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Demulsification Behavior of Alkali and Organic Acid in Zinc Extraction

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Abstract: Alkali agents could be used to enhance the extraction of zinc from solution of high concentration, but excess alkali can sensitively lead to emulsification of the solution. In this paper, the emulsification in the extraction process, demulsification, and extraction with different additives and its action mechanism were studied. The results indicate that the associated addition of alkali and organic acid could eliminate emulsification and improve zinc extraction. The extraction ratio of zinc reached 99.61% under the conditions of 104 mL/L organic acid, 80 g/L alkali, and 40% extractant concentration. Zinc hydroxide formed from hydroxyl and zinc ion at sensitively increased pH was the cause of emulsification during extraction. Associated addition of alkali and organic acid could contribute to the control solution pH in the range of 3.0–4.0, which is lower than that of the formation of zinc hydroxide, and therefore, improve zinc extraction.

Keywords: demulsification; zinc extraction; saponification pre-treatment; alkali and organic acid; zinc hydroxide

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1. Introduction

As an important separation method that is widely applied in many industries such as petrochemical, pharmaceutical, and hydrometallurgical, solvent extraction has quite a few favourable advantages for separation and recovery of valuable metals from solutions [1–3]. Accordingly, it is commonly used for separating and concentrating for metals such as zinc, copper, nickel, cobalt, uranium, and other metal ions [4]. In hydrometallurgy, several extraction methods including cationic extraction [5–7], neutral extraction [8,9], anions extraction [10,11], and synergistic extraction [12,13] have been reported. As for zinc, which is usually in the form of sulfate in solutions and occurring as Zn^{2+} , cationic extraction has been widely considered to be most suitable because of its high selectivity.

Recently, some phosphorus extractants such as D2EHPA, TBP, and Cyanex272 have been marketed and applied extensively in extraction technology [14–16]. Among them, the most common reagent is D2EHPA. The general reaction for the extraction by an organophosphorus acid is displayed in Equation (1).

where M^{x+} is the metal cation, RH is the extractant, and m is the association degree of extractant. For the extraction of zinc sulfate with D2EHPA, $n = 1.5$ and m depend on the diluent ($m = 1$ for aromatic and $m = 2$ for aliphatic [17]).

A hydrometallurgical treatment on the recovery of zinc from a low concentration leachate zinc extraction with D2EHPA (di-2-ethylhexyl phosphoric acid) has been studied by Vahidi et al., in which the operation variables such as pH, D2EHPA concentration, temperature, aqueous/organic (A/O) phase ratio, tri-butyl phosphate (TBP) concentration, and sodium sulfate concentration have been considered. The result demonstrated that all zinc

was extracted from the aqueous solution at pH 2.5 with 20% *w/w* D2EHPA concentration in kerosene [18,19]. Zinc was preferentially extracted with D2EHPA at low pH (below 2.5) and in a short time (5 min). The continuous operation containing three extraction stages and three stripping stages, operated in a counter-current manner, has demonstrated that zinc could be removed quantitatively and selectively from the effluent (overall efficiency higher than 98%). Chen et al. studied zinc extraction using the D2EHPA reagent from zinc containing a low acid waste solution [20]. The result demonstrated that zinc can be efficiently extracted, and zinc concentration in the solution was reduced from 2.2 g/L to 0.003 g/L.

In the process of zinc extraction with D2EHPA, the extraction reaction is greatly influenced by the pH value of solution, while the substitution of hydrogen ions may lead to a decrease in pH. For solutions of low zinc, the pH decrease may not be so noticeable as to affect the extraction [21]. However, for high zinc solutions, the pH decrease is so marked that the zinc extraction equilibrium is substantially influenced, which significantly reduces zinc extraction ratio. Therefore, extraction of zinc in high concentration solutions should be accompanied by control of pH to ensure high extraction recovery. However, direct addition of common alkali reagents may cause sensitive reaction to the solution pH so that a quick pH increase usually, uncontrollably, takes place, leading to emulsification, which destroys the phase separation.

