Flotation Separation of Cadmium by NaCl-KI-Butyl Rhodamine B System

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Abstract. The flotation separation behaviors and conditions of Cadmium(Ⅱ) by NaCl-KI-Bu-RhB system are studied. The results show that when the amount of NaCl is 1.0 g, the amount of 0.001mol/L Bu-RhB solution is 1.50 mL and 0.1 mol/L KI solution is 0.75 mL, Cadmium(Ⅱ) is floated quantitatively at pH 2.0. While Mn²⁺, Ni²⁺, Zn²⁺ and Co²⁺ could not be floated. The method of flotation separation of trace Cadmium(Ⅱ) is established. The flotation separation of Cadmium(Ⅱ) in the sample of synthetic water is performed, and the recoveries are 103.0% ~ 109.2%.

1. Introduction
Cadmium(Ⅱ) is a highly toxic and accumulative heavy metal which seriously harms to human health, and it is one of the main pollutants in the environment. The studies of separation/enrichment methods of trace Cadmium(Ⅱ) have been paid much attention by chemical researchers. Up to now, solvent extraction[1-3], solid phase extraction[4], cloud point extraction[5], liquid membrane separation[6], ion exchange separation[7], etc have been reported for the separation/enrichment of Cadmium(Ⅱ).

In NaCl-KI-Bu-RhB system, the (Bu-RhB)₂(CdI₄) sediment which produced by Cd²⁺, I⁻ and Bu-RhB cation (Bu-RhB⁺) was floated above the water phase and Cd²⁺ was floated quantitatively at pH 2.0, while Mn²⁺, Ni²⁺, Zn²⁺ and Co²⁺ could not be floated. So, a method for flotation separation of Cd²⁺ was established. The flotation separation of Cd²⁺ in the sample of synthetic water is performed and the results are satisfactory.

2. Experimental

2.1. Equipment and reagents
723S spectrophotometer; UV-2401 UV-visible spectrophotometer.
Butyl Rhodamine B(Bu-RhB) solution: 0.001 mol/L. KI solution: 0.1 mol/L. 4-(2-pyridylazo) resorcinol (PAR) ethanol solution: 1.0×10⁻³ mol·L⁻¹. Borax solution: 0.1 mol/L. Cd²⁺: 50.0µg·mL⁻¹, is prepared by appropriately diluting the standard solution of Cd²⁺ (1.000 g·L⁻¹). The buffer solutions of different pH was prepared as references [8].

2.2. Method
In 25 mL ground color comparison tube, 50µg Cd²⁺, 0.75 mL KI solution and 1.50 mL Bu-RhB solution are added. Then adjust the pH(2.0), dilute to 10.00 mL. 2.0 g NaCl is added, oscillationed sufficiently and kept still for a moment. 1.00 mL salt water sample, 1.5 mL PAR ethanol solution and
3.0 mL borax solution are added into another 25 mL ground color comparison tube. The content of Cd\(^{2+}\) is determined at 495 nm with reagent as blank, or the precipitation by filtration is dissolved in ethanol, and the content of Cd\(^{2+}\) is determined in the same method. The flotation yield (E%) is calculated.

3. Results and discussion

3.1. The dosage of Bu-RhB

50 µg Cd\(^{2+}\) and 3.00 mL KI solution are applied to the proposed method, the effect of Bu-RhB dosage on the flotation yield of Cd\(^{2+}\) was studied (figure 1). The results show that the flotation yield of Cd\(^{2+}\) is zero when the solution not Bu-RhB. The flotation yield of Cd\(^{2+}\) increased with the increase of Bu-RhB dosage. When Bu-RhB is 1.50 mL or more, Cd\(^{2+}\) can be completely floated (or the flotation yield of Cd\(^{2+}\) is 100%). So, 1.50 mL Bu-RhB solution is chosen.

3.2. The dosage of KI

When Cd\(^{2+}\) is 50 µg and Bu-RhB solution is 1.50 mL, the effect of KI dosage on the flotation yield of Cd\(^{2+}\) is shown in Figure 2. It can be seen from Figure 2 that the flotation yield of Cd\(^{2+}\) is zero without KI. It indicate that Bu-RhB could not float Cd\(^{2+}\). When the solution add KI, Cd\(^{2+}\) react with I\(^{-}\) and Bu-RhB\(^{+}\) to form (Bu-RhB\(_2\))(CdI\(_4\)) sediment, it leads to the the flotation yield of Cd\(^{2+}\) increase. When the dosage of KI is up to 0.75 mL, the flotation yield of Cd\(^{2+}\) is 100% (or Cd\(^{2+}\) can be completely floated. Furthermore, superfluous KI would not affect the flotation yield of Cd\(^{2+}\). Hence, 0.75 mL KI solution is selected.

