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## Separation Science and Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713708471>

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Online publication date: 08 July 2010

**To cite this Article** Stoica, Ligia and Oproiu, Gabriela Carmen(2005) 'Cu(II) Recovery from Aqueous Systems by Flotation', Separation Science and Technology, 39: 4, 893 — 909

**To link to this Article: DOI:** 10.1081/SS-120028452

**URL:** <http://dx.doi.org/10.1081/SS-120028452>

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## Cu(II) Recovery from Aqueous Systems by Flotation

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### ABSTRACT

Ionmolecular and colloidal inorganic particles representing both pollutants and sources of useful substances require the separation from aqueous systems by modern techniques that also permit their removal and recovery. Ion flotation and precipitate flotation are considered as separation methods with wide application, especially for the small concentration ranges of noxious components, indicating high environmental and economical performances. The present paper presents the results of a research study concerning Cu(II) recovery from aqueous model systems by the precipitate flotation method, dissolved air flotation (DAF), with an anionic-type collector  $C_{18}H_{33}O_2Na$ —sodium oleate (NaOL). The separation mechanism by the collector–Cu(II) interaction at optimum conditions

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was studied. A comparison of chemical analysis results with electronic and vibration spectra and thermal analysis for isolated species was also made. The results of the experimental data plead for the Cu(II) recovery separation from aqueous systems and its recovery as oxide after thermal decomposition of the species contained in the foam.

**Key Words:** Copper; Separation; Recovery; Precipitate flotation; Sodium oleate.

## INTRODUCTION

Wastewater arising from various metal-processing operations have a complex composition, being impure in various ways. Therefore, they require the application of efficient and economic purification methods. Concerning the impurities of metallic ion, these pollutants are dangerous but, simultaneously, they may represent a source of useful substances. For the improvement of environmental quality, regarding the useful substances, several methods of recover-separation have been developed, generally, nonconventional procedures based on interfaces mass transfer. The group of separation methods using adsorptive bubbles, which also includes ion-molecular and colloidal particle flotation, represents an alternative to the classical methods.<sup>[1-3]</sup>

Precipitate flotation is an efficient and economical separation method and comprises separation of hydrophobic species (hydroxides, sulfides, etc.) existing or formed in aqueous systems. In the precipitate flotation process, the aqueous hydrophilic ion species become hydrophobic, by precipitation with an other reagent than the tensioactive agent (the collector). The precipitate's hydrophobicity can be increased when it is treated with a tensioactive agent (the collector) in lower quantities than the stoichiometrical ones.<sup>[4,5]</sup> The collector has a heteropolar structure with linear chain ( $C > 8$ ) and a polar group, which causes it to interact with the insoluble hydroxospecies of the colligand  $M^{n+}$ , generally surface inactive. In this manner the product formed by the collector-colligand interaction, or sublate, becomes surface active, being concentrated in foam, owing to the mobile phase.

The efficiency of the flotation process depends on chemical factors (pH, molar ratio collector:colligand  $C_C : C_{M^{n+}}$ ,  $M^{n+}$  concentration), the gas flow, and the hydrodynamic and the mass transfer factors.<sup>[6]</sup>

The  $Cu^{2+}$  cations are present in aqueous solution at low pH values as stable aqueous complex  $[M(OH_2)_4]^{2+}$ . In the presence of collectors, the  $Cu^{2+}$ -collector interactions are important and the process becomes more complex. The polymeric hydroxospecies that result from olation and/or the hydrolysis process  $[M_p(OH)_y(OH_2)_x]^{n-p-y}$  are involved in the flocculation



process.<sup>[7-9]</sup> Flotation permits the separation of these complex species in which the collector has a double role—by apolar part it is fixed at air bubble and by polar part it interacts with insoluble species from the system.

Metallic ion separation from diluted solution by precipitate flotation is studied especially for those systems that contain the tensioactive species as impurity. Collector tensioactive properties are based on structures having long alkyl chains (C<sub>8</sub>–C<sub>18</sub>). The anionic collector sodium oleate (NaOL), CH<sub>3</sub>(CH<sub>2</sub>)<sub>7</sub>–CH=CH–(CH<sub>2</sub>)<sub>7</sub>–COO<sup>–</sup>Na<sup>+</sup>/CH<sub>3</sub>(CH<sub>2</sub>)<sub>7</sub>–CH=CH–(CH<sub>2</sub>)<sub>7</sub>COOH, present in some aqueous systems, belongs to this group. It is necessary to know the form of the collector in the particular aqueous system because this could influence the collector function as tensioactive and complexant agent.

Literature data<sup>[7,10]</sup> show that for RCOO<sup>–</sup>/RCOOH systems at pH < 4, the fatty acids in protonated form are present in aqueous systems; at pH = 10, the carboxyl molecules are fully ionized. At pH = 5, the proportion of ionization is about 50%.

The knowledge of the real separation–concentration mechanism and the understanding of the active factor's influence is very important in the realization of an optimum separation control of the flotation process.

