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## Precipitate Flotation of Aluminum and Copper

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**Abstract:** Ion molecular 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 Al(III) and Cu(II) separation from aqueous systems by the precipitate flotation method using carbonate as precipitant agent and oleic acid as surfactant. The parameters, influencing the flotation process, namely: solution pH, metal ion, surfactant and carbonate concentrations, ionic strength, temperature and foreign ions were examined. The procedure was successfully applied to recover  $\text{Al}^{3+}$  and  $\text{Cu}^{2+}$  ions from natural water samples.

**Key words:** Aluminum, copper, precipitate flotation, oleic acid, natural waters

## INTRODUCTION

The current pattern of industrial activity alters the natural flow of materials and introduces novel chemicals into the environment (Fasal and Hasnain, 2004; Igwe and Abia, 2006). The rate at which effluents are discharged into the environment especially water bodies have been increased as a result of urbanization. Toxic metal ions are dangerous contaminants that are accumulated by the living organisms and, up to now, there are no widely accepted methods to have them removed. Therefore, the best solution is preventing the entrance of toxic metals in the ecosystem (Chubar *et al.*, 2003). Furthermore, the removal of toxic metal ions and recovery of valuable metal ions from mine wastewaters, soils and waters have been important in economic and environmental viewpoints (Seki *et al.*, 1997; Monteagudo and Ortiz, 2000; Capponi *et al.*, 2006).

Aluminum is an abundant metal in the earth's crust; in the industrialized world the metal is the second only to iron in its usage and its compounds can justifiably be said to touch our lives daily (Downs, 1993). Because aluminum salts are still used as flocculating agents in potable water treatment units (Kemmer, 1988) there is a strong need for aluminum monitoring in treated and raw waters (Srinivasan *et al.*, 1999). It is now well known that this metal is harmful to several organisms, such as fish (Birchall *et al.*, 1989), zoo-plankton (Havens, 1992), algae (Gensemer, 1991) and plants (Parker *et al.*, 1989). Moreover, there are potential health risks associated with the intake of dissolved aluminum which play an active role in the development and advancement of senile dementia of Alzheimer type (Flaten, 2001; Miu and Benga, 2006), renal insufficiency, pulmonary fibrosis, microcytic anemia and disturbances of sleeping (Descocotes, 1988). Owing to these potential risks, European Community legislation on the quality of water for human consumption sets a MAC (maximum admissible concentration) level of  $200 \mu\text{g L}^{-1}$  and guide-line level, around which Member States should set their quality standards, of  $50 \mu\text{g L}^{-1}$  (Bensen *et al.*, 1990).

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Copper has received a considerable attention owing to its uses in metallurgy and chemical industries. Moreover, it is an essential constituent of about thirty enzymes and glycol-proteins and is required for the synthesis of hemoglobin and for some biological processes. It also promotes iron absorption from the gastrointestinal system, is involved in the transport of iron from tissues into plasma, helps to maintain myelin in the nervous system, is important in the formation of bone and brain tissues and is necessary for other many important functions (Sorensen, 1991; Khalifa *et al.*, 2001). When levels of Cu exceed certain values, however, defense mechanisms to protect against excess Cu are overcome and toxicity results. Therefore, it is necessary to develop a rapid, effective and simple treatment process for removing aluminum and copper from water and wastewater.

Numerous techniques for the separation, removal and control of metal toxicants have been reported (Ghazy, 1995; Blöcher, 2003). Although adsorption has been well established as a technology for removing toxic compounds from wastes or wastewaters (Lazaridis *et al.*, 2004), the process may face filter-blocking problems. Also, sedimentation is a relatively slow process when dealing with biological materials that are usually of low density. Flotation as a separation process has recently received a considerable interest owing to its simplicity, rapidity, economy, good separation yields ( $R > 95\%$ ) for small impurity agent concentrations ( $10^{-6}$ - $10^{-2}$  mol L<sup>-1</sup>), a large possibility of application for species having different nature and structure, flexibility and friability of equipment and processing for recovery purpose (Stoica *et al.*, 1998). It is believed that this process will be soon incorporated as a clean technology to treat water and wastewater (Capponi *et al.*, 2006). Therefore, flotation technique (viz. precipitate flotation) was chosen for this investigation.

Precipitate flotation (Filippov *et al.*, 2000; Ghazy *et al.*, 2006a; Capponi *et al.*, 2006) is a foam separation process used to remove surface inactive substances from aqueous dispersions. The component to be removed is precipitated before the addition of a surfactant, collector. This may be accomplished by adding any substance that forms an insoluble compound. Since surfactant needs only to react with ions on the surface, small amounts of collector are required. Moreover, in this process the separation is obtained at the interface of the bulk and foam phases without the assistance from the extended phase, having the advantage of producing dry foam of small volume and thus allowing the use of compact equipment (Ghazy *et al.*, 2006a). Therefore, the objective of the present work was to investigate the feasibility of developing the use of carbonate ion as a coagulant and precipitating agent for aluminum and copper(II) removal from aqueous media and natural water samples by precipitate flotation, under the recommended conditions.

