



Liquid-Liquid Extraction of Metal Ions Using Aqueous Biphasic Systems

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Abstract

An investigation was conducted for the study of extraction of metal ions using aqueous biphasic systems. The extraction of iron, zinc and copper from aqueous sulphate media at different kinds of extractants SCN^- , Cl^- and I^- , different values of pH of the feed solution, phase ratio, concentration of metals, concentration of extractant, concentration of polymer, and concentration of salt was investigated. Atomic absorption spectrophotometer was used to measure the concentration of iron, zinc and copper in the aqueous phase throughout the experiments. The results of the extraction experiments showed the use of SCN^- as extractant, pH=2.5, phase ratio=1.5, concentration of metals 1g/l, concentration of extractant 0.06 %, concentration of polymer =50 %, and concentration of salt=20% gave the highest value of percent removed. Also increase of extractant concentration increases the percent removed. The results clarified that increasing the metal ions concentration in the aqueous phase causes to decrease the percent removed. The addition of an inorganic salt (sodium sulphate) up to (20%) increased the dehydration of polymer chains and then increases the percent removed.

الخلاصة

تم في هذا البحث دراسة عملية استخلاص ايونات المعادن من محاليتها المائية باستخدام انظمة الطورين المائية. تتضمن الدراسة استخلاص ايونات الحديد، الزنك والنحاس من وسط محلول كبريتي تحت ظروف مختلفة وهي: نوع المذيب SCN^- , Cl^- , I^- ، pH المحلول ، نسبة الطور، تركيز المعادن تركيز المذيب المستخدم ، تركيز البوليمر ، وتركيز الملح .

تم تحليل النتائج باستخدام جهاز الامتصاص الذري ، وظهرت التجارب ان استخدام (SCN^-) كمذيب و pH (2.5) ونسبة الطور (1.5) وتركيز المعادن (1 غم /لتر) وتركيز المذيب (0.06 % حجما) وتركيز البوليمر (50 % وزنا) وتركيز الملح (20 %) تعطي اعلى قيمة لنسبة الازالة للمعادن، كذلك بزيادة تركيز المذيب يزداد معامل الاستخلاص وان زيادة تركيز ايونات المعادن في المحلول المائي تسبب نقصان في معامل الاستخلاص . ان اضافة الملح غير العضوي (كبريتات الصوديوم) لغاية 20 % تسبب زيادة لنسبة الازالة.

Introduction

Traditional solvent extraction is one of the most useful techniques that are being used for selective removal and recovery of metal ions from aqueous solutions and it is largely applied in the purification processes in numerous chemical and metallurgical industries [Dean J.R.1998].

In liquid-liquid extraction system, water immiscible and miscible solvents are employed. Cationic or anionic forms of metals are complexed into an organophilic compounds or an ion-pairs by chelation or using ion-pairing agents. If the water immiscible solvent and an aqueous solution containing a hydrophobic species are brought into contact, the chelate or an ion-pair is transferred into the organic phase [Thurman E. M. and Mills M.S.1998].

Advantages of liquid-liquid extraction are simplicity and rapidity. The solvents are not highly flammable and easily recoverable. They are stable, transparent to UV, not emulsifying during extraction as selective as possible. Disadvantages of liquid-liquid extraction methods are emulsion formation, different extraction efficiencies for various compounds with various extracting agents, and low sensitivity. In these processes, metal ion containing solution contacts with a large amount of selective solvent. After extraction, stripping follows this process. Solvent extraction is very difficult for the separation of quantitatively of metal ions because of low driving force, and then a large amount of solvent is required. These make the extraction and stripping of desired species very expensive [Triangl P.1983].

Even with today's environmental standards a number of extraction systems still utilize toxic and flammable organic diluents. When the diluent is coupled with a highly selective extractant the cost of the solvent system can become very expensive [Walter H. and Johansson G.1994].

