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Study on the removal of chromium(III) by solvent extraction

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ABSTRACT

The extraction of chromium(III) from aqueous waste solution by extractants 2-ethylhexyl phosphonic acid-mono-2-ethylhexyl ester (HEHPEHE), di(2-ethylhexyl) phosphoric acid (D2EHPA), and mixture of D2EHPA with other extractants is carried out, respectively. It is found that the extractant HEHPEHE exhibited high extraction selectivity for chromium(III) from aqueous waste solution. Based on the molecular structure of HEHPEHE, it is confirmed that the extraction mechanism of chromium(III) by HEHPEHE is mainly determined by cation exchange and chelation. Furthermore, the influences of major factors, such as the initial pH, the initial concentration of extractant, phase ratio, and the extraction temperature on the extraction efficiency of chromium(III) are also investigated and the appropriate process conditions are obtained. At the appropriate conditions, the extraction efficiency of chromium(III) above 99% can be achieved and the treated aqueous waste solution can be discharged directly without polluting the environment.

Keywords: Extraction process; HEHPEHE; Chromium(III)

1. Introduction

The extensive use of chromium in leather tanning, metallurgy, electroplating, and other industries has resulted in the release of aqueous chromium to the subsurface at numerous sites [1]. Chromium is an element with mutagenic, teratogenic, and cancerogenic properties [2–6]. The most common oxidation states of chromium are +3 and +6. Chromium(III) cannot be absorbed easily, and it can form complexes with proteins in the external layer of skin and accumulation in the lung causes lung cancer. Thus, scholars pay more and more attention to the removal and recovery of chromium(III) because of the growing importance to environmental protection problems.

The current work investigates the potential of the cationic extractant for the separation of chromium(III) from aqueous waste solution. HEHPEHE and D2EHPA as effective extractants have been widely used for the extraction of zinc, beryllium, copper, vanadium, indium, gallium, and rare earth elements [7–15]. Dejun Fei [16,17] successfully employed cationic extractant D2EHPA and p-tert-butylcalix[4]arene acetate as extractant by emulsion liquid membrane (ELM) to remove chromium(III) effectively from aqueous waste solution, which can be discharged directly after extraction treatment. However, due to the stability of ELM and regeneration of the extractant, this approach need more work to achieve for industrialization. Consequently, the cationic extractant HEHPEHE herein is employed as extractant to remove chromium(III) for wastewater treatment which has great significance.

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2. Experimental

2.1. Materials and equipment

The diluent used in this work is aviation kerosene which was bought from Luo yang Zhongda Chemical Company (China). HEHPEHE, D2EHPA, TOA, and TBP were employed as extractants which were produced by Luo yang Zhongda Chemical Company (China) (AR grade). Chromium(III) nitrate nonahydrate and sodium hydroxide were purchased from Ke Long Chemical Company (China) (AR grade). Distilled water was produced by Aquapro making-water machine (ABZ1-1001-P) in laboratory. PHSJ-5 pH meter was bought from Shanghai Precision & Scientific Instrument Co. Ltd.

2.2. Parameters that can affect the extraction process

To study chromium(III) removal efficiency and advantages of the extraction process, it is necessary to optimize various parameters that can affect the process. The optimized parameters were the HEHPEHE volume content, the reaction temperature, the phase volume ratio, the stirring speed, the reaction time, and the initial pH of aqueous waste solution.

2.3. Analysis

The concentration of chromium(III) was determined by atomic absorption spectrophotometry (GF3000).

3. Result and discussion

Extraction efficiency (E) is defined as followed:

$$E = \frac{M_{(A_1)}^{Cr^{3+}} - M_{(A_2)}^{Cr^{3+}}}{M_{(A_1)}^{Cr^{3+}}} \times 100\% \qquad (1)$$

E represents the efficiency of extraction process;

$M_{(A_1)}^{Cr^{3+}}$: Mole of chromium(III) in initial solution, mol;

$M_{(A_2)}^{Cr^{3+}}$: Mole of chromium(III) in the raffinate, mol.

3.1. Influences of extractants

The extraction of chromium(III) from aqueous waste solution was carried out by various extractants. In the mixed extractant, the molar ratio of D2EHPA and another extractant was kept at 1:1 ratio. The results demonstrates that the extraction selectivity of HEHPEHE for chromium(III) from aqueous waste solution is outstanding as shown in Table 1. Therefore, HEHPEHE is applied in the further experiments.

