rise to 77%. The adsorption mechanism was also discussed.

Algae cells are capable of adsorbing different metals from a variety of solution environments (Ray H. Crist, et al., 1988). This biosorption phenomena has been the subject of increased research activity for a variety of reasons, including concern over metal recovery techniques from processes and industrial streams, contaminated water treatment methods, toxic trace metal accumulation in the food chain, and precious metal recovery methods.

Experimental results showed that Scenedesmus Obliquus (SO) had an ability to accumulate and biodegrade organic pollutants, such as 2,4–dinitrophenol (Klekner V., et al., 1992), DDT (Lin Y., et al., 1984) and dimethyl phthalate (Yian Hai, et al., 1996) and adsorb metals, such as Au (III) and Tc from dilute solutions. But uptake of V (V) by SO has not been reported. In this paper conditions for the preconcentration of V(V) by SO. The adsorption mechanism is also discussed in this paper.

MATERIALS AND METHODS

800–centrifuge medical appliances plant, (Jinan, China), Hitachi 850 spectrofluorophotometer (Japan) and UV–240 spectrophotometer (Shimadzu, Japan) were used.

V(V) stocking solution (3.0×10^{-3} mol/L) was prepared by dissolving

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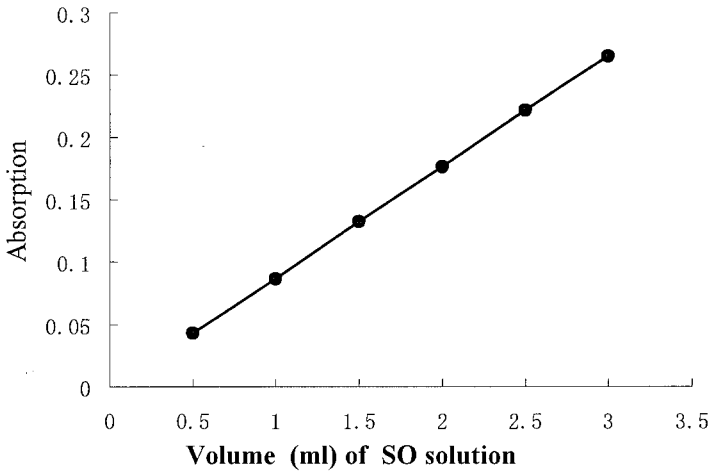

Figure 1. Relationship between absorption and volumes of SO solution

0.0351 g NH_4VO_3 (Shanghai Reagent Head Company Third Branch factory) in 6 mol/L NaOH solution and was neutralized with 9 mol/L H_2SO_4, then the solution was diluted to 100 ml with demineralized distilled water. Scenedesmus Obliquus was obtained from the Research Center for Eco-environmental Sciences, Academia Sinica, Beijing, China. The medium solution consisted of $(NH_4)_2SO_4$, 0.200 g; superphosphate, 0.030 g; $MgSO_4$, 0.080 g; $NaHCO_3$, 0.100 g; KCl, 0.025 g; 1% $FeCl_3$ solution, 0.15 ml; soil extraction solution, 0.50 ml; and distilled water, 1000 ml (Zhou Y.X., et al., 1989). The initial pH of the medium, adjusted to 7.0. Zn^{2+} solution (1.0×10^{-3} mol/L), was prepared by dissolving 0.0125 g $ZnCO_3$ (J.T. Baker Chemical Co., Phillipsburg, New Jersey) in 100 ml of water. EDTA solution (0.01 mol/L) was prepared by dissolving 0.3722 g ethyle-diaminetetraacetic acid disodium salt($C_{10}H_{14}N_2O_3Na_2\cdot2H_2O$) in 100 ml of water. Sulfuric acid solution (3.0×10^{-3} mol/L)(Jinan Reagent factory).

RESULTS AND DISCUSSION

Algae were grown in medium solution (see above section of materials) and were kept in a culture room at 24°C with the light intensity of 4000±100 Lux continuously.

