Cu(II) separation from diluted aqueous solutions by flotation with atypical collectors \textit{anti} and \textit{syn} 2-hydroxy-3,5-di-tert-butyl-benzaldoxime

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Abstract: The paper is a contribution to the development of the flotation separation area, concerning in the proposal of new atypical collectors (\textit{anti} and \textit{syn} 2-hydroxy-3,5-di-tert-butyl-benzaldoxime) for the metallic ions separation from diluted aqueous systems. A case study (R\%) was studied and the optimal parameters were established. The insoluble species of Cu(II), isolated by flotation were characterised by physical-chemical methods, for establishing the Cu(II)-collector interaction. The experimental results showed the efficiency of both collectors for Cu(II) removal (\%R~100). This systematic research based on structure-properties-floatability correlation, allow to these atypical collectors to be also tested for other metallic ions.

Keywords: flotation; Cu(II); 2-hydroxy-3,5-di-tert-butyl-benzaldoxime; diluted aqueous solution.


Biographical notes: Ligia Stoica, Professor at “Politehnica” University of Bucharest. She teaches the courses “Inorganic Chemistry” and “Pollutants recovering-separation processes”. She obtained her PhD Degree in Chemical Engineering with the thesis “Separation and concentration of some ions by flotation”. She initiated and developed the domain of ion flotation and related techniques in Romania. She is supervising BSc, MSc and PhD and she organised ion flotation laboratory. She published a monographic book in ion and molecular flotation area and has 160 published papers, 14 invention brevets and 110 scientific communications to her credit. She has flotation research projects and she is evaluating expert.
1 Introduction

The presence of inorganic pollutants, especially heavy metal ions in the different aqueous systems, has a negative impact on the environment with dangerous consequences. These pollutants must be removed before evacuation into emissary by efficient and low-cost techniques below the maximum allowable limits. In this respect, one can act towards the use of highly successful ‘clean technologies’ that should simultaneously assure the liquid media quality.

The group of separation methods by adsorptive bubbles, which include ion flotation, represents an effective alternative sustained by the fast rate of separation, low cost, small volumes of wastes that allow recovery of valuable species and so on (Stoica, 1997). The metallic ions – hydrophilic species – can be removed from aqueous systems by ion flotation, with their recovery by this method imposing their hydrophobisation. The modification of the hydrophilic–hydrophobic balance of ionic species that can be constituted as a separable component by flotation can be achieved by many modes (Matis et al., 2003; Doyle, 2003; Lazaridis et al., 2004), generally by Surface-Active Agent (STA) intervention, commonly called ‘collector’.

The selection of the adequate collector in view of the quantitative separation of a metallic ion from diluted aqueous solutions by flotation is based on two important characteristics:

- **ligand function**, fulfilled by the presence of one polar group in collector molecule (–NH₂, –COOH, –OH, –SH, etc.), that can coordinate the metallic ions, forming insoluble complexes

- **STA function**, assured by a long linear alkylhydrocarbonate chain (C > 8).

In the recent years, it can be noticed in the literature, orientation to multipolar collectors, generally analytical organic reagents, with two or more polar chelating groups, which thus increase their donor capacity, with effect on the separation efficiency. Generally, the organic chelating reagents are used in analytical chemistry as extraction reagents. Grafting an alkyl radical to such a chelating reagent associates to its surface-active properties, which are important for metallic ion flotation.

A class of chelating organic compounds for the metallic ions with affinity for donor O and N atoms are α-aromatic hydroxyoximes. There is literature data that demonstrates the excellent ligand function of α-aromatic hydroxyoximes, successfully used in metallic ions separation techniques as solvent extraction (Ainscow et al., 1999; Radushev et al., 2002; Sudderth et al., 2002; Menacho et al., 1996; Jong Sung and Jongheop, 1999;
Cu(II) separation from diluted aqueous solutions by flotation

Green and Mueller, 2000; Virnig et al., 2004; Buch et al., 2002; Warren et al., 2003; Jones, 2002).

The aim of this paper consists of the proposal of two atypical collectors (anti and syn 2-hydroxy-3,5-diterbutyl-benzaldoxime) – for metallic ions separation from aqueous diluted solutions by flotation (DAF technique) and to include these new reagents in the category of collectors for the ion flotation and related methods. A case study for Cu(II) ion is presented.

The anti and syn isomer of BuA contains in its molecule two polar groups situated in the immediate steric vicinity (–OH, =N–OH) and presents the advantage of a tertbutyl radical with electron donor properties in the third position (neighbour of OH group) that leads to a predominant increase of electronic effects. This directly results in an increase of reagent collecting capacity, by a rapid deprotonation of the phenolic OH and a rapid coordination of the metallic ion to the phenolic oxygen atom. These aspects are supported by:

- compound low solubility, accentuated by the two tertbutyl groups
- classification of metallic ions after Ahrland and series Irving-Williams (Stoica, 1997), according to which Cu(II) ions present affinity for the donor O and N atoms
- the selectivity of these collectors vs. Cu(II) ion, in a first interpretation, can be anticipated using acid–base properties of metallic ions (HSAB theory), which allows the estimation of affinity for a ligand.

2 Materials and methods

Reagents. CuSO₄·5H₂O (Merck) stock solution 0.05 M, used subsequently for the preparation of working solutions in the concentration range 20–500 mg/L; C₆H₅–C(N–OH)–CH(OH)–C₆H₅ (α-benzoinoxime, α-BO); C₆H₅(OH)(C₉H₁₉)(CH=N–OH) (2-hydroxy-5-nonyl-benzaldoxime, BA); C₆H₂(OH)(tC₄H₉)₂(CH=N–OH) (anti and syn BuA, synthesised by the authors) solutions 0.05 M in ethanol p.a.; solutions of KOH 1M and 0.1 M for pH adjustment.

