# Extraction of Cd, Cu, Fe, and Zn metal ions mixture using PEG-inorganic salt aqueous two phase systems in the presence of iodide (KI) and Thiocyanate (KSCN) ions as Extractants

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## Abstract

The extraction behavior of (Cd (II), Cu (II), Fe (II), and Zn (II)) metal ions was studied in an aqueous biphasic system formed from poly ethylene glycol and sodium Sulphate in the presence of iodide (KI) and thiocyanate (KSCN) as extractants. The extraction percentage was determined at constant temperature of 25$^{o}$C, PH of 2.5 and mixing time of 10 min. and as a function of the following variables:

- Concentration of (KI) or (KSCN) solvents between (0.1-0.7) ml of 2 g/l solution.
- Volumetric phase ratio of PEG to $Na_2SO_4$ in the range of (0.5-3).
- Initial concentrations of the metal ions between (0.5-0.15) ml of 1 g/l metal solution added.

The extraction percentage (%) of metals is mainly increased with the increasing of each concentration of the extractant, phase ratio, and the initial concentrations of the metal ions. The extraction percentage of (Cu (II), Fe (II), and Zn (II)) was higher for the system containing ($SCN^-$) than ($I^-$), while the extraction (%) of Cd (II) was higher in the system containing ($I^-$) than ($SCN^-$). The mixtures consist of (0.5) ml of initial concentration of metal ions, (0.7) ml of (KSCN), (3) of ($PEG/Na_2SO_4$) volumetric phase ratio had the best results of the extraction of (Cd, Cu, Fe, and Zn) which equal to (87, 92, 92, and 80) % respectively.

## الخلاصة

تم دراسة أستخلاص أيونات معادن (الكادميوم, النحاس, الحديد و الزنك) ثنائية التكافؤ كمزيج في أنظمة المحاليل المائية ثنائية الطور والمتكونة من البولي أثيلين كلايكول ومحلول ملح كبريتات الصوديوم بوجود أيونات اليود والثايوسيانات كمستخلصات. أوجدت النسب المئوية للاستخلاص بدلالة كل من المتغيرات التالية:

- تراكيز المذيبات المستخدمة, يوديد البوتاسيوم وثايوسيانات البوتاسيوم وتتراوح بين (0.1−0.7) ملیلتر من 2 غرام / لتر تركيز أبتدائي لمحلول المذيب.
- نسبة الطور الحجمية (محلول بولي أثيلين كلايكول/ محلول ملح كبريتات الصوديوم) بين (0.5−3).
- التراكيز الابتدائية لايونات الفلزات وتتراوح بين (0.5−0.15) ميلتر من 1غرام / للتر كتركيز أبتدائي لمحلول أيونات المعادن يضاف الى المحلول.

أن النسبة المئوية لاستخلاص أيونات الفلزات تزداد بصورة رئيسية بزيادة كل من تراكيز المذيبات المستخدمة, نسبة الطور بين البوليمر والملح والتراكيز الابتدائية لأيونات المعادن.

أن النسبة المئوية لأستخلاص أيونات فلز كل من (النحاس, الحديد, و الزنك) ثنائية التكافؤ تكون أعلى قيمة في الانظمة المحتوية على أيونات الثايوسيانيد عنها في الانظمة المحتوية على أيونات اليود بينما تكون النسبة المئية لأستخلاص أيونات الكادميوم ثنائية التكافؤ أعلى قيمة في الانظمة المحتوية على أيونات اليود عنها في الانظمة المحتوية على أيونات الثايوسيانات.

أن أفضل النسب المئوية لأستخلاص أيونات فلزات (الكادميوم,النحاس,الحديد و الزنك) كانت للخلطات المتكونة من (0.5) ملیلتر من 1 غرام / لتر تركيز أبتدائي لمحلول أيونات الفلزات, (0.7) ملیلتر من 2 غرام / لتر تركيز أبتدائي لمحلول أيونات الثايوسيانات و (3) نسبة طور حجمي بين البولي أثيلين كلايكول وملح كبريتات الصوديوم حيث وصلت الى (87,92,92,80) % على التوالي.