The quantity of algae was expressed by the absorption of algae solution at 650 nm. In 10ml volumetric flask, adding a series of

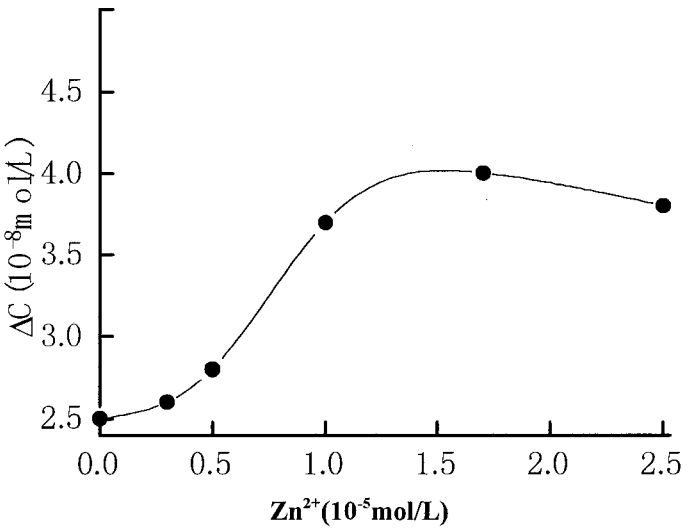

Figure 2. Effect of Zn^{2+} on the amount of adsorption of V(V)

volumes of SO solution, then the solution was diluted to 10 ml and absorption was measured at 650 nm. The results are shown in Figure 1 and the relationship between absorption and volumes of SO solution can be expressed as:

$$A = 0.089V \qquad (1)$$

To a 10-ml volumetric flask, appropriate SO solution and 2.0 ml of 3.0×10^{-7} mol/L V (V) solution were added. The mixture was diluted to the mark with water and sonicated for 20 min. The suspended algae were then centrifuged and the supernatant was decanted for fluorometric analysis. The amount of V (V) in the supernatant was subtracted from the sum of V (V) added and the difference was considered as the uptake of V (V) (ΔC). A linear relationship was obtained with the correlation coefficient of 0.9916 and the linear equation was:

$$\Delta C = 1.55\times10^{-8}\ Vso - 1.0\times10^{-9} \qquad (2)$$

(the unit of ΔC was mol/L, the unit of Vso was ml.)

To a 10ml volumetric flask, 2.0 ml of SO solution and appropriate 3.0×10^{-7} mol/L V (V) solution were added. The procedure followed was the same as above. The results showed that a linear relationship was obtained with the correlation coefficient of 0.9974 and the linear

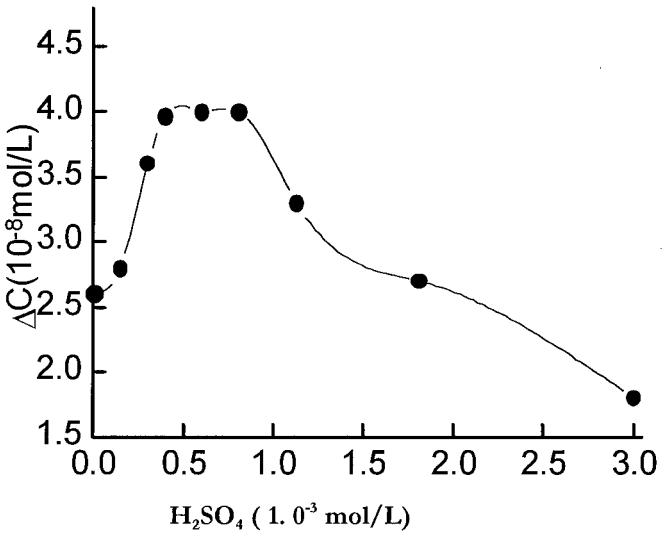

Figure 3. Effect of H_2SO_4 concentration on the amount of adsorption of V(V)

equation was:

$$\Delta C = 0.43\ Cv \qquad (3)$$

The slope represents the adsorption rate, so the V (V) adsorption rate of SO was 43%.