Equipments. Thermostated stalagmometer and picnometers; flotation unit with dissolved air and cell size h = 30 cm, φₜᵢₜ = 4.5 cm (Stoica, 1997; Stoica and Oproiu, 2004); pH-meter A 250 ORION; atomic absorption spectrophotometer PAY UNICAM SP9; FT – IR spectrometer 620, Jasco, Japan (range 4000–400 cm⁻¹), KBr pellets of spectral grade (Merck), ~0.3 g KBr + ~0.003 g analysed substance; spectrometer UV–VIS–NIR V 570, Jasco, Japan (range 200–2300 nm); diffuse reflection analysis performed with the device ILN – 472 endowed with integrating sphere; derivatograph Erdey-Paulik (TG = Thermogravimetric analysis; DTG = Derivate Thermogravimetric analysis; ATG = differential thermal analysis): temperature interval: tᵢ = 24°C; tᵢ = 1000°C, with ∆t = 10°C/min, sample mass taken at work, mᵢ = 50–100 mg, measure channel sensitivity: Sᵣ = 250 µV, Sᵣ = 500 µV, Sᵣ = 500 µV, Sᵣ = 500 µV, balance sensitivity, Sᵢ = 500 mg, paper speed for recording: vᵢ = 2 mm/min.
2.1 Methodology

The surface tension was determined with the stalagmometric method, and was calculated
by the relation:

$$\sigma = \sigma_0 \frac{n_0 \cdot d}{n \cdot d_0}$$

Flotation experiments (DAF technique) performed and aimed to separate Cu(II) from
diluted aqueous systems (model samples), in the presence of anti and syn BuA had in
view: study of the factors that influence separation efficiency for determining the
optimum separation parameters (solution pH, collector and Cu(II) concentrations, flow
gas, dilution ratio, separation equilibrium).

The insoluble species formed (sublate) by Cu(II) interaction with anti and syn BuA
were characterised by coordination-chemistry-specific methods (FT-IR and reflexion
electronic spectra, thermal analysis and elemental chemical analysis) to establish the
probable sublate composition, the geometry and stoichiometry.

The concentration of residual metallic ion was determined from decanted samples, by
atomic absorption spectrometry (the sensitivity of the method is 10⁻⁹ g). The separation
efficiency ($R\%$) was calculated with the relation:

$$R\% = \left(1 - \frac{C_{\text{Cu(II)}}}{C_{\text{Cu(II)}}}\right) \times 100.$$

For processing of experimental data, Microsoft Excel, Corel Draw software (for graphic
representation) and Student method (for statistical processing) have been used.

3 Results and discussion

Surface-active properties. Starting from the two above-mentioned basic characteristics
of the collectors, the surface-active properties have been tested by surface tensions
determination of anti and syn BuA aqueous solutions. The isotherms of surface tension
$\sigma = f(C)$ for the two collectors were compared with those of $\alpha$-benzoinoxime and
2-hydroxy-5-nonyl-benzaldoxime (Figure 1):

- Only 2-hydroxy-5-nonyl-benzaldoxime shows the conventional collector
  characteristics, being a compound with heteropolar structure; the curve $\sigma = f(C)$
  has a descendent trend $\sigma_{\text{BA min}} = 37.9 \times 10^{-3}$ N m⁻¹ owing to the existence in its
  structure of the linear hydrocarbonate chain ($-C_9H_{19}$) and the two polar chelating
  groups ($-\text{OH}, =\text{N}\text{─OH}$)
- Even $\alpha$-benzoinoxime does not present a linear hydrocarbonate chain; the
  phenyl group determines a decrease of surface tension confirmed by descendent
  allure of isotherm curves and by surface tension values of aqueous solutions
  ($\sigma_{\text{BO min}} = 38.7 \times 10^{-3}$ N m⁻¹, Figure 1) that supports the possibility of its use as
  collector reagent for the separation of metallic ions from diluted aqueous solutions;
  $\alpha$-BO supplies the ligand function, its molecule having functional groups of oxime
  and hydroxyl type
anti and syn BuA isomers partially exhibit the characteristics of a conventional collector ($\sigma_{\text{anti BuA min.}} = 51.6 \times 10^{-3} \text{ N} \cdot \text{m}^{-1}$, $\sigma_{\text{syn BuA min.}} = 44.7 \times 10^{-3} \text{ N} \cdot \text{m}^{-1}$, Figure 1), being compounds with hetero-polar structure (specific for STA), but with short and branched hydrocarbonate chain ($<C_8$), although the characteristics of these reagents support the possibility of their application in the field of flotation, curve trend $\sigma = f(C)$ being also descendent.

**Figure 1** Dependence $\sigma = f(C)$ of collector reagents solutions

Therefore, the selected anti and syn BuA can be tested as collectors, based on their chelating activity and less on their surface-active properties, for the recovering separation, by flotation of metallic ions from diluted aqueous solutions. Cu(II) separation from aqueous solutions with $\alpha$-benzoinoxime and 2-hydroxy-5-nonyl-benzaldoxime previously reported by the authors (Stoica et al., 2006, 2007) led to expected results obtaining separation efficiencies $> 98\%$ (in the case of $\alpha$-BO) and $> 99\%$ (in the case of BA). In this paper, a case study regarding the collector function of the two atypical isomers anti and syn BuA for the Cu(II) separation from diluted solutions by flotation was considered appropriate. The term ‘atypical’ is sustained by their structure:

- two non-polar groups with branched chain and with $C < 8$
- two polar groups ($–\text{OH}, =\text{N–OH}$) in ortho position favourable for the formation of a heterocyclic with Cu(II) species of the system.

### 3.1 Influencing factors

**pH flotation.** In aqueous solutions, the metallic cations are present as aqua-complexes $[\text{M(H}_2\text{O)}_n]^n^+$. For any chemical aquaspecies, there exists a certain pH at which ion flotation is achieved with a maximum separation efficiency; this differs from species to species and corresponds to the minimum hydrating point (Stoica, 1997). For a better interpretation of pH influence on Cu(II) separation with the two collectors, Figure 2 comparatively presents the equilibrium diagram of the Cu(II) species to different pH values and the separation efficiency (R%) obtained in the flotation process. The hydrated Cu(II) forms are stable at low pH values. pH increase favours the aqua-complex deprotonation equilibrium with the formation of hydroxo-aqua-complexes polymer species that finally pass in insoluble hydroxospecies. Therefore, by olation and oxolation
the hydrophilic–hydrophobic balance moves in the sense of hydrophobic accentuation and the floatability increase (Stoica, 1997).