## Introduction

The extraction and recovery of ions from aqueous solutions has traditionally been done using extraction with organic solvents (Graber, at. el., 2000)

In recent years, aqueous biphasic systems (ABS) have come into use for the same purpose, especially those formed of polyethylene glycol (PEG), water, and an inorganic salt. One of the main advantages of these systems besides of liquid-liquid extraction is that the separation and the recovery of metal ions occurs between two aqueous immiscible phases instead of toxic organic solvents which is not beneficial to the environment (Roger, 1995 and Albertson,1986).

Polyethylene glycol is a nonpolluting, noninflammable, durable solvent, which is available commercially in large quantities at relatively low cost, making it attractive for use in extractive processes.

Aqueous biphasic systems (ABS) are formed by using water-soluble polymers. The formation of an ABS can be achieved by using three kinds of ABSs: polymer–polymer systems, polymer-salt systems, and more recently salt-salt systems (Cabezas, H. 1996).

The polymer-salt system is employed in the present study, in which Sodium Sulphate is concentrated in the lower aqueous phase and PEG in the upper aqueous phase. The metal ion extraction in aqueous PEG- $Na_2SO_4$ two phase systems depends on:

- The formed aqueous two – phase system characteristics (determined by the type and molecular mass of PEG, type of inorganic salt and their concentrations, system PH, temperature, presence of neutral or charged inert species).
- The properties of metallic extracted species (hydration degree, charge dimension, etc.) (Iris, at. el. 1994 and Robin, 1995).

The present work studied the percent extraction behavior of some metal ions in PEG-$Na_2SO_4$ aqueous two phase system as a function of iodide and thyiocyanate ion added to the system, the phase ratio and initial concentration of the metal ions were also investigated.

## Experimental

### Materials

**a.** The PEG used in this study was PEG-8000 (average molecular mass = 8000). Stock solutions of 30% (w/w) PEG were prepared by dissolving of suitable quantity of PEG in deionized water.

**b.** The stock solution of inorganic salts (15% (w/w) $Na_2SO_4$) was prepared by dissolving of Suitable quantity of $Na_2SO_4$ in deionized water.

**c.** The 1 gm/L solution of metal ions (Cd (II), Cu (II), Zn (II), and Fe(II)) were obtained by metal sulphate salt dissolving of 1 gm of each metal Sulphate in deionized water.

**d.** The 4 gm/L solution inorganic extractants were prepared by dissolving of suitable quantity of Thiocyanate (KSCN) or Potassium iodide (KI) in deionized water.

### Procedure

**1.** Aqueous two – phase systems were prepared by mixing (5 ml) of PEG solution with (10 ml) of $Na_2SO_4$.

**2.** (0.1,0.3,0.5,0.7ml) of (4 g/ml) KI and mixture of the four metals [Cd(II)=0.5, Zn(II)=0.5, Cu(II)=0.25, Fe(II)=0.25 ml] added to the PEG-$Na_2SO_4$ Solution.

**3.** With constant temperature ($25^0$C) using temperature controller in a water path and PH (2.5) taken by adding small amount of $H_2SO_4$ concentrated solution to

the mixture, the system was shaken for (10 minute) followed by (10 minute) of Centrifugation at (2000 rpm).

4. Just before analysis, the two immiscible phases were carefully separated with Pasteur pipettes and placed into separated tubes.
5. Equal volumes (1ml) for each phase were measured for Cd (II), Zn (II), Cu (II), and Fe (II) by means of atomic absorption spectrometer model (PERKIN – ELMER 5000).
6. By Replacing the Extractant agent (KI) with (KSCN) the procedure above was repeated with (0.1, 0.3, 0.5, 0.7 ml) of KSCN Solution.
7. Phase ratio (PEG/ $Na_2SO_4$) was studied for the mixtures which had the best extraction% of the metals with (0.5, 1, 2 and 3).
8. Finally variable concentrations of metal ions were studied for the mixtures which had the best percent removed of the metals acting from stage (7), by changing the concentration of one metal with (0.5, 0.25, 0.5, and 0.1) and fix the amount of the other metals. And so on for the other metals.