According to the literature [22], the causes for emulsification could be divided into two categories. One is the generation of surfactants, the other is the generation of precipitates. Both of them reduce the interfacial tension and lead to emulsification. In zinc extraction, the generation of precipitates at unfavorably higher pH, mainly hydroxides, turns out to be the main cause for emulsification. When zinc extraction is conducted to solutions with relatively low concentration, a certain saponification treatment could be applied to avoid emulsification and achieve a good extraction ratio [11]. However, in cases of higher zinc concentration, the emulsification cannot be effectively controlled by only applying a saponification treatment.

This paper focus on the emulsification in zinc extraction with D2EHPA extractant from solutions with zinc up to 30 g/L. Demulsification techniques were studied to eliminate the emulsification so as to intensify the zinc extraction.

2. Materials and Methods

2.1. Materials and Reagents

The chemical reagents in the aqueous phase such as zinc sulfate, ammonium hydroxide, glacial acetic acid, and sodium hydroxide are all of analytical reagent grade, and were provided by Guangzhou luyuan Chemical and Glass Instrument Co. Ltd., Guangzhou, China. The extractant bis(2-ethylhexyl) thiophosphoric acid (D2EHPA) was supplied by Zhengzhou Qinshi Technologies Co. Ltd., Zhengzhou, China, and used without further purification. The extractant was dissolved in sulfonated kerosene provided by Shenzhen Yishun Petrochemical industry Co. Ltd., Shenzhen, China. After dilution, the organic phase was washed with deionized water to remove the soluble impurities. Redistilled water prepared by a water purification system (UPR-I-5/10/15T, Wuhan Youpu Instrument Co., LTD, Wuhan, China) was used throughout all experiments.

2.2. Experimental Methods

2.2.1. Extraction Tests

The extraction tests were carried out at the temperature of 25 ± 0.5 °C with an aqueous: organic (A:O) ratio of 1:1. The two phases were mixed with mechanical agitation for 10 min. Then, put it in a separating funnel and kept stationary for 3 min to induce the phase separation. The content of zinc and pH value in the aqueous phase were determined.

2.2.2. Saponification Test

The organic phase and a certain amount of saponifier solution was placed in a beaker, and the solution was stirred at 200 rpm for a certain time. Unless otherwise stated, all the experiments were carried out at 25 ± 0.5 °C by heating in an external water bath. After the experiment was finished, the solution was placed in a separating funnel, and kept stationary for 8 min to separate the aqueous phase and organic phase. The volume of aqueous phase and organic phase was measured, and the concentration of Zn in the aqueous phase was also analyzed to determine the saponification ratio. The organic phase was used in the subsequent experiments.

2.3. Analytical Method

The concentration of zinc in aqueous solutions, after coming into contact with the organic extractant, were analyzed using inductively coupled plasma-atomic adsorption spectrometry (PS-6, Barid; Milwaukee, WI, USA). The pH values of solution were measured with a pH meter (PHSJ-4A). The extracted amounts from the organic extractants were calculated through the concentration differences in the aqueous solutions before and after extraction. The organic matter and emulsion were analyzed by a Fourier Transform Infrared Spectrometer (IRAffinity-1, Bruker; Billerica, MA, USA).

The saturation capacity represents the maximum load that the system can carry in stable conditions. Thus, it is necessary to study the saturation capacity of extractant for the purpose of extraction process. The saturation capacity of extractant was determined under the conditions of Zn(II) concentration 8 g/L, initial pH 3.0, A/O ratio 50:50, stirring speed 1000 rpm, and extraction time 15 min. After being stationary for 10 min, the organic phase and raffinate was separated, and the concentration of zinc in the raffinate was also determined. Then, the organic phase was mixed with a fresh solution containing zinc for extraction, phase separation, and detection. The extraction of zinc was repeated several times until the concentration of zinc ions in the raffinate remained unchanged, and the organic phase was considered to reach saturation.

3. Results and Discussion

3.1. Zinc Extraction with D2EHPA Extractant

The effect of zinc concentration on zinc extraction with D2EHPA extractant was studied under the conditions of 20% D2EHPA, pH 3.0, O/A ratio 50:50, 1000 rpm, and 10 min. As the results demonstrate in Figure 1, zinc extraction ratio decreased with zinc concentration increase in the range of 2–15 g/L, due to the inevitably noticeable decrease of solution pH. When zinc concentration was higher than 15 g/L, the pH of raffinate remained unchanged, while the extraction of zinc kept decreasing. Such a change in pH indicated that no more hydrogen ion is substituted into the solution at zinc concentrations above 15 g/L, demonstrating that the further extraction of zinc did not take place because of the saturation of zinc in the oil phase. Accordingly, the decrease of the extraction ratio was only due to the increase of total zinc quantity in the solutions.

