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Solvent extraction of uranium from aqueous solutions by α-benzoinoxime

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Abstract Solvent extraction of uranium with α-benzoinoxime from aqueous solutions has been systematically investigated. The extraction equilibration was very fast and achieved at 60 s for uranium. The extraction of uranium was pH-dependent using α-benzoinoxime as extractant. The effect concentration of uranium and α-benzoinoxime was studied. The uranium loaded in the organic phase can be stripped efficiently with 93 % yield using 0.1 M HCl as the stripping agent in a single stripping step. A good selectivity for uranium was observed through α-benzoinoxime as extractant from aqueous solution with other interfering cation ions. Present study suggested that α-benzoinoxime can be used as a potential extractant for separation of uranium from aqueous solution using centrifugal extractor in industrial application.

Keywords Uranium · Solvent extraction · Stripping · Centrifugal extractor

Introduction

Uranium is one of the most dangerous heavy metals in the environment because of its chemical toxicity and radioactivity. Hence, studies on the separation of uranium from waste solutions are very important. Solvent extraction method has been one of the important techniques in concentrating and purification of uranium [1–7]. Oxyimines, >C=N–OH, also abbreviated as oximes, is an important class of chelating agents, which was frequently used in extractive and analytical chemistry for many metal ions [8–14]. α-Benzoinoxime is a simple oximes and it is a typical extracting agent for molybdenum, tungsten and vanadium [15–19] since it reacts with these metal elements to form stable chelate complexes. In our previous studies [20, 21], we also found that α-benzoinoxime was really a good extractant for Mo and W. However, this property has not been widely used for extraction of uranium, which was usually considered as a pseudo homologs element of group 6. Until now, to the best of our knowledge, only two works mentioned the separation of uranium by using α-benzoinoxime as extractant [15, 22]. Therefore, this paper extends the solvent extraction research of α-benzoinoxime to uranium. The impact of organic diluents, initial pH, shaking time, initial uranium concentration and α-benzoinoxime concentration on the extraction uranium and stripping of uranium were systematically investigated and discussed. Moreover, in order to elucidate its practical application as a selective extractant for U(VI), the selective extraction studies were examined under the optimum conditions. Finally, uranium extraction with α-benzoinoxime was also performed using miniature centrifugal extractor in the present work.

Experimental

Materials

A stock solution of 1 g/L U(VI) was prepared by dissolving an appropriate amount of $UO_2(NO_3)_2 \cdot 6H_2O$ in deionized

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Table 1 The effect of diluents on uranium ion extraction

Diluents	*E* (%)	Dielectric constant
1,2-Dichloroethane	51.73	10.37
Chloroform	92.56	4.7
1,1,2,2,-Tetrachloroethane	43.25	8.2
Ethyl acetate	11.80	6
n-Butyl ether	15.81	3.1
Butyl acetate	1.1	5.01
Octanol	1.4	10.34

[α-Benzoinoxime] = 1.52×10^{-2} M, [U(VI)] = 4.2×10^{-4} M, pH 5

water. Uranium solution used in the extraction experiment was diluted from stock solution. α-Benzoinoxime was purchased from Alfa Aesar Co., Ltd. (Tianjin, China). The initial pH of working solutions was adjusted by the addition of HCl or NaOH solution. All of the reagents were of analytical reagent grade and without further purification.

General procedure

The extraction experiments were performed at $T = 25 \pm 2$ °C. Three mL of the aqueous solution containing 1.52×10^{-4} M uranium ions was contacted with an equal volume of α-benzoinoxime solution in chloroform in a 10 mL tube with screw cap under shaking for certain time. After separation of two phases, uranium concentration of aqueous phases was determined by the spectrophotometer at 650 nm with arsenazo-III. The concentration of uranium ions in the organic phase were calculated from the difference between the uranium ions concentrations in the aqueous phase before and after extraction. Each extraction experiment was performed in triplicate.