A relationship between ΔC and CvVso was obtained with the correlation coefficient of 0.9962 and the linear equation was:

$$\Delta C = 0.23\ CvVso + 0.06 \qquad (4)$$

If equation (1) was introduced, equation (4) can also be expressed as:

$$\Delta C = 2.58\ CvA + 0.06 \qquad (5).$$

The effect of EDTA and Zn^{2+} on the adsorption was investigated. The results showed that EDTA had no effect on the adsorption, but Zn^{2+} can raise the adsorption rate remarkably.

When 2.0 ml of SO solution and 2.0 ml of 3.0×10^{-7} mol/L V (V) were added, the effect of Zn^{2+} on the adsorption was shown in Fig 2. It can be seen from Fig 2 that maximum and constant adsorption was obtained when Zn^{2+} concentration was above 1.0×10^{-5} mol/L.

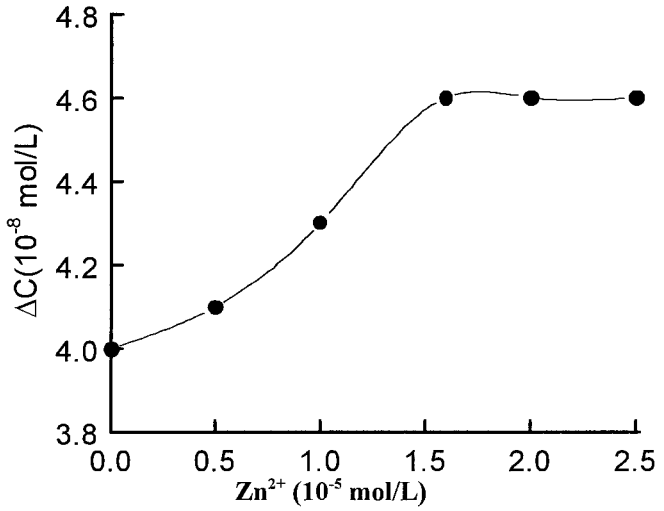

Figure 4. Effect of Zn^{2+} concentration (with H_2SO_4 added) on the amount of adsorption of V(V)

The adsorption curve was drawn when 2.0 ml of SO solution and 2.0 ml of 1.0×10^{-4} mol/L Zn^{2+} were added. The results showed that a linear relationship between ΔC and Cv was obtained with the correlation coefficient of 0.9963 and the linear equation was:

$$\Delta C = 0.61Cv - 4.7\times10^{-12} \qquad (6)$$

So the adsorption rate rose from 43% to 61% if Zn^{2+} was added.

The effect of sulfuric acid concentration on the adsorption is shown in Fig 3. The results showed that the adsorption reached a maximum value in the range of $4.0\times10^{-4} \sim 8.0\times10^{-4}$ mol/L H_2SO_4. So 6.0×10^{-4} mol/L H_2SO_4 was selected. Under the optimum acidity condition a linear adsorption curve was obtained with the correlation coefficient of 0.9989 and the linear equation was:

$$\Delta C = 0.66\ Cv + 4.0\times10^{-10} \qquad (7)$$

So the adsorption rate rose from 43% to 66% if H_2SO_4 was added.