As reported in the literature [21], the equilibrium partition ratio is related to the pH value, and the equilibrium partition ratio is higher at higher pH. The more zinc in initial solutions, the more hydrogen ions substituted, and a lower pH value as well as a lower extraction ratio resulted. Therefore, the prevention of pH decrease by substituting hydrogen ions plays a key role in ensuring high zinc extraction. In cases of higher zinc solution, development of effective techniques to control solution pH is of great significance.

As calculated, Zn(II) can be precipitated to Zn(OH)₂ at pH 6.0, and thus, the maximum amount of alkali without precipitation of Zn(OH)₂ is 45 g/L in a solution of 30 g/L zinc. In order to adjust the pH of raffinate, zinc extraction with the addition of alkali NaOH was carried out, and the results are displayed in Table 1. With the dosage of alkali increased from 0 g/L to 19.2 g/L, the pH value of raffinate increased slowly up to 2.5, and zinc extraction accordingly increased. However, with the alkali dosage further increased to above 24 g/L, the pH increase became quicker and ultimately uncontrollable. Although

the equilibrium ratio still increased, emulsification appeared, and phase separation was badly impacted. Therefore, the direct addition of common alkali sodium hydroxide may cause a sensitive reaction and an uncontrollable increase to the solution pH; alternative methods for pH control are urgently needed.

Figure 1. The effect of zinc concentration on zinc extraction. Conditions: initial pH 3.0, D2EHPA concentration 20%, O/A ratio 50:50, stirring speed 1000 rpm, and time 10 min.

Table 1. Effect of alkali dosage on zinc extraction from a zinc concentration of 30 g/L solution.

Alkali Dosage (g/L)	Extraction (%)	pH Value of Raffinate	Extraction Phenomenon
0	23.92	1.334	-
4.8	30.85	1.491	-
9.6	37.95	1.711	-
14.4	44.71	2.018	-
19.2	53.47	2.511	-
24	56.08	3.240	emulsification
28	65.78	6.555	emulsification
32	79.89	6.726	emulsification

3.2. Demulsification

3.2.1. Demulsification by Saponification Pre-Treatment of Extractant

In order to prevent the sensitive quick increase of solution pH, the organic phase with extractant D2EHPA was pretreated by saponification. The experiments were performed under the condition of 20% D2EHPA, pH 3.0, O/A ratio 50:50, 1000 rpm, and 10 min. The effect of alkali dosage on extractant saponification and zinc extraction are displayed in Table 2. It was found that emulsification could be alleviated to some extent by a saponification pre-treatment of the extractant. The emulsification caused by the direction addition of alkali at 24 g/L did not appear at the same dosage of alkali by saponification. However, at a higher dosage of alkali, such as 28 g/L, emulsification appeared again. Although the saponification pre-treatment of extractant could not entirely avoid emulsification, it allows more addition of alkali. Therefore, a saponification pre-treatment of extractant can be applied for demulsification in cases of zinc extraction at lower concentrations whose alkali addition for pH control are no more than 24 g/L, but for higher zinc concentrations, further demulsification measures are desired.

Table 2. The effect of alkali dosage on the saponification of extractant and zinc extraction.

Alkali Dosage (g/L)	Saponification Ratio (%)	Extraction (%)	The pH of Raffinate	Extraction Phenomenon
0	0	23.92	1.334	-
4.8	20	30.16	1.534	-
9.6	40	36.07	1.719	-
14.4	60	41.51	2.012	-
19.2	80	50.19	2.548	-
24	100	57.47	3.082	-
28	100	60.40	5.573	emulsification
32	100	61.87	6.087	emulsification

3.2.2. Demulsification by Addition of Sodium Salt of Organic Acid

For further demulsification in cases of higher zinc concentration, the addition of sodium salt of organic acid was studied in addition to the saponification pre-treatment of extractant. The experiments of demulsification were carried out under the conditions of 20% D2EHPA, 3.0 M NaOH, saponification ratio of 80%, and saponification time 8 min. Accordingly, zinc extraction experiments at 30 g/L were carried out to evaluate the effect of demulsification on zinc extraction.

