Extraction of Copper from Aqueous Solutions Using Sodium Diethyldithiocarbamate as the Extracting Agent

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Copper is toxic to living organisms and is listed as a major pollutant by the U.S. Environmental Protection Agency (EPA) and liquid-liquid extraction has shown great capabilities for its removal from aqueous extraction, particularly when adequate extracting agents and diluents are used.

The present work concerns chelate extraction of copper traces from aqueous solutions by means of Sodium Diethyldithiocarbamate (NaDDC) as the extractant. The effect of several parameters such as the mass of the extractant, the shaking time, the ratio of the organic phase volume to that of the aqueous one, the pH of the aqueous solution, on the copper extraction from synthesised solutions, was investigate.

The SDDT mass in presence of chloroform as the diluent was increased gradually from 1 to 12 mg, fixing the initial concentration of metal, the volumes of the aqueous and organic phases, the shaking time and the stirring velocity. The extraction ratio increased up to a value of 99.94 % as the SDDT mass increased up to 9 mg, before reaching a constant value.

The aqueous and organic phases should be well agitated, increasing the contact and homogenising the concentrations of the different species in order that the complexation reaction would not be limited by diffusion. This parameter was varied from 5 up to 120 min and for an extractant mass equal to 7 mg, the extraction percentages were not far from an average value of 90 %.

The volume ratio of the organic phase to that of the aqueous one was varied from 0.2 up to 4, keeping all the other parameters constant. The optimum value of the volume ratio was 1:1 corresponding to an extraction percentage of 92.45 %.

The pH of the aqueous solution before extraction was varied from 2 to 11 and the extraction percentage increased reaching a value 99.39 % for pH= 9. For a pH greater than 9, a decrease was observed.

The analysis of the organic phases obtained after separation by UV-visible spectrophotometer confirmed the formation of $Cu(DDC)_2$ complex in Chloroform, assuming a dissociation as $[(C_2H_5)_2NCSS]^-$ and Na^+ in the aqueous phase.

1. Introduction

Copper is a widely used metal in different industries such as plating, mining and smelting, brass manufacture, electroplating industries, petroleum refining, etc. Cupric ion (Cu^{2+}) is the most frequently encountered copper form in the environment. It is also toxic to living organisms and is listed as a major pollutant by the US Environmental Protection Agency (EPA) (Chang et al, 2010).

In fact high doses of copper can cause serious toxicological diseases since it can be deposited in the brain, skin, liver and pancreas. It will then lead to nausea, vomiting, headache, diarrhoea, respiratory difficulties, liver and kidney failure, and death (Lippard, 1990). The world Health Organization recommended a maximum acceptable concentration of Cu(II) in drinking water less than 1.3 mg/L (Dezuane, 1997).

Different techniques can be used to remove Cu(II) from aqueous solutions and one can cite chemical precipitation, coagulation-flocculation, flotation, ion exchange, electro oxidation, membrane filtration, biosorption and extraction which is the main concern of the present study. It has shown great capabilities, particularly when adequate extracting agents and diluents are used and it is simply based on the transfer of a solute from an aqueous phase to an organic one (Chang et al, 2010).

Chelating agents such as ethylenediaminetetraacetic acid (EDTA), nitriloacetic acid (NTA), diethylenetriamine pentaacetic acid (DTPA) and S,S-ethylene-diaminedisuccinic acid (EDDS) have been extensively investigated according to their ability to increase metal extraction through the formation of strong metal–ligand complexes (Luciano et al.,2012). Chelate extraction by means of a well established copper extractant, namely sodium diethyldithiocarbamate (NaDDC), enables the removal of even traces from an aqueous solution into a small volume of organic solvent (Hiraide et al., 1992). In fact, dithiocarbamates have the property of giving strongly brown colored water-insoluble copper (II) chelates which can be extracted by a variety of organic solvents.

Therefore the present study concerns the effect of several parameters such as the mass of the extractant, the shaking time, the ratio of the organic phase volume to that of the aqueous one, the pH of the aqueous solution, on the copper extraction from synthesised solutions.