3.3. Flotation mechanism

Base on the results above, it can be seen that only KI and Bu-RhB exist at the same time, Cd\(^{2+}\) reacts with I\(^{-}\) and Bu-RhB\(^{+}\) to form (Bu-RhB\(_2\))(CdI\(_4\)) sediment and be floated. Therefore, the flotation mechanism of Cd\(^{2+}\) is as follows:

(1) Cd\(^{2+}\) reacts with I\(^{-}\) to form complex anion CdI\(_4^{2-}\):
Cd^{2+} + 4I^- → CdI_4^{2-}  
(Water phase)  
(Water phase)  

(2) CdI_4^{2-} reacts with Bu-RhB^+ to form (Bu-RhB)_2(CdI)_4 sediment which float above water phase and form flotation solid phase. So, Cd^{2+} is completely floated.

CdI_4^{2-} + 2 Bu-RhB^+ → (Bu-RhB)_2(CdI)_4  
(Water phase)  
(Flotation phase)  

3.4. Effect of different salts
When Cd^{2+} is 50µg, Bu-RhB solution is 1.50 mL and KI solution is 0.75 mL, the effects of NaCl, KNO_3, (NH_4)_2SO_4 and NaBr on liquid-solid disengagement and the flotation yield of Cd^{2+} are investigated. The results are shown in Table 1.

| Salt     | The dosage of salt/g | The flotation yield of Cd^{2+}/% | Separate-phase and its effect                |
|----------|----------------------|----------------------------------|---------------------------------------------|
| NaCl     | 1.0                  | 100.0                            | Liquid-solid interface clear, phase separation fast and phase separation effect is best |
|          | 2.0                  | 100.0                            |                                              |
|          | 3.0                  | 89.0                             |                                              |
|          | 1.0                  | 80.2                             | Liquid-solid interface clear, phase separation faster and phase separation effect is general |
| KNO_3    | 2.0                  | 99.0                             |                                              |
|          | 3.0                  | 98.2                             |                                              |
|          | 1.0                  | 100.0                            | Liquid-solid interface is not clear, phase separation slow and phase separation effect is worst |
| (NH_4)_2SO_4 | 2.0              | 100.0                            |                                              |
|          | 3.0                  | 100.0                            |                                              |
|          | 1.0                  | 44.6                             | Liquid-solid interface clear, phase separation slow and phase separation effect is general |
| KBr      | 2.0                  | 94.6                             |                                              |
|          | 1.0                  | 92.0                             |                                              |

From the Table 1, we can see that when (NH_4)_2SO_4 exists in the solution, liquid-solid interface is not clear, phase separation slow and phase separation effect is worst. KNO_3 and KBr decreased the flotation yield of Cd^{2+} in a certain extent and separation effect is general. When the presence of NaCl in the solution, liquid-solid interface is clear, phase separation fast and phase separation effect is best. When NaCl dosage is 1.0g, 2.0g, the flotation yield of Cd^{2+} are 100%. Therefore, 1.0g NaCl is chosen.

3.5. Effect of pH
When metal ion is 50µg, NaCl is 1.0 g, Bu-RhB solution is 1.50 mL and KI solution is 0.75 mL, the effects of pH on the flotation yield of different metal ions are studied. The results are shown in Table 2.

| metal ion | 1.0 | 2.0 | 3.0 | 4.0 | 5.0 | 6.0 | 7.0 |
|-----------|-----|-----|-----|-----|-----|-----|-----|
| Cd^{2+}   | 100%| 100%| 100%| 96.4%| 89.4%| 100%| 100%|
| Mn^{2+}   | -10.9%| 2.0%| -1.6%| 6.0%| -19.4%| 4.0%| 4.2%|
| Ni^{2+}   | 4.1%| -6.4%| -12.9%| 0.9%| 7.4%| 5.5%| 7.3%|
| Zn^{2+}   | 10.0%| 6.7%| 10.0%| 6.7%| 5.3%| 7.9%| 4.7%|
| Co^{2+}   | 5.9%| 4.5%| -12.9%| -5.2%| 6.3%| -2.1%| 0.8%|

The results show that at pH 1.0~3.0 and pH 6.0~7.0, the flotation yield of Cd^{2+} is not affected, or the flotation yield of Cd^{2+} remain 100%. When pH=2.0, the flotation rates of Mn^{2+}, Ni^{2+}, Zn^{2+} and Co^{2+} are lower. Therefore, by controlling pH=2.0, Cd^{2+} could be separated from Mn^{2+}, Ni^{2+}, Zn^{2+} and Co^{2+}. 
3.6. Flotation separation experiments

By controlling pH=2.0, when NaCl is 1.0 g, Bu-RhB solution is 1.50 mL and KI solution is 0.75 mL, the flotation separation of Cd²⁺ in the sample of synthetic water is performed. The flotation separation results are shown in Table 3 and Table 4.