As displayed in Figure 2, a demulsification effect was favorably attained and the demulsified ratio increased as sodium salt of organic acid dosage increased in its initial stage of 0–8 g/L; afterward, it was roughly steady. In addition, Table 3 indicates that, with the increase of sodium salt of organic acid after saponification, demulsification was attained even at a high alkali dosage of 32 g/L and the extraction ratios were increased compared to Table 2.

Figure 2. The relationship between the content of a salt compounded with alkali and weak acid and the ratio of demulsification (Conditions: 20% D2EHPA extractant, 3 M NaOH, 80% saponification ratio, and time 8 min).

Table 3. The extraction of zinc after saponification pre-treatment and demulsification.

Alkali Dosage (g/L)	Saponification Ratio (%)	Salt Dosage (g/L)	Demulsification Ratio (%)	Extraction (%)	pH of Raffinate
19.2	80	8	80	54.40	2.636
24	100	10	70	60.12	3.641
28	—	12	50	63.90	6.428
32	—	13	50	63.96	6.672

The sodium salt of organic acid that is made of alkali and a weak organic acid served to stabilize the solution pH by combining the substituted hydrogen ions during zinc extraction,

which allowed a lower dosage of alkali in saponification so that the emulsification was favorably alleviated.

3.3. Zinc Extraction with D2EHPA by Direct Addition of Alkali and Organic Acid

As above mentioned, zinc extraction was badly influenced by emulsification, and demulsification could be favorably attained by the saponification pre-treatment of extractant in association with the addition of alkali salt of a weak organic acid. Since both saponification and the salt additive involved the use of alkali sodium hydroxide and the addition of organic acid had a marked effect on demulsification, it is reasonable to infer that the main effect on demulsification was the associated performance of alkali and organic acid. Based on this idea, the direct extraction of zinc without extractant saponification by the simultaneous addition of alkali and organic acid was studied.

3.3.1. Effect of Organic Acid Dosage

Table 4 displays the effect of acid dosage on zinc extraction at the alkali dosage of 40 g/L under the conditions of 20% D2EHPA, pH 3.0, O/A ratio 50:50, extraction time 10 min, phase separation time 3 min, and 1000 rpm. When acid dosage was lower than 52 mL/L, emulsification appeared in the extraction. As the results demonstrate, at the alkali dosage of 40 g/L, when organic acid dosage increased above 52 mL/L, emulsification in the extraction process was avoided and the extraction was accomplished. Meanwhile, a zinc extraction ratio decrease was observed with an increase in organic acid above 52 mL/L, which could be attributed to the decrease of pH. The increase of extraction ratio should be increased by further optimization of other factors.

Table 4. The effect of acid dosage on zinc extraction at alkali dosage of 40 g/L.

Organic Acid Dosage (mL/L).	Extraction (%)	pH of Raffinate	Extraction Phenomenon
20	-	-	emulsification
40	-	-	emulsification
52	61.79	3.063	-
100	56.00	2.935	-

3.3.2. Effect of Alkali Dosage

In Table 5, the effect of alkali dosage on zinc extraction is presented at an acid dosage of 52 mL/L. It is apparent that raffinate pH and zinc extraction went up when alkali dosage increased in the range of 8–40 g/L. It indicates that the dosage of alkali exceeds the range of organic acid to adjust the pH value, and emulsification will appear, while emulsification occurred at the alkali dosage above 40 g/L. Therefore, weak acid with 52 mL/L and alkali with 40 g/L are the best dosage for zinc extraction.

Table 5. The effect of alkali dosage on zinc extraction at acid dosage at 52 mL/L.

Alkali Dosage (g/L)	Extraction (%)	pH of Raffinate	Extraction Phenomenon
8	34.32	2.013	-
24	52.48	2.793	-
32	55.18	2.902	-
40	61.79	3.063	-
48	-	-	emulsification

3.3.3. Effect of Extractant Concentration

It is noticed that, as mentioned above, zinc extraction ratios were all at relatively low levels. Since those experiments were conducted at a low extractant concentration, the low zinc extraction ratios could be considered to be limited by the capacity of the

extractant. Therefore, a higher extractant concentration could be expected to increase the extraction ratio.