The present research was conducted on “model” systems prepared from CuSO<sub>4</sub>·5H<sub>2</sub>O p.a. for:

1. The study of the principal influencing factors (pH, C<sub>c</sub>, C<sub>Cu(II)</sub>) in Cu(II) separation by precipitate flotation; this allows evaluation of optimum separation conditions, which were also applied and verified on real aqueous systems (wastewater from copper plating and mine wastewater).
2. The interaction mechanism between Cu(II)-insoluble species and collector separated at optimum conditions; this characterization allows the valuation of the final separated product use possible.

## EXPERIMENTAL

The optimal separation conditions were established using the dissolved air flotation (DAF) methodology.

### Equipment

- Laboratory apparatus DAF<sup>[11]</sup> contains a flotation cell connected at a pressure vessel made of special steel in order to resist at high values of pressure (to 8 atm). Also, the apparatus has an air-compressed supply



system, a water supply system, stirring control system, manometer, water- and air-dissolved admission tap, and thermostat.

- ORION 290 A pH meter (USA).
- Electrical stirrer (4803-02, Cole Parmer, USA).
- Atomic absorption spectrophotometer (AAS) PYE UNICAM SP 9.
- Perkin-Elmer spectrophotometer for IR spectra.
- VIS-VSU-2G spectrophotometer for reflexion electronic spectra (Carl Zeiss, Jena, Germany).
- Paulik-Paulik Erdey derivatograph (Hungary).

### Reagents

- $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  p.a., Merck (stock model, solution of  $2\text{ g L}^{-1}$ ), in distilled water was used to prepare working solutions, according to  $\text{Cu}^{2+}$  concentrations in real systems ( $10\text{--}100\text{ mg L}^{-1}$ ).
- Anionic collector: sodium oleate Fluka p.a. 0.2% solution.
- $\text{NaOH}$  (COMCHIM, Romania) p.a., 6 and 2M solutions as precipitation reagent.

### Methods

The experimental studies were carried out using  $\text{CuSO}_4 \text{aq}$  samples ( $100\text{ mg L}^{-1}$ ,  $V = 0.3\text{ L}$ ). A 6 and 2M  $\text{NaOH}$  solution was used in order to obtain  $\text{Cu}(\text{II})$  hydroxide species for optimum pH separation value ( $\text{pH} \sim 7$ ). The samples containing  $\text{Cu}(\text{II})$  hydroxide species were treated with collector reagent ( $\text{NaOL}$ ) under continuous stirring and then introduced into the flotation cell where the separation process by air bubbles was achieved. To generate airbubbles, pressurized water ( $p = 4 \cdot 10^5 \text{ N m}^{-2}$ ,  $V_{\text{sample}} : V_{\text{water}} = 3 : 1$ ) was used. Every 10 sec, 2mL of the dispersion was sampled and the concentration of  $\text{Cu}^{2+}$  was determined by AAS. For determination of  $\text{Cu}^{2+}$  as soluble species, the samples were treated with 0.05 mL concentrated  $\text{H}_2\text{SO}_4$ .

The efficiency of the separation  $R$  was expressed as:

$$R = (1 - C_t/C_0)100 \quad (1)$$

The initial concentration of  $\text{Cu}^{2+}$ ,  $C_0$ , and the concentration at the time  $t$ ,  $C_t$ , expressed in  $\text{mg L}^{-1}$ , were determined by AAS. The colligand-collector interaction study was performed using coordinative chemistry-specific methodology: chemical analysis, electronic and vibration spectra, and thermal analysis. The foam obtained at optimal values of the pH and different molar ratio  $C_c : C_{\text{Cu}(\text{II})}$  was isolated and a comparison of chemical analysis results



with electronic and vibration spectra and thermal analysis for isolated species was made.

Chemical elementary analysis of the sublate was made using the follow methods: Cu(II) was determinate gravimetrically,  $\text{SO}_4^{2-}$  was determined gravimetrically as  $\text{BaSO}_4$ , and sodium was determined flamephotometrically.

IR spectra were performed using a Perkin–Elmer spectrophotometer by pelleting techniques with potassium bromide in the range  $400\text{--}4000\text{ cm}^{-1}$ .

Thermal analysis was performed with a Paulik-Paulik–Erdey derivatograph, with simultaneous registration of thermogravimetric (TG) analysis  $\Delta m = f(T)$ , thermodifferential gravimetric (TDG) analysis, and differential thermal analysis (DTA),  $\Delta T = f(\tau)$  curves, in the range  $20\text{--}900^\circ\text{C}$ . Tests were made in air atmosphere, with a temperature increase rate of  $10^\circ\text{C min}^{-1}$ , TDG sensitivity = 500 mg, DTA sensitivity = 1/10, platinum crucibles, and a standard  $\text{Al}_2\text{O}_3$  sample calcinated at  $1000^\circ\text{C}$ .

The separation stages in Cu(II) aqueous systems recovery by precipitate flotation are presented in Fig. 1.