Results and discussion

Effect of organic diluents on extraction

The organic phase diluents can influence metal ions extraction because both physical and chemical interactions exist between diluents and extractant. Various diluents such as chloroform, 1,2-dichloroethane, 1,1,2,2,-tetrachloroethane, ethyl acetate, *n*-butyl ether, butyl acetate and octanol were tested to evaluate their adequacy for the extraction of U(VI) with α-benzoinoxime. Table 1 presents the results of uranium extraction and the best extraction yield (92.56 %) was obtained with chloroform as diluents. Boutamine et al. [15] also found that chloroform as organic diluents can lead to the higher recovery for uranium. Usually the dielectric constant of organic diluents was used to explain the effect of organic diluents on extraction. But for this experiment, it seems that the extraction efficiency was independent of dielectric constant. Maybe other factors including the solubility of diluents in aqueous, steric hindrance of diluents and so on influence the extraction. Hence, it cannot be interpreted only on the basis of polarity of the diluents. A similar observation was found in extraction of uranium by using *N*-octanoylpiperidine as an extractant from nitric acid solution [23].

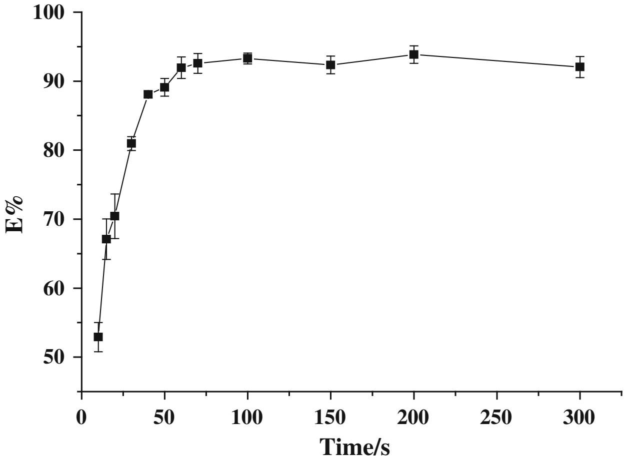

Fig. 1 The influence of shaking time on uranium extraction ([α-benzoinoxime] = 1.52×10^{-2} M, [U(VI)] = 4.2×10^{-4} M, pH 5)

Effect of shaking time on extraction

The kinetics of extraction of uranium with α-benzoinoxime was performed by determining the extraction yield as a function of shaking time between the two phases. Figure 1 shows a plot of the extraction yield versus shaking time for the extraction of U(VI) with 1.52×10^{-2} M α-benzoinoxime from pH 5 solution. It was found that this extraction system is very fast and the extraction equilibrium can be achieved at 60 s for U(VI) with the extraction efficiency of about 92 %. Thus, the extraction of U(VI) can be completed within 60 s. Hence, in subsequent solvent extraction experiments, 5 min was selected as the shaking time which was sufficient to achieve extraction equilibrium.

Effect of pH on extraction

The pH is a very critical parameter in extraction process. First of all, pH has an effect on the uranium species in solution and will therefore have a direct an impact on the complexation of uranium with α-benzoinoxime. At lower pH values, the predominant species is UO_2^{2+}. To find the optimum pH value for maximum extraction, the influence of initial pH on the extraction of U(VI) using α-benzoinoxime was investigated. As shown in Fig. 2, the

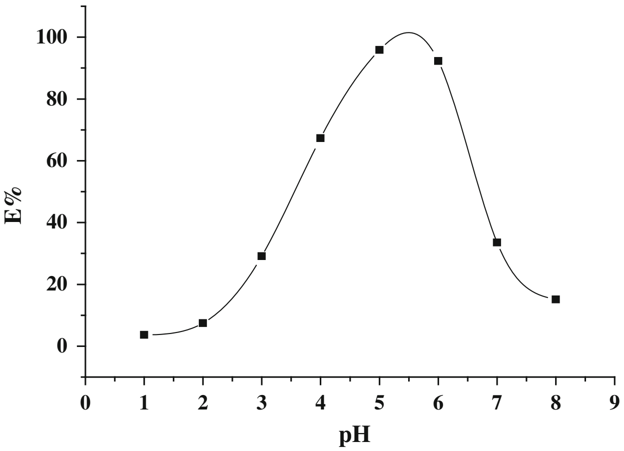

Fig. 2 The effect of pH on uranium ion extraction ([α-benzoinoxime] = 1.52×10^{-2} M, [U(VI)] = 4.2×10^{-4} M, shaking time = 5 min)