The effect of extractant concentration on zinc extraction is displayed in Table 6; with the increase of extractant concentration, the zinc extraction ratio was significantly raised. Under the condition of 40% extractant concentration, 104 mL/L organic acid, and 80 g/L alkali, the zinc extraction ratio reached 99.61%, demonstrating that the zinc in the solution was almost entirely extracted. Nevertheless, the direct extraction of zinc by simultaneous direct addition of alkali and organic acid perfectly stabilized solution pH without emulsification, which effectively ensured a high extraction ratio at high zinc concentrations up to 30 g/L.

Table 6. The effect of D2EHPA extractant concentration on zinc extraction.

Extractant (%)	Alkali Dosage (g/L)	Organic Acid Dosage (mL/L)	Extraction %	pH of Raffinate
20	40	52	61.79	3.063
	48	64	61.93	3.188
	56	76	62.62	3.298
30	40	52	79.39	2.692
	56	72	86.88	3.159
	64	84	87.64	3.287
40	40	52	91.34	2.350
	48	64	96.64	2.770
	64	84	98.29	3.242
	80	104	99.61	3.370

3.4. Mechanism of Intensified Extraction with Associated Additives of Alkali and Organic Acid

3.4.1. Saturation Capacity

The saturation capacity of an extractant with and without the addition of alkali and organic acid have been investigated, and the results are displayed in Figure 3. Apparently, the saturation capacity of an extractant increased with the increase of the extractant concentration, and the saturation capacity had a linear relationship with the extractant concentration. Besides, the saturation capacity of the extractant with the addition of alkali and organic acid is relatively higher than that without additives; this indicates that the addition of alkali and weak acid could not only adjust the solution pH, but also improve the saturation capacity of the extractant.

Figure 3. The saturation capacity of an extractant with and without the compound additive of organic acid and strong alkali (Conditions: zinc concentration 8 g/L, initial pH 3.0, A/O ratio 50:50, stirring speed 1000 rpm, and extraction time 15 min).

3.4.2. FTIR Spectroscopy

The FTIR spectroscopies of the organic phase without and with addition of alkali and organic acid are in Figure 4a,b, respectively. It is clear from Figure 4a that the peak of P-O-H bond in the D2EHPA extractant disappeared, which indicated that the hydrogen bond in D2EHPA was completely broken, and the P=O bond was not associated with the hydrogen bond in D2EHPA after extraction. The peak of the P=O bond shifted to 1197.58 cm^{-1} and demonstrated that P=O still existed in the form of an associative, and the bond energy of P=O was weakened. After extraction, the zinc ions could associate with the P=O bond in the organic phase. The peak of the C-O bond was moved to 1105.01 cm^{-1} due to the coordination of the P=O bond with the zinc ion [23–25]. For the addition of alkali and organic acid, the peak of P-O-H bond still existed, and the peak of P=O was transferred to 1205.49 cm^{-1} . Furthermore, the vibration absorption peak of organic acid appeared at 1634.92 cm^{-1} , and it indicated that organic acid salts appeared in the organic phase after extraction.

Figure 4. The FTIR spectroscopy for organic phase: (a) without addition of organic acid and strong alkali, and (b) with addition of organic acid and alkali. A, stretching vibration of C-H; B, bending vibration of C-H; C, P-O-H bond vibrations of hydrogen bond association; D, coupled vibration of P=O bond; E stretching vibration of C-; G, stretching vibration of P-O; H, stretching vibration of P-O-C; J, O-H vibration; K, vibration of organic acid.

In conclusion, the P=O bond in the D2EHPA extractant was not fully coordinated with the zinc ion, and a part of the D2EHPA extractant still existed in the form of a dimer in zinc extraction with the compound additive of alkali and organic acid. Moreover, the presence of alkali and weak acid in the extraction could not only adjust the pH value, but also improve the saturation capacity of the D2EHPA extractant. As a result, the zinc extraction could be improved by adding a compound additive of alkali and organic acid.