Table 1
Influences of extractants

Extractants	Extraction efficiency (%)
D2EHPA	25.5
D2EHPA and TOA	16.5
D2EHPA and TBP	5.0
D2EHPA and HEHPEHE	29.6
HEHPEHE	40.9

Notes: Diluent: kerosene; phase ratio (A/O): 1:1; extractant volume fraction (%): 10%; stirring speed: 350r/min; initial chromium(III) concentration: 600 mg/L; initial pH of aqueous waste solution: 3; reaction time: 30 min; reaction temperature: 30℃.

3.2. Effect of HEHPEHE volume fraction (%)

Fig. 1 shows the effect of HEHPEHE volume concentration on the extraction efficiency. It is seen that the amount of extractant increases as increasing HEHPEHE volume concentration in solvent phase. Therefore, the number of free extractant molecules taking part in the extraction reaction will also increase. However, when the HEHPEHE concentration increases to certain value, as the extraction reaction reaches equilibrium, the extraction efficiency will remain almost unchanged as shown in Fig. 1.

3.3. Effect of phase ratio (A/O)

Fig. 2 displays the effect of phase ratio (A/O) on the extraction efficiency. The phase ratio (A/O) has a significant effect on extraction efficiency (E). This effect is studied by changing the phase ratio (A/O)

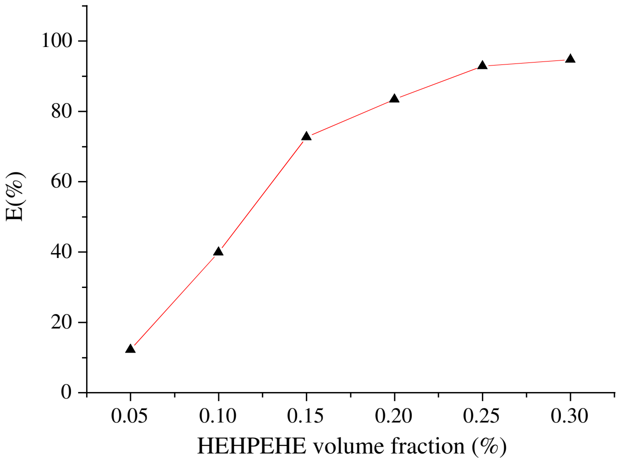

Fig. 1. The extraction efficiency (E) vs. the HEHPEHE volume fraction (%).
Notes: Diluent: kerosene; phase ratio (A/O) = 1:1; stirring speed: 350 r/min; initial chromium(III) concentration: 600 mg/L; initial pH of aqueous waste solution: 3; reaction time: 30 min; reaction temperature: 30℃.

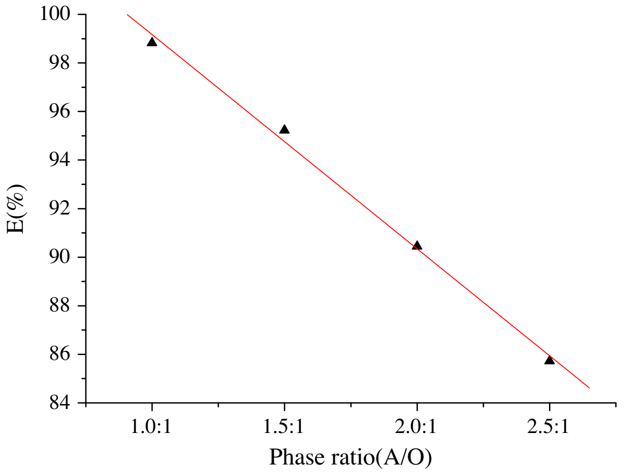

Fig. 2. The extraction efficiency (*E*) vs. the phase ratio (A/O).
Notes: Diluent: kerosene; HEHPEHE volume fraction (%): 30%; stirring speed: 350 r/min; initial chromium(III) concentration: 600 mg/L; initial pH of aqueous waste solution: 3; reaction time: 30 min; reaction temperature: 30℃.

from 2.5:1 to 1:1. The results presented in Fig. 2 clearly show that the phase ratio (A/O) of 1:1 gives the highest extraction of chromium(III). The possible reason [16] is that for the fixed chromium(III) concentration in solution, decreasing phase ratio (A/O) in extraction process can enhance the amount of solvent and extractant. Subsequently, the extraction efficiency of chromium(III) is improved with the decrease of phase ratio (A/O).