The effect of H_2SO_4 and Zn^{2+} added together on the adsorption was studied. When the concentration of H_2SO_4 added was 3.0×10^{-4} mol/L,the effect of Zn^{2+} concentration on the adsorption was shown in Fig 4. It can be seen that the adsorption reached a maximum value when Zn^{2+} concentration was above 1.6×10^{-5} mol/L. So 2.0×10^{-5} mol/L Zn^{2+} was selected. When the concentration of Zn^{2+} was 2.0×10^{-5} mol/L, the effect of H_2SO_4 concentration on the adsorption of V(V)

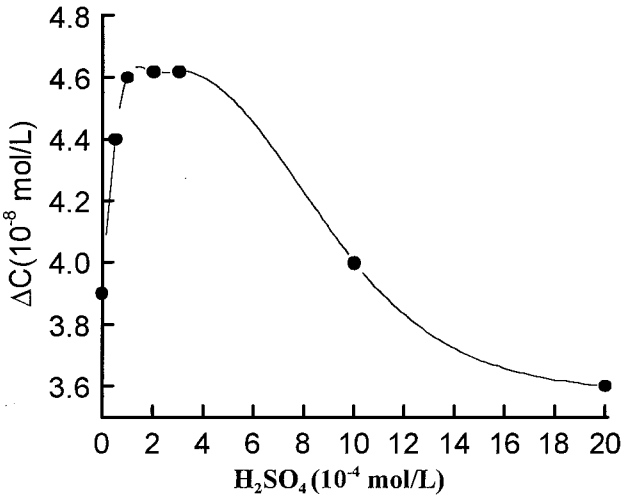

Figure 5. Effect of sulfuric acid concentration (with Zn^{2+} added) on the amount of adsorption of V(V)

was shown in Fig 5. It can be seen that the adsorption reached a maximum value in the range of 1.0×10^{-4}~3.0×10^{-4} mol/L H_2SO_4. So 2.0×10^{-4} mol/L H_2SO_4 was selected.

The adsorption curve was drawn when 2.0×10^{-4} mol/L H_2SO_4 and 2.0×10^{-5} mol/L Zn^{2+} were added together . As can be seen, a linear relationship between ΔC and Cv was obtained with the correlation coefficient of 0.9984 and the linear equation was:

$$\Delta C = 0.77\ Cv + 1.6\times10^{-10} \qquad (8)$$

So the adsorption rate rose from 43% to 77% if H_2SO_4 and Zn^{2+} were added together.

The desorption experiment was conducted. The results showed that SO lost adsorption capacity when H_2SO_4 added was above 0.3 mol/L.

In the adsorption experiment, the supernatant was decanted for fluorometric analysis to obtain ΔC as adsorption. The lees was flushed by deionized water, then the solution was centrifuged and the lees was transferred into a 10 ml volumetric flask with water, then 2.0 ml of 3.0 mol/L $H_2SO_4$was added and the mixture was diluted to the mark and sonicated for 20 min, then centrifuged and the supernatant was decanted for fluorometric analysis to obtain $C_{recovery}$. The recovery efficiency was calculated by $C_{recovery}/(C_0 - \Delta C)\cdot100\%$ in which C_0 represented the concentration of V (V) added. The results showed that

the recovery efficiency was between 94 – 97%, which proved that the ΔC considered as adsorbance was reasonable.

In neutral medium or under optimum acidity condition (pH≅3), V (V) existed as oxo acid anion, which can be bonded with the cation group on the algae cell. Acid added could accelerate the protonation of amino on the algae cell. The amount of the cation group increased. So the adsorption rate rose. But when the acid concentration was above 0.3 mol/L (pH<1), V (V) existed as VO_2^+ and the anion group on the algae cell was saturated by H^+. It was difficult for V (V) to substitute H^+, so the algae lost adsorption capacity.

Zn^{2+} could be adsorbed fast and stable by algae when pH ≥5 and desorbed when pH ≤2 (Darnall D.W., et al., 1986). In neutral medium Zn^{2+} could be adsorbed stable by the anion group of algae . In the process of V (V) adsorption, Zn^{2+} acted probably as an adsorption bridge. V (V) was adsorbed in the form of algae–Zn–V (V), which made the adsorption rate rise. When H_2SO_4 and Zn^{2+} were added together, under the optimum acidity condition (pH≅4), Zn^{2+} still could be adsorbed by algae and acted as adsorption bridge, which made the adsorption rate rise of V(V).

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