The goal of Technology is to enable the (chemical) industry to continue to lead in technology development, manufacturing and profitability, while optimizing health and safety and ensuring environmental stewardship. New separations technologies developed for pollution prevention may also find application in pollution remediation, helping to clean up already contaminated sites. Aqueous biphasic systems (ABS) consist of two immiscible phases formed when certain water-soluble polymers are combined with one another or with certain inorganic salts in specific concentrations. As two-phase systems they are suitable for carrying out liquid-liquid separations of various solutes such as biomolecules, metal ions, and particulates. In ABS the major component in each of the two phases is water, and because of this non-denaturing environment these systems have been widely employed in biological separations for over 40 years [Rogers R.D. and Eitema M.A.1995]. There are three kinds of (ABS): polymer-polymer systems, polymer-salt systems, and more recently salt-salt systems. The literature has reported equilibrium data for different (ABS) formed by poly ethylene glycol (PEG) of different average molar masses and inorganic salt [Bridges N.J. at.el.2007].



Separation processes are applied in various types of industries including chemical, pharmaceutical, and food. Classic methods involving liquid-liquid extraction use an organic solvent and an aqueous solution as the two immiscible phases for the fractionation and purification of molecules. However, these systems are very toxic and present risks to human health. An alternative to substitute organic two-phase systems, based on the beginning of green chemistry, is aqueous biphasic systems (ABS). They are formed by the mixture of a polymer + water + salt or two water-soluble polymers differing in chemical structure. This methodology has been widely used to separate metallic ions and biological materials such as viruses, nucleic acids, and proteins. These characteristics are important because an organic solvent is not used in the separation processes [Martins J. et al. 2008].

Experimental

Materials

The PEG used in this study was PEG-3000 (average molecular mass = 3000). Stock solutions of 10%, 20%, 30% and 40% (w/w) PEG were prepared by dissolving of suitable quantity of PEG in deionized water. The stock solution of inorganic salt (Na_2SO_4) (5%, 10%, 15% and 20% (w/w) Na_2SO_4) was prepared by dissolving in deionized water. The solution of metal ions was prepared by dissolving CuSO_4 , Fe_2SO_4 and ZnSO_4 in deionized water to reach the required concentration of metal of about (1g/l) for each metal. The extractant used was prepared by dissolving KI, KCl, and KSCN in deionized water to reach the extractant ions. The different pH values were obtained by adding small volumes of acid (H_2SO_4) or base (NaOH) concentrated solutions, which were considered in the total solution mass.

Methods

Aqueous two-phase system was prepared by mixing equal volumes (20 ml) of PEG stock solution and inorganic salt stock solutions (20%w/w). The other variables were pH (2), metal concentration (1g/l), extractant concentration (0.05%), polymer concentration (40%) and salt concentration (20%). The effect of extractant type on the percent removed was investigated by using KI, KCl, and KSCN. The system was mixed for (15 minute) followed by (10 minute) of Centrifugation at (2000 rpm). Just before analysis, the two immiscible phases were carefully separated with Pasteur pipettes and placed into separated tubes. Equal volumes (1ml) for each phase were measured for ZN (II), CU (II), and Fe (III) by means of atomic absorption spectrophotometer model (AA-670, Shimadzu corporation, Japan). Phase ratio (PEG/ Na_2SO_4) was studied for the mixtures which had the best percent removed of the metals with (0.5, 1, 1.5, 2, 2.5 and 3) (Polymer /inorganic salt ratio). Study the effect of other variables on percent removed, different pH values (1, 1.5, 2, 2.5, 3, 3.5 and 4), concentration of metals (0.5-3g/l), concentration of extractant (0.01-0.06 extractant vol. / salt vol. %), concentration of polymer (10-50 %) and finally concentration of salt (5-20 %).

Results and Discussion

Effect of Extractant Type

The effect of extractant type on the percent removed was investigated. The operating conditions were (pH = 2, metal concentration = 1g/l, phase ratio = 1, extractant concentration = 0.05%, polymer concentration = 40% and salt concentration = 20%) being kept constant.