3.4. Effect of reaction time

The extraction efficiency (*E*) of chromium(III) with different reaction time by solvent extraction is presented in Fig. 3. The results indicate that the extraction efficiency of chromium(III) can be enhanced with the increase of reaction time. The equilibrium time for the emulsification extraction of chromium(III) is observed to be 30–35 min. Therefore, the equilibrium time of 30 min is used for extraction to ensure complete reaction.

3.5. Effect of stirring speed

Fig. 4 shows the effect of stirring speed on extraction efficiency. As the stirring speed increases, a smaller globule size will lead to a larger interfacial transfer area between the feed and the solvent phase. This increased transfer area allows the extraction to occur at a higher rate. However, Fig. 4 shows that the stirring speed does not affect the extraction efficiency

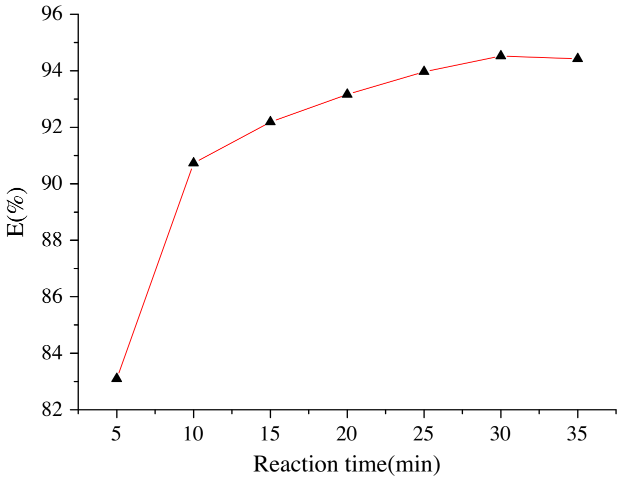

Fig. 3. The extraction efficiency (*E*) vs. the reaction time.
Notes: Diluent: kerosene; phase ratio (A/O) = 1:1; HEHPEHE volume fraction (%): 30%; stirring speed: 350 r/min; initial chromium(III) concentration: 600 mg/L; initial pH of aqueous waste solution: 3; reaction temperature: 30℃.

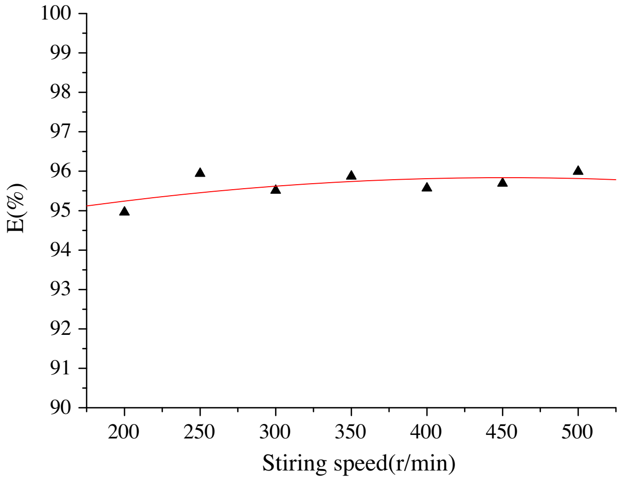

Fig. 4. The extraction efficiency (*E*) vs. the stirring speed.
Notes: Diluent: kerosene; phase ratio (A/O) = 1:1; HEHPEHE volume fraction (%): 30%; reaction time: 30 min; initial chromium(III) concentration: 600 mg/L; initial pH of aqueous waste solution: 3; reaction temperature: 30℃.

too much when the stirring speed reaches 250 r/min. Therefore, the optimum value for stirring speed is found to be 250 r/min.