## RESULTS AND DISCUSSIONS

### Optimal Separation Conditions

#### Flotation pH

The concentrating tendency of hydroxide-type species depends on the flotation pH. In order to find the optimal flotation pH value in the separation process, the recovery efficiency dependence of pH [ $\%R = f(\text{pH})$ ] in the range (6–8.5) was studied. The preliminary tests obtained in the range  $\text{pH} = 1\text{--}6$  showed that the NaOL could not remove Cu(II) from solution with good results. At  $\text{pH} > 6$ ,  $\text{Cu(OH)}_2$  was formed and Cu(II) could be floated as hydroxide species.

Cu(II) solution ( $100\text{ mg L}^{-1}$ ) was precipitated using a 6 and 2 M NaOH solution. The precipitate was mixed with NaOL as collector reagent, stirred continuously, then followed by flotation.

Experimental data presented in Fig. 2 show that the maximum yield  $R = 99.2\%$  was obtained at  $\text{pH} \sim 7$  (6.8–7.2).

#### Collector Concentration

In precipitate flotation, the collector concentration is generally under stoichiometrical and has to be established in correlation with maximum  $\%R$ ;



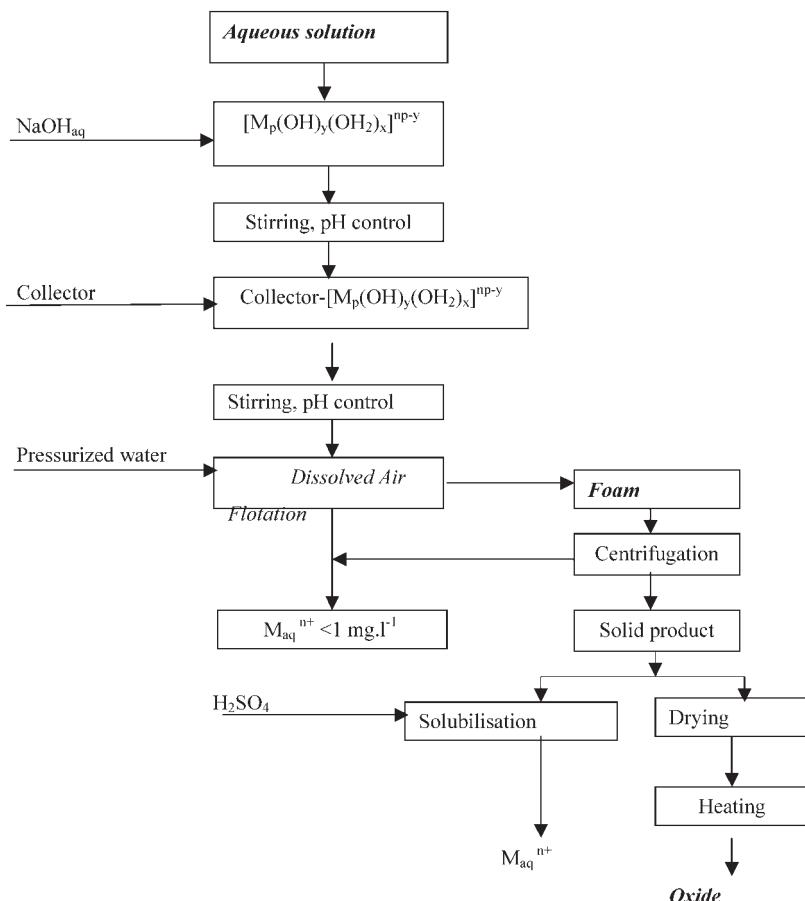
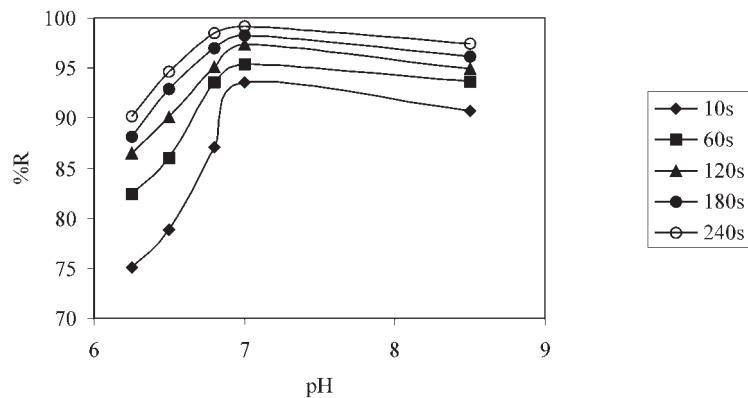


Figure 1. Separation scheme of flotation processes (DAF).

finally, the collector concentration in aqueous solutions must be under allowed limits. Cu(II) solution ( $100 \text{ mg L}^{-1}$ ) was studied at different collector-colligand molar ratios at the optimum pH  $\sim 7$ . Table 1 shows the relationship  $\%R = f(C_C : C_{\text{Cu(II)}})$ . The optimum collector-colligand molar ratio is  $C_C : C_{\text{Cu(II)}} = 10^{-1}$  and a  $\%R = 99.2$  is obtained.

For molar ratios collector-colligand  $C_C : C_{\text{Cu(II)}} < 10^{-1}$ ,  $\%R > 85.3\%$  and could be applied in order for Cu(II) recovery from wastewater with low consumption of collector. No supplementary addition of collector is required.