## Results And Discussion

### Effect of extractant type and concentration

Figs. 1 and 2 show the extraction of metal ions as a function of amount of KI and KSCN solution added respectively. The percentage removed of Cd (II), Cu (II), Fe (II), and Zn(II) are equal to (16,14,13 and 28)% respectively in the prepared mixtures contained (0.1) ml of KI solution, and reaches to (88,41,59,and 35)% in the mixtures contained (0.7) ml of KI solution. While the percentage removed of Cd (II), Cu (II), Fe (II), and Zn(II) is equal to (36,37,38,and 37.5)% respectively in the prepared mixtures contained (0.1) ml of KSCN solution, and reaches to (61,75,66,and 72)% In the mixtures contained (0.7) ml of KSCN solution.

In the beginning the experimental results indicate that the extraction of the four metals above is very low, because the metal ions remain predominantly in the salt -rich phase of the extraction system, this means that in the extraction of these metals, chemical interactions between the metal ions and the PEG molecules are not involved (Laura Bulgariu, 2004). An increase in the extraction into the top PEG-rich phase with the increasing of the amount of the inorganic anions (KI, KSCN) respectively was observed from the metal ions above.

In the extraction system with ($I^-$) a quantitatively extraction can be attained only for Cd (II), on the other hand Cu (II), Fe (II), and Zn (II) ions are quantitatively extracted when a sufficient amount of $SCN^-$ is added to the system, this is presumably due to the difference in the stability constant between the Thiocyanate complex and the iodide one (Masami Shibukawa, 2001). Also the $SCN^-$ ions have the strongest bonding with the polymer surface, this tends to raise the cloud point (the interface between the two-phase systems) at lower salt concentration and increases the polymer net charge , and hence solubility (Laura Bulgaria, 2008).