The results obtained from this set are listed in Table 1, showing that using thiocyanate as an extractant give the highest

value of percent removed. The distribution behavior of Fe (III), Cu (II), and Zn (II) was studied in an aqueous two-phase system formed from a polyethylene glycol and sodium sulphate in the presence of thiocyanate, chloride, and iodide ions. From the distribution ratios determined as a function of the iodide, chloride or thiocyanate concentration. In the SCN^- system Cu(II), Zn(II) distribute into the PEG-rich phase predominantly as $\text{Cu}(\text{SCN})_4^{-2}$, $\text{Zn}(\text{SCN})_4^{-2}$ and Fe(III) as $\text{Fe}(\text{SCN})_4^-$, respectively. The extractabilities of the metal ions depend not only on the stabilities of the metal thiocyanate, chloride or iodide complexes but also on those of their sulphate complexes. This is presumably due to the difference in the stability constant between the thiocyanate complex and the iodide or chloride. It has also been suggested that the extractability of a metal ion with complexing anions in aqueous two-phase systems formed by a polymer and an inorganic salt depends not only on the complexing ability of the extracting anions but also that of the anion of the phase-forming salt [Masami Shibukawa et al. 2001].

Effect The pH of The Solution

The effect of pH solution on the percent removal was investigated. Keeping other variables constant (metal concentration = 1 g/l, phase ratio = 1, extractant concentration = 0.05%, polymer concentration = 40% and salt concentration = 20%). The results as shown in Fig.(1) indicate that increasing the pH lead to an increase in the percent removed up to a limit then decreases. Thus, pH = 2.5 gave the highest value of percentage of metals removal. The decrease in recovery beyond pH = 2.5 is due to hydrolysis of the metal. This might be attributed to a reverse action due to unstable complex formation between the

metal species and the thiocyanate which will lead to a reduction in the percent removed. In general, decreasing the pH of the salt stock solution has the effect of increasing the hydrophobicity of the PEG-rich phase and, thus, enhancement of the efficiency of metal ion extraction increases with increasing acidity of the salt stock solution [Bulgariu L. and Bulgariu D. 2007] and [Bulgariu L. and Bulgariu D. 2008].

Effect of Phase Ratio

The effect of phase ratio on the percent removed was investigated. From the previous section pH (2.5) is used at this set. Keeping other variables constant (metal concentration = 1 g/l, extractant concentration = 0.05%, polymer concentration = 40% and salt concentration = 20%). The results obtained showed that phase ratio of (1.5) gave the highest value for the system as indicated in Fig. (2), this may be attributed to the large difference in the concentration of the two phase systems, so that the solute extraction is increased because of the solute hydration. Further support the above conclusion where this figure represent the percentage removal of metals (Fe=66.25, Zn=75.99 and Cu=85.25), the percentage of metals removal increases up to a limit then it remains nearly constant. The behavior because when the concentration of the PEG polymer is increased the stronger hydrogen bonding between the PEG molecules and the water is increased, causing raise in the cloud point (the interface between the two phase systems) [Rogers R.D. and Eitema M.A.1995].



Effect of The Metals Concentration

The effect of metals concentration on the percent removed was investigated. From the results of previous sections as it were noticed, pH (2.5) and phase ratio (1.5) gave the highest percent removed. These conditions were used in this section. Keeping other variables constant (extractant concentration =0.05%, polymer concentration = 40% and salt concentration=20%). Increasing the metals concentration in the feed, the extraction percentage of metal removed decrease. These results could clearly be seen in Fig. (3), the formation of an extractant-metal complexing in the PEG will produce a lower concentration of free extractant. A certain number of extraction molecules associated with each metal ion, thus upon keeping other variable constant, the concentration in the solvent will remain almost constant in spite of its increase in the aqueous phase [Bulgariu L. and Bulgariu D. 2007].