3.6. Effect of initial pH of aqueous waste solution

As the cationic extractant HEHPEHE (HA) contains dissociable H^+, H^+ will be replaced when HA reacts with chromium(III). So the reaction mechanism of extracting chromium(III) with HA could be attributed to the cation exchange. In general, the extraction reaction can be described as follows [18]:

$$\mathrm{nqCr}^{3+}_{(a)} + \frac{q(s+3n)}{m}(\mathrm{HA})_{m(o)} \rightarrow (\mathrm{Cr}_n A_{3n} \cdot \mathrm{sHA})_{q(o)} + 3\mathrm{nqH}^{+}_{(a)}$$

$$K = \frac{[(\mathrm{Cr}_n\mathrm{A}_{3n}.\mathrm{sHA})_q]_{(0)}[\mathrm{H}^+]^{3nq}_{(a)}}{[\mathrm{Cr}^{3+}]^{nq}_{(a)}[(\mathrm{HA})_m]^{\frac{q(s+3n)}{m}}_{(0)}} \tag{2}$$

where m is the aggregation number of HEHPEHE. The equilibrium constant K is given as follows:

$$[(\mathrm{Cr}_n A_{3n} \cdot \mathrm{sHA})_q]_{(o)} = \frac{1}{\mathrm{qn}}[\mathrm{Cr}^{3+}]_{(o)} \tag{3}$$

And the distribution ratio of chromium(III) can be expressed as follows:

$$D = \frac{[\mathrm{Cr}^{3+}]_{(o)}}{[\mathrm{Cr}^{3+}]_{(a)}} \tag{4}$$

$$\log\mathrm{D} = \log\mathrm{K} + 3\mathrm{nqpH} + \log\mathrm{nq} + \frac{q(s+3n)}{m}\log[(\mathrm{HA})_{\mathrm{m}}]_{(o)} + (\mathrm{nq} - 1)\log[\mathrm{Cr}^{3+}]_a \tag{5}$$

The plot of logD-pH as shown in Fig. 5 is a straight line with the slope of approximately 0.2078, suggesting $3\mathrm{nq} \approx 0.2$, which indicates that the chelate complex of ($\mathrm{CrA_3.2HA}$) can be obtained. So the extraction mechanisms of chromium(III) with HA accords with the cation exchange [19,20] and chelation. So the extraction reaction can be described as follows:

$$\mathrm{Cr}^{3+}_{(a)} + 5(\mathrm{HA})_{(o)} \rightarrow (\mathrm{CrA}_3 \cdot 2\mathrm{HA})_{(o)} + 3\mathrm{H}^{+}_{(a)} \tag{6}$$

According to Eq. (5), the intercept value 0.901 can also be obtained, and the extraction equilibrium constant K value is 1.807. Therefore, the extraction distribution ratio (D) of chromium(III) increases rapidly as the initial pH of aqueous waste solution rises in the extraction system, as shown in Fig. 5. However, considering the economic cost and extraction efficiency, the pH value of 4.5 for extraction is appropriate.

3.7. Effect of reaction temperature

Fig. 6 shows the effect of reaction temperature on extraction distribution ratio (logD). The distribution ratio (D) increases as the temperature rises. It can be seen from Fig. 6 that a linear relationship between logD and $10^3\mathrm{T}^{-1}$ is obtained in this experiment. From the van't Hoff equation [21]:

$\mathrm{dlogD/d(1/T)} = -\Delta H/(2.303\mathrm{R}) + \mathrm{const}$, ΔH value 1.167×10^{-2} ($\mathrm{J\,mol^{-1}}$) can be calculated, which shows that the extraction of chromium(III) with HEHPEHE is endothermic. And from the equations $\Delta G = -\mathrm{RTlnK}$ and $\Delta G = \Delta H - T\Delta S$, the ΔG value is -1.490×10^3 ($\mathrm{J\,mol^{-1}}$) ($T = 303\,\mathrm{K}$) and the ΔS value is 4.917 ($\mathrm{J\,mol^{-1}\,K^{-1}}$) ($T = 303\,\mathrm{K}$).

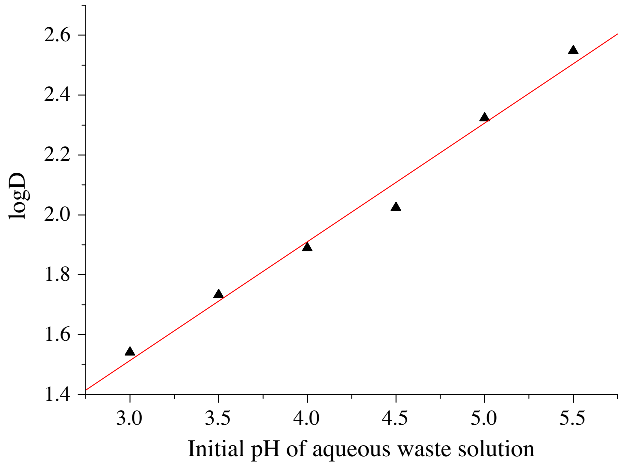

Fig. 5. The extraction efficiency (*E*) vs. the initial pH of aqueous waste solution.
Notes: Diluent: kerosene; phase ratio (A/O) = 1:1; HEHPEHE volume fraction (%): 30%; reaction time: 30 min; stirring speed: 350 r/min; initial chromium(III) concentration: 600 mg/L; reaction temperature: 30℃.