2. Experimental

2.1 Reagents
Copper sulphate pentahydrate ($CuSO_4.5H_2O$, ≥99.6 % purity), NaDDC ($NaS_2CN(C_2H_5)_2.3H_2O$, ≥ 99.6 % purity), Chloroform ($CHCl_3$), Nitric acid (HNO_3, 63 % purity) and Sodium hydroxide (NaOH, ≥ 99.6 % purity) were supplied by PRS Panreac. Water was distilled locally using a GFL 2001/4 distillation.

2.2 Apparatus
A mechanical shaker (ProLabo Oscill 8) was used to mix the aqueous and organic phases and a pH meter (Standard pH meter, pHM210) was used to measure the pH of aqueous solution. The concentration of Cu(II) in the aqueous phase, after extraction, was measured with a flame atomic absorption spectrophotometer (Ray Leigh WFX-130). UV-vis spectra were obtained by means of a Shimadzu 1601 UV/vis spectrophotometer.

2.3 Extraction procedure
A volume of 25 mL of prepared aqueous solution of Cu^{2+} containing a fixed amount of NaDDC was mixed with a fixed volume of the solvent in a glass stoppered bottle which was shaken for a fixed time to reach equilibrium, using a mechanical shaker.

The pH of an aqueous solution was adjusted to a desired value by adding dilute HNO_3 or NaOH solutions. After phase disengagement the raffinate was separated and the metal concentration in the aqueous phase was measured by means of the flame atomic absorption spectrophotometer, after appropriate filtration and dilution. The concentration of Copper in the organic phase was calculated from the difference between the initial and final metal concentrations in the aqueous phase.

The obtained results are expressed in terms of the extraction ratio R (%) or the partition coefficient D which are expressed as follows:

$$R(\%) = \frac{[Cu]_{0.aq} - [Cu]_{f.aq}}{[Cu]_{0.aq}} \times 100 \tag{1}$$

$$D = \frac{[Cu]_{0.aq} - [Cu]_{f.aq}}{[Cu]_{f.aq}} \tag{2}$$

Where $[Cu]_{0.aq}$ and $[Cu]_{f.aq}$ are the initial and the final Cu (II) concentrations in the aqueous phase, respectively.

All experiments were carried at room temperature and they were repeated at least twice in order to ensure the reproducibility of the results.

3. Results and discussion

3.1 Effect of extractant mass
The influence of the SDDT mass in presence of chloroform as the diluent, was examined, fixing the initial concentration of metal $[Cu^{2+}]_0$, the volumes V_{aq} and V_{org} of the aqueous and organic phases the shaking time and the stirring velocity.

The extractant mass was increased gradually from 1 to 12 mg. The initial solution pH_0, was measured and found equal to a constant value of 5.25, excluding the formation of copper hydroxide $Cu(OH)_2$ which takes place at higher pH values.

As shown in Figure 1, the extraction ratio R increased up to a value of 99.94 % as the NaDDC extractant mass increased up to 9 mg, before reaching a constant value where any further extractant addition would be in excess.
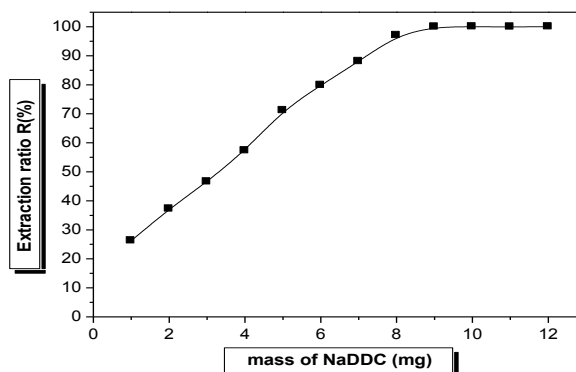

Figure 1: Effect of extractant mass on the extraction ratio; conditions: $[Cu^{2+}]_0 = 50$ mg/ ; $V_{aq} = 25$ ml/L; $V_{org} = 25$ mL; agitation time = 60 min ; agitation speed = 478 rpm ; $pH_0 = 5.25$.

