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Experimental Study of the Extraction of Copper(II) from Sulphuric Acid by Means of Sodium Diethyldithiocarbamate (SDDT)

S.Touati, A.H. Meniai

Abstract—The present work presents the extraction of copper(II) from sulphuric acid solutions with Sodium diethyldithiocarbamate (SDDT), and six different organic diluents: Dichloromethane, Chloroform, Carbon tetrachloride, Toluene, xylene and Cyclohexane, were tested. The pair SDDT/Chloroform showed to be the most selective in removing the copper cations, and hence was considered throughout the experimental study.

The effects of operating parameters such as the initial concentration of the extracting agent, the agitation time, the agitation speed and the acid concentration were considered.

For an initial concentration of Cu (II) of 63 ppm in a 0.5 M sulphuric acid solution, both with a mass of the extracting agent of 20 mg, an extraction percentage of about 97.8 % and a distribution coefficient of 44.42 were obtained, respectively, confirming the performance of the SDDT-Chloroform pair.

Keywords—Copper (II), Distribution coefficient, Extraction, SDDT, Sulphuric acid.

I. INTRODUCTION

S ULFURIC acid is an important chemical which is involved in many sensitive industrial fields such as textile, car batteries manufacturing, production of fertilizers through superphosphate and ammonium sulphate, metallurgical, fabrication of explosive materials, etc. However, very often any freshly produced or recycled sulphuric acid is contaminated by heavy metal cations, mainly Fe^{3+}, Zn^{2+} and Cu^{2+} [1]. These impurities must be imperatively removed, requiring then a treatment of the acid. Various techniques do exist to achieve this task and one can cite filtration, flotation, electrolysis, precipitation and liquid-liquid extraction which is the main topic of the present study.

In fact in the literature many research works were reported and dealt with the elimination of heavy metal cations like iron, cobalt, nickel, cadmium, etc. from sulphuric acid solutions, using liquid-liquid extraction and the main conclusion was that the efficiency of this separation technique depended upon the considered complexing agent. Consequently this has been the main motivating factor to carry out the present

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experimental work where the elimination of Cu^{+2} from synthesized sulphuric acid solutions of 0.5M at 25 °C, is considered with sodium diethyl dithiocarbamate (SDDT) as the complexing agent to form Cu $(C_{10}H_{20}N_2S_4)$ $(Cu(DDT)_2)$ [2], at a pH of 8.5, a value within the range of 4 to 11 as suggested by [2], [3].

The approach is similar to that generally used for the extraction of heavy metals in an acidic medium, by organophosphorus and oximes extractants [4], [5].

The extraction is based on the following two main steps:
1) A complex formation between the present ionic species in the solution and the complexing agent;
2) A phase separation after a migration of the formed complexes into the organic phase.

However in the literature, some research workers insinuated that a high acidity may lead to a decomposition of SDDT giving CS_2 [6], [7].

II. EXPERIMENTAL

A. Chemicals

Sulphuric acid of 98 % purity was provided by PRS Panreac Quimica SA. Copper with fixed concentration was added as hydrated copper sulphate $CuSO_4$, $5H_2O$, and obtained also from the same source, in order to obtain a sulphuric acid solution contaminated with the corresponding cation Cu^{2+}. Locally bi-distilled water by means of a GFL 2001/4 distillation unit was used to dilute the sulphuric solutions to desired different concentrations. Sodium diethyldithiocarbamate (SDDT) of 98 % purity was purchased from Sigma Aldrich and used as the extractant. The commercial organic diluent was Chloroform and was also purchased from Sigma Aldrich.

B. Experimental methods

The elimination extraction process of the copper (II) cations from sulphuric acid solutions was carried out batchwise, according to the following steps:
- A given volume of a sulphuric acid solution contaminated with copper (II) cations was mixed with a fixed amount of the extracting agent (SDDT) in an Erlen Meyer and the resulting mixture was vigorously shaken using a Prolab Oscill8 shaker;
- Organic solvent was added and the resulting mixture was agitated by means of a mechanical agitator at a preset

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agitation speed and for a long contact time, enhancing mass transfer;

- The system was kept at rest to allow for equilibrium;
- Separation of the two phases by decantation;
- The aqueous phase is then analysed by means of a Rayleigh WFX-130 atomic absorption in order to determine the copper (II) concentration. A priori, a calibration curve was prepared by using standard solutions. The concentration of the copper in the organic phase was obtained from a material balance by calculating the difference between its concentration in the aqueous phase before and after extraction.