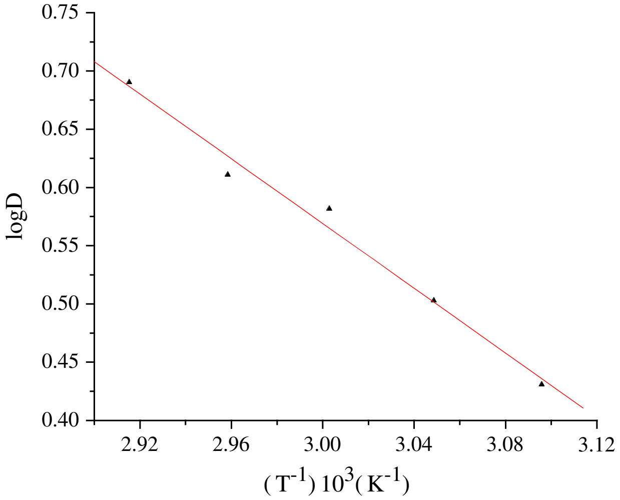

Fig. 6. The extraction distribution ratio (logD) vs. the reaction temperature.
Notes: Diluent: kerosene; phase ratio (A/O) = 1:1; HEHPEHE volume fraction (%): 30%; reaction time: 30 min; initial chromium(III) concentration: 600 mg/L; initial pH of aqueous waste solution: 3; stirring speed: 350 r/min.

4. Conclusion

Based on the results of removing chromium(III) from aqueous waste solution by solvent extraction of HEHPEHE, the following specific conclusions can be drawn:

(1) Solvent extraction technology is an effective method to remove chromium(III) from aqueous waste solution with HEHPEHE as extractant.
(2) The optimal process conditions are as follows: The HEHPEHE volume fraction is 30%, the reaction temperature is 25℃, the phase volume ratio (A/O) is 1:1, the stirring speed is 300r/min, and the initial pH of aqueous waste solution is 4.5.
(3) The mechanism of the extraction of chromium(III) with HA accords with the cation exchange and chelation.
(4) The thermodynamic data of the extraction reaction are as follows: $\Delta H = 1.167 \times 10^{-2}$ ($\mathrm{J\,mol^{-1}}$); -1.490×10^{3} ($\mathrm{J\,mol^{-1}}$) ($T = 303\,\mathrm{K}$); and $\Delta S = 4.917$ ($\mathrm{J\,mol^{-1}\,K^{-1}}$) ($T = 303\,\mathrm{K}$).

5. Actual verification

In the actual verification experiments, a kind of practical chromium(III) waste solution containing 350 mg/L chromium(III) is neutralized firstly to be at pH = 4.5 with acetic acid and sodium acetate. About 250 ml of the neutralized solution is then put into a 1,000 ml jacketed beaker which is then extracted under the above mentioned optimal conditions. After two-stage extraction, the concentration of chromium(III) in the waste water is less than 0.5 mg/L, and an extraction efficiency of above 99.9% can be obtained, the treated aqueous waste solution can be discharged directly without polluting the environment.

