



Ion Flotation of Copper(II) and Lead(II) from Environmental Water Samples

¹GHAZY, S. E.; ¹EL-MORSY, S. M.; ²RAGAB, A. H.

¹Chemistry Department, Faculty of Science, Mansoura University, P.O. Box ,66 Mansoura, Egypt

²New Mansoura Water Treatment Plant, Mansoura City, Egypt. E-mail: ghazyse@mans.edu.eg, shabanghazy@yahoo.com

ABSTRACT: The present study aims to develop a simple, rapid and economic procedure for copper(II) and lead(II) removal under the optimum conditions investigated. It is based on the complex formation between Cu^{2+} and Pb^{2+} ions and diphenylcarbazone (HDPC) followed by flotation with oleic acid (HOL) surfactant. The different parameters (namely: solution pH, HDPC, HOL, copper and lead concentrations, ionic strength, temperature and the presence of foreign ions) influencing the flotation process were examined. Nearly, 100% of Cu^{2+} and Pb^{2+} ions were removed from aqueous solutions at pHs 6 and 7, respectively at room temperature (~25 °C). The procedure was successfully applied to recover almost copper(II) and lead(II) spiked to some natural water samples. Due to the rapid, simple and economic nature of the procedure, a flotation mechanism is suggested for metal removal in wastewater systems. @ JASEM

Environmental pollution, mainly in the aquatic systems, due to developments in industry, is one of the most significant problems of this century. Many industrial wastewater streams (ca. the metal working, semiconductor, and copper industries, mine water, etc.) contain heavy metals, which are of great environmental concern and must be removed prior to water discharge or water recycling. Copper has received considerable attention owing to its uses in metallurgy, chemical industries and is necessary for other many biological important functions (Freematle, 1989; Khalifa et al., 2001). When levels of Cu exceed certain values, however, defense mechanisms to protect against excess Cu are overcome and toxicity results. The reported list of toxic Cu species (Sorenson, 1991) often includes $\text{Cu}(\text{OH})^+$, $\text{Cu}_2(\text{OH})_2^{2+}$ and CuCO_3 . However, without doubt, Cu^{2+} ions that are present in various aqueous solutions (their presence is a function of pH) are considered to be the most toxic of dissolved copper species (Freematle, 1989; Khalifa et al., 2001; Sorenson, 1991). Excess copper in water is not only harmful to human beings, but also interferes with the self-purification of bulk water (Ghazy et al., 2006) and adverse effect on the microbiological treatment of wastewater (Ghazy et al., 2001).

Lead is a natural compound that exists in elemental, inorganic, and organic forms. It is used in mining, smelting, refining, battery manufacturing, soldering, electrical wiring, home demolition and construction, painting, ceramic glazing, and the making of stained glass. The increasing presence of lead is very problematic to surface water and underground water due to their mobility and great toxicity (Meunier et al., 2003; Yan and Viraraghavan, 2003). The heavy metal lead is among the most common pollutant found in industrial effluents. Even at low concentration, this metal can be toxic to organisms, including humans and can damage the nervous system, kidneys, and reproductive system, particularly in children (Sheng et al., 2004). Also, lead is known to have a toxic effect on the neuronal system and the

function of the brain cells (Ho et al., 2001; Freedman et al., 1990; Goldstein, 1990). The U.S. Environmental Protection Agency (EPA) requires lead not to exceed 0.015mg.l^{-1} in drinking water (ATSDR, 1999). Therefore, from the viewpoint of pollution, environmental chemistry, and geochemistry, it is necessary to establish a rapid, and simple procedure for copper and lead removal. Numerous techniques for the separation, removal and control of metal toxicants have been reported (Blöcher et al., 2003; Ghazy, 1995; Leyden and Wegscheider, 1981). Although, adsorption has been well established as a technology for removing toxic compounds from wastes or wastewaters (Zouboulis et al., 1994), 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 ($10^{-6} - 10^{-2} \text{ mol l}^{-1}$), 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 (Rubio et al., 2002). Therefore, flotation technique was selected for this investigation.

Ion flotation involves the removal of surface-inactive ions (colligend) from aqueous solutions by adding surfactants which act as collectors. The subsequent passage of gas bubbles through the solution transfers the surface-active ions to the top (. Doyle, 2003; Lazaridis, 2004) Compared to other separation methods, ion flotation has advantages in its ease of operation and low costs. It shows particular promise for treating large volumes of dilute aqueous solutions (Doyle and Lui, 2003). Although some work have been carried out for ion flotation of copper (Khalifa et al., 2001; Lazaridis, 2004; Doyle and Lui 2003; Ghazy and Kabil, 1994;

Stalidis et al., 1989; Stoica et al., 2001; Liu and Doyle, 2001a; Girek et al., 2004) and lead (Lui and Doyle, 2001b; Matis and Mavros, 1991) from aqueous, fresh and wastewaters, and that diphenylcarbazone (HDPC) was used as a complexing agent for spectrophotometric determination of metal cations (Balt and Van Dalen, 1963; Steven, 1966; Trinder, 1966), no attention has been paid towards the use of HDPC as complexing agent for the flotation of Cu(II) and Pb(II). Therefore, the objective of the present work was to investigate the feasibility of developing the use of HDPC as chelating agent for Cu(II) and Pb(II) removal from aqueous media by ion flotation, under the recommended conditions, in the presence of oleic acid as a surfactant.