Table 2 The effect of phase ratio on uranium ion extraction

Phase ratio[a]	E (%)
2/1	93.89
1/1	92.87
1/2	90.80
1/3	83.51
1/4	76.3
1/5	66.63

[a] Phase ratio = $V_{\text{organic phase}}:V_{\text{aqueous phase}}$

variation in pH influences the extraction efficiency to a large extent. With the increasing pH, the extraction efficiency of uranium increases and reaches about 95 % at pH 5, then drops down sharply when the initial pH of the aqueous solution exceeds 6. This result is in good agreement with the data reported in the literature [15] but different from the result of the group 6 elements Mo and W using the same extraction system [20, 21]. Therefore, pH 5.0 was selected for the further experiments.

Effect of phase ratio on extraction

In order to choose a suitable phase ratio, different ratio of organic phase and aqueous phase was investigated. Table 2 demonstrates the effect of phase ratio on uranium ion extraction. It is clear that the extraction is dependent on the phase ratio and the value of E % decreases with the increase of the volume of aqueous phase. The phase volume ratio O/A was kept at 1:1 in the extraction experiment.

Table 3 The effect of stripping agents on uranium back extraction

Stripping agents	Concentration (M)	Back-extraction (%)
HCl	0.01	57.48 ± 6.5
HCl	0.05	88.16 ± 2.7
HCl	0.1	92.64 ± 1.5
$NaHCO_3$	0.1	35.72 ± 5.9
Na_2CO_3	0.1	52.51 ± 2.6

Effect of initial uranium and α-benzoinoxime concentration on extraction

The influence of initial uranium concentration was investigated at a fixed concentration of α-benzoinoxime (1.52×10^{-2} M). The uranium extraction is nearly invariable with the extraction efficiency of about 92 % when the concentration of initial uranium ion increases from 1.26×10^{-4} to 6.30×10^{-4} M. From experimental results of the slopes of log *D* versus log [U], it can be deduced that only one uranium ion is present for each of the extracted species under investigation.

In order to assess the extraction ability of α-benzoinoxime, the distribution ratio *D* of uranium(VI) ions was determined at room temperature between aqueous solution (pH 5) and chloroform phases as a function of the extractant concentration in the organic phase. With varying concentrations of α-benzoinoxime (from 0.2×10^{-2} to 1.52×10^{-2} M) in chloroform, uranium extraction increases and the percentage of extraction increases from 54 to 95 %. This trend confirms the participation of α-benzoinoxime molecules in the extraction. The plot of log *D* versus log [α-benzoimoxime] gave a slope of 2.21, which implied that two molecule extractant participate the extraction process under investigation.

Stripping studies

In any extraction process it is necessary to back-extract the metal ion from the loaded organic phase. A loaded organic solution containing U(VI) after extraction was employed for stripping tests. Table 3 exhibits the result of different stripping agents on uranium back extraction. The results reveal that when contacted with a 0.1 M HCl solution at phase ratio (A/O) of 1/1, 92.64 % U was stripped from the loaded organic phase in a single stripping step. The results demonstrated that the back-extraction efficiency is not satisfactory when alkaline agents (Na_2CO_3 and $NaHCO_3$) were applied as stripping agents to recover uranium. Therefore, it is easy to strip uranium ions using 0.1 M HCl solution with an efficiency of about 93 % from the loaded organic solution in a single stripping step.