Therefore a safe mass of 7 mg of the extractant agent was adopted in order to avoid the migration of any excess of NaDDC into the aqueous phase after extraction. The resulting extraction ratio was close to 90 %.

3.2 Effect of shaking time

Since the extraction is a mass transfer process, agitation time may have a certain effect on the Cu(II) recovery. Also the two aqueous and organic phases should be well agitated, increasing the contact between them and homogenising the concentrations of the different species in order that the complexation reaction would not be limited by diffusion. Therefore this parameter was varied from 5 up to 120 min, keeping all the others constant.
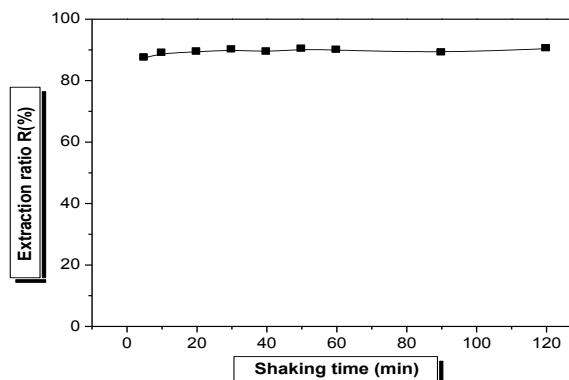

Figure 2: Effect of shaking time on the extraction ratio. Conditions: $[Cu^{2+}]_0 = 50$ mg/L, m NaDDC = 7mg, V_{aq}=25ml, V_{org}= 25ml , va=478rpm, pH_0=5.34

The results are shown in Figure 2 where for an extractant mass equal to 7 mg, the extraction percentages are not far from an average value of 90% in the considered time range, indicating a low effect on the Cu (II) recovery. This value was reached after only 10 minutes of shaking, indicating a negligible chemical

resistance with an instantaneous migration of the resulting complex into the organic phase. A contact time of 30 min was considered to ensure equilibrium.

3.3 Effect of the ratio V_{org}/V_{aq}

The volume ratio V_{org}/V_{aq} of the organic phase to that of the aqueous one, was varied from 0.2 up to 4, keeping all the other parameters constant. The results are shown in Figure 3.
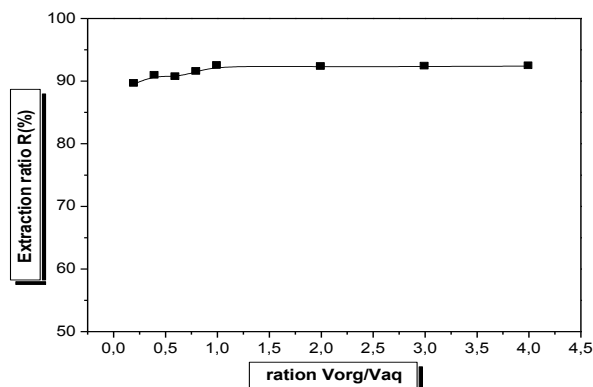

Figure 3: Effect of the ratio V_{org}/V_{aq} on the extraction ratio; conditions: $[Cu^{2+}]_0 = 50$ mg/L, m NaDDC = 7 mg , agitation time = 30 min, agitation speed = 478 rpm, $pH_0 = 5.46$

The relationship between the extraction percentage, the partition coefficient and the volume ratio V_{org}/V_{aq} can be expressed as follows (Didi, 2004):

$$R(\%) = 100.D/(D + V_{aq}/V_{org})$$
(3)

The extraction percentage is proportional to the value of Vorg/Vaq until a certain limit where R becomes constant. This is in agreement with the obtained results and the optimum value of the volume ratio *Vorg/Vaq* is 1:1 corresponding to an extraction percentage of 92.45 %. Therefore this volume ratio was retained for the further experiments.