## MATERIALS AND METHODS

### Reagents and Solutions

Unless otherwise stated, all reagents used were of analytical-reagent grades. All aqueous solutions were prepared in double distilled water. Aluminum stock solution ( $3.7 \times 10^{-2}$  mol L<sup>-1</sup>) was prepared from  $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  (BDH Ltd., Poole, England) by dissolving 17.59 g in double distilled water containing 5 mL of concentrated  $\text{H}_2\text{SO}_4$  and diluting to 1 L. Chrome Azurol S (CAS) and 1% ascorbic acid were freshly prepared. Copper sulfate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  or  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , (BDH limited, Poole, England) was used as the source of divalent copper. A copper stock solution ( $1.6 \times 10^{-2}$  mol L<sup>-1</sup>) was prepared. Oleic acid (HOL) was used directly as received. Its stock solution ( $6.36 \times 10^{-2}$  mol L<sup>-1</sup>) was prepared from the food grade with sp. gr. 0.895 (provided from J.T. Baker Chemical Co.) by dispersing 20 mL HOL in 1 L of kerosene. Further dilutions of the former stock solutions were prepared daily as required. pH of the solutions during experiments was adjusted with  $\text{H}_2\text{SO}_4$  and/or NaOH.

### Apparatus

The flotation cell (a cylindrical tube of 29 cm length and 1.5 cm inner diameter, provided with a stopcock at the bottom and a stopper at the top) used was the same as has been described

earlier (Ghazy and Kabil, 1994). The pH values of the solutions were measured using ORION (model 720 A) digital pH meter connected with a glass electrode. The low concentration of Cu(II) was determined by using Pekin-Elmer 2380 Atomic Absorption Spectrophotometer with air-acetylene flame at 327.4 nm while higher concentration was determined iodometrically (Ghazy *et al.*, 2004).

### Procedure

A suitable aliquot containing known amount of Al(III) or Cu(II), specified for each investigation, was mixed with a suitable amount of carbonate followed by addition of 3 mL of double distilled water. After adjusting the pH with H<sub>2</sub>SO<sub>4</sub> and/or NaOH to the required value, the solution was transferred to the flotation cell and the total volume was made up to 10 mL with double distilled water. The cell was shaken well for few seconds, to ensure precipitation. To this, 3 mL of HOL (of known concentration) was added. The cell was then inverted upside down twenty times by hand. Meanwhile, the stopper of the cell was removed to permit air movement. After allowing it to stand for 5 min for complete flotation, the residual Al<sup>3+</sup> ion content in the mother liquor was analyzed spectrophotometrically using CAS at 545 nm as has been described by Marczenko (1986) while that of Cu<sup>2+</sup> was determined using AAS at 217.0 nm.

The floatability (F) of Al<sup>3+</sup> or Cu<sup>2+</sup> ions was determined from the relationship:

$$F = (C_i - C_f)/C_i \times 100\% \quad (1)$$

where, C<sub>i</sub> and C<sub>f</sub> denote the initial and final concentrations of Al<sup>3+</sup> or Cu<sup>2+</sup> ions in the mother liquor, respectively. All experiments were carried out at room temperature (25±1°C).

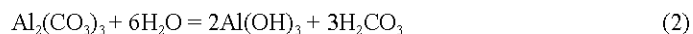
## RESULTS AND DISCUSSION

An initial series of experiments was carried out at pH 7 using 2×10<sup>-4</sup> mol L<sup>-1</sup> of Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub> or (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> as precipitating agents and 6×10<sup>-3</sup> mol L<sup>-1</sup> of HOL surfactant to establish the optimum conditions for the flotation of 5×10<sup>-5</sup> mol L<sup>-1</sup> Al<sup>3+</sup> or 7.87×10<sup>-5</sup> mol L<sup>-1</sup> Cu<sup>2+</sup> ions. The obtained data showed that Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> gave the same results in all the experiments with respect to Al<sup>3+</sup> ions. Therefore, in this study Na<sub>2</sub>CO<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> were only taken into consideration for flotation experiments of aluminum while the three carbonates are used for copper flotation.

### Effect of pH of the Medium

According to our previous knowledge of flotation processes and the fact that the pH of the medium is a highly significant factor in this respect, therefore, it was the first variable to be optimized. Flotation experiments (using 2×10<sup>-4</sup> mol L<sup>-1</sup> of Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub> or (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> as precipitating agents and 6×10<sup>-3</sup> mol L<sup>-1</sup> of HOL surfactant) were carried out to establish the optimum pH for the flotation of 5×10<sup>-5</sup> mol L<sup>-1</sup> Al<sup>3+</sup> or 7.87×10<sup>-5</sup> mol L<sup>-1</sup> Cu<sup>2+</sup> ions. As can be seen, the floatability gradually increases as the pH of the solution increases.

