ION FLOTATION AND VARIANTS - UNCONVENTIONAL SEPARATION AND RECOVERING METHOD IN WASTEWATER TREATMENT PROCESS

Carolina CONSTANTIN*
Ligia STOICA*

*UNIVERSITY “POLITEHNICA” OF BUCHAREST, FACULTY OF APPLIED CHEMISTRY AND MATERIALS SCIENCE
ION FLATION is one of adsorptive bubble separation technique, involves the removal of surface inactive ions from homogenous and heterogenous aqueous solutions by the introduction of a surfactant and the subsequent passage of gas microdisperse bubble through the solution.

In separation process the properties of participant phase are important:
✓ Liquid phase of superficial tension;
✓ High hydrofobya and low density for foam concentrated species;
✓ Homogene dimension of gas bubbles;
✓ The optimum gas flow for the concentrate of bubble-particle in foam.
1. Analytical information obtained (Diagnosis)

It applied method with next characteristics:

- Selectivity
- Sensibility
- Specificity
- Precizion

2. Separation process selection

Depend on:
- System composition
- Components concentrations
- System characteristics

3. Separation process in technological scope

3.1. Aqueous system depollution

- Comp. conc. under admissible limit

3.2. Aqueous system recovering depollution

- Final conc. under admissible limit
- Recovering product increase the efficiency of process and reduce the cost

4. Separation process in analytical scope

- Achieve in scope of compound concentration
- As step after quantitative determination of an element
FLOTATION CHARACTERISTICHS

- **Species density** (as nature and structure) susceptible to be separate;
- **High separation efficiency** for the diluted solution ($10^{-6}$-$10^{-2}$ M) of separable species;
- **Simplicity, economicity, rapidity**;
- **Installation Flexibility and fiability**;
- **Reactive low reduce** for formed some hydroxospecies insoluble with high hydrophobic and low specific weight;
- **Used compounds recovering by foam manufacture**.
COLLECTOR-$[\text{M(H}_2\text{O)}_x]^{n+}$ INTERACTION in its flotation variant

TSA (COLECTOR) = Tensioactive agent with long hydrophobe chain ($\leq C_{12}$) and a polar group who can interaction with $M_{aq}^{n+}$ species resulting an insoluble species (sublate), which will be separate and concentrate in foam.
In case of hydrolizable metals, if decrease pH, the species \( \text{M(OH}_2\text{)}_x^{n+} \) are implicated in successive deprotonation reactions with formation of polimeric aquahydroxospecies and precipitate hydroxid \( \text{[M}_p\text{(OH)}_y\text{(OH}_2\text{)}_x]^{n_p} \) finally. These reactions are known as olare and oxolare.

**Exemple:**

\[
\text{[Cr(OH}_2\text{)}_6]^{3+} - \text{H}^+ \quad \text{Cr} \quad (\text{OH}_2)_5^{2+} - \text{H}^+ \quad \text{Cr} \quad (\text{OH}_2)_4^+ \\
- \text{H}^+ \quad \text{Cr} \quad (\text{OH}_2)_3^{-} \quad \text{Cr} \quad (\text{OH}_2)_2^{-} \\
- \text{H}^+ \quad \text{Cr} \quad (\text{OH})_3^{-} \quad \text{Cr} \quad (\text{OH})_3^{-}
\]
Ion flotation and its variant, as precipitate flotation, are considerate separation method with multiple application possibility, in special for low concentration domain of toxic compounds, having the ecological and economical performance.
Ion flotation systematic research aims at chemical and process influence factors.
Systematical study of flotation covers two main interest area:

- Environmental protect, aqueous system decontamination and metallic ions recovering as useful compounds;
- Synthesis method on moisture way for oxidic precursors.
## Results regarding the separation of inorganic pollutants by flotation in Chemistry Inorganic Department-UPB