**Figure 2.** Recovery efficiency as function of pH in Cu(II) separation,  $C_C : C_{\text{Cu(II)}} = 10^{-1}$ ,  $V_{\text{sample}} : V_{\text{water}} = 3 : 1$  at different time of flotation.

### Cu(II) Concentration

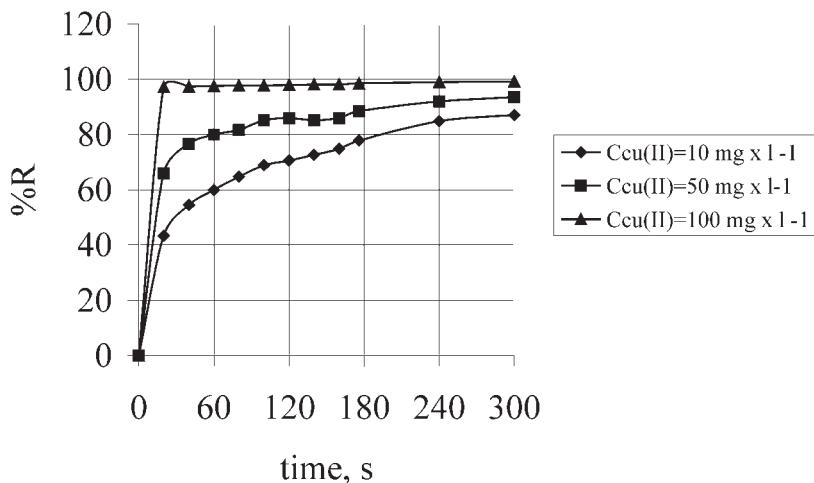
The concentration range of copper in aqueous solution for which the DAF method at  $\text{pH} \sim 7$  and molar ratio  $C_C : C_{\text{Cu(II)}} = 10^{-1}$  has the maximum yield was also studied. The necessary air volume is provided by sample dilution with pressurized water at  $4 \cdot 10^5 \text{ N m}^{-2}$ , to a dilution ratio that depends on colligand concentration.

Experimental results presented in Fig. 3 show that DAF allows Cu(II) recovery from aqueous system with anionic collector (NaOL) in the range of

**Table 1.** Recovery efficiency as function of collector–colligand concentration in Cu(II) separation;  $C_{\text{Cu(II)}} = 100 \text{ mg L}^{-1}$ ,  $V_{\text{sample}} : V_{\text{water}} = 3 : 1$ ,  $t = 5 \text{ min}$ ,  $p = 4 \times 10^5 \text{ N m}^{-2}$ .

Time (sec)	$C_C : C_{\text{Cu(II)}}$					
	$10^{-1}$		$10^{-2}$		$10^{-3}$	
	$C (\text{mg L}^{-1})$	%R	$C (\text{mg L}^{-1})$	%R	$C (\text{mg L}^{-1})$	%R
10	4.75	93.6	8.36	88.74	5.71	85.3
60	1.72	97.7	1.99	96.93	3.98	94.66
120	1.54	98.2	1.78	97.6	3.12	95.89
180	1.27	98.7	1.47	98.02	2.27	96.95
300	0.58	99.2	0.96	98.7	1.6	97.86





**Figure 3.** Recovery efficiency as function of initial Cu concentration in Cu(II) separation,  $C_C : C_{\text{Cu(II)}} = 10^{-1}$ , pH = 7,  $V_{\text{sample}} : V_{\text{water}} = 3 : 1$ .

10–100 mg L<sup>-1</sup> with maximum  $R = 99.2\%$  for an initial Cu(II) concentration of 100 mg L<sup>-1</sup>.

### Gas Flow

The influence of gas flow on the efficiency of the separation was studied. The necessary gas flow in DAF separation has been obtained according to Henry–Dalton's law, by pressurizing the diluting water followed by releasing the pressure in the flotation cell. The experimental results obtained for  $C_{\text{Cu(II)}} = 100 \text{ mg L}^{-1}$ , at pH  $\sim 7$ , indicate that the optimum dilution ratio was 3 : 1 for the samples pressurized at  $4 \cdot 10^5 \text{ N m}^{-2}$ . An increase over this pressure is not necessary.

### Foam Processing

The foam processing for copper recovery represents an important stage of the experimental research. The resulting foam volume depends on the Cu(II) concentration, the collector type, the collector–colligand molar ratio, and the  $V_{\text{sample}} : V_{\text{water}}$  dilution ratio. Foam processing results in a Cu(II)–NaOL system at pH  $\sim 7$ , a molar ratio of  $C_C : C_{\text{Cu(II)}} = 10^{-1}$ , and  $C_{\text{Cu(II)}} = 100$



$\text{mg L}^{-1}$  is presented in Table 2. The results show that Cu(II) is recovered in the foam with  $R \sim 98.4\%$ .