All the experiments were carried out at constant temperature of 25 °C.

III. RESULTS AND DISCUSSION

A. Effect of the Extracting Agent Type

The performance of the metallic ion extraction from a given sulphuric acid solution depends upon the type and nature of the extracting agent. Therefore this effect was investigated by considering three different extracting compounds, namely, Dibenzoylmethane (DBM), Benzoylacetone (BA) and Sodium Diethyldithiocarbamate (SDDT), in Chloroform as diluent, where a mass of 50 mg of each was mixed into a volume of 10ml of 0.5M of sulphuric acid solution, for an initial Cu (II) concentration of 63 ppm, an organic to aqueous phase ratio equal to 1 and an agitation time of 30 minutes at a speed of 200 rpm.

The results are shown in Figure 1and 2 where it is clear that the SDDT gives by far the best extraction percentage (85.46%) and distribution coefficient (44.42) and thus confirming the chelating properties of this compound, as reported in the literature for the extraction of other metallic cations like Copper (II) [8].
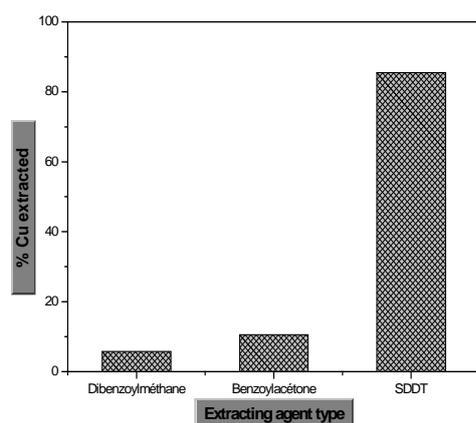

Fig.1 Effect of extracting agent type on the extraction yield: $[H_2SO_4]_0$=0.5M, $[Cu]^{2+}$=63ppm, aq/O =1; agitation time=30min; agitation speed=200 rpm
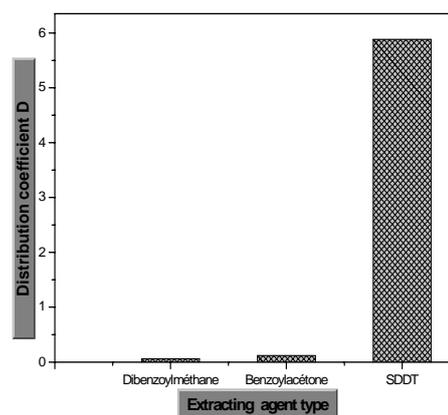

Fig.2. Effect of extracting agent type on the distribution coefficient: $[H_2SO_4]_0$=0.5M, $[Cu]^{2+}$=63ppm, aq/O =1; agitation time=30min; agitation speed=200 rpm

B. Effect of the Organic Diluents

The effect of the nature of the organic solvent on the Cu(II) extraction from sulphuric acid solutions by means of the SDDT was also investigated. The concentration of Cu(II) in the 0.5M sulphuric acid solutions was 63 ppm and the mass of the extracting agent was 20 mg. Six different solvents were tested as shown in the following figure 3:
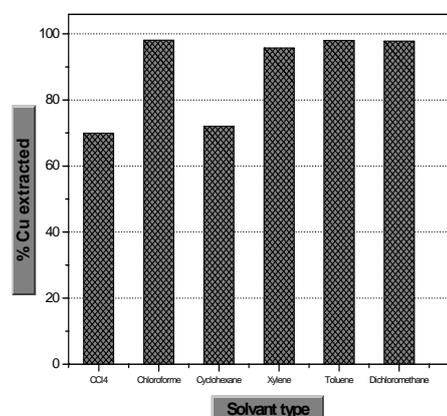

Fig.3 Effect of organic diluents on the extraction yield: $[H_2SO_4]_0$=0.5M, $[Cu]^{2+}$=63ppm, aq/O =1; agitation time=30min; agitation speed=600 rpm and SDDT as extractant

Figure 3 shows that chloroform, dichloromethane, toluene and xylene give a good output but we know very well that the choice of a solvent in extraction depends on several parameters such as the miscibility and the boiling point.

The table I shows that although the dichloromethane, toluene and xylene give almost the same output that chloroform but the pair Chloroform-SDDT remains the best combination for its boiling point and its solubility in water and hence justifying and encouraging its use in the present work.