3.4.3. Demulsification with Associated Additive of Organic Acid and Strong Alkali

As mentioned above, the emulsification did not occur in zinc extraction with the addition of enough weak acid. Therefore, the emulsification in extraction with the addition of alkali was discussed in this section. FTIR analysis was performed on the emulsion produced in the extraction with the addition of alkali, and the results are displayed in Figure 5. It can be observed that the peaks of P-O-H in the form of hydrogen-bonding association appeared, and it indicates that a new association of O-H bond and P=O occurred in the emulsion. The new stretch at 3442.41 cm^{-1} and 3186.79 cm^{-1} could be assigned to the stretching vibration of O-H in water and O-H in the form of association, respectively. It indicated that a new O-H bond in the form of association existed in the emulsion. Therefore, the P=O bond in the emulsion existed in the free state and association state. When the zinc extraction was lower than 100%, the emulsification contained zinc hydroxide. The action of hydroxyl with the reactive bond of D2EHPA-Zn salt caused multi-molecular polymerization in the organic phase. The viscosity of the organic phase increased, resulting in emulsification. However, the pH value of the extraction solution with the addition of alkali and organic acid was lower than that of the formation of zinc hydroxide, eliminating emulsification in the extraction process.

Figure 5. FTIR spectroscopy for an emulsion formed in extraction with the addition of a strong alkali. A, stretching vibration of C-H; B, bending vibration of C-H; C, P-O-H bond vibrations of hydrogen bond association; D, coupled vibration of P=O bond; E, coupled vibration of P-O-C bond; F, coupled vibration of P-O-C bond; G, O-H vibration.

4. Conclusions

Emulsification was apt to occur in zinc extraction with D2EHPA from zinc solution of high concentration with direct addition of alkali to control solution pH. The saponification pre-treatment of extractant and the addition of sodium salt of organic acid were helpful to demulsification. On this basis, the associated addition of alkali and organic acid applied directly to zinc extraction effectively served to adjust the solution pH and eliminate emulsification, which ensured a smooth extraction of zinc at high concentrations. Under the condition of 40% extractant concentration, 104 mL/L organic acid, and 80 g/L alkali, the zinc extraction favorably reached 99.61%.

The emulsification in the extraction process was mainly due to the formation of zinc hydroxide at sensitively increased pHs with addition of alkali. With the effect of associated additives of alkali and organic acid, solution pH could be controlled in the range of 3.0–4.0, which is far below that of the formation of zinc hydroxide, being the main mechanism in improvement of extraction without emulsification.

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References

1. Rydberg, J.; Musikas, C.; Chopping, G.R. Introduction to Solvent Extraction. In *Principles and Practices of Solvent Extraction*; Marcel Dekker Inc.: New York, NY, USA, 1992; pp. 1–17.
2. Owusu, G. Selective extractions Zn and Cd from Zn-Cd-Co-Ni sulphate solution using di-2-ethylhexyl phosphoric acid extractant. *Hydrometallurgy* **1998**, *47*, 205–215. [[CrossRef](#)]