Maximum flotation of Al<sup>3+</sup> ions (~ 100%) was obtained in the pH ranges 4-9 for Na<sub>2</sub>CO<sub>3</sub> and 4.5-10 for (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> (Fig. 1). It must be taken into consideration that carbonate ions may precipitate aluminum hydroxide according to the following equation (Ghazy *et al.*, 2006 b):



Moreover, as a function of solution pH (Vogel, 1977; Champbell *et al.*, 1983), aluminum species may exist as soluble hydroxo-complexes (Al(OH)<sup>2+</sup>, Al(OH)<sub>2</sub><sup>+</sup> and Al(OH)<sub>4</sub><sup>-</sup> Al(OH)<sub>3</sub><sup>0</sup> and poly hydroxo-complexes (Al<sub>n</sub>(OH)<sub>m</sub><sup>(3n-m)+</sup>) in addition to the insoluble colloidal aluminum hydroxide Al(OH)<sub>3</sub>(s). Between pH 4 and 9, aluminum species being made hydrophobic by combination with un-dissociated

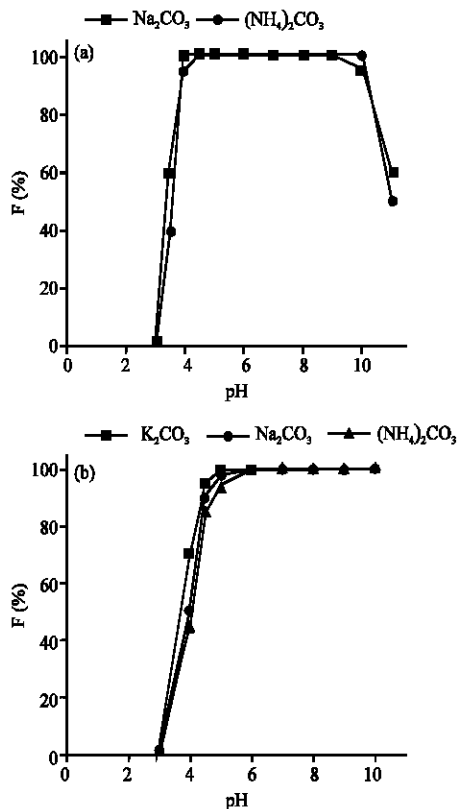


Fig. 1: Floatability (%) of  $5 \times 10^{-5} \text{ mol L}^{-1} \text{ Al}^{3+}$  (a) and  $7.87 \times 10^{-5} \text{ mol L}^{-1} \text{ Cu}^{2+}$  (b) at different pH values using  $2 \times 10^{-4} \text{ mol L}^{-1} \text{ CO}_3^{2-}$  and  $6 \times 10^{-3} \text{ mol L}^{-1} \text{ HOL}$

oleic acid, that begins to dissociate at  $\text{pH} = 5.2$  (Ghazy *et al.*, 2006b), through hydrogen bonding and/or chemically with oleate anions. These hydrophobic aggregates are floated to solution surface with the aid of air bubbles. Maximum floatability of  $\text{Cu}^{2+}$  ions ( $\sim 100\%$ ) was attained in the pH ranges 4.5-10 for  $\text{K}_2\text{CO}_3$  and 6-10 for  $\text{Na}_2\text{CO}_3$  and  $(\text{NH}_4)_2\text{CO}_3$  (Fig. 1b).

Below pH 3, the floatability diminishes. Such poverty may be due to the solubility of the precipitates of aluminum and copper. In alkaline medium, at  $\text{pH} > 10$ , the removal of  $\text{Al}^{3+}$  and  $\text{Cu}^{2+}$  ions decreases which may be attributed to the formation of soluble  $\text{Al}(\text{OH})_4^-$  and  $\text{Cu}(\text{OH})_4^{2-}$  that are not capable of the interaction with the negatively charged oleate anions.

Finally, in this precipitate flotation the fundamental process may be the interaction of the HOL surfactant with the colloidal precipitates of aluminum and copper. This process renders the surface hydrophobic and so enables the precipitates to be held at the air-water interface and floated to the surface. Accordingly pH 7 was recommended for other experiments carried out in this investigation.