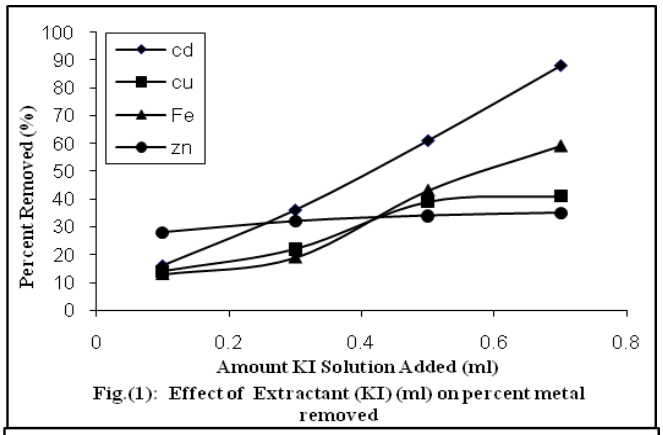



Fig.(1): Effect of Extractant (KI) (ml) on percent metal removed

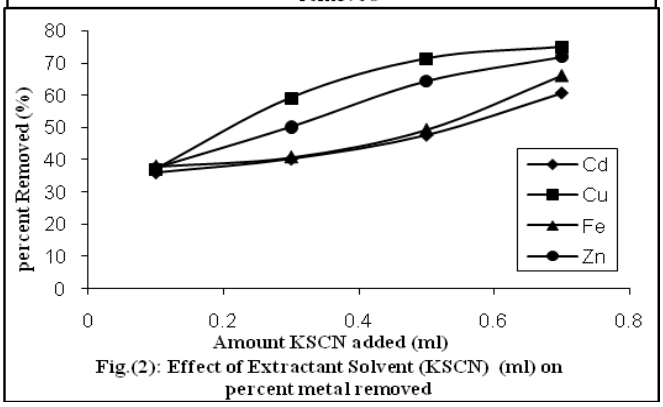



Fig.(2): Effect of Extractant Solvent (KSCN) (ml) on percent metal removed

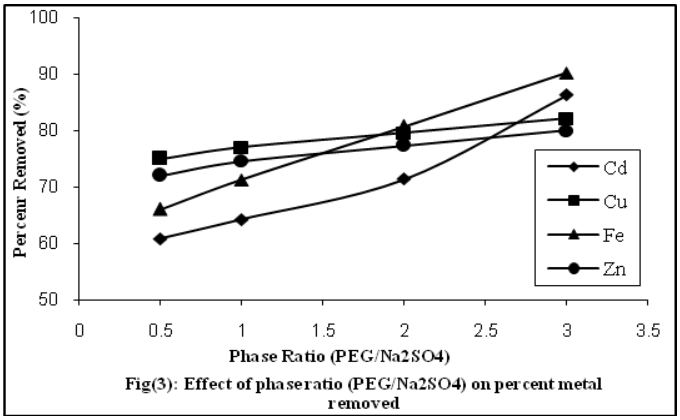
**Effect of the phase ratio**

In previous studies it was shown that the $Na_2SO_4$ can be used as the forming salt because it exerts a strong salting out effect on PEG and high solubility in water, besides that the PEG polymer not only effects on the distribution of the solute between the phases but also effect on the physical characteristics of the ABS (Robin, 1996).

Also 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 (Dean, 1995).

Fig. 4 shows the percentage removed of Cd (II), Cu (II), Fe (II), and Zn (II) metal ions as a function of phase ratio. The percentage removed of Cd (II), Cu (II), Fe (II), and Zn(II) is equal to (61,75,66,and 72)% respectively in the prepared mixtures contained (0.5) phase ratio of (PEG/$Na_2SO_4$), and reaches to (86,82,90,and 80)% in the mixtures contained (3) phase ratio of (PEG/$Na_2SO_4$). Overall results above indicate that the extraction of the metals above increases with increasing of PEG/$Na_2SO_4$ volumetric phase ratio. 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 (Graber, 2007).

Besides, 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) (Robin Rogers, 1995).




Fig(3): Effect of phaseratio (PEG/Na2SO4) on percent metal removed

## Effect of metals concentration

Figs. 4, 5, 6, and 7 show the effect of initial metal ions concentration on the percentage removed. The percentage removed of each (Cd (II),Cu (II), Fe (II), and Zn (II)) is equal to (87, 92, 92, and 80)% respectively for the mixtures contained (0.5)ml of each of the metals, while in the mixtures contained (0.15) ml of the metals above the metals extraction (%) is equal to (71, 72, 71, and 70)%.

Over all behavior indicate that the percentage removed of metal ions is decrease with decreasing of the concentration of the metals in the prepared mixtures because of the increasing of the solute hydration coming from decreasing the size of the metals in the mixtures leading to decreasing the chemical interaction between the metals and the polymer (Laura Bulgariu, 2005 and Laura Bulgaria, 2007).

The difference in the extraction of Zn (II) (%) is very narrow range usefulness in the mixtures contained between (0.5-0.15) ml initial concentrations of Zn because the mixtures were saturated with Zn ions.