| Mixed ions | Dosage of metal ions (µg) | Contents of metal ions in water phase (µg) | Flotation yield (E/%) |
|------------|---------------------------|------------------------------------------|----------------------|
|            | Cd | Me | Cd | Me |                  |                  |
| Cd²⁺-Mn²⁺  | 50 | 50 | 0  | 20  | 48.1             | 99.6             | 3.7               |
|            | 50 | 200 | 0  | 205.1 | 100             | -2.5             |
|            | 50 | 500 | 0  | 484.5 | 99.8             | 3.1              |
| Cd²⁺-Ni²⁺  | 50 | 50 | 0  | 50.2 | 99.6             | -0.5             |
|            | 50 | 200 | 0  | 192.7 | 99.4             | 3.7              |
|            | 50 | 500 | 0  | 454.4 | 99.8             | 9.1              |
| Cd²⁺-Zn²⁺  | 50 | 50 | 0  | 48.3 | 99.6             | 3.4              |
|            | 50 | 200 | 0  | 190.1 | 99.6             | 5.0              |
|            | 50 | 500 | 0  | 504.3 | 99.6             | -0.9             |
| Cd²⁺-Co²⁺  | 50 | 50 | 0  | 54.3 | 99.8             | -8.6             |
|            | 50 | 200 | 0  | 212.6 | 99.6             | -6.3             |
|            | 50 | 500 | 0  | 431.0 | 99.6             | 13.8             |

Me represents other ions except Cd²⁺.

| Number of the synthesized samples | 1       | 2       | 3       |
|----------------------------------|---------|---------|---------|
| Dosage of Cd²⁺ (µg)              | 50.0    | 100.0   | 200.0   |
| Dosage of Mn²⁺, Ni²⁺, Zn²⁺, and Co²⁺ (µg) | 50.0    | 200.0   | 500.0   |
| Cd²⁺ content in solid phase (µg) | 51.5    | 107.7   | 218.3   |
| Flotation yield E of Cd²⁺ (%)    | 103.0   | 107.7   | 109.2   |

4. Conclusion

In this paper, a method for the flotation separation of trace Cadmium(II) was reported. At pH 2.0, in NaCl-KI-Bu-RhB system, Cd²⁺ can quantitatively form the (Bu-RhB)₂(CdI₄) sediment and be floated. In the same conditions, Mn²⁺, Ni²⁺, Zn²⁺ and Co²⁺ can not be floated. Therefore, the flotation separation of Cd²⁺ from Mn²⁺, Ni²⁺, Zn²⁺ and Co²⁺ can be achieved. The proposed method has been successfully applied to the flotation separation of Cd²⁺ in the sample of synthetic water, and the recoveries are 103.0%~109.2%.

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References

[1] Alfonso O, Aurora M, Francisco Z, et al. (2002) Studies on liquid-liquid extraction of nickel(II), zinc(II), cadmium(II), mercury(II) and lead(II) with 1-phenyl-3-hydroxy-4-dodecylthiocarbonylate-5-pyrazolone[J]. Microchim. Acta., 140, 201–203.

[2] Mousa S B, Altakrory A, Abdel Raouf M W, et al. (1998) Extraction and separation of zinc and cadmium chlorides by TOPO from mixed media. J Radioanal Nucl Chem., 227(1-2):143-146.

[3] Sandhya D, Subramanian M S. (1997) Extractive separation of trace amounts of mercury, cadmium and zinc. J Radioanal Nucl Chem., 224(1-2):53-57.
[4] Xiang G Q, Huang Y, Luo Y F. (2009) Solid phase extraction of trace cadmium and lead in food samples using modified peanut shell prior to determination by flame atomic absorption spectrometry[J]. Microchim. Acta., 165, 237–242.

[5] Liang P, Li J, Yang X Y. (2005) Cloud point extraction preconcentration of trace cadmium as 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone complex and determination by flame atomic absorption spectrometry[J]. Microchim. Acta., 152, 47–51.

[6] Farhadi K, Shamsipur M. (2005) Separation Study of Cadmium as CdI₄²⁻ through a Bulk Liquid Membrane Containing Ketoconazole and Oleic Acid. Anal.sci., 21:501-505.

[7] Zbigniew S, Rajmund D. (2004) Ion Exchange Behavior of Cadmium, Mercury, Silver and Zinc on Retardion 11A8 and Chelex 100 Ion Exchangers in Ammonia Medium and Its Application for Radiochemical Separations. Microchim Acta., 144; 103–114.

[8] Chang,W.-B.;Li,K.-A. (1981) Brief Handbook of Analytical Chemistry;Beijing University Press: Beijing, p262.