<table>
<thead>
<tr>
<th>$M_{aq}^{n+}$</th>
<th>Initial Conc. $M_{aq}^{n+}$, M</th>
<th>TSA</th>
<th>Flot. Meth.</th>
<th>Research results</th>
<th>Refe.</th>
</tr>
</thead>
</table>
| Cu(II)       | $3 \times 10^{-2} - 3 \times 10^{-4}$ | • Stearylamine  
• Laurylamine (LA)  
• Sodium stearate  
• Sodium laurate  
• Sodium dodecylsulphate  
• Romegal CM  
• Imidazolyne  
• Hydroxamyc acids  
• Lauric acid amidoamine  
• Oleic acid | PF | • Depolution  
$C_f < 0.2 \text{ mg dm}^{-3}$;  
• Recovery Cu(II)  
%R=92-99  
%R=92-99  
%R=94-99  
%R=96-99  
%R=96-99  
%R=90-97  
%R=90-97 | 1  
3-9  
26-30 |
| Ti(IV)       | $2 \times 10^{-2} - 3 \times 10^{-5}$ | • Dodecylamine  
• Stearylamine | PF | • Recovery Ti(IV)  
%R=95-98 | 3  
10  
11 |
<table>
<thead>
<tr>
<th>$M_{aq}^{n+}$</th>
<th>Initial conc. $M_{aq}^{n+}$, M</th>
<th>TSA</th>
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<th>Refe.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(II) Fe(III) Ni(II)</td>
<td>3 $10^{-2}$ - $10^{-4}$ 2 $10^{-2}$ - $10^{-4}$ 1 $10^{-2}$ - $10^{-4}$</td>
<td>Dodecylamine</td>
<td>Sel.F</td>
<td>Recovery as oxides</td>
<td>12, 13, 14, 31</td>
</tr>
<tr>
<td>Co(II) Mn(II) Cd(II)</td>
<td>10$^{-3}$ - $10^{-4}$</td>
<td>Sodium 2-ethylhexanomate</td>
<td>PF</td>
<td>Recovery Co(II), Mn(II), Cd(II)</td>
<td>15, 16, 17</td>
</tr>
<tr>
<td>MoO$_4^{2-}$</td>
<td>10$^{-3}$ - $10^{-4}$</td>
<td>Romegal CM acetate  Dodecylamine</td>
<td>PF Fe(OH)$_3$ support</td>
<td>Recovery MoO$_4^{2-}$, from waste water resulted in uranium ores processing</td>
<td>18</td>
</tr>
<tr>
<td>Pd(II)</td>
<td>10$^{-2}$ - $10^{-5}$</td>
<td>Dodecylamine</td>
<td>PF</td>
<td>Recovery Pd(II) Water decontamination  Pd valorification</td>
<td>19  20</td>
</tr>
<tr>
<td>$M_{aq}^{n+}$</td>
<td>Initial conc. $M_{aq}^{n+}$, M</td>
<td>TSA</td>
<td>Flot. Meth.</td>
<td>Research results i</td>
<td>Ref.</td>
</tr>
<tr>
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<td>-----</td>
</tr>
</tbody>
</table>
| Cd(II)         | $10^{-2}$ - $10^{-4}$ | · Romegal CM  
· LA | PF-EF | · Recovery Cd(II) | 21, 22 |
| Cr(III)        | $2 \times 10^{-2}$ - $10^{-4}$ | · Sodium dodecylsulphate | PF | · Recovery Cr(III) | 23 |
| Cr(VI)         | $10^{-3}$ - $10^{-5}$ | · Dodecylamine  
· Quaternar ammonium salt | ACF | · %R >99  
· Reducing concentration in water | 24 33 |
| $\text{AsO}_4^{3-}$ | $10^{-3}$ - $10^{-5}$ | · Dodecylamine  
· Quaternar ammonium salt | ACF | · %R >99  
· Reducing concentration in water | 24 33 |
| $\text{Ra}^{2+}$ | <$10^{-5}$ | · Dodecylamine | ACF | · %R >99  
· Reducing concentration in water | 25 |

Notes: PF=Precipitate Flotation; EF=Electroflotation; SelF=Selective Flotation; ACF=Adsorption Colloid Flotation
The physical and chemical investigation on isolated species lead to information about their structure. The results of physico-chemical investigation on some isolated metallic ions hydroxospecies by PF are presented in the next table.

On the basis of these information, it can make estimations on separation mechanism, recovering form and correct leadership of all processes.
### Interaction hydroxospecie-STA and product final hydroxospecie-STA and final product obtained by foam thermical manufacture, Inorganic Chemistry Department