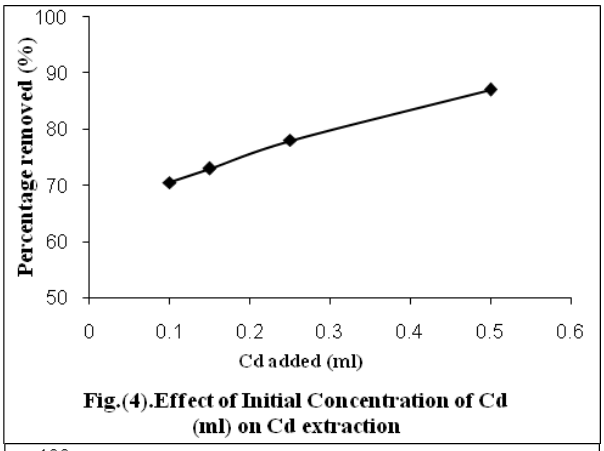



**Fig.(4).Effect of Initial Concentration of Cd (ml) on Cd extraction**

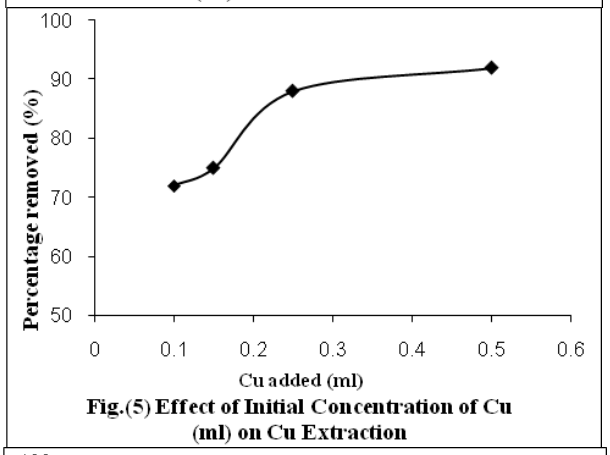



**Fig.(5) Effect of Initial Concentration of Cu (ml) on Cu Extraction**

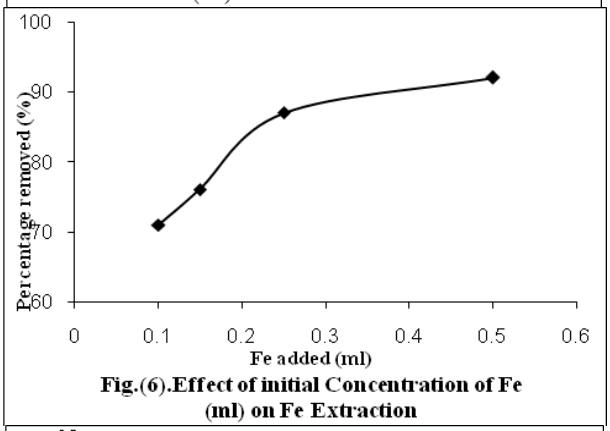



**Fig.(6).Effect of initial Concentration of Fe (ml) on Fe Extraction**

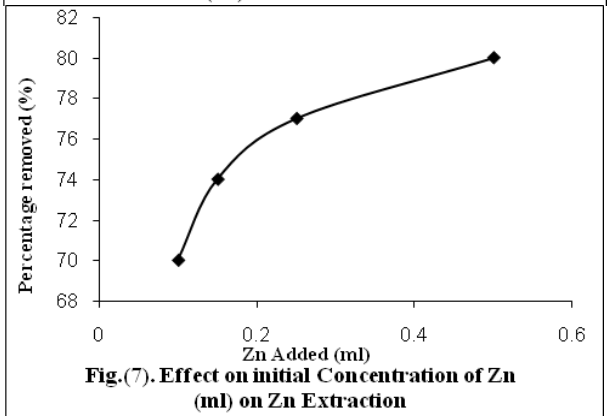



**Fig.(7). Effect on initial Concentration of Zn (ml) on Zn Extraction**

## Conclusions

- The mixing conditions (temperature, PH, time) of the mixtures had the correct selection to obtain efficient metal ions extraction.
- The extraction of metal ions was increased with the increasing of initial concentrations of (KI) and (KSCN) solvents, phase ratio (PEG /$Na_2SO_4$), and the initial concentrations of the metals added to the mixtures.
- The metals extraction (%) by using (KSCN) as an extractant is greater than the extraction by using (KI), because of the difference in the stability constant between the Thiocyanate complex and the iodide one.
- Efficient extraction reached between (80-92)% was obtained in the mixture had the experimental conditions of (0.5ml) of metals solution, (0.7ml) of (KI ) or (KSCN) solutions, and ($PEG_{3000}$/$Na_2SO_4$) equal to (3) volumetric phase ratio.
- The difference in the extraction of Zn (II) (%) is very narrow range usefulness in the mixtures contained between (0.5-0.15) ml initial concentrations of Zn because the mixtures were saturated with Zn ions.

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