**Figure 2** (a) Dependence $R = f$(pH) in *anti* BuA – Cu(II) and (b) *syn* BuA – Cu(II) systems

![Graph](image)

$C_{i\text{Cu(II)}} = 200 \text{ mg/L}; V_{\text{sample}} = 150 \text{ mL}; V_{\text{press. water}} = 3 : 1; P = 4.5 \times 10^5 \text{ N/m}^2; t_{\text{flotation}} = 300 \text{ s}.$

The flotation experiments performed for the determination of optimum separation pH of Cu(II) ions with collectors *anti* and *syn* BuA were achieved in the range $4.5 \leq \text{pH} \leq 9.5,$ on model solutions that contain initial concentrations of 200 mg/L Cu(II), at four molar ratios $C_{\text{STA}} : C_{\text{Cu(II)}} = 1.1 : 1; 1 : 1; 5 \times 10^{-1} : 1$ and $1 \times 10^{-1} : 1.$ The obtained results, presented in Figure 2(a) and (b), indicate:

- at $\sim 3.5 \leq \text{pH} \leq 6$ a low floatability of Cu(II) species is observed ($R\% < 74,$ for *anti* BuA, $R\% < 80,$ for *sin* BuA), simultaneously with obtaining $C_{\text{Cu(II)}}$ in residual solution $\leq 38 \text{ mg/L}$ and $\leq 29 \text{ mg/L}$ for *anti* BuA and *sin* BuA, respectively
- from pH $\sim 6.5,$ corresponding to Cu(OH)$_2$ precipitation, a sudden increase of the separation efficiency ($R\% > 99$) occurs, simultaneously with the decrease of the residual concentration of Cu(II) ($C_{\text{Cu(II)}} < 0.7 \text{ mg/L}$ for *anti* BuA and $C_{\text{Cu(II)}} < 0.4$ for *syn* BuA)
- maximum separation efficiencies of Cu(II) with *anti* BuA ($99.6 < R\% < 99.9,$ with $0.08 < C_{\text{Cu(II)}} \text{ mg/L} < 0.50$) are obtained in the pH range 7–9, and with *syn* BuA ($99.71 < R\% < 99.96$) in the range $7 \leq \text{pH} \leq 9.5,$ for all $C_{\text{anti/syn BuA}} : C_{\text{Cu(II)}}$ molar ratios.
**Collector concentration.** The influence of collector concentration on the ion flotation process was investigated by the dependence $R\% = f(C_{\text{anti}/\text{syn BuA}} : C_{\text{Cu(II)}})$ based on the experiments performed in solutions with $C_{\text{Cu(II)}} = 200$ mg/L, at pH values between $8 \leq \text{pH} \leq 9.5$, at $1.1 : 1$; $1 : 1$; $5 \times 10^{-1} : 1$ and $1 \times 10^{-1} : 1$ molar ratios (Table 1).

### Table 1  Influence of $C_{\text{anti}/\text{sin BuA}} : C_{\text{Cu(II)}}$ molar ratio on Cu(II) separation efficiency, by flotation (DAF)

<table>
<thead>
<tr>
<th>BuA : Cu(II) molar ratio</th>
<th>$C_{\text{corr Cu(II)}}$ (mg/L)</th>
<th>pH</th>
<th>$C_{\text{f Cu(II)}}$ (mg/L)</th>
<th>$R%$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>anti</td>
<td>sin</td>
<td>anti</td>
<td>sin</td>
</tr>
<tr>
<td>1.1 : 1</td>
<td>137.36</td>
<td>139.02</td>
<td>8.0</td>
<td>8.5</td>
</tr>
<tr>
<td></td>
<td>137.24</td>
<td>138.82</td>
<td>8.5</td>
<td>9.0</td>
</tr>
<tr>
<td></td>
<td>137.05</td>
<td>138.44</td>
<td>9.0</td>
<td>9.5</td>
</tr>
<tr>
<td>1 : 1</td>
<td>134.89</td>
<td>135.75</td>
<td>8.0</td>
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<td></td>
<td>133.99</td>
<td>135.32</td>
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<td></td>
<td>133.87</td>
<td>134.89</td>
<td>9.0</td>
<td>9.5</td>
</tr>
<tr>
<td>$5 \times 10^{-1} : 1$</td>
<td>137.36</td>
<td>141.31</td>
<td>8.0</td>
<td>8.5</td>
</tr>
<tr>
<td></td>
<td>136.86</td>
<td>141.38</td>
<td>8.5</td>
<td>9.0</td>
</tr>
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<td>136.42</td>
<td>141.24</td>
<td>9.0</td>
<td>9.5</td>
</tr>
<tr>
<td>$1 \times 10^{-1} : 1$</td>
<td>139.86</td>
<td>143.27</td>
<td>8.0</td>
<td>8.5</td>
</tr>
<tr>
<td></td>
<td>138.89</td>
<td>143.06</td>
<td>8.5</td>
<td>9.0</td>
</tr>
<tr>
<td></td>
<td>138.76</td>
<td>142.92</td>
<td>9.0</td>
<td>9.5</td>
</tr>
</tbody>
</table>

$C_{\text{Cu(II)}} = 200$ mg/L; $V_{\text{sample}} = 150$ mL; pH = 8–9 (for anti BuA), respectively 8.5–9.5 (for sin BuA); $V_{\text{sample}} : V_{\text{press. water}} = 3 : 1$; $P = 4.5 \times 10^5$ N/m$^2$; $\tau_{\text{flotation}} = 300$ s.