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. 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 stock copper solution of 1000 mg l^{-1} concentration was prepared and the working solutions were made by diluting the former with double distilled water. A lead nitrate $\text{Pb}(\text{NO}_3)_2$ (Aldrich) stock solution of 780 mg l^{-1} concentration was prepared. The working solutions were made by diluting with doubly distilled water. Oleic acid (HOL) was used directly as received. Its stock solution, $6.36 \times 10^{-2} \text{ mol l}^{-1}$, 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. Diphenylcarbazone (HDPC) stock solution (Koch-Light Laboratories LTD, England), $1.0 \times 10^{-2} \text{ mol l}^{-1}$, was prepared by dissolving the requisite amount in the least amount of ethyl alcohol and completing to 100 ml with doubly distilled water daily before use. The pH of the solutions during experiments was adjusted with HCl, HNO_3 , H_2SO_4 and/or NaOH.

Apparatus

The flotation and separation cells were of two types (Ghazy and Kabil, 1994). Type (a) was a cylindrical tube of 29 cm length and 1.2 cm inner diameter with a stopcock at the bottom and a stopper at the top. This cell was used to study the different factors affecting the separation of the investigated ions from aqueous solutions. Type (b) was a glass cylinder of 6 cm inner diameter and 45 cm length with a stopcock at the bottom and a quick-fit stopper at the top. This cell was used to study the separation of the investigated ions from 1 l of some natural water samples. The pH values of the solutions were measured using ORION (model 720 A) pH meter. The concentrations of Cu(II) and Pb(II) were determined using Pekin-Elmer 2380

Atomic Absorption Spectrophotometer with air-acetylene flame at 324.7 and 217.0 nm, respectively. The stirring of the solutions was performed with a magnetic stirrer Model VEHP, Scientifica, Italy.

Recommended procedures

A suitable aliquot containing known amount of Cu(II) or Pb(II) specified for each investigation, was mixed with a suitable amount of DPC followed by addition of 3 ml of double distilled water. After adjusting the pH to the required value, the solution was transferred to the flotation cell (a) and the total volume was made up to 10 ml with doubly distilled water. The cell was shaken well for few seconds, to ensure complexation. 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 concentration of Cu(II) or Pb(II) in the mother liquor was determined. The floatability (F) of Cu(II) was determined from the relationship:

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

where C_i and C_f denote the initial and final concentrations of Cu(II) or Pb(II) in the mother liquor, respectively. All experiments were carried out at room temperature ($25 \pm 1^\circ\text{C}$).

To assess the applicability of the procedure, another series of experiments was conducted on 1 l suspension of clear and pre-filtered natural water samples with an initial pH adjusted to 7.0. These suspensions were placed in flotation cell (b) containing 6.4 or 12.8 mg of Cu^{2+} or Pb^{2+} ions, $4 \times 10^{-4} \text{ mol l}^{-1}$ HDPC, 10 ml of $1 \times 10^{-4} \text{ mol l}^{-1}$ HOL and stirred magnetically for 10 min at 250 rpm.

RESULTS AND DISCUSSION

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. Initial series of experiments were carried out to investigate the suitable acid (ca. HNO_3 , HCl or H_2SO_4) for controlling pH in the flotation of Cu^{2+} or Pb^{2+} ions. It was found that maximum floatation efficiency of Cu^{2+} or Pb^{2+} ions was attained in the presence of HNO_3 . Therefore, control of pH was carried out with HNO_3 throughout. Moreover, the floatability did not exceed 40% in the presence of HOL only. Hence, trials were made to float Cu^{2+} and Pb^{2+} ions in the presence of other additives such as HDPC.

Several experiments were carried out to investigate the relation between the floatability of $1 \times 10^{-4} \text{ mol l}^{-1}$ Cu^{2+} or Pb^{2+} ions and pH (adjusted by HNO_3) using the systems: i) $2 \times 10^{-3} \text{ mol l}^{-1}$ of HOL without additives; ii) $2 \times 10^{-4} \text{ mol l}^{-1}$ HDPC + $1 \times 10^{-3} \text{ mol l}^{-1}$

HOL. The results obtained are plotted in Figure 1 (a and b).

On using HDPC, the floatability of Cu^{2+} increases up to ~ 100 %, reaches its maximum value in the pH range 5 - 6 and then decreases (Figure 1a) while

that of Pb^{2+} reaches its maximum value in the range 6.5 – 8.0. Therefore, pHs 6 and 7 were optimized for the flotation experiments of Cu^{2+} and Pb^{2+} ions, respectively.