3.4 Effect of the initial pH

 For this case the pH_0 of the aqueous solution before extraction was varied from 2 to 11 by using solutions of HNO_3 (0.1M) and NaOH (0.1M).
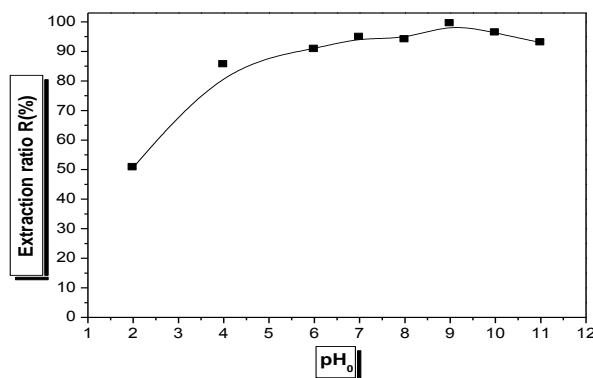

Figure 4: Effect of the pH on the extraction ratio R $[Cu^{2+}]_0 = 50$ mg/L, m NaDDC = 7 mg, $V_{aq} = 25mL$, $V_{org} = 25mL$, agitation time = 30 min, agitation speed = 478 rpm

According to Figure 4, the extraction percentage increased with the increase of the pH reaching a value 99.39% for pH= 9, which is close enough to value of 8.5 recommended by the literature (Brozovic-Pohl et

al, 1992) for similar extraction systems. The decrease of the ratio in a more alkaline medium (pH greater than 9) occurs when the hydrolysis of the cation in aqueous phase is important enough to disrupt the formed chelate, enabling the element to pass back into the aqueous phase (Poitrenaud, 1984), hence decreasing the extraction percentage.

The organic phases obtained after separation were analyzed simultaneously by UV-visible spectrophotometer. Figure 5 shows the visible spectra of Cu^{2+} extracted by NaDDC in the organic layers. There is a fairly good coincidence concerning the shape of the spectra and in the maximum wavelength λ_{max} equal to 436 nm, confirming the formation of $Cu(DDC)_2$ complex (Jankiewicz et al, 1999).
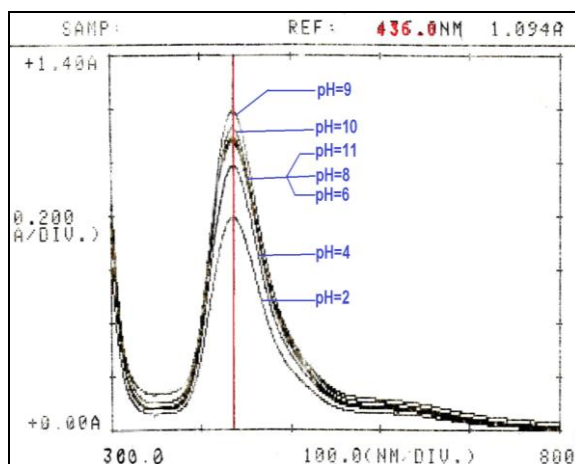

Figure 5: Absorption spectra of the organic phase containing Cu^{2+} extracted by NaDDC at different pH_0

The difference in absorbance between the spectra is due to the effect of the initial pH fixed in the aqueous phase what is in concord with the results presented in Figure 4. Thus a pH equal to 9 seems to be the optimal value.

3.5 Extraction mechanism

It is confirmed that the extraction of the metal as $Cu(DDC)_2$ in Chloroform, assuming that the extractant can dissociate in the aqueous phase as $[(C_2H_5)_2NCSS]^-$ and Na^+ (Rathore et al., 2006).