In anti BuA–Cu(II) system, for all the four studied molar ratios, the separation efficiency is high ($R\% \geq 99.6$) at pH ~8.5 and residual concentrations of Cu(II) $0.54 \leq C_{\text{f Cu(II)}} \leq 0.08$. The maximum separation efficiency was obtained for $C_{\text{anti BuA}} : C_{\text{Cu(II)}} = 1 : 10^{-1} : 1$ and pH = 8.5 ($R\% = 99.94$), with $C_{\text{f Cu(II)}} = 0.08$ mg/L.

In syn BuA–Cu(II) system:

- for $C_{\text{syn BuA}} : C_{\text{Cu(II)}} = 1.1 : 1$ and $1 : 1$ molar ratios, the separation efficiency was maximum: $99.84 \leq R\% \leq 99.96$, with a final Cu(II) concentration, $0.22 \leq C_{\text{f Cu(II)}} \leq 0.05$

- for understoichiometric molar ratios, separation efficiency has similar values, $99.90 \leq R\% \leq 99.94$, with $0.15 \leq C_{\text{f Cu(II)}} \leq 0.09$ (8.5 $\leq \text{pH} \leq 9.5$).

Experiments for collector: Cu(II) molar ratios $<10^{-1}$ were not justified because we wanted to obtain insoluble chelates as unitary compounds in this stage. To apply these collectors on real samples, the ratios less than $10^{-1}$ can be used owing to the pronounced floatability of formed mixture (Stoica, 1997). The molar ratios $\geq 1 : 1$ are applied only for isolation of unitary compound (e.g., for oxidic compounds synthesis).

As it will be proved further, at understoichiometric molar ratios, the froth is not a unitary compound. However, for depollution purpose an understoichiometric consumption represents an advantage of the separation method.
Cu(II) concentration. For the determination of the concentration range of Cu(II) in which flotation takes place with maximum efficiency, experiments were performed at two stoichiometric and understoichiometric molar ratios, keeping pH constant (pH = 8.5 and 9.5, respectively), in the range 20 ≤ \( C_{i\text{Cu(II)}} \) mg/L ≤ 500 (Table 2).

- For anti BuA–Cu(II) system (Table 2), an increase of separation efficiency with the increase of initial concentration of Cu(II), up to a value of 200 mg/L was observed. It seems that at low Cu(II) concentrations (20 mg/L), anti BuA forms chelating complex with more difficulty. For \( C_{i\text{Cu(II)}} = 500 \) mg/L, almost similar results are obtained with \( C_{i\text{Cu(II)}} = 200 \) mg/L, but the high concentrations are not justified in these conditions, as they require considerable collector reagent quantities.

- For syn BuA–Cu(II) system, good results are obtained for both stoichiometric and understoichiometric molar ratios, for the whole range of used concentrations (20–500 mg/L): 99.90 ≤ \( R \% \) ≤ 99.99 and 0.15 ≤ \( C_{f\text{Cu(II)}} \) mg/L ≤ 0.03.

Table 2 Influence of \( C_{i\text{Cu(II)}} \) on Cu(II) separation efficiency, by flotation (DAF)

<table>
<thead>
<tr>
<th>BuA : Cu(II) molar ratio</th>
<th>( C_{i\text{Cu(II)}} ) (mg/L)</th>
<th>( C_{\text{correction Cu(II)}} ) (mg/L)</th>
<th>( C_{f\text{Cu(II)}} ) (mg/L)</th>
<th>( R % )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 : 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>14.85</td>
<td>14.81</td>
<td>1.66</td>
</tr>
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<td>200</td>
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<tr>
<td></td>
<td>500</td>
<td>311.20</td>
<td>301.81</td>
<td>3.68</td>
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<tr>
<td>5 × 10⁻¹ : 1</td>
<td>20</td>
<td>14.90</td>
<td>14.83</td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td>50</td>
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<td>36.58</td>
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<td>344.35</td>
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<td>3.25</td>
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</table>

\( V_{\text{sample}} = 150 \) mL; \( pH = 8.5 \) (for anti BuA), respectively 9.5 (for sin BuA); 
\( V_{\text{sample}} : V_{\text{press. water}} = 3 : 1; P = 4.5 \times 10^5 \) N/m²; \( \tau_{\text{flotation}} = 300 \) s.

No data for \( C_{\text{Cu(II)}} > 500 \) mg/L have been presented because it is well known from previous papers (Stoica, 1997; Stoica and Oproiu, 2004) that for such concentrations, separation parameters are different or it is necessary for a new flotation stage.
The necessary gas flow. In the DAF separation, the necessary gas flow has been obtained by pressurising the dilution water \((P = 3–5 \times 10^5 \text{ N/m}^2)\) followed by pressure release in the flotation cell. Gas bubbles must have dimensional homogeneity and an optimum flow rate, to concentrate the sublate and to avoid the collapse of the foam. The experimental results with regard to the influence of the required air on the flotation efficiency (Table 3) were correlated with sublate foam height.

Table 3  Influence of pressure on Cu(II) separation efficiency, by flotation (DAF)

<table>
<thead>
<tr>
<th>BuA : Cu(II) molar ratio</th>
<th>(C_i) correction Cu(II) (mg/L)</th>
<th>(P \cdot 10^5) (N/m²)</th>
<th>(C_f) Cu(II) (mg/L)</th>
<th>(R) (%)</th>
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<td>sin</td>
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<td>3</td>
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<td>3.5</td>
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<td>4</td>
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<td>0.09</td>
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<td>0.05</td>
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<td>99.83</td>
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</table>

\(C_i\) Cu(II) = 200 mg/L; \(V_{\text{sample}}\) = 150 mL; pH = 8.5 (for \(anti\) BuA), respectively 9.5 (for \(sin\) BuA); \(V_{\text{press. water}} = 3 : 1\); \(P = 4.5 \times 10^5 \text{ N/m}^2\); \(\tau_{\text{flotation}} = 300 \text{ s}\).

The experimental data (Table 3) show high separation efficiencies for all the five used pressures and for both studied molar ratios. Maximum separation efficiencies were obtained for \(P = 4.5 \times 10^5 \text{ N/m}^2\) : \(99.83 \leq R\% \leq 99.87\) (for \(anti\) BuA–Cu(II) system) and \(99.85 \leq R\% \leq 99.97\) (for \(syn\) BuA–Cu(II) system).