Effect of The Extractant Concentration

The effect of extractant concentration on the percent removed was investigated. From the results of previous sections as it were noticed, pH (2.5), phase ratio (1.5) and metal concentration (1g/l) gave the highest percent removed. These conditions were used these experiments. Keeping other variables constant (polymer concentration = 40% and salt concentration =20%).Percentage of metal removed plotted vs. extractant concentration in the Fig. (4) Showed that upon increasing the extractant concentration, the percentage of metals removed increased and the best values were (Fe=69.61, Zn=77.35 and

Cu=89.23). This is due to the polar nature of the extractant, which might cause an interaction between the extractant and the metal. Thus, the formation of an extractant-metal complexing in the PEG will produce a lower concentration of free extractant.

Effect of the Poly Ethylene Glycol Concentration(PEG)

The effect of the poly ethylene glycol concentration on the percent removed was investigated. Wide range of the extraction coefficient values was obtained using different poly ethylene glycol concentration. Fig. (5) Shows that increasing poly ethylene glycol concentrations increase the values of percentage of metals removal (Fe=70.71, Zn=81.25 and Cu=91.42).

The metal ion, initially present in salt-rich phase as anionic or neutral species will interact with inorganic extractants, most probably at interface, and the formed species will be then partitioned into PEG rich phase. In our opinion, the formation of extractable species occurs step by step, until his hydration degree becomes comparable with the hydration environment of PEG-rich phase from extraction system [Bulgariu L. and Bulgariu D. 2007]

Effect of Salt Concentration (Na_2SO_4)

The effect of salt concentration on the percent removed was investigated. The results obtained shows that salt concentration (20%) gave the highest value for the system as indicated in Fig.(6) the percentage of metal removal increases as the salt percent increases (Fe=70.71%, Zn=81.25% and Cu=91.42%).

The formation of aqueous two-phase system of PEG and a certain inorganic salt

can be explained on the basis of the competition for hydration between the two components. The addition of an inorganic salt increases the dehydration of the polymer chains, due to the salting-out effect and phase separation. Thus, two immiscible aqueous phases are obtained: an upper one – rich in PEG, having the same role as the organic phase in traditional extraction systems, and a lower one, rich in the inorganic salt [Bulgariu L. and Bulgariu D. 2008].

Conclusions

1. It was found that (SCN^-) ion is more active extractant than Cl^- and I^- ions for extraction of metal ions.
2. The results indicate that increasing the pH of the solution lead to increase the percent removal of the metal ions up to about 2.5 then decrease ,and the phase ratio of (1.5) gave the highest percent removal of metal ions
3. The results showed that and on increasing the metals concentration in the feed, the percentage of metal removed decreases.
4. The results indicate that the percent removal of metal ions increases with increasing the extractant concentration, increasing of poly ethylene glycol concentrations and addition of an inorganic salt
5. Two immiscible aqueous phases are obtained: an upper one – rich in PEG, having the same role as the organic phase in traditional extraction systems, and a lower one, rich in the inorganic salt.

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Table (1) Effect of Extractant Type

| Extractant | %Removed Fe. | %Removed Zn. | %Removed Cu. |
|------------------|--------------|--------------|--------------|
| SCN ⁻ | 63.12 | 72.23 | 84.77 |
| Cl ⁻ | 48.32 | 51.22 | 57.46 |
| I ⁻ | 8.19 | 9.18 | 49.44 |

