Separation and recovery of heavy metals from waste water using synergistic solvent extraction

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Abstract. Heavy metal wastewater pollution is one of the three major water pollutions in the world. The zinc hydrometallurgy smelting process usually discharge large quantities of heavy metal wastewater into the environment. In this paper, a synergistic solvent extraction process has been developed to recover copper, nickel, zinc and cadmium respectively from calcium and magnesium. The synergistic organic system contained 0.50 M Versatic 10 and 0.5 M Mextral 984H in DT100. Adjusting pH to 2.0 at 40 °C, the copper will be extracted preferentially with the extraction rate more than 99%. Continuing to adjust pH to 4.2 at 40 °C, the nickel will be extracted secondly with an extraction rate more than 98%; the zinc and cadmium in raffinate could be extracted separately while pH is about 6.5.

1. Introduction

With rapid development of the mining and smelting industry in China, wastewater generated by this process was largely emitted into the soil and water bodies. This waste water contains heavy metals such as Zn (II), Cu (II), Ni (II), Hg (II), Cd (II), Co (II) and As (II). It not only affects the quality of the atmosphere, but also threatens the health of human beings by way of the food chain[1,2]. Heavy metal wastewater pollution had been one of the three major water pollutions in the world, and the zinc hydrometallurgy smelting process usually discharges large quantities of wastewater into the environment[3]. Currently, the most common heavy metal wastewater treatment techniques are chemical reaction methods[4,5]. This usually engenders hydroxide precipitation, sulfide precipitation and heavy metal chelating precipitation. So far, the most widely used chemical precipitation technique is hydroxide precipitation[6], because it can remove any heavy metals other than mercury, and the process is usually simple and low cost. However, hydroxide precipitation generates large volumes of relatively low density sludge and both the metals and acid resource cannot be efficiently recovered for recycle[7]. Finding a way to clean the heavy metals from wastewater and recover resourceful metals is the most significant task.

Recently, people began to apply solvent extraction technology into wastewater treatment, as it can provide the selectivity necessary to create valuable product streams suitable for recycle or reuse. Compared to the solvent extraction system, the synergistic solvent extraction system can simplify the extraction process, and recover three or more metal ions respectively at the same time in the complex solution system[8].

In this paper, the synergistic solvent extraction system was developed using Versatic 10, Mextral 984H and DT 100 for the effective and efficient recover copper, nickel, zinc and cadmium.
respectively from the main impurities, magnesium, calcium. All three reagents are commercially available.

2. Materials and methods

2.1. Feed Solutions

The composition of a synthetic aqueous feed solution is shown in Table 1. It was prepared by dissolving analytical grade metal sulphate salts in de-ionized water including CuSO₄·5H₂O, NiSO₄·6H₂O, ZnSO₄·7H₂O, 3CdSO₄·8H₂O, MgSO₄·7H₂O, and CaSO₄·2H₂O. Its profile is similar to a certain zinc hydrometallurgical wastewater.

| Concentrations (mg/L) | Cu    | Ni    | Zn    | Cd    | Ca    | Mg    | pH |
|-----------------------|-------|-------|-------|-------|-------|-------|----|
|                       | 1803.6| 507.5 | 5288.5| 736.7 | 481.4 | 11084.6| 3.3|

2.2. Organic Solutions

The synergistic organic system consisted of 0.50 M Versatic 10 and 0.5 M Mextral 984H in DT100. Versatic 10 was supplied by Shell Chemicals, Mextral 984H and Mextral DT100 were supplied by Kopperchem of China. Versatic 10 was 2-methyl-2-ethylheptanoic acid. Mextral 984H was a mixture of 2-hydroxy-5-nonyl-acetophenone oxime and 5-nonyl-salicylaldoxime in a high flash point hydrocarbon diluent. Mextral DT100 (containing >99% aliphatics and <0.5% aromatics) was used as the diluent for all organic systems tested.

2.3. Experimental Procedure

All batch experiments were carried out in glass bottles. The pH of the solution, adjusted to the desired value by adding drops of 5 M NaOH, was measured by an on-line pH monitor. The two phases were mixed for enough time to ensure that equilibrium was reached. After phase separation, the metal concentrations in the raffinate were detected by inductively coupled plasmaatomic emission spectroscopy (ICP-AES), and the metal concentrations in the organic phase were calculated by mass balance.

3. Results and discussion

3.1. Extraction pH Isotherms of Versatic 10

![Figure 1. Extraction pH isotherms of metals with 0.5 M Versatic 10 in Mextral DT100 and the synthetic solution at an A/O ratio of 1:1 and 40C.](image-url)
As it is shown in Figure 1, in low pH values, Cu was well extracted; in a pH profile of <8.0. The metal extraction order is Cu > Zn > Cd > Ni > Ca > Mg, and it is shown a better extraction for a single metal ions. But the heavy metal ions were extracted within the range of high pH values, where metal hydrolysis occurred. The separation factors between the desirable metals with calcite are small which could introduce the generation of gypsum in aqueous solution if operated under this condition. By comparing the half extraction(pH_{50}), pH_{50}^{Zn}=5.8, pH_{50}^{Cd}=6.1, pH_{50}^{Ni}=6.45, pH_{50}^{Ca}=6.9, the pH values are so close that it would be difficult to recover the valuable metals from others with only a few steps, and using the cascade process to extract these metals would be costly.