Another series of experiments were achieved for the confirmation of the previous researches in which a 3 : 1 ratio was used between sample volume subjected to flotation process and the pressurised water volume introduced in the system (Table 4). For these experiments, two molar ratios \(C_{anti/syn \text{ BuA}} : C_{\text{Cu(II)}}\) were used, and all the other influencing parameters of the flotation process were kept constant.

The ratio between sample floated volume and pressurised water volume introduced in the flotation cell for the \(anti\) and \(syn\) BuA–Cu(II) systems does not show an important variation, as the results were similar for all the performed tests by variation \(V_{\text{sample}} : V_{\text{press. water}} = 3 : 1 \div 1 : 1.5\) (Table 4), obtaining a maximum separation efficiencies (99.76 ≤ \(R\%\) ≤ 99.94, for \(anti\) BuA–Cu(II) and 99.82 ≤ \(R\%\) ≤ 99.92, for \(syn\) BuA–Cu(II)).
**Table 4**  Influence of $V_{\text{sample}} : V_{\text{press. water}}$ dilution ratio on the Cu(II) separation efficiency, by flotation (DAF)

<table>
<thead>
<tr>
<th>BuA : Cu(II) molar ratio</th>
<th>$C_{\text{Cu(II)}}$ (mg/L)</th>
<th>$V_{\text{sample}} : V_{\text{press. water}}$</th>
<th>$C_{\text{Cu(II)}}$ (mg/L)</th>
<th>$R$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$C_{\text{Cu(II)}}$</td>
<td>$anti$</td>
<td>$sin$</td>
<td>anti</td>
</tr>
<tr>
<td>1 : 1</td>
<td>135.50</td>
<td>137.99</td>
<td>3 : 1</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>121.75</td>
<td>123.76</td>
<td>2 : 1</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>110.54</td>
<td>112.19</td>
<td>1.5 : 1</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>93.34</td>
<td>94.52</td>
<td>1 : 1</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>75.68</td>
<td>76.45</td>
<td>1 : 1.5</td>
<td>0.18</td>
</tr>
<tr>
<td>5 : $10^{-1}$ : 1</td>
<td>139.15</td>
<td>139.73</td>
<td>3 : 1</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>124.69</td>
<td>125.16</td>
<td>2 : 1</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>112.95</td>
<td>113.34</td>
<td>1.5 : 1</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>95.06</td>
<td>95.33</td>
<td>1 : 1</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>76.80</td>
<td>76.98</td>
<td>1 : 1.5</td>
<td>0.12</td>
</tr>
</tbody>
</table>

$C_{\text{Cu(II)}} = 200 \text{ mg/L}; V_{\text{sample}} = 150 \text{ mL}; pH = 8.5 \text{ (for } \text{anti BuA), respectively 9.5 \text{ (for } \text{sin BuA); P} = 4.5 \times 10^5 \text{ N/m}^2; t_{\text{flotation}} = 300 \text{ s.}$

**Separation equilibrium.** The study of separation equilibrium performed at optimum parameters has in view the evolution of the separation efficiency in time. For both systems anti and syn BuA : Cu(II), the separation equilibrium is rapidly installed with ~60 s being sufficient to obtain maximum separation parameters ($R\% > 99.9$) for both studied molar ratios (Figure 3(a) and (b)).

From the study of the influencing factors, the following operating parameters result: pH = 8.5 (for anti BuA) and 9.5 (for syn BuA); initial concentrations of Cu(II) = 50–500 mg/L; $V_{\text{sample}} : V_{\text{press. water}}$ dilution ratio = 3 : 1 and $P = 4.5 \times 10^5 \text{ N/m}^2$ for both isomers. We can conclude that $C_{\text{anti/syn BuA : Cu(II)}}$ molar ratio for unitary compounds formation with maximum efficiency is 1 : 1, but the maximum results with reduced consumption can be obtained at $10^{-1} : 1$ molar ratio (and probably lower).

**Figure 3**  Dependence $C_{\text{Cu(II)}} = f(t)$ and $R = f(t)$ in anti BuA – Cu(II); (a) and syn BuA – Cu(II) and (b) systems

(a)
Figure 3  Dependence $C_f^{Cu(II)} = f(t)$ and $R = f(t)$ in anti BuA – Cu(II): (a) and syn BuA – Cu(II) and (b) systems (continued)

(b)

$C_i^{Cu(II)} = 200 \text{ mg/L}; \ V_{\text{sample}} = 150 \text{ mL}; \ \text{pH} = 8.5$ respectively 9.5; \ $V_{\text{sample}} : V_{\text{press. water}} = 3 : 1; \ P = 4.5 \times 10^5 \text{ N/m}^2$.

The optimum parameters established for both anti and syn BuA–Cu(II) systems, at $C_{\text{anti/syn BuA}} : C_{\text{Cu(II)}} = 1 : 1$ and $5 \times 10^{-1} : 1$ molar ratios, respectively, were reproduced on six identical samples. The results obtained for $C_f^{Cu(II)}$ and $R\%$ after statistics processing (Student) were:

- for anti BuA – Cu(II): there is 99% probability to obtain: $C_f^{Cu(II)} = 0.175 \pm 0.136$, $R\% = 99.87 \pm 0.09$, respectively and 95% probability to obtain $C_f^{Cu(II)} = 0.123 \pm 0.040$, $R\% = 99.91 \pm 0.03$
- for syn BuA – Cu(II): there is 99% probability to obtain $C_f^{Cu(II)} = 0.112 \pm 0.089$, $R\% = 99.92 \pm 0.06$ respectively and 95% probability to obtain $C_f^{Cu(II)} = 0.108 \pm 0.043$, $R\% = 99.92 \pm 0.03$.