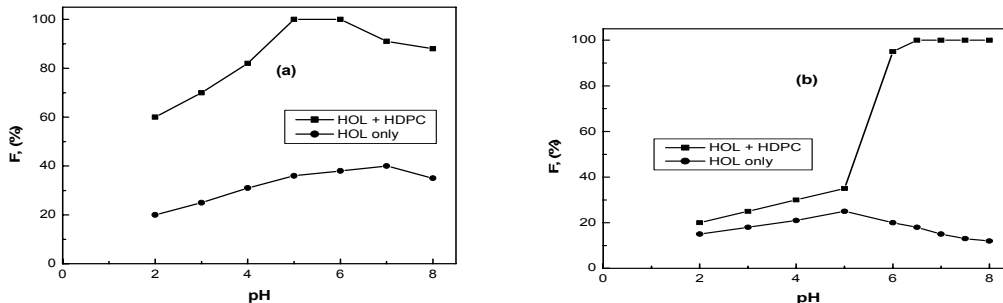


Figure 1. Floatability (%) of $1 \times 10^{-4} \text{ mol l}^{-1} \text{ Cu}^{2+}$ ions (a) or Pb^{2+} ions (b) at different pH values using $2 \times 10^{-4} \text{ mol l}^{-1}$ of HDPC and $1 \times 10^{-3} \text{ mol l}^{-1}$ of HOL.

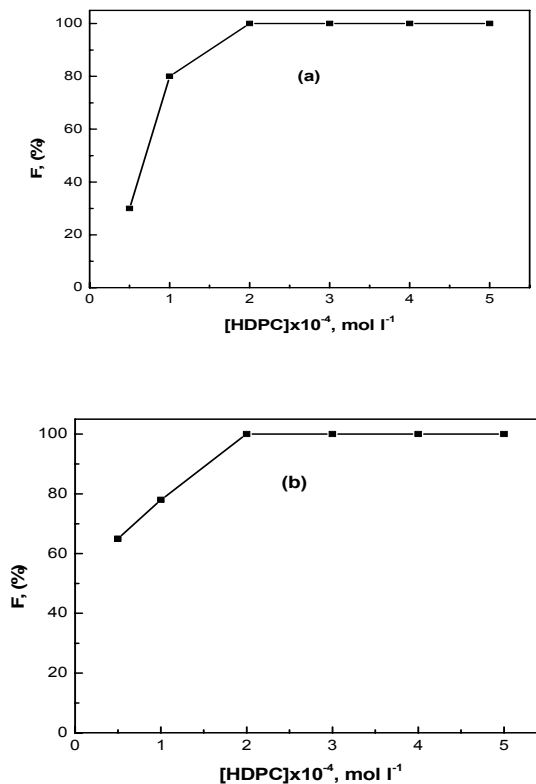


Figure 2. Floatability (%) of $1 \times 10^{-4} \text{ mol l}^{-1} \text{ Cu}^{2+}$ ions at pH 6 (a) or Pb^{2+} ions at pH 7 (b) using different concentrations of HDPC and $1 \times 10^{-3} \text{ mol l}^{-1}$ of HOL.

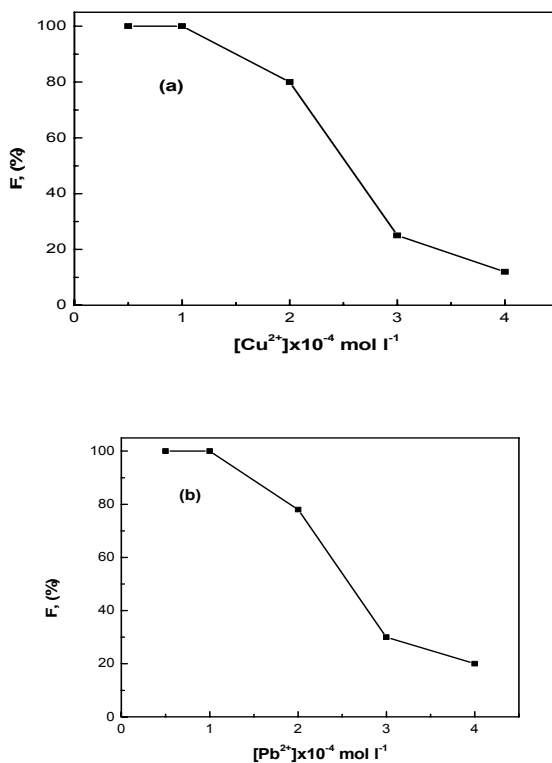


Figure 3. Floatability (%) of different concentrations of Cu²⁺ ions at pH 6 (a) or Pb²⁺ ions at pH 7 (b) using 2×10⁻⁴ mol l⁻¹ of HDPC and 1×10⁻³ mol l⁻¹ of HOL.