### **Cu(II) Separation from Real Samples (Wastewaters)**

The proposed processing scheme based on “model” systems was used for a real wastewater sample provided from the copper plating industry. By processing the sample according to the stages listed in Fig. 1, at the optimum pH, and with the experimental conditions ( $C_{\text{Cu(II)}} = 100 \text{ mg L}^{-1}$ ,  $C_C : C_{\text{Cu(II)}} = 10^{-1}$ ,  $V_{\text{sample}} : V_{\text{water}} = 3 : 1$ ), a separation recovery of  $R > 96\%$  was obtained. The high efficiency of the Cu(II) separation recommends the use of the anionic type collector, NaOL, applied in the DAF technique.

### **The Nature of Collector–Colligand Interaction**

The knowledge of the real separation–concentration mechanism and understanding of active factor’s influence is very important in the realization of an optimum separation control of the flotation process.

In order to establish the nature of collector–colligand interaction, the insoluble sublates isolated at optimal pH values and different molar ratios  $C_C : C_{\text{Cu(II)}}$  were studied by elemental chemical analysis. The results are presented in Table 3. They show that for molar ratio  $C_{\text{NaOL}} : C_{\text{Cu(II)}} \leq 10^{-1}$  the sublate is probably an oleate-hydroxo-sulfate compound, and for a molar ratio  $C_{\text{NaOL}} : C_{\text{Cu(II)}} \geq 1$  the sublate is probably a mixture of hydroxo-sulfate and hydroxo-oleate-sulfate species (sample 1 was analyzed in the absence of the collector).

In order to achieve a better characterization of the separated compounds, the sublate composition was studied.

**Table 2.** Cu(II) recovery in foam;  $C_{\text{Cu(II)}} = 100 \text{ mg L}^{-1}$ ,  $C_C : C_{\text{Cu(II)}} = 10^{-1}$ ,  $V_{\text{sample}} : V_{\text{water}} = 3 : 1$ , pH = 7.

Sample volume (L)	Cu(II)		Foam analysis			Cu(II) residual	
	mg L <sup>-1</sup>	Total (mg/ $V_{\text{sample}}$ )	CuSO <sub>4</sub> (mg)	Cu(II) (mg)	R (%)	mg L <sup>-1</sup> calc	mg L <sup>-1</sup> exp
2	25	50	82.0	49.2	98.4	0.41	0.25
2	25	50	80.7	48.4	96.2	0.82	0.70
2	25	50	81.7	49.0	98.0	0.50	0.25
2	25	50	77.2	46.3	92.6	1.85	0.50



**Table 3.** The elemental chemical analysis of different Cu(II)-NaOL sublates.

Sample	$C_e : C_{Cu(II)}$	Cu% (calc/exp)	$SO_4^{2-}$ (calc/exp)	Na% (calc/exp)	Chemical formula proposed
1	—	43.04/44.1	21.52/22.31	—	$CuSO_4 \cdot 5H_2O \cdot 2Cu(OH)_2$ or $Cu_3(OH)_4SO_4 \cdot (H_2O)_5$
2	$10^{-3}$	50.61/51.2	19.56/19.48	—	Oleate complex
3	$10^{-2}$	48.33/49.1	18.72/18.28	—	Oleate complex
4	$10^{-1}$	39.5/40.83	12.99/13.66	—	Mixture of hydroxo-sulfate and hydroxo-oleate-sulfate species
5	1	9.23/10.83	4.62/3.85	6.64/5.4	$[Cu_3L_6(OH)_4SO_4]Na_6 \cdot 2H_2O$
6	2	9.23/10.06	4.62/3.25	6.64/5.02	$[Cu_3L_6(OH)_4SO_4]Na_6 \cdot 2H_2O$

*Note:* L  $\rightarrow$   $CH_3-(CH_2)_7-CH=CH-(CH_2)_7COO^-$  (collector).



### IR Spectra

The experimental data registered for collector, sublate without collector, and sublate with collector provides information on the coordinative species formed by collector and on the existence of the other ions inside or outside the coordinative field.

The characteristic IR frequencies for the  $\text{CuSO}_4$  isolated at optimum pH  $\sim 7$  and for the three obtained sublates are presented in Table 4. The sublates are comparable to some reference data.<sup>[12]</sup> IR spectra and data presented in Table 4 reveal the absence of valence vibration— $\nu_{\text{COO}^-}$  ( $1700-1750 \text{ cm}^{-1}$ ) characteristic for unsaturated acids and the absence of the other vibration frequencies specific for saturated carboxylic acids. This could prove the absence of this species in the acid form (COOH).

The presence of characteristic spectra of  $(\text{COO}^-)$  species slightly shifted in comparison with literature data, involving the possibility of coordination of the oleate by oxygen as donor atom.

The presence of characteristic vibration spectra of  $\text{OH}^-$  species represents proof of the existence of this group in all separated sublates. Also, the OH groups show an absorption band below  $1100 \text{ cm}^{-1}$ . For one of the Cu(II) compounds, this band is at about  $955 \text{ cm}^{-1}$ . The band from  $900$  to  $1000 \text{ cm}^{-1}$  could be assigned to the stretch vibration of the M—O bond of carboxylic group.