#### Effect of Precipitating Carbonate and Metal Ion Concentrations

The effect of carbonate concentrations on the floatability of  $5 \times 10^{-5} \text{ mol L}^{-1} \text{ Al(III)}$  and  $7.87 \times 10^{-5} \text{ mol L}^{-1} \text{ Cu(II)}$  using  $6 \times 10^{-3} \text{ mol L}^{-1} \text{ HOL}$  at pH 7 was investigated. Floatability of  $\text{Al(III)}$  and  $\text{Cu(II)}$  increases as  $\text{CO}_3^{2-}$  concentration increases. Maximum floatability of  $\text{Al}^{3+}$  ions ( $\sim 100\%$ ) was obtained in the concentration ranges  $8.3 \times 10^{-5}$ - $5 \times 10^{-4} \text{ mol L}^{-1}$  for  $\text{Na}_2\text{CO}_3$  and  $5 \times 10^{-4}$ - $6.7 \times 10^{-4} \text{ mol L}^{-1}$  for  $(\text{NH}_4)_2\text{CO}_3$ , respectively (Fig. 2). Maximum floatability of  $\text{Cu}^{2+}$

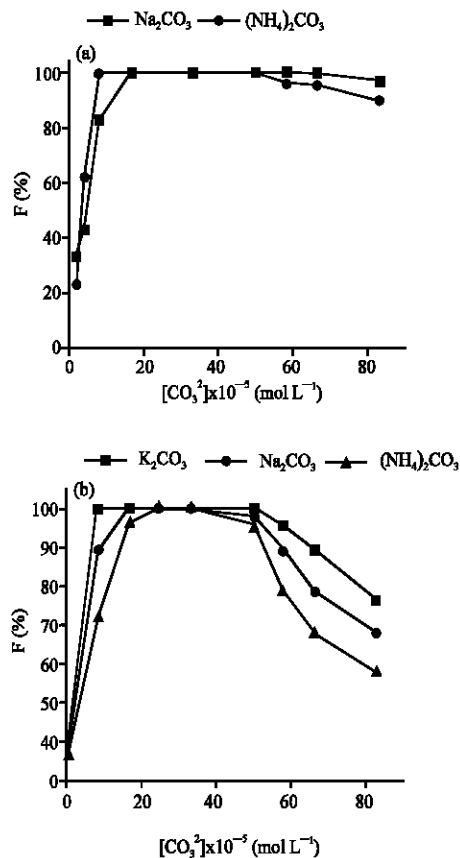
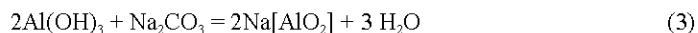


Fig. 2: Floatability (%) of  $5 \times 10^{-5} \text{ mol L}^{-1} \text{ Al}^{3+}$  (a) and  $7.87 \times 10^{-5} \text{ mol L}^{-1} \text{ Cu}^{2+}$  (b) using different concentrations of  $CO_3^{2-}$  ions and  $6 \times 10^{-3} \text{ mol L}^{-1}$  HOL at pH 7

ions ( $\sim 100\%$ ) was attained in the concentration ranges  $8.3 \times 10^{-5}$ - $5 \times 10^{-4} \text{ mol L}^{-1}$  for  $K_2CO_3$ ,  $2 \times 10^{-4}$ - $4.2 \times 10^{-4} \text{ mol L}^{-1}$  for  $(NH_4)_2CO_3$  and  $1.3 \times 10^{-4}$ - $4.2 \times 10^{-4} \text{ mol L}^{-1}$  for  $Na_2CO_3$ , respectively. At higher carbonate concentrations, more than  $6.7 \times 10^{-4} \text{ mol L}^{-1}$ , the floatability of  $Al^{3+}$  and  $Cu^{2+}$  ions decreases which may be attributed to the formation of soluble aluminate according to the following equation (Ghazy *et al.*, 2006a, b):



and/or formation of potassium-, sodium-or ammonium oleate as a white precipitate dispersed in the whole bulk of solution not capable of floating. Therefore, a carbonate concentration of  $2 \times 10^{-4} \text{ mol L}^{-1}$  was used throughout.

Parallel series of experiments were carried out to float different concentrations of  $Al(III)$  and  $Cu(II)$  using  $2 \times 10^{-4} \text{ mol L}^{-1} \text{ CO}_3^{2-}$  and  $6 \times 10^{-3} \text{ mol L}^{-1}$  HOL at pH 7. Close inspection of the figure shows that the maximum flotation ( $\sim 100\%$ ) of  $Al(III)$  and  $Cu(II)$  was decreased as their concentrations increased. This may be attributed to the fact that there is no sufficient amount of carbonate ions to precipitate quantitatively all  $Al(III)$  and  $Cu(II)$  ions (Fig. 3a, b).