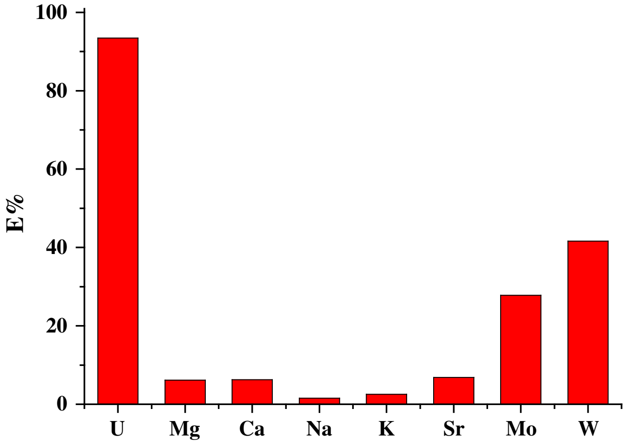

Fig. 3 Competitive extraction of coexistent ions onto α-benzoinoxime (50 mg/L for every ions, pH 5, time = 10 min, 1.52×10^{-2} M α-benzoinoxime in chloroform)

Selective extraction

The effect of coexisting metal ions on the extraction of U(VI) by α-benzoinoxime was examined to evaluate the selectivity of α-benzoinoxime towards U(VI) (Fig. 3). The concentration of each metal ion in the aqueous phase before and after was measured by ICP-AES. Because the concentration of uranium only can be determined by the spectrophotometer in our experiment, other colored metal ions including Fe^{2+}, Ni^{2+}, V^{5+} and Cu^{2+} can not be coexisted with uranium in the solution. Therefore, we just separately examine the extraction of Fe^{2+}, Ni^{2+}, V^{5+} and Cu^{2+} in the optimum extraction condition for uranium ([α-benzoinoxime] = 1.52×10^{-2} M, pH 5 of aqueous phase). The extraction efficiency of Fe^{2+}, Ni^{2+}, V^{5+} and Cu^{2+} is 13.17, 2.76, 8.76 and 51.37 %, respectively. From the result, we can see that the presence of Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Fe^{2+}, Ni^{2+} and V^{5+} do not hardly interfere with the extraction of U(VI) under this experiment. However, Mo, W and Cu cation ions will disturb the extraction of U(VI) to some extent in the present study. In our previous study [21], we also found a little extraction of Mo and W in the weak acid solution using α-benzoinoxime as extractant. Moreover, Boutamine et al. [15] also reported that the maximum extraction of Fe, Ni and Cu is at around pH 10. Hence, α-benzoinoxime as an extraction and separation agent can be used in the recovery of uranium from waste solution.

Centrifugal extractor experiment

The centrifugal extractor is a new type of high efficient auto liquid–liquid extractive equipment, which has many advantages and a great future for industrial application [24–27]. In order to evaluate the feasibility of this extraction system, extraction of uranium by α-benzoinoxime from solution was studied using ϕ10 mm centrifugal extractor under the experimental conditions (aqueous solution: 25 mg/L uranium solution of pH 5, organic solution: 0.1 % α-benzoinoxime in chloroform). The extraction stage efficiency of single-stage centrifugal extractor was only about 68 %. However, the extraction yield of two-stage cascade increased to about 90 % when the rotor speed was 5,000 r/min, and the flow ratio of two phases was 1 L/min. This result shows that uranium can be separated from aqueous solution using centrifugal extractor under the present extraction system.