3.2 Interaction of anti and syn 2-hydroxy-3,5-di-tert-butyl-benzaldoxime – Cu(II)

The insoluble species concentrated in foam, at optimum parameters: pH flotation, stirring time, $C_i^{Cu(II)}$, $C_{\text{anti/syn BuA}} : C_{\text{Cu(II)}}$ molar ratio, dilution ratio, pressure and time were investigated by physical–chemical analysis (FT-IR and reflexion electronic spectroscopy, thermal analysis and elemental chemical analysis) for establishing interaction between collectors and Cu(II) species for the determination of their composition and structure, at stoichiometric and understoichiometric ratios, respectively.

FT-IR spectra of the free collectors (anti and syn BuA) of the compounds of copper hydroxide obtained under stoichiometric and understoichiometric conditions are presented in Figures 4(a)–(d) and 5(a)–(d).
The spectra comparison of the collector $\text{anti} \: \text{BuA}$ with those of the sublate obtained at $C_{\text{anti BuA}} : C_{\text{Cu(II)}} = 1 : 1$ (Figure 4(a)–(c)) indicates:
the sharpened peak from 3437.14 cm\(^{-1}\) of the free collector spectrum, attributed to phenolic \(\nu_{\text{O-H}}\) not associated, almost disappears as intensity

- in the spectrum of sublate, a weak band at 3429.32 cm\(^{-1}\) is noticed because of the deprotonation of phenolic hydroxyl bond and the bonding of Cu(II) ion to phenolic oxygen

- the Cu–O bond can be explained by the displacement of the characteristic frequency for the extension vibration of the C–O phenolic bond from 1242.16 cm\(^{-1}\) (in \textit{anti} BuA) to 1255.16 cm\(^{-1}\) in the sublate

- the extension vibration of azometinic bond appears in the free collector at 1608.26 cm\(^{-1}\) and in the sublate appears with the same intensity but slowly modified with \(\nu_{\text{C=N}} = 1604.37\) cm\(^{-1}\), which would suggest a weak coordination of Cu(II) to the N donor atom of oximino group

- the average intensity peak from 1006.19 cm\(^{-1}\) characteristic for the N–O bond of oximino group appears in the complex \textit{anti} BuA: Cu(II), with a weak intensity displaced with \(\sim 23\) cm\(^{-1}\) (1029.20 cm\(^{-1}\)) that indicates the coordination of Cu(II) to oximic oxygen.

Comparison of the spectrum of the compound obtained at the understoichiometric molar ratio \((C_{\text{anti BuA}}: C_{\text{Cu(II)}} = 1 \times 10^{-1} : 1)\) with the spectrum of \textit{anti} BuA and that of the metallic hydroxide (Figure 4(a), (b) and (d)) leads to the following remarks:

- in the sublate spectrum, \(\nu_{\text{O-H}}\) phenolic appears as a large band, with a frequency displaced to a value smaller with \(\sim 47\) cm\(^{-1}\) (\(\nu_{\text{O-H,as}} = 3389.28\) cm\(^{-1}\)), that can be due to the deprotonation of the phenolic OH group, simultaneously with the Cu(II) ion bond to the phenolic oxygen atom; the displacement \(\nu_{\text{C-O(H)}}\) from 1242.15 cm\(^{-1}\) to 1255.41 cm\(^{-1}\) confirms the Cu–O phenolic bond.

- the absorption bands of \(\nu_{\text{C=N}}\) and \(\nu_{\text{N-O}}\) oximino group appear in the free collector spectrum with an average intensity at 1608.26 cm\(^{-1}\) and 1006.19 cm\(^{-1}\), respectively; in sublate spectrum these bands appear with a smaller intensity and shifted (\(\nu_{\text{C=N}} = 1605.44\) cm\(^{-1}\) and \(\nu_{\text{N-O}} = 1031.35\) cm\(^{-1}\)); these changes suggest a coordination of Cu(II) both to donor N atom of oximino group and to oximic oxygen.

- in the spectrum of the sublate are found Cu(OH)\(_2\) and aquahydrospecies of Cu(II) (\(\nu_{\text{M–OH,sr H}_2\text{O}}\)) bands, that suggest the presence of some hydrospecies of Cu(II).

The information obtained by the comparison of the two spectra (\textit{anti} BuA and Cu(OH)\(_2\)) with the spectrum of the sublate obtained at a \(C_{\text{anti BuA}} : C_{\text{Cu(II)}} = 1 : 1\) would suggest the coordination of Cu(II) ion to the phenolic oxygen and to both O and N donors atoms of oximino group.

By comparing the spectra of understoichiometric sublate, \textit{anti} BuA collector, and metallic hydroxide, it can be presumed that a mixture of copper oximate with Cu(II) aquahydroxospecies is obtained.

Comparison of the FT-IR spectra of \textit{syn} BuA–Cu(II) insoluble species, at \(C_{\text{syn BuA}} : C_{\text{Cu(II)}} = 1 : 1, 5 \times 10^{-1} : 1\), with the spectrum of the free collector and the spectrum of the metallic hydroxide (Figure 5(a)–(d)) indicate the following:
the characteristic band for O–H phenolic bond is displaced in the two compounds to frequencies smaller by ~44 cm⁻¹ (3393.51 cm⁻¹) in the stoichiometric sublate and with ~38 cm⁻¹ (3399.41 cm⁻¹) in the understoichiometric sublate (C_{syn BuA} : C_{Cu(II)} = 5 \times 10^{-1} : 1) that suggest the deprotonation of the phenolic OH group and the coordination to the Cu(II) ion

these arguments are sustained by the fact that the band from 1242.24 cm⁻¹, specific for the vibration ν_{C–O(H)} phenolic of syn BuA is displaced by complexation to frequencies higher with ~12 cm⁻¹ (1254.46 cm⁻¹ in the stoichiometric compound and 1254.44 cm⁻¹ in the understoichiometric compound)

vibration of azometinic group of the collector ν_{C=N} = 1608.29 cm⁻¹ is displaced to frequencies smaller by ~4 cm⁻¹, by complexing: ν_{C=N} = 1604 cm⁻¹, in both isolated compounds

the sharpened peak characteristic of the N–O bond of oxime group syn BuA from 1006.28 cm⁻¹ is displaced in the two compounds to frequencies higher with ~20 cm⁻¹ (1026.53 cm⁻¹ in the stoichiometric compound and 1026.47 cm⁻¹ in the understoichiometric one

IR spectra of both sublates isolated in this system also contain the ν_{OH}, δ_{OH}, ρ_{H2O} and γ_{H2O} absorption bands that indicate the presence of coordinated water

Thus, it can be evaluated that all these modifications in the absorption bands of O–H, C=N, C–O(H) and N–O bonds (specific for syn BuA collector) are due to their implication in the coordination with the Cu(II) ion.