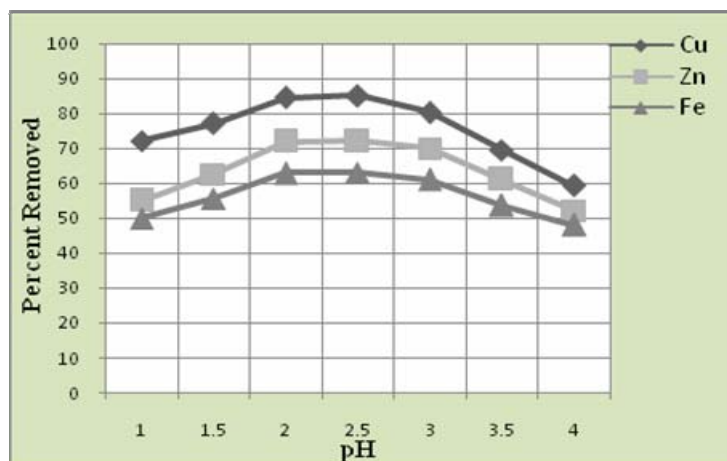


Figure 1: Percent removed vs. pH of the solution, at phase ratio =1, metal concentration =1g/l, extractant concentration =0.05%, polymer concentration = 40% and salt concentration=20%.

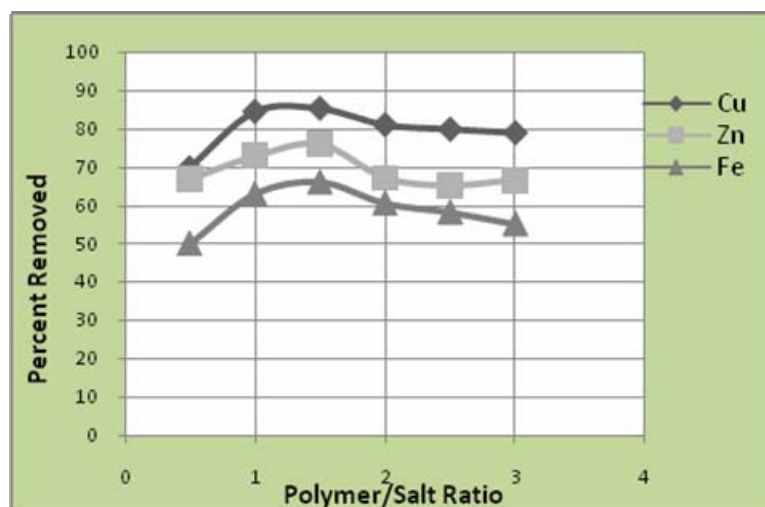


Figure 2 Percent removed vs. phase ratio, pH=2.5, metal concentration=1g/l, extractant concentration =0.05%, polymer concentration=40% and salt concentration = 20 %.

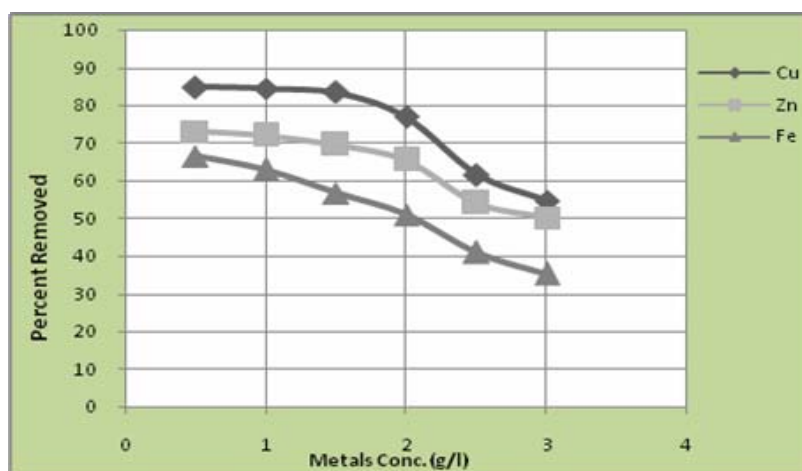


Figure 3 Percent removed vs. metal concentration in the feed, at pH=2.5, phase ratio=1.5, extractant concentration=0.05%, polymer concentration=40% and salt concentration=20%.