Conclusions

In this study, the extractability of uranium was investigated in α-benzoinoxime/chloroform system. It can be said that α-benzoinoxime is an efficient extracting reagent for uranium from aqueous solution with a maximum extraction yield about 95 %. The initial pH of aqueous solution influenced uranium extraction. The distribution ratio for uranium increased with increasing extractant concentration. The extraction process is quite fast as the equilibration time was found to be 60 s. Selective experiments indicated that α-benzoinoxime can extract uranium ions in the presence of other competing ions. Moreover, it is easy to strip uranium ions using 0.1 M HCl solution with an efficiency of about 93 % from the loaded organic solution in a single stripping step. Additional studies showed that α-benzoinoxime can be used as a potential extractant for separation of uranium from aqueous solution using centrifugal extractor in industrial application. Hence, α-benzoinoxime could be a good candidate as an extractant to remove the toxic and radioactive U(VI) from waste solution.

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References

1. Mohite BS, Mane SG, Sawant SM (2001) J Radioanal Nucl Chem 249:613–616
2. Yang YZ, Feng SY (2002) J Radioanal Nucl Chem 253:161–164
3. Lapka JL, Paulenova A, Alyapyshev MY, Babain VA, Herbst RS, Law JD (2009) Radiochim Acta 97:291–296
4. Quinn JE, Wilkins D, Soldenhoff KH (2013) Hydrometallurgy 134–135:74–79
5. Kanekar AS, Pathak PN, Mohapatra PK, Manchanda VK (2010) J Radioanal Nucl Chem 283:789–796
6. Hu PZ, Qian LJ, He YX, Wang HL, Wu WS (2013) J Radioanal Nucl Chem 297:133–137

7. Zhong XM, Wu YH (2012) J Radioanal Nucl Chem 292:355–360
8. Tian G, Geng JX, Jin YD, Wang CL, Li SQ, Chen Z, Wang H, Zhao YS, Li SJ (2011) J Hazard Mater 190:442–450
9. Shafa-Amry NN, Khalili FI, Ebraheem KAK, Mubarak MS (2006) React Funct Polym 66:789–794
10. Gameiro MLF, Machado RM, Ismael MRC, Reis MTA, Carvalho JMR (2010) J Hazard Mater 183:165–175
11. Park KH, Kim HI, Parhi PK (2010) Sep Purif Technol 74:294–299
12. Choi SH, Nho YC (2000) Radiat Phys Chem 57:187–193
13. Das S, Pandey AK, Athawale AA, Manchanda VK (2009) J Phys Chem B 113:6328–6335
14. James D, Venkateswaran G, Rao TP (2009) Microporous Mesoporous Mater 119:165–170
15. Boutamine S, Hank Z, Meklati M, Benali-Baitich O (1994) J Radioanal Nucl Chem 185:347–353
16. Hoenes HJ, Stone KG (1960) Talanta 4:250–263
17. McDonald MJ, Carson SD, Naranjo GE, Wemple JA (2000) Ind Eng Chem Res 39:3146–3150
18. Hwang DS, Choung WM, Kim YK, Park JH, Park SJ (2002) J Radioanal Nucl Chem 254:255–262
19. Wish L (1962) Anal Chem 34:625–627
20. Fan FL, Lei FA, Zhang LN, Lin MS, Bai J, Wu XL, Ding HJ, Li XF, Qin Z (2009) Radiochim Acta 97:297–302
21. Fan FL, Lei FA, Zhang LN, Lin MS, Bai J, Wu XL, Ding HJ, Li XF, Ding YQ, Qin Z (2009) Solv Extr Ion Exch 27:434–446
22. Ghasemi JB, Zolfonoun E (2010) Talanta 80:1191–1197
23. Shao H, Han JT, Sun GX, Bao BR, Yang YH, Sun SX (2000) J Radioanal Nucl Chem 246:233–235
24. Zhou JZ, Duan WH, Xu JQ, Yang YY (2007) Chin J Chem Eng 15:209–214
25. Zhu JQ, Chen J, Li CY, Fei WY (2007) Sep Purif Technol 56:237–240
26. Duan WH, Cheng Q, Zhou XZ, Zhou JZ (2009) Prog Nucl Energy 51:313–318
27. Tamhane TV, Joshi JB, Mudali UK, Natarajan R, Patil RN (2012) Chem Eng J 207–208:462–472