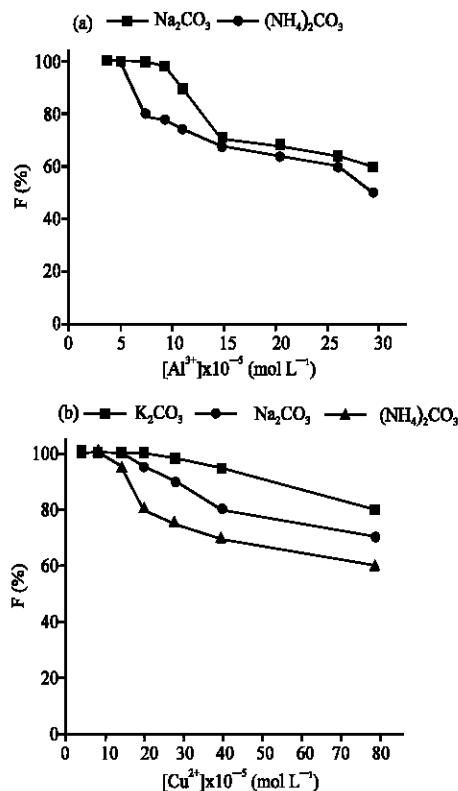


Fig. 3: Floatability (%) of different concentrations of  $\text{Al}^{3+}$  ions (a) and  $\text{Cu}^{2+}$  ions (b) using  $2 \times 10^{-4} \text{ mol L}^{-1} \text{ CO}_3^{2-}$  and  $6 \times 10^{-3} \text{ mol L}^{-1} \text{ HOL}$  at pH 7

#### Effect of Surfactant Concentration

The effect of surfactant concentration (HOL) on the floatability of  $5 \times 10^{-5} \text{ mol L}^{-1} \text{ Al}^{3+}$  and  $7.87 \times 10^{-5} \text{ mol L}^{-1} \text{ Cu}^{2+}$  using  $2 \times 10^{-4} \text{ mol L}^{-1} \text{ CO}_3^{2-}$  at pH 7 (Fig. 4). As can be seen, the floatability decreases at lower concentrations of surfactant, reaching maximum value (~100%) in the optimum concentration range and again decreases at higher concentrations.

Flotation of  $\text{Al(III)}$  increases with increasing surfactant concentration reaching its maximum value for both carbonates in the concentration range  $1 \times 10^{-6}$ – $1 \times 10^{-2} \text{ mol L}^{-1} \text{ HOL}$ . Flotation of  $\text{Cu(II)}$  increases with increasing surfactant concentration reaching its maximum value for the three carbonates in the concentration range  $4 \times 10^{-3}$ – $6 \times 10^{-2} \text{ mol L}^{-1} \text{ HOL}$  (Fig. 4a, b).

At lower surfactant concentration, the  $\text{Al(III)}$  and  $\text{Cu(II)}$  flotation decrease may be due to the presence of insufficient amount of surfactant for complete flotation. At higher surfactant concentration the decrease in the separation of  $\text{Al(III)}$  and  $\text{Cu(II)}$  may be attributed to the fact that the surfactant changes the state of the precipitates, from coagulation precipitation through coagulation flotation to re-dispersion with an increase in the amount of HOL added (Rubin and Johnson, 1967). Moreover, the poor flotation at high surfactant concentration is caused by the formation on the air bubble surface of a stable, hydrated envelope of surfactant or, perhaps, by forming a hydrate micelle coating on the solid surface (Klassen and Mokrossov, 1969). As a result, the hydrophobicity of this surface was not satisfactory for flotation which agrees well with literature data (Rubin and Johnson, 1967). The surfactant concentration of  $6 \times 10^{-3} \text{ mol L}^{-1}$  was fixed as an optimum value through the experiments of flotation of  $\text{Al}^{3+}$  and  $\text{Cu}^{2+}$  ions.