3.2. Extraction pH Isotherms of Mextral 984H

![Figure 2. Extraction pH isotherms of metals with 0.5 M Mextral 984H in Mextral DT100 and the synthetic solution at an A/O ratio of 1:1 and 40°C.](image)

Figure 2 shows that in a pH profile of <7.5, the metal extraction order is Cu > Ni > Zn > Cd > Ca > Mg. The extraction of Ca and Mg were lower than 15%. Cu was well extracted at low pH values; the others with higher extraction only occurred at the high pH values. It was also difficult to recover copper, nickel, zinc, and cadmium by using Mextral 984H.

3.3. Extraction pH Isotherms of the Synergistic system

![Figure 3. Extraction pH isotherms of metals with 0.5 M Mextral 984H & 0.5 M Versatic 10 in Mextral DT100 and the synthetic solution at an A/O ratio of 1:1 and 40°C.](image)
Figure 3 shows that adding Mextral 984H to Versatic 10 resulted in very large synergistic shifts with heavy metal ions. As a general rule, it is unusual for an extractant to cause a ΔpH $^{50}$ greater than 1. The synergistic shifts for copper were greater than 2. However, the nickel ΔpH $^{50}$ shifted scale was small, only 0.5 pH units, the ΔpH $^{99}$ increased more than 2 pH units. The pH isotherms of zinc also shifted, but not very significantly, towards lower pH. The pH isotherms of cadmium also shifted 1.5 pH units to lower pH. Magnesium and calcium shifted either but the change scale is small. According to figure 3, the technique process could be divided into 3 stages. In the 1st, the copper in feed solution could be extracted totally by controlling the pH at about 2.0, while other ions were hardly extracted. In the 2nd, nickel is extracted at a pH of about 5.0, and finally zinc and cadmium at a pH of about 6.5.

![Figure 4](image1.png)

**Figure 4.** Extraction pH isotherms of metals without copper.

As is shown in figure 4, after extracting copper, the extraction pH of isotherms of other metals shifted. The pH isotherm of nickel shifted 1.0 pH units to a lower pH. The pH isotherm of zinc and cadmium also shifted a little to a lower pH. According to figure 4, after extracting copper, the nickel could be extracted totally by controlling the pH at about 4.0, while other ions are hardly extracted. The zinc and cadmium could be extracted at a pH of about 6.25.

![Figure 5](image2.png)

**Figure 5.** Extraction pH isotherms of metals without copper and nickel.
Figure 5 shows that after extracting copper and nickel, the extraction pH of isotherms of zinc and cadmium did not shift again. They would be extracted at a pH of about 6.0. However, this synergistic system cannot recover zinc and cadmium directly, and calcium will be significantly extracted under these conditions. Many other extraction systems which had been used in industry, such as D2EHPA, can extract zinc and cadmium separately from calcium and magnesium[9].

4. Conclusions
A single solvent extraction system such as Versatic10 or Mextral 984H, cannot recycle heavy metals separately in complex waste water. The synergistic organic system consisting of 0.50 M Versatic10 and 0.5 M Mextral 984H in DT100 can deal with a certain waste water which contains Zn (II), Cu (II), Ni (II), Ca(II), Mg(II) efficiently, and as extraction proceeds, some improved change of extraction pH isotherms of metal ions will occur. At an A/O ratio of 1:1 and 40°C, the copper could be extracted while pH is about 2.0, nickel will be preferentially extracted while pH is about 4.2, zinc and cadmium could be recovered while pH is about 6.5.

References
[1] Cheng S P. Heavy metal pollution in China: Origin, pattern and control[J]. *Environmental Science and Pollution Research*, 2003, 10(3): 192-198.
[2] Guo J F, Lu Y J. Progress of heavy metal wastewater treatment technology[J]. *Nonferrous Metals Processing*, 2006, 35(4): 48-50.
[3] Wang T, Li X G, Du Q Y. Research progresses in treatment technologies for heavy metal ion containing wastewater[J]. *Environmental Protection of Chemical Industry*, 2008, 28(4): 323-325.
[4] Li Y, Yang G Y. Present status of treatment and utilization of heavy metal wastewater[J]. *Environmental Protection for Electric Power*, 2009, 25(4): 50-51.
[5] Ma Q, Zhang X L. Advances in new technology for heavy metal wastewater treatment at home and abroad[J]. *Chinese Journal of Environmental Engineering*, 2007, 1(7): 10.
[6] Chai L Y, Li Q Z, Li M; Liang Y J, Peng B, Min X B. Research advances on reduction and treatment technology of pollutants discharged from zinc smelting[J]. *Nonferrous Metals Science and Engineering*, 2013, 4(4): 1-10.
[7] Fu F, Wang Q. Removal of heavy metal ions from wastewaters: A review[J]. *Journal of Environmental Management*. 2011, 92(3): 407-418.
[8] Zhang M J. The Extraction of Metal and Other Useful Components in the Solution[M]. *Metallurgical Industry Press*, 1995.
[9] Ma R J. Principle of Hydrometallurgy[M]. *Metallurgical Industry Press*, 2007.