<table>
<thead>
<tr>
<th>M_{aq}^{n+}</th>
<th>Molar ratio C_C:C_M</th>
<th>pH</th>
<th>Isolated species</th>
<th>Final product</th>
<th>Bibliog</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(II)</td>
<td>- 1 1</td>
<td>9,0</td>
<td>Cu(OH_2)CuSO_4</td>
<td>CuO</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[Cu(LA)_2(OH)_4(OH_2)]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti(IV)</td>
<td>2 10^{-4}</td>
<td>7,0</td>
<td>[Ti_2O_2(OH)_6(OH_2)(LA)_2]</td>
<td>TiO_2</td>
<td>3</td>
</tr>
<tr>
<td>Pd(II)</td>
<td>- 10^{-2} 10^{-1} 1</td>
<td>6,5</td>
<td>Pd(OH)_2 H_2O</td>
<td>PdO sau Pd metallic</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Start aminic complex forming</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Hydroxido-hydroamino species</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[Pd(LA)_2(OH)_2] 2H_2O</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[Pd(LA)_2(OH)_2] 2H_2O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$M_{aq}^{n+}$</td>
<td>Raport molar $C_C:C_M$</td>
<td>pH</td>
<td>Isolated species</td>
<td>Final product</td>
<td>Bibliog</td>
</tr>
<tr>
<td>--------------</td>
<td>------------------------</td>
<td>----</td>
<td>-----------------</td>
<td>--------------</td>
<td>---------</td>
</tr>
</tbody>
</table>
| Cd(II)       | $10^{-4} - 10^{-3}$    | 9,5 | • Cd(OH$_2$)CuSO$_4$  
• Start aminic complex forming  
• Mixture of amino and sulphate hydroxospecies  
• [Cd$_2$(OH)SO$_4$(LA)$_2$(OH$_2$)$_2$] | CdO | 21 |
|              | $10^{-2} - 10^{-3}$    |     |                 |              |         |
|              | 1                      |     |                 |              |         |
| Cr(III)      | $10^{-2}$              | 9,3 | • [Cr$_2$(OH)$_6$(H$_2$O)$_4$]  
• Hydroxo-amino species  
• [Cr$_2$(OH)$_6$(H$_2$O)$_2$(LA)$_2$] | Cr$_2$O$_3$ | 11 |
<p>|              | $10^{-1}$              |     |                 |              | 23 |
|              | 1                      |     |                 |              |         |</p>
<table>
<thead>
<tr>
<th>$M_{aq}^{n+}$</th>
<th>Raport molar C$_C$:C$_M$</th>
<th>pH</th>
<th>Isolated species</th>
<th>Final product</th>
<th>Bibliog</th>
</tr>
</thead>
</table>
| La(III)      | 5 $10^{-2}$ 2,5 $10^{-1}$ 5 $10^{-1}$ 1 | 9,75 | •Mixture of hydroxo and hydroxoamino complexes
  •[La$_2$(OH)$_6$(H$_2$O)$_2$(LA)$_2$] | La$_2$O$_3$ | 11 |
| Ni(II)       | - 10$^{-4}$ - 10$^{-3}$ 10$^{-2}$ - 10$^{-3}$ 1 2 | 9,5 | •[Ni$_2$(H$_2$O)$_7$(OH)$_2$SO$_4$]
  •Start amino hydroxo complex and hydroxoamino species forming
  •[Ni$_2$(H$_2$O)$_4$(LA)$_2$(OH)$_2$SO$_4$]
  •[Ni$_2$(H$_2$O)$_4$(LA)$_2$(OH)$_2$SO$_4$] | NiO | 12 31 |
<table>
<thead>
<tr>
<th>$\text{M}_{\text{aq}}^{n+}$</th>
<th>Raport molar $C_C:C_M$</th>
<th>pH</th>
<th>Isolated species</th>
<th>Final product</th>
<th>Bibliog</th>
</tr>
</thead>
</table>
| Co(II)                   | -                     | 9,5 | • $[\text{Co}_2(\text{H}_2\text{O})(\text{OH})_2\text{SO}_4]$  
• Start amino hydroxo complex and hydroxoamino species forming  
• $[\text{Co}_3(\text{H}_2\text{O})(\text{LA})_2\text{SO}_4]$ 2H$_2$O | CoO | 12  
13 |

**Nota:** LA=dodeciliamine; isolated species to molar ratio $C_C:C_M \geq 1$ are well defined compounds; isolated species to molar ratio $C_C:C_M \ll 1$ are mixed compounds.
• On mondial plan (SUA, Japan, South Africa, Germany, France, Russia, Greece, Poland, India, Coreea, Maroc etc) it notice a divers interest of specialists given of SEPARATION METHOD BY ADSORPTIVE BUBBLE in generally, and for ION FLOTATION, in specially materialized, both scientific contribution with experimental character and elaboration of large working with monographic character for process theory, application domains, experience from world centers and domain perspective.

• On national plan this domain was development in Inorganic Chemistry Department, pioneer domaine in applicative chemistry leads by Prof. STOICA LIGIA, materialized by PhD thesis, course and master practical work, dissertation work, contracts, projects, published scientific paper, invention brevet.
CONCLUSIONS

- The separation method by adsorptive bubble in generally and ion flotation in specially represent an alternative in recovering depollution of aqueous systems from different industry. This affirmation is confirm by obtained results in frame of contracts and projects presented in this presentation.
Selective bibliografy

THANK YOU FOR YOUR ATENTION!