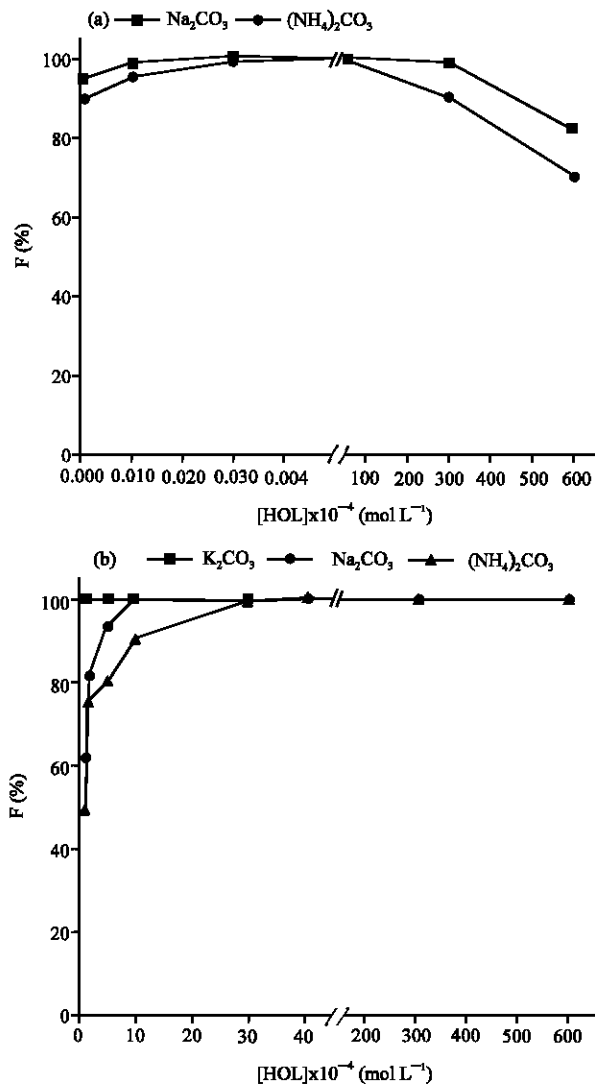


Fig. 4: Floatability (%) of  $5 \times 10^{-5}$  mol L $^{-1}$   $\text{Al}^{3+}$  (a) and  $7.87 \times 10^{-5}$  mol L $^{-1}$   $\text{Cu}^{2+}$  (b) using different concentrations of HOL and  $2 \times 10^{-4}$  mol L $^{-1}$  of carbonate ions at pH 7

#### Effect of Temperature

The effect of temperature on the floatability of  $5 \times 10^{-5}$  mol L $^{-1}$   $\text{Al}^{3+}$  and  $7.87 \times 10^{-5}$  mol L $^{-1}$   $\text{Cu}^{2+}$  using  $2 \times 10^{-4}$  mol L $^{-1}$   $\text{CO}_3^{2-}$  and  $6 \times 10^{-3}$  mol L $^{-1}$  HOL at pH 7 was studied over a wide range 10-80°C. In order to do this, Al(III) or Cu(II), the surfactant and carbonate solutions were either heated or cooled to the same temperature in a water bath. The carbonate and HOL solutions were quickly poured into Al(III) or Cu(II) solution. The mixture was introduced into the flotation cell jacketed with 1 cm thick fiberglass insulation. The flotation procedure was then followed. The obtained data show that the variation of temperature in this range has no marked effect on the flotation efficiency of Al(III) or Cu(II); it just made an acceleration of the flotation process which may be attributed to coagulation of the precipitates. Since most industrial influents are usually hot, the simple procedure presented here

may find its application in the removal of Al(III) and Cu(II) ions directly from industrial wastewaters. Therefore, subsequent, measurements were carried out at room temperature, ca.  $25 \pm 1^\circ\text{C}$ .

### Effect of Ionic Strength

The effect of ionic strength on the floatability of  $5 \times 10^{-5} \text{ mol L}^{-1} \text{ Al}^{3+}$  and  $7.87 \times 10^{-5} \text{ mol L}^{-1} \text{ Cu}^{2+}$  using  $2 \times 10^{-4} \text{ mol L}^{-1} \text{ CO}_3^{2-}$  and  $6 \times 10^{-3} \text{ mol L}^{-1} \text{ HOL}$  at pH 7. The cations and anions which nearly resemble that present in natural waters are taken into consideration. As can be seen, all the salts added to the floating medium have no effect on flotation efficiency. Only  $\text{CaCl}_2$  and  $\text{MgCl}_2$  decrease the flotation efficiency to some extent owing to the formation of calcium and magnesium oleates resulting in a decrease of the concentration of oleic acid surfactant needed for flotation. The adverse effect of  $\text{CaCl}_2$  and  $\text{MgCl}_2$  can be overcome by adding slight excess of oleic acid surfactant (Table 1).

### Effect of Foreign Ions

Under the optimized conditions determined as above, the floatability of  $5 \times 10^{-5} \text{ mol L}^{-1} \text{ Al}^{3+}$  and  $7.87 \times 10^{-5} \text{ mol L}^{-1} \text{ Cu}^{2+}$  was carried out using  $2 \times 10^{-4} \text{ mol L}^{-1} \text{ CO}_3^{2-}$  and  $6 \times 10^{-3} \text{ mol L}^{-1} \text{ HOL}$  at pH 7. High concentrations of various cations and anions usually found in some water samples were investigated. All cations were used as their sulfates or chlorides whereas the anions were used as their sodium salts. The interference from the foreign ions were indicated as a molar ratio (foreign ion: $\text{Al}^{3+}$  or  $\text{Cu}^{2+}$ ). The tolerable amounts of each ion giving a maximum error of  $\pm 2\%$  in the flotation efficiency (Table 2). It can be seen that the ions investigated did not interfere. However, it should be noted that higher concentrations of  $\text{Cu}^{2+}$  (in aluminum investigation),  $\text{Al}^{3+}$  (in copper investigation),  $\text{Zn}^{2+}$  or  $\text{Hg}^{2+}$  could have interference effect on the removal process. These interferences (which may be due to the formation of insoluble oleates of these cations or the competition between these foreign cations and Al(III) or Cu(II) for precipitation with the  $\text{CO}_3^{2-}$ ) were overcome by the addition of slight excess of surfactant and/or  $\text{CO}_3^{2-}$ . This agrees well with literature data (Ghazy, 1995) that heavy metals and polyvalent metal ions form, with anionic surfactant, curds or lime-soap precipitates that reduce the effective concentration and adversely affect performance. Thus, the recommended procedure could be fairly employed for the removal of Al(III) and Cu(II) from various complex water samples.