The interaction between Cu(II) and collector could be deduced from the existence of the vibration frequency of the Cu—O bond, which appears at  $435-440 \text{ cm}^{-1}$  as a medium-intensity band.

IR spectra sustain the idea of Cu(II) hexacoordination corresponding to the proposed formula and show that all ligand have oxygen as a donor atom. Reflexion electronic spectra study gives additional information about the structural characterization of the separated species.

Figure 4 presents the reflexion electronic spectra of Cu(II) insoluble species in the absence of collector and of the sublate at  $C_C : C_{\text{Cu(II)}} = 10^{-3}$  and sublate at molar ratio  $C_C : C_{\text{Cu(II)}} = 2$ . Basic Cu(II) sulfate spectrum is a characteristic hexacoordinated combination of Cu(II) presenting an absorption band at  $\sim 14,200 \text{ cm}^{-1}$  (700 nm). The band from 700 nm exists in all studied spectra sustained by presence of an octahedral surround of Cu(II).

Sublate 2 spectrum obtained at molar ratio  $C_C : C_{\text{Cu(II)}} = 10^{-3}$  is not very different from basic sublate spectrum because of low concentration of the collector. Sublate 6 spectrum obtained at molar ratio  $C_C : C_{\text{Cu(II)}} = 2$  is different from the other two, presenting a supplementary band at  $26,600 \text{ cm}^{-1}$  (375 nm), which is probably a ligand band.

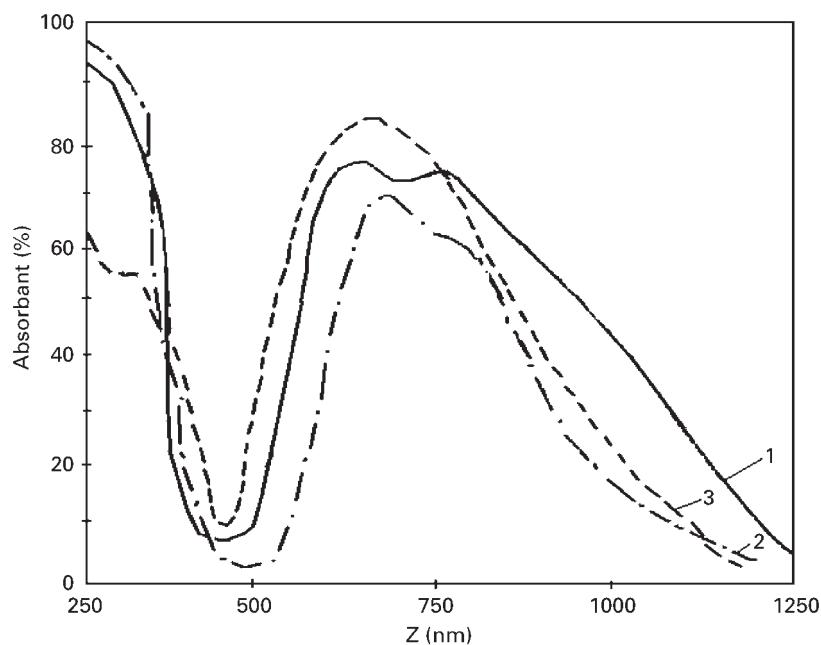
The slight shift of the bands from 700 nm to lower  $\lambda$  values in sublates at molar ratio  $C_C : C_{\text{Cu(II)}} = 10^{-3}$  and  $C_C : C_{\text{Cu(II)}} = 2$  spectra compared with



Table 4. IR characteristic frequencies of the studied compounds and their probable assignments (cm<sup>-1</sup>).

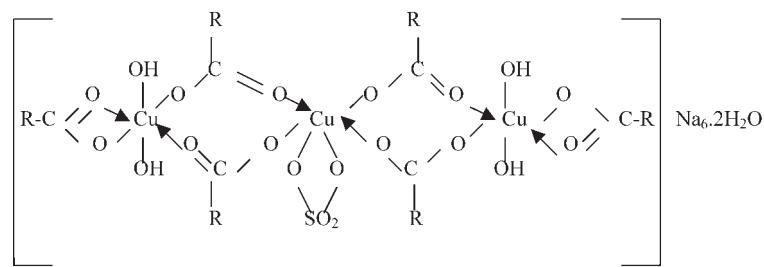
	Literature	Compound			
		C <sub>18</sub> H <sub>33</sub> O <sub>2</sub> collector	Cu <sup>2+</sup> (pH = 7)	C <sub>C</sub> : C <sub>Cu(II)</sub> = 10 <sup>-1</sup>	C <sub>C</sub> : C <sub>Cu(II)</sub> = 2
$\nu_{C=O}$	1,300–1,400	1,300–1,400	—	1,420	1,415
sym	1,590–1,610	1,560–1,610	—	1,570	1,580
asym	1,620–1,680	1,620–1,680	—	1,640	1,670
$\nu_{C=C}$					
CH <sub>3</sub>	2,956/2,870	2,956/2,870	—	2,900/2,855	2,990/2,940
$\nu_{as/s}$	1,460/1,330	1,460/1,330	—	1,420/1,490	1,418/1,490
$\delta_{as/s}$	720–750	720–750	—	740	750
$\nu_{(CH2)n}$	3,200–3,500	—	3,200–3,500	3,270–3,560	3,250–3,540
$\nu_{OHstr}$	970–1,100	—	985	990	980
$\delta_{M-OH}$	440	—	440	440	435
$\nu_{Cu-O}$					
SO <sub>4</sub> <sup>2-</sup>					
$\nu_3$	1,104	—	1,125	1,090/1,130	1,090/1,125
$\nu_4$	613	—	620	615/610	620/615