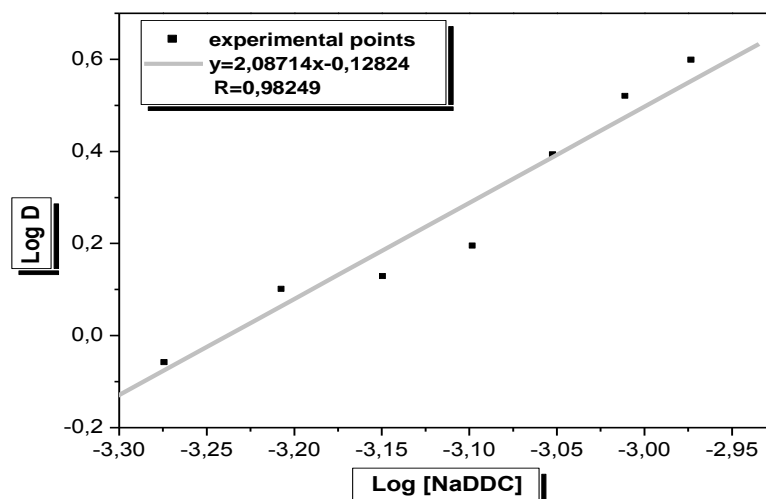*Figure 6: Determination of stoechiometry of reaction; conditions: $[Cu^{2+}]_0 = 50$ mg/L, $V_{aq} = 25$ mL, $V_{org} = 25$ mL , agitation time = 60 min, agitation speed = 478 rpm, $pH_0 = 5.25$.*

The proposed chemical scheme of the Cu(II) is as follows (Touati and Meniai, 2011):

$$Cu^{2+} + 2NaDDC \Leftrightarrow \overline{Cu(DDC)}_2 + 2Na^+ \tag{4}$$

The plotted variation of Log D according to the variation of Log [NaDDC] from the data of Figure 1 can be fitted reasonably well to a linear plot (see Figure 6) with a calculated slope of 2,08714, justifying the suggested stoechiometry.

4. Conclusion

The results confirms that Sodium diethyldithiocarbamate (NaDDC) can be used efficiently in the elimination of Cu(II) from aqueous systems by solvent extraction, with Chloroform as the diluent, where extraction percentages over 97 % could be achieved at the optimum determined operating conditions. The results also showed that the extraction percentage increased as the pH increased up to 9 and then decreased in the alkaline region. Similarly the extraction ratio R increased up to a value of 99.94 % as the extractant agent mass increased up to 9 mg.

References

Chang H. S., Tjoon T. T., Norli I., 2010, Extraction of Cu (II) from aqueous solutions by vegetable oil-based organic solvents, Journal of Hazardous Materials, 181, 868-872.

Lippard S. J., 1990, Progress in Inorganic Chemistry, Vol. 38: Bioinorganic Chemistry, Ed. John Wiley and Sons, New York, USA..

Dezuane J., 1997, Handbook of Drinking Water Quality, 2nd Edition, Van Nostrand Reinhold, New York.

Luciano A., Viotti P. and Mancini G., 2012, A numerical model to study pulsing soil flushing: validation and application to a real contaminated soil, Chemical Engineering Transactions, 28, 151-156 DOI:10.3303/CET1228026

Hiraide M., Hommi H., Kawaguchi H., 1992, Diethyldithiocarbamate (DTTC) extraction of Copper (II) and Iron (III) associated with humic substances in water Journal of Analytical Chemistry, 342, 387-390.

Didi M. A., 2004, Science and Technology of organo-phosphorus extractants, Office des publications universitaires 38, Algiers, Algeria (in French)

Brozovic-Pohl H., Altorfer X. Perlia A., 1992, A new (limit) test for heavy metals, Journal of Analytical Chemistry 343, 348-351.

Poitrenaud C., 1987, Liquid-liquid Extraction, Technique de l'ingénieur, 1425 (in French).

Jankiewicz B., Ptszynski B., Turek A., 1999, Spectrophotometric determination of Copper (II) in samples of soil from selected allotment gardens in Lodz, Polish Journal of Environmental Studies, 8, 1, 35-38.

Rathore H. S., Kumar M., Ishratullah K., 2006, Metal ion chromatography on sodium Diethyldithiocarbamate, Indian Journal of Chemical Technology 13, 84.

Touati S., Meniai A-H, 2011, Identification of the formed complex after extraction of Copper (II) from Sulphuric Acid by means of Sodium diethyldithiocarbamate (SDDT), Chemical Engineering Transactions, 25, 219-224, DOI:103303/CET1125037