### Recovery of $\text{Al}^{3+}$ and $\text{Cu}^{2+}$ Ions Added to Some Water Samples

To investigate the applicability of the recommended procedure, the recoveries of known amounts of Al(III) or Cu(II) added to natural water samples taken up from different locations were examined. The experiments were carried out using 1 L of clear, uncontaminated samples, filtered through  $0.45 \mu\text{m}$

Table 1: Effect of ionic strength on the floatability (%), of  $5 \times 10^{-5} \text{ mol L}^{-1} \text{ Al}^{3+}$  and  $7.87 \times 10^{-5} \text{ mol L}^{-1} \text{ Cu}^{2+}$  from aqueous solutions using  $6 \times 10^{-3} \text{ mol L}^{-1} \text{ HOL}$  and  $2 \times 10^{-4} \text{ mol L}^{-1} \text{ CO}_3^{2-}$  at pH 7

| Salts                    | Concentration<br>( $\text{mol L}^{-1}$ ) | F (%)                    |                              |                         |                          |                              |
|--------------------------|------------------------------------------|--------------------------|------------------------------|-------------------------|--------------------------|------------------------------|
|                          |                                          | $\text{Al}^{3+}$         |                              | $\text{Cu}^{2+}$        |                          |                              |
|                          |                                          | $\text{Na}_2\text{CO}_3$ | $(\text{NH}_4)_2\text{CO}_3$ | $\text{K}_2\text{CO}_3$ | $\text{Na}_2\text{CO}_3$ | $(\text{NH}_4)_2\text{CO}_3$ |
| NaCl                     | 0.1                                      | 100.0                    | 100.0                        | 100.0                   | 100.0                    | 100.0                        |
|                          | 0.5                                      | 100.0                    | 100.0                        | 100.0                   | 100.0                    | 100.0                        |
| KCl                      | 0.1                                      | 100.0                    | 100.0                        | 100.0                   | 100.0                    | 100.0                        |
|                          | 0.5                                      | 98.0                     | 97.0                         | 100.0                   | 100.0                    | 100.0                        |
| $\text{Na}_2\text{SO}_4$ | 0.1                                      | 100.0                    | 100.0                        | 100.0                   | 100.0                    | 100.0                        |
|                          | 0.5                                      | 98.0                     | 97.0                         | 100.0                   | 100.0                    | 98.0                         |
| $\text{MgCl}_2$          | 0.1                                      | 100.0                    | 100.0                        | 100.0                   | 100.0                    | 98.0                         |
|                          | 0.5                                      | 100.0                    | 98.0                         | 95.0                    | 100.0                    | 93.0                         |
| $\text{CaCl}_2$          | 0.1                                      | 100.0                    | 100.0                        | 100.0                   | 100.0                    | 100.0                        |
|                          | 0.5                                      | 100.0                    | 96.0                         | 98.0                    | 100.0                    | 95.0                         |

Table 2: Effect of some foreign ions on the floatability (%) of  $5 \times 10^{-5}$  mol L<sup>-1</sup> Al<sup>3+</sup> and  $7.87 \times 10^{-5}$  mol L<sup>-1</sup> Cu<sup>2+</sup> from aqueous solutions using  $6 \times 10^{-3}$  mol L<sup>-1</sup> HOL and  $2 \times 10^{-4}$  mol L<sup>-1</sup> CO<sub>3</sub><sup>2-</sup> at pH 7