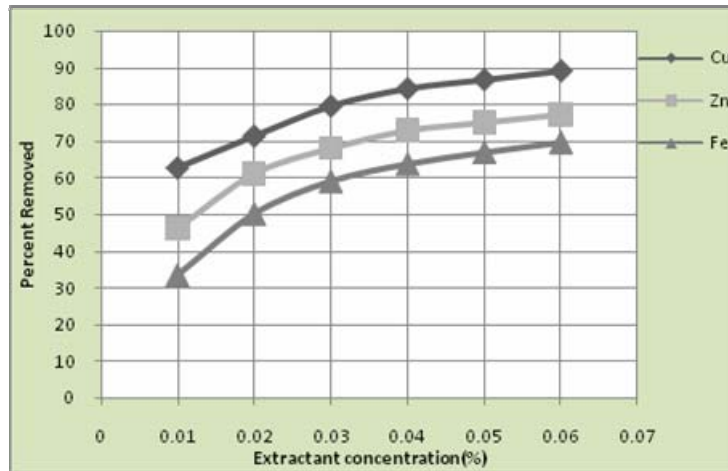


Figure 4 Percent removed vs. extractant concentration, at pH=2.5, phase ratio =1.5, metal concentration = 1g/l, polymer concentration = 40% and salt concentration=20%.

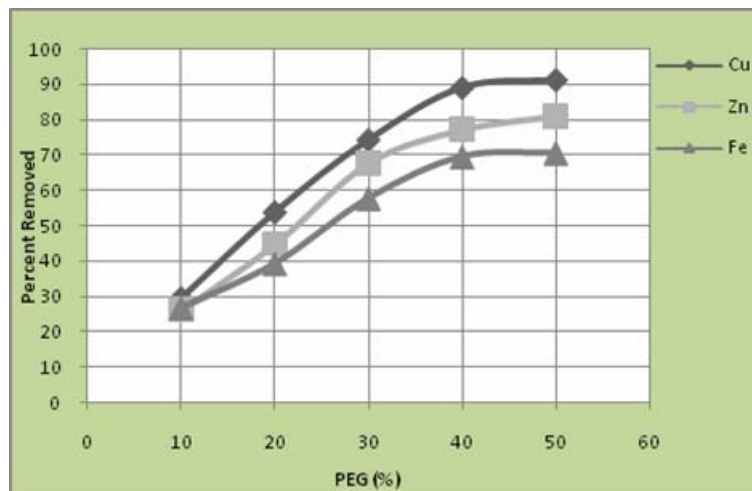


Figure 5 Percent removed vs. polymer concentration, at pH=2.5, phase ratio =1.5, metal concentration =1g/l, extractant concentration =0.06%and salt concentration=20%.

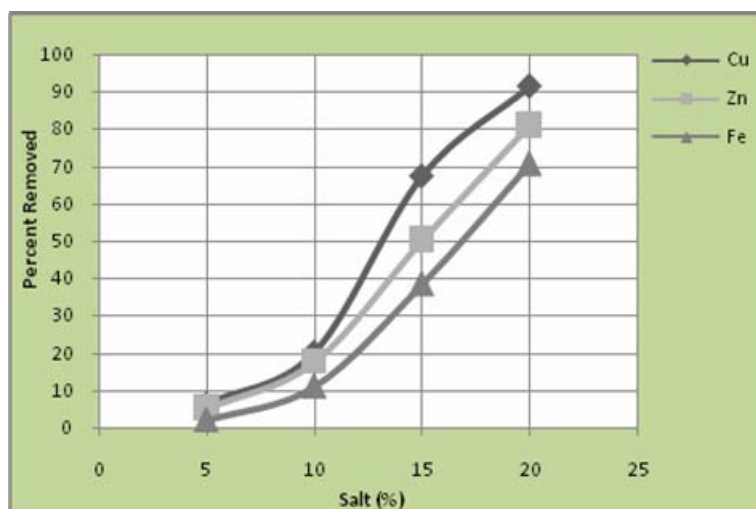


Figure 6 Percent removed vs. salt concentration, at pH=2.5, phase ratio =1.5, metal concentration =1g/l, extractant concentration=0.06% and polymer concentration =50%.