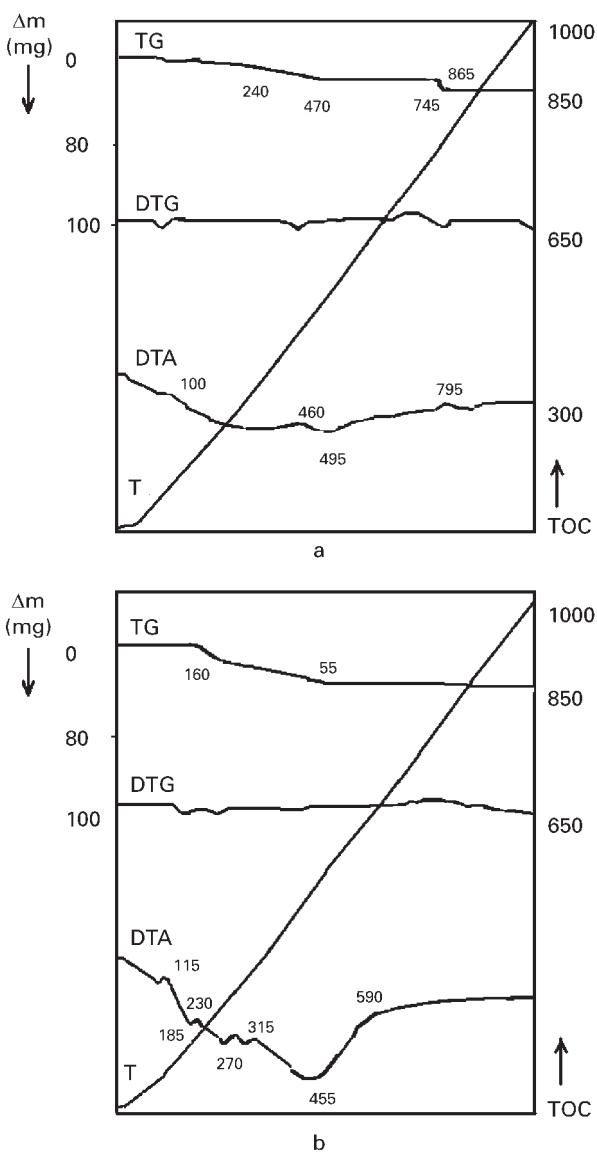
**Figure 4.** Electronic reflectance spectra: 1, basic Cu(II) sulphate; 2, sublate at molar ratio  $C_C : C_{\text{Cu(II)}} = 10^{-3}$ ; 3, sublate  $C_C : C_{\text{Cu(II)}} = 2$ .

those of Cu(II) basic salt and can sustain the ligand coordination. The spectra results sustain the idea of Cu(II) hexacoordination corresponding to the proposed formula and show that two carboxylic groups and two hydroxyl groups surround the Cu(II). The probable structure of the separated compound is as follows:



Differential thermal analysis of insoluble separated sublates gives additional information regarding thermal decomposition. The TG curves show three decomposition steps associated with three DTA curves endo-effects (Fig. 5).





**Figure 5.** Derivatogram for: (a) basic Cu(II) sulphate  $[\text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}]$ , (b) sublate at molar ratio  $C_C : C_{\text{Cu}(\text{II})} = 2$ , (c) derivatogram for collector.



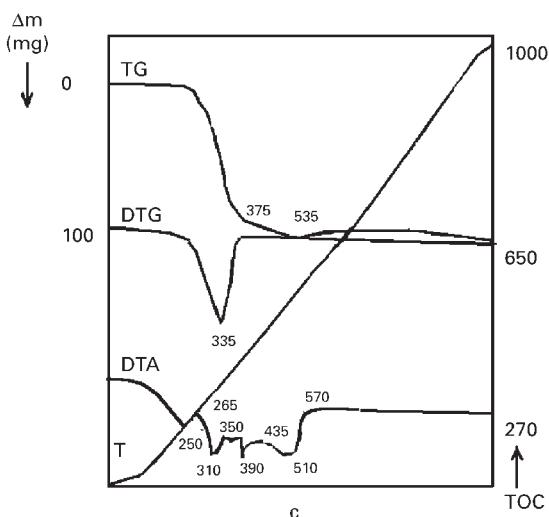


Figure 5. Continued.