| Foreign ions                                | Al <sup>3+</sup>          |       | Cu <sup>2+</sup>          |       |
|---------------------------------------------|---------------------------|-------|---------------------------|-------|
|                                             | [Ion]/[Al <sup>3+</sup> ] | F (%) | [Ion]/[Cu <sup>2+</sup> ] | F (%) |
| K <sup>+</sup>                              | 10000.0                   | 99.9  | 6353.2                    | 99.9  |
| Na <sup>+</sup>                             | 10000.0                   | 100.0 | 6353.2                    | 100.0 |
| Ba <sup>2+</sup>                            | 1000.0                    | 100.0 | 635.3                     | 100.0 |
| Ag <sup>+</sup>                             | 1000.0                    | 99.7  | 635.3                     | 99.7  |
| Sr <sup>2+</sup>                            | 1000.0                    | 100.0 | 508.3                     | 100.0 |
| Mg <sup>2+</sup>                            | 2500.0                    | 100.0 | 1270.6                    | 100.0 |
| Ni <sup>2+</sup>                            | 1000.0                    | 99.9  | 38.2                      | 99.7  |
| Co <sup>2+</sup>                            | 1000.0                    | 99.8  | 38.4                      | 99.9  |
| Mn <sup>2+</sup>                            | 1000.0                    | 99.7  | 114.4                     | 99.9  |
| Cd <sup>2+</sup>                            | 400.0                     | 99.8  | 25.4                      | 99.9  |
| Ca <sup>2+</sup>                            | 1000.0                    | 99.9  | 381.2                     | 99.8  |
| NH <sub>4</sub> <sup>+</sup>                | 1000.0                    | 99.7  | 635.3                     | 99.7  |
| Hg <sup>2+</sup>                            | 7.0                       | 99.9  | 4.5                       | 99.7  |
| Zn <sup>2+</sup>                            | 7.0                       | 100.0 | 12.7                      | 100.0 |
| Cu <sup>2+</sup>                            | 3.2                       | 99.7  | -                         | -     |
| Al <sup>3+</sup>                            | -                         | -     | 1.9                       | 99.7  |
| SO <sub>4</sub> <sup>2-</sup>               | 10000.0                   | 99.8  | 6353.2                    | 99.8  |
| NO <sub>3</sub> <sup>-</sup>                | 10000.0                   | 100.0 | 6353.2                    | 100.0 |
| Cl <sup>-</sup>                             | 10000.0                   | 100.0 | 6353.2                    | 100.0 |
| S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> | 1000.0                    | 100.0 | 635.3                     | 100.0 |
| CH <sub>3</sub> COO <sup>-</sup>            | 1000.0                    | 100.0 | 635.3                     | 100.0 |
| HCOO <sup>-</sup>                           | 1000.0                    | 100.0 | 635.3                     | 100.0 |
| C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> | 172.0                     | 99.9  | 109.3                     | 99.9  |
| B <sub>4</sub> O <sub>7</sub> <sup>2-</sup> | 60.0                      | 100.0 | 457.4                     | 100.0 |

Table 3: Recovery of Al<sup>3+</sup> and Cu<sup>2+</sup> ions added to 1 L of various water samples using 10 mL of  $6 \times 10^{-3}$  mol L<sup>-1</sup> HOL and  $2 \times 10^{-4}$  mol L<sup>-1</sup> of CO<sub>3</sub><sup>2-</sup> at pH 7

| Samples (location)              | Al <sup>3+</sup> or Cu <sup>2+</sup> added (mg) | Al <sup>3+</sup> found (mg) | Re (%) | RSD (%) | Cu <sup>2+</sup> found (mg) | Re (%) | RSD (%) |
|---------------------------------|-------------------------------------------------|-----------------------------|--------|---------|-----------------------------|--------|---------|
| Distilled water                 | 1.35                                            | 1.35                        | 100.0  | 2.5     | 1.35                        | 100.0  | 2.3     |
| Tap water (Our laboratory)      | 1.35                                            | 1.35                        | 100.0  | 2.4     | 1.35                        | 100.0  | 2.5     |
| Nile water (Mansoura City)      | 1.35                                            | 1.33                        | 98.5   | 2.4     | 1.30                        | 96.3   | 2.1     |
| Sea water (Gamasa)              | 1.35                                            | 1.30                        | 96.3   | 2.5     | 1.29                        | 95.6   | 2.6     |
| (Ras El-Barr)                   | 1.35                                            | 1.33                        | 98.5   | 2.3     | 1.32                        | 97.8   | 2.2     |
| (Alexandria)                    | 1.35                                            | 1.32                        | 97.8   | 2.4     | 1.35                        | 100.0  | 2.1     |
| Lake water (Manzalah)           | 1.35                                            | 1.32                        | 97.8   | 2.6     | 1.37                        | 101.5  | 3.1     |
| Underground water (Cinbillween) | 1.35                                            | 1.35                        | 100.0  | 2.4     | 1.35                        | 100.0  | 2.1     |

(a) The mean of five replicate measurements

filters after acidifying to 0.2 M with sulfuric acid immediately after collection. Recovery data indicated that the method could be successfully applied for the separation of Al(III) or Cu(II) at lower levels from natural water samples containing large amounts of salt matrix under the recommended conditions with a relative standard deviation RSD (%) did not exceed 3.1% (Table 3).

## CONCLUSIONS

Flotation technique, which has advantages (compared with other separation methods) of being simple, inexpensive, less time consuming and expected to be soon incorporated as a clean technology to treat water and wastewater has been applied in this investigation. The removal of Al(III) and Cu(II) attained ~100% at natural pH ~ 7, room temperature and in the presence of CO<sub>3</sub><sup>2-</sup> ions as precipitating agents. The procedure could be applied to hot wastewater since it can not be affected by raising the

temperature up to 80°C. Moreover, the recommended procedure was successfully applied to some natural water samples and was nearly free from interferences of some selected foreign ions.

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