Acknowledgments

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References

[1] N.K. Djane, K. Ndungu, C. Johnsson, H. Sartz, T. Tornstrom, L. Mathiasson, Chromium speciation waters using serially connected supported liquid membranes, Talanta 48 (1999) 1121–1132.
[2] T.J. O'Brien, S. Ceryah, S.R. Paterino, Complexities of chromium carcinogenesis:role of cellular response, repair and recovery mechanism, Mutat. Res. 533 (2003) 3–4.
[3] K.C. Tagliari, V.M. Vargos, K. Zimiani, R. Cecchini, Oxidative stress damage in the liver of fish and rats receiving an intrapertioneal injection of hexavalent chromium as evaluated by chemiluminescence, Environ. Toxicol. Pharmacol. 17 (2004) 149–150.
[4] R. Swietlik, Speciation and Transformations of Anthropogenic Chromium in the Environment Polluted by Tannery Wastes, Radom University of Technology, Radom, (2001) in Polish.
[5] A. Molik, J. Siepak, R. Swietlik, J. Dojlido, Identification of chromium species in tanning solutions, Pol. J. Environ. Stud. 13 (2001) 311–312.
[6] Nilgun Balkaya, Nilden Bektas, Chromium(VI) adsorption from dilute aqueous solution by wool, Desalin. Water Treat. 3 (2009) 43–49.
[7] G.M. Ritcey, A.W. Ashbrook, Solvent Extraction: Principles and Applications to Process Metallurgy, Vol. 1, Elsevier, New York, NY, 1984, pp. 106–107.
[8] Y.C. Hoh, W.S. Chuang, B.-D. Lee, C.-C. Chang, The separation of manganese from cobalt by D2EHPA, Hydrometallurgy 12 (1984) 375–386.
[9] L.F. Cook, W.W. Szmokaluk, Refining of cobalt and nickel sulfate solution by solvent extraction using di-(2-ethyl hexyl.) phosphoric acid, in: Proceedings ISEC' 71, Soc. Chem. Ind. London, 1 (1971) 451–462.
[10] G.M. Ritcey. Process options using solvent extraction for the processing of laterites, in: Nickel '96, Kalgorlie, September 1996, pp. 251–258.
[11] P.D.A. Clark, P.M. Cole, M.H. Fox, Purification of nickel sulphate using di-(2-ethyl hexyl) phosphoric acid, In: D.H. Lonsdail, M.J. Slater (Eds), ISEC'93, Solvent Extraction in the Process Industry, Society of Chemical Industry, London, pp. 175–182, 1993.
[12] B.H. Yao, N. Yukio, S. Masatada, N. Akihiko, H. Kiyoshi, Solvent extraction of metal ions and separation of nickel(II) from other metal ions by organophosphorus acids, Solvent Extr. Ion Exch. 5 (1996) 849–970.
[13] A. Feather, K.C. Sole, D.B. Dreisinger, Pilot-plant investigation of manganese removal and cobalt purification by solvent extraction, in: ISEC' 99, Barcelona, Spain, 1999, pp. 56–59.
[14] B.R. Reddy, J.R. Kumar, A.V. Reddy, D.N. Priya, Solvent extraction of Zr(IV) from acidic chloride solution using 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (PC288A), Hydrometallurgy 72 (2004) 303–303.
[15] B.R. Reddy, J.R. Kumar, A.V. Reddy, Solvent extraction of tetravalent hafnium from acidic chloride solutions using 2-ethyl hexylphosphonic acid mono-2-ethyl hexyl ester (PC288A), Miner. Eng. 17 (2004) 553–555.
[16] Luo Jian-Hong Feide-Jun, Ya-Gu Dang, Extraction of Cr3+ with p-tert-Butylca lix[4] arene Acetate from artificial tannery waste water, Chin. J. Appl. Chem. 25(2) (2008) 157–161.
[17] Lifeng Zhao, Dejun Fei et al., Studies on the extraction of chromium(III) by emulsion liquid membrane, J. Hazard. Mater. 178 (2010) 130–135.
[18] Amit Keshav, L. Wasewar Kailas, Chand Shri, Recovery of propionic acid by reactive extraction 1. Equilibrium; Effect of pH and temperature; Water co-extraction, Desalin. Water Treat. 3 (2009) 91–98.
[19] Y.D. Wang, M. Cheng, L.L. Xu, Y.Y. Dai, Removal of phenol from dilute solutions by predispersed solvent extraction, Chinese J. of Chem. Eng. 2 (2000) 103–107.
[20] D.D. Van, L. Pinoy, E. Courtijn, F. Verpoort, Influence of acetate ions and the role of the diluents on the extraction of copper(II), nickel(II), cobalt(II), magnesium(II) and iron(II, III) with different types of extractants, Hydrometallurgy 78 (2005) 92–106.
[21] E.O. Out, R. Chiarizia, Thermodynamics of the extraction of metal ions by dialkyl-substituted diphosphonic acids. II. The U(VI) and Sr(II) case, Solvent Extr. Ion Exch. 6 (2001) 1017–1036.