Collector derivatograms show its gradual decomposition. The three exothermic effects ( $265^{\circ}\text{C}$ ,  $350^{\circ}\text{C}$ ,  $435^{\circ}\text{C}$ ) and the three endothermic effects (at  $310^{\circ}\text{C}$ ,  $390^{\circ}\text{C}$ ,  $510^{\circ}\text{C}$ ) can be assigned to the decomposition and oxidation of the organic residue. [Fig. 5(c)]. Weight losses calculated from the TG curves are similar to those obtained by stoichiometrical calculation and correspond to CuO formation.

The thermodifferential analysis of sublates obtained at molar ratio  $C_{\text{C}} : C_{\text{Cu(II)}} = 2$  and without collector presents a loss of weight of about 86.71% ( $C_{\text{C}} : C_{\text{Cu(II)}} = 2$ ) and 45.23% (without collector), respectively; the corresponding theoretical losses of weight from the proposed formulae are 88.45% and 46.18%, respectively. The absence of RES signal (the absence of paramagnetism) could be interpreted by obtaining some dimmer groups with diamagnetic coupling spin.

The physicochemical data presented above sustained the coordinative nature of a collector-colligand interaction in the separation process of Cu(II) salts by flotation with NaOL. At very small concentrations of NaOL, the role of collector is as ten-side only, but at higher concentrations the collector is not only a ten-side agent but a complexing agent, too.

## CONCLUSIONS

Dissolved air flotation is a depollutant separation process and its main advantages are: high efficiencies ( $R > 95\%$ ), rapidity, accessibility, and the



possibility of removal and recovery of organic and inorganic species. The present paper proposes a Cu(II) recovery method from aqueous systems by precipitate flotation (DAF) using as collector reagent NaOL. The efficiency of Cu(II) separation by precipitate flotation with anionic collector NaOL is maximum  $R = 99.2\%$ , at optimum pH (pH  $\sim 7$ ), and at a molar ratio collector colligand of  $C_C : C_{Cu(II)} = 10^{-1}$ .

Good results from the ecological point of view were obtained for initial Cu(II) concentrations in the range  $10\text{--}100\text{ mg L}^{-1}$  and final concentrations after flotation are less than  $1\text{ mg L}^{-1}$ . The physical-chemical data presented sustained the coordinative nature of a collector-colligand interaction in the separation process of Cu(II) salts by flotation with NaOL. The interaction of insoluble species with NaOL leads to a probable sublate's structure, and thermal analysis shows the possibility of obtaining the oxide from the sublate that was isolated at optimal conditions. The study of the collector-Cu(II) interaction could explain the separation mechanism and could sustain the industrial application of the Cu(II) removed in the form obtained in the process.

## REFERENCES

1. Lemlich, R. *Adsorptive Bubbles Separation Techniques*; Academic Press: London, 1972.
2. Matis, K.A.; Zouboulis, A.I.; Lazaridis, N.K. Removal and recovery of metals from dilute solutions: applications of flotation techniques. In *Mineral Processing and the Environment*; Gallios, G.P., Matis, K.A., Eds.; NATO ASI Series, 1996; Vol. 2, 43, 165–196.
3. Lazaridis, N.K.; Matis, K.A.; Stalidis, G.A.; Mavros, P. Dissolved-air flotation of metal ions. *Separ. Sci. Technol.* **1992**, 27 (13), 1743–1758.
4. Sebba, F. *Ion Flotation*; Elsevier: New York, 1962.
5. Stumm, W. *Chemistry of the Solid Water Interface*; A Wiley Interscience Publication, John Wiley & Sons, Inc.: New York, Chichester, Brisbane, Toronto, Singapore, 1992.
6. Wang, Yun Dong; Wen, Hanzhen; Huang Ying Yi; Dai, You Yuan. Separation of Cu(II) from aqueous solution by using colloidal gas aphrons. *J. Chem. Eng. Jpn.* **2001**, 34 (9), 127–130.
7. Ghazy, S.E.; Samra, S.E.; El-Morsy, S.M. Removal of Cu(II) from aqueous solutions by flotation using limestone fines as the sorbent and oleic acid as the surfactant. *Adsorption Sci. Technol.* **2001**, 19 (2), 175–185.
8. Zubareva, G.I. Selection of highly effective collectors of various classes for flotation removal of metal ions from industrial wastewater. *Khimicheskaya Promyshlennost* **2000**, 672 (10), 46–48.

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9. Rubio, J.; Tessele, F. Removal of heavy metal ions by adsorptive particulate flotation. *Miner. Eng.* **1997**, *10* (7), 671–679.
10. Hughes, T.C. Fatty hydroxamic acids and salts suitable for froth flotation of ores. *Pct. Int. Appl. Wo 02 10, 122 (Cl. C07C259/06)*, 7 Feb. 2002; AU APPL. 2000/551, 3 Oct. 2000.
11. Stoica, L.; Catuneanu, R.; Nicolau, M.; Bretan, V. Recovery of metallic ions from wastewater by flotation. *Revue Roumaine De Chimie* **1990**, *1*, 31–39.
12. Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; Wiley Interscience Publ.: New York, 1986.

Received August 2002

Revised January 2003



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