In the spectrum, the presence of the sublate obtained at the molar ratio C_{syn BuA} : C_{Cu(II)} = 5 \times 10^{-1} : 1 of the absorption bands characteristic for the syn BuA collector (ν_{O–OH} phenolic, ν_{C=N}, ν_{C–O(H)} and ν_{N–O}), as well as the similarity noticed by the comparison of the spectrum of the stoichiometric sublate with the understoichiometric one, would suggest the probable formation of a complex mixture of syn BuA–Cu(II) with Cu(II) aquahydroxospecies.

Reflexion electronic spectra. Information on the stereochemistry of the isolated chemical species for the two systems anti and syn BuA–Cu(II), at the two molar ratios, were obtained by reflexion electronic spectra. In Figures 6 and 7, only the interested domain (UV–VIS) is presented.

the electronic spectra of the anti BuA–Cu(II) sublates at both molar ratios contain the d–d bands characteristic for the Cu(II) ion d⁰ in a plane square geometry:

\[ B_{2g}(xy) \rightarrow B_{1g}(x^2y^2) \sim 700 \text{ nm}; \quad A_{1g}(z^2) \rightarrow B_{1g}(x^2y^2) \sim 490 \text{ nm} \]

in the syn BuA–Cu(II) system, electronic spectra are similar to those of Cu(OH)₂; and contain the d–d characteristic Cu(II) bands in a distortional tetrahedral geometry; the large band from 640–660 nm is obtained by the superposition of the transits:

\[ ^2A(E_g) \rightarrow ^2A(T_{2g}); \quad ^2A(E_g) \rightarrow ^2B(T_{2g}). \]
In each complex spectra (Figures 6 and 7), two intense bands at 282, 368 nm (stoichiometric molar ratio) and 286, 358 nm (understoichiometric molar ratio) for \textit{anti} BuA–Cu(II) system (Figure 6(b) and (c)) and 292, 374 nm (stoichiometric molar ratio) for \textit{syn} BuA–Cu(II) system.
ratio) and 292, 348 nm (understoichiometric molar ratio) for syn BuA–Cu(II) system (Figure 7(b) and (c)) have been assigned to the ligand.

The different stereochemistry that adopts the $d^9$ Cu(II) ion in isolated compounds with the two syn/anti isomers, i.e., the plane square in anti BuA and tetrahedral in syn BuA can be, most probably, due to space positioning of OH oximic group.

**Thermal analysis.** The thermal analysis allows evaluations on the stability and thermal behaviour of isolated substrates, in the 24–1000°C range. For a correct interpretation, the thermograms of the organic collectors (anti and syn BuA) and of the copper hydroxide under the same working conditions (Figures 8(a)–(c) and 9(a)–(c)) were also recorded.

**Figure 8** Thermal analysis for anti BuA – Cu(II): (a) anti BuA; (b) anti BuA : Cu(II) = 1 : 1 and (c) anti BuA : Cu(II) = $1 \times 10^{-1} : 1$.
The examination of TG, DTG and DTA curves of Cu(OH)$_2$ shows the presence of some endothermic processes due to lattice water loss and of hydroxyl groups. The endo-effect from 754°C accompanied by a small mass loss could be due to a reduction process of CuO ($2\text{CuO} \rightarrow \text{Cu}_2\text{O} + \frac{1}{2}\text{O}_2$).

Anti BuA (Figure 8(a)) starts to decompose at about 197°C. The decomposition takes place in two stages and finishes to about 527°C with a total mass loss, $\Delta m_t = 98\%$.

The thermal decomposition of the syn BuA collector (Figure 9(a)) takes place similarly to that of the anti isomer.

The thermogram of the sublate isolated in the flotation process to a C$_{\text{anti BuA}}$ : C$_{\text{Cu(II)}}$ = 1 : 1 molar ratio (Figure 8(b)) shows the existence of exothermal processes accompanied by mass losses at $t_1 = 189^\circ\text{C}$, $t_2 = 344^\circ\text{C}$ and $t_3 = 577^\circ\text{C}$, probably due to the decomposition of the anti BuA collector and the burning product elimination. The process finishes at about 577°C with a total loss $\Delta m_t = 78\%$ and the formation as
stable product of copper oxide (plateau on TG). The mass loss recorded on TG curve is in good agreement with the calculated one ($\Delta m_i = 76\%$), that confirms the formula proposed for the isolated species at this molar ratio.

The examination of TG, DTG and DTA curves of the stoichiometric sublate (Figure 9(b)) shows that the thermal decomposition begins at $156^\circ$C and takes place in two stages accompanied by mass losses. On DTA curve several endo and exothermic effects are recorded due to the organic compound burning and release of burning gases. The process finishes at about $630^\circ$C, recording a level that corresponds to the formation of stable oxide, CuO.

The obtained sublate for the $C_{\text{anti BuA}} : C_{\text{Cu(II)}} = 1 \times 10^{-1} : 1$ ratio (Figure 8(c)) is decomposed in two stages accompanied by mass losses: first stage, at $\sim 237^\circ$C, endothermic process corresponds to the elimination of bonded water (hydroxyl group); in the second stage, at about $430^\circ$C, the decomposition of the sublate by an exothermal process takes place; the mass loss of about 38.75% shows that a unitary compound is not formed. The obtained sublate at a $C_{\text{syn BuA}} : C_{\text{Cu(II)}} = 5 \cdot 10^{-1} : 1$ molar ratio (Figure 9(c)) is decomposed in two stages $t_1 = 208–285^\circ$C and $t_2 = 421^\circ$C by exothermal processes (DTA). The total mass loss recorded on TG of about 33% confirms that the isolated sublate at understoichiometric ratio mainly consists in hydrospecies of copper and less organic collector.