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TABLE I
SOLVENTS PROPERTIES [8]

Solvent	Solubility at 20°C	Boiling point °C
Dichloromethane	13.00	40
Trichloromethane (Chloroform)	08.22	61.1
Tétrachlorure de carbone CCl$_4$	0.80	76.7
Toluene	Non miscible	111
Cyclohexane	Non miscible	81
Xylene	Non miscible	138.5

C. Effect of the Initial Concentration of the Extracting Agent

To investigate the effect of the initial concentration of the extracting agent SDDT, its mass was varied from 1.8 to 251.5mg, while fixing the phase volume ratio to 1, an agitation time of 30 minutes, an agitation speed of 600 rpm, an initial acid concentration of 0.5M and a Cu (II) concentration of 63ppm. From Figure 4 it can be seen that the extraction percentage increases up to 97.8 %, as the mass of the extracting agent increases up to 20 mg and then exhibit saturation like behaviour. This indicates that the mass of 20 mg is an optimal value to use in the present study.
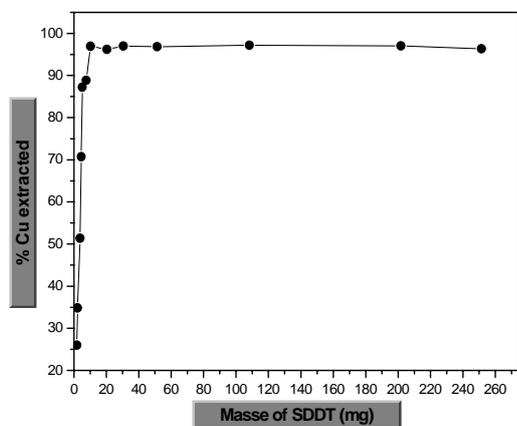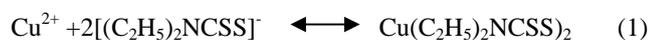

Fig.4 Effect of mass extracting agent on the extraction yield
$[H_2SO_4]_0$=0.5M, $[Cu]^{2+}$=63ppm, aq/O =1, agitation time=30min, agitation speed=600 rpm

D. The Process Chemistry

Assuming that the sodium diethyldithiocarbamate can dissociate in the aqueous phase as $[(C_2H_5)_2NCSS]^-$ and Na^+, the proposed chemical scheme of the copper(II) is as follows [9], [10]:

$$Cu^{2+} +2[(C_2H_5)_2NCSS]^- \longleftrightarrow Cu(C_2H_5)_2NCSS)_2 \qquad (1)$$

The plotted data of Figure 4 can be fitted reasonably well to a linear plot with a calculated slope of 1.855 , not far from 2 which may be interpreted as the number of $[(C_2H_5)_2NCSS]^-$ and hence confirming the stoichiometry shown in Equation 1
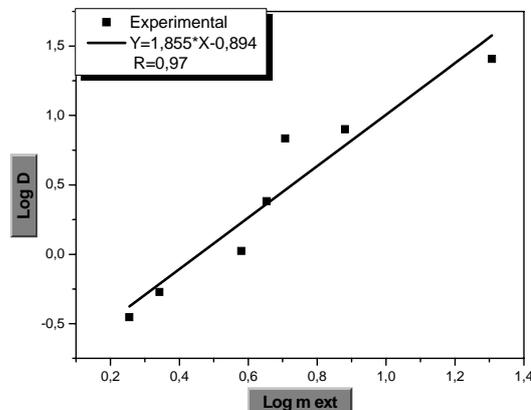

Fig.5 Stoichiometry of reaction
$[H_2SO_4]_0$=0.5M, $[Cu]^{2+}$=63ppm, aq/O =1, agitation time=30min, agitation speed=600 rpm