3. Kongolo, O.; Mwema, M.D.; Banza, A.N.; Gock, E. Cobalt and zinc recovery from copper sulphate solution by solvent extraction. *Miner. Eng.* **2003**, *16*, 1371–1374. [[CrossRef](#)]
4. Faubel, W.; Ali, S.A. Separation and purification of fission products from process streams of irradiated nuclear fuel. *Radiochim. Acta.* **1986**, *40*, 1–5.
5. Zamani, A.A.; Amani, A.A.; Zarabadi, A.S.; Yaftian, M.R. Water soluble crown ethers: Selective masking agents for improving extraction-separation of zinc and lead cations. *J. Incl. Phenom. Macro.* **2009**, *63*, 327–334. [[CrossRef](#)]
6. Ali, A.M.I.; Ahmad, I.M.; Daoud, J.A. CYANEX 272 for the extraction and recovery of zinc from aqueous waste solution using a mixer-settler unit. *Separ. Purif. Technol.* **2006**, *47*, 135–140. [[CrossRef](#)]
7. Park, Y.J.; Fray, D.J. Separation of zinc and nickel ions in a strong acid through liquid–liquid extraction. *J. Hazard. Mater.* **2009**, *163*, 259–265. [[CrossRef](#)] [[PubMed](#)]
8. Marcelo, B.M.; Sonia, D.F.R.; Fernando, S.M.; Jeaneth, D.S.B. Selective extraction of zinc(II) over iron(II) from spent hydrochloric acid pickling effluents by liquid–liquid extraction. *J. Hazard. Mater.* **2008**, *150*, 669–678.
9. Abdelhamid, M.; Djafer, B. The solvent extraction of zinc, cadmium and chromium from phosphoric acid solutions by tri-nbutyl phosphate in kerosene diluent. *Separ. Purif. Technol.* **2007**, *56*, 220–224.
10. Tang, B.; Zhu, Y.C.; Bai, X.M.; Cai, B.; Chen, L.Q.; Zhang, J.H. Study on separation of zinc from iron in waste sulfuric acid pickle liquor by solvent extraction. *Min. Metall. Eng.* **2003**, *5*, 47–49. (In Chinese)
11. Yang, Y.; Shi, X.; Li, Q.; Jiang, T.; Wang, W.; Nie, H. Research on Control of pH in Solvent Extraction of Zinc by D2EHPA (P204). In Proceedings of the 19th International Biohydrometallurgy Symposium, Changsha, China, 18–22 September 2011.
12. Luo, F.; Li, D.; Wei, P. Synergistic extraction of zinc(II) and cadmium(II) with mixtures of primary amine N1923 and neutral organophosphorous derivatives. *Hydrometallurgy* **2004**, *3*, 31–40. [[CrossRef](#)]
13. Keshavarz, A.E.; Moradkhani, D.; Oradkhani, D.; Darvishi, D.; Askari, B.M.; Behnian, C.D. Synergistic effect of MEHPA on co-extraction of zinc and cadmium with DEHPA. *Miner. Eng.* **2004**, *17*, 89–92. [[CrossRef](#)]
14. Principe, F.; Demopoulos, G.P. Comparative study of iron(III) separation from zinc sulphate–sulphuric acid solutions using the organophosphorus extractants, OPAP and D2EHPA: Part I: Extraction. *Hydrometallurgy* **2004**, *74*, 93–102. [[CrossRef](#)]
15. Rice, N.M.; Smith, M.R. The recovery of zinc, cadmium and mercury(II) by solvent extraction. *J. Appl. Chem. Biotechnol.* **1975**, *25*, 379–402. [[CrossRef](#)]
16. Forrest, C.; Orrest, C.; Hughes, M.A. The separation of Zn from Cu by DEHPA—an equilibrium study. *Hydrometallurgy* **1978**, *3*, 327–342. [[CrossRef](#)]
17. Kolarik, Z. Critical evaluation of some equilibrium constants involving acidic organophosphorus extractant. *Pure Appl. Chem.* **1982**, *54*, 2593–2674. [[CrossRef](#)]
18. Vahidi, E.; Rashchi, F.; Moradkhani, D. Recovery of zinc from an industrial zinc leach residue by solvent extraction using D2EHPA. *Miner. Eng.* **2009**, *22*, 204–206. [[CrossRef](#)]
19. Pereira, D.D.; Rocha, S.D.; Mansur, M.B. Recovery of zinc sulphate from industrial effluents by liquid–liquid extraction using D2EHPA (di-2-ethylhexyl phosphoric acid). *Sep. Purif. Technol.* **2007**, *53*, 89–96. [[CrossRef](#)]
20. Chen, S.; Lai, X. A study on extracting zinc out of low acid waste solution from copper leaching process by using D2EHPA agent. *Copp. Eng.* **2007**, *20*, 21–23. (In Chinese)
21. Tang, J. Technology and Mechanism of Recovery Zinc from Zn-Bearing Waste Stream by Solvent Extraction. Master's Thesis, Central South University, Changsha, China, 2008.
22. Liu, X. Research on Mechanism and Prevention of Interfacial Emulsion Formation in Copper Solvent Extraction Process. Ph.D. Thesis, Central South University, Changsha, China, 2001.
23. Brown, E.N.; White, S.R.; Sottos, N.R. Microcapsule induced toughening in a self-healing polymer composite. *J. Mater. Sci.* **2004**, *39*, 1703–1710. [[CrossRef](#)]
24. Biniak, S.; Szymanski, G.; Siedlewski, J.; Świątkowski, A. The characterization of activated carbons with oxygen and nitrogen surface groups. *Carbon* **1997**, *35*, 1799–1810. [[CrossRef](#)]
25. Shi, X. Technology and Mechanism on Solvent Extraction of Zinc from High Concentration Zinc Solution by P204. Master's Thesis, Central South University, Changsha, China, 2011.