**Elemental chemical analysis.** Table 5 contains the results of the elemental chemical analysis of the studied sublates, which correlated with the results of previously performed physical–chemical analysis, leading to the determination of a probable formula of the isolated sublate in the flotation process for a $C_{\text{anti/syn BuA}} : C_{\text{Cu(II)}} = 1 : 1$ molar ratio.

<table>
<thead>
<tr>
<th>Sublate</th>
<th>Cu%</th>
<th>N%</th>
<th>Probable sublate composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>exp.</td>
<td>calc.</td>
<td>exp.</td>
</tr>
<tr>
<td>$C_{\text{anti BuA}} : C_{\text{Cu(II)}} = 1 : 1$</td>
<td>19.70</td>
<td>21.33</td>
<td>19.57</td>
</tr>
<tr>
<td>$C_{\text{anti BuA}} : C_{\text{Cu(II)}} = 5 \cdot 10^{-1} : 1$</td>
<td>42.26</td>
<td>35.18</td>
<td>–</td>
</tr>
</tbody>
</table>

By the corroboration of the physical–chemical analyses results, it can be evaluated that the sublates isolated in the systems *anti* and *syn* BuA–Cu(II), at molar ratios $C_{\text{anti/syn BuA}} : C_{\text{Cu(II)}} = 1 : 1$ are binuclear complexes type of Cu(II) of [Cu$_3$(BuA)$_2$(H$_2$O)$_2$] in which the organic collector functions as tridentate ligand (ONO) in bridge. The probable formula assigned to the formed sublate by the study of the two systems at a $C_{\text{anti/syn BuA}} : C_{\text{Cu(II)}} = 1 : 1$ molar ratio is:

### 4 Conclusion

In this paper, a case study on the behaviour of “atypical” collectors for the flotation of Cu(II) ions (*anti* and *syn* BuA) from model aqueous systems is presented.
The experimental results obtained for the two anti BuA–Cu(II), syn BuA–Cu(II) systems proved a high collecting capacity of both chelating reagents, owing to the presence in their structure of two radicals with short (C₄) and branched chain and of two polar chelating groups (–OH, =N–OH).

The formed flocs show good floatability only for a weakly basic pH (Figures 2(a) and (b)), that enables the de-protonation of phenolic OH group (Figures (4) and (5)), favouring the Cu(II) complexation. The obtained results in the Cu(II) separation from aqueous monocomponent systems, by the interaction of Cu(II) species present at pH > 7, with anti and syn BuA followed by flotation are promising: the separation efficiency being high, at understoichiometric molar ratio: \( R\% = 99.91 \pm 0.03 \), with \( C_{Cu(II)} = 0.123 \pm 0.040 \) for the anti BuA collector and \( R\% = 99.92 \pm 0.03 \), with \( C_{Cu(II)} = 0.108 \pm 0.043 \) for the syn BuA collector.

The high separation efficiency of Cu(II) with the two isomers is the result of complexation as Cu(II) insoluble chelate (at \( C_{anti/syn\ BuA}:C_{Cu(II)} = 1:1 \)), or as aqual hydroxospecies and adequate chelates (at \( 1 \times 10^{-1}:1 \), respectively \( 5 \times 10^{-1}:1 \)); when in the system the collector is insufficient to interact quantitatively with Cu(II) from the aqueous solution.

Although these collector reagents does not have a linear hydrocarbonate chain with \( C > 8 \) in their structure, the presence of two chelating polar groups with N and O donors atoms in the molecule in favourable positions for the formation of some stable chelate complexes increases the range of metallic ions that could be separated by flotation, simultaneously or selectively. In addition, a reason that sustain more the usage of these collectors in flotation process is sustained by the their relatively low cost, because they are obtained from accessible raw materials provided as secondary products from different organic technology (e.g., tertbutylphenol).

The fact that high separation efficiency are obtained at understoichiometric collector:Cu(II) molar ratios confer to these reagents the properties that support their belonging to the flotation reagents category.

References


**Nomenclature**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma$</td>
<td>Surface tension (N·m$^{-1}$); $\sigma_0 = \sigma_{\text{H}_2\text{O}} = 72.8 \times 10^{-3}$ N·m$^{-1}$</td>
</tr>
<tr>
<td>$n$</td>
<td>Number of drops for investigated solutions; $n_0 = \text{number of drops for distillate water}$</td>
</tr>
<tr>
<td>$D$</td>
<td>Investigated solutions density (Kg·L$^{-3}$); $d_0 = d_{\text{H}_2\text{O}}$</td>
</tr>
<tr>
<td>$C_i$ (Cu(II))</td>
<td>Cu(II) initial concentration (mg·L$^{-1}$); $C_{i,\text{Cu(II)}} = \text{Cu(II) initial concentration (mg·L}^{-1}$</td>
</tr>
<tr>
<td>$C_f$ (Cu(II))</td>
<td>Cu(II) final (residual) concentration (mg·L$^{-1}$); $C_{f,\text{Cu(II)}} = \text{Cu(II) final (residual) concentration (mg·L}^{-1}$</td>
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<tr>
<td>$C_{i,\text{correction Cu(II)}}$</td>
<td>Cu(II) concentration after dilution (mg·L$^{-1}$)</td>
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<td>$P$</td>
<td>Pressure (N·m$^{-2}$); $V_{\text{sample}} : V_{\text{press-water}} = \text{sample : pressurised water dilution ratio}; t = \text{time (s)}$</td>
</tr>
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<td>$R$</td>
<td>Separation efficiency (%), reflectance (%); $T = \text{transmittance (%)}$, temperature (°C)</td>
</tr>
<tr>
<td>$\Delta m$</td>
<td>Mass loss (mg)</td>
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</table>