E. Effect of Agitation Time

Since the extraction is a mass transfer process, agitation may have a certain effect on the Cu (II) recovery. This parameter was varied from 5 to 120 minutes, keeping all the others constant. The results are shown in the following figure where the extraction percentage values are not far from an average value of 97% in the considered time range, indicating a low effect on the Cu (II) recovery. However the highest percentage of 97.8% was reached after 10 minutes of shaking and hence can be considered as an optimal time value.
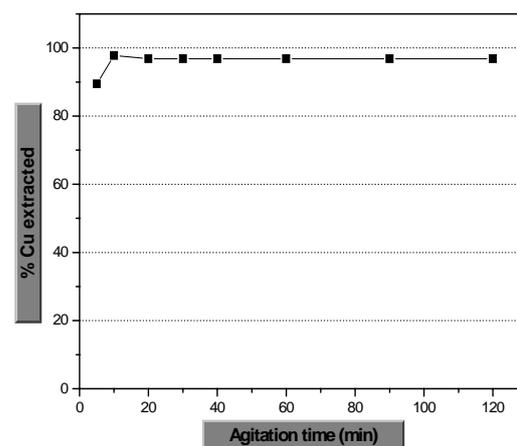

Fig.5 Effect of agitation time on the extraction percentage:
$[H_2SO_4]_0$=0.5M, $[Cu]^{2+}$=63ppm, aq/O =1, agitation speed =600 rpm

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F. Effect of the Acid Concentration

To examine the effect of the acid concentration, its value was changed from 0.5 to 6M, while fixing the other parameter values.
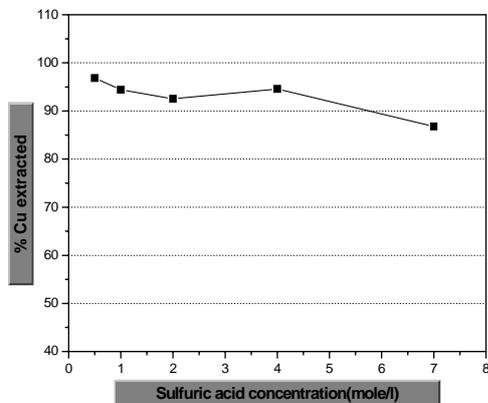

Fig.6 Effect of concentration acid on the extraction yield: $[Cu]^{2+}$=63ppm, aq/O =1, agitation speed =600rpm, agitation time=30min

It is clear from the Figure 6 that the extraction percentage of Cu (II) decreases with the increase of the acid concentration. This can be explained by the great decomposition of the SDDT in a strong acidic medium, and hence depriving Cu (II) ions from being complexed. This is confirmed by the literature where it is confirmed that SDDT does not present any affinity for strong oxidising agents. Even in aqueous solutions, it shows a decomposition which is enhanced with the presence of an acid [11].

G. Effect of Agitation Speed

In extraction, time to reach balance is controlled by the transfer of matter. It depends on the diffusion, of surface and the nature of the interface between the two phases and it can be to accelerate by agitation.
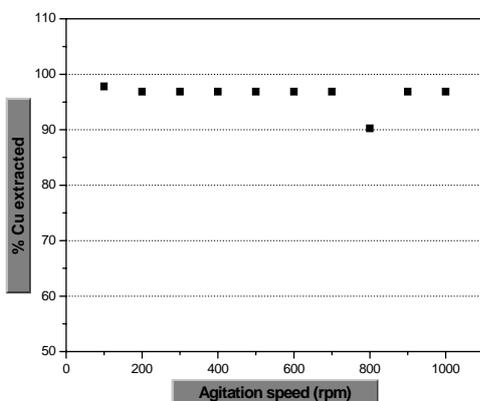

Fig.6. Effect of agitation speed on the extraction percentage: $[H_2SO_4]_0$=0.5M, $[Cu]^{2+}$=63ppm, aq/O =1, agitation time =30 min

In this test we will see the influence of stirring velocity on the extraction yield of the copper from the acid solution.

For that all the parameters are fixed and only the agitation speed is changed from 100 to 1000 rpm.

According to the Figure 6 it notes that the stirring velocity does not have an influence on the extraction yield because the time necessary to reach balance is very fast, it is of 10 min.

IV. CONCLUSION

The results confirms that the sodium diethyldithiocarbamate (SDDT) can be used efficiently in the purification of sulphuric acid when eliminating the heavy metals cations such as Cu^{2+}, by liquid-liquid extraction, with Chloroform as the diluent. In fact with acid concentrations between 0.2 and 7M and at a pH in the range of 0.45 to 1.66, an extraction rate between 86.7% and 97 % could be achieved.

Finally, through this study, it can ascertained that the SDDT can be safely used as a complexing agent for the elimination of Cu^{2+} from sulphuric acid solutions of different molar concentrations by liquid-liquid extraction, at a pH less than 4 and the resulting complex is $Cu(C_{10}H_{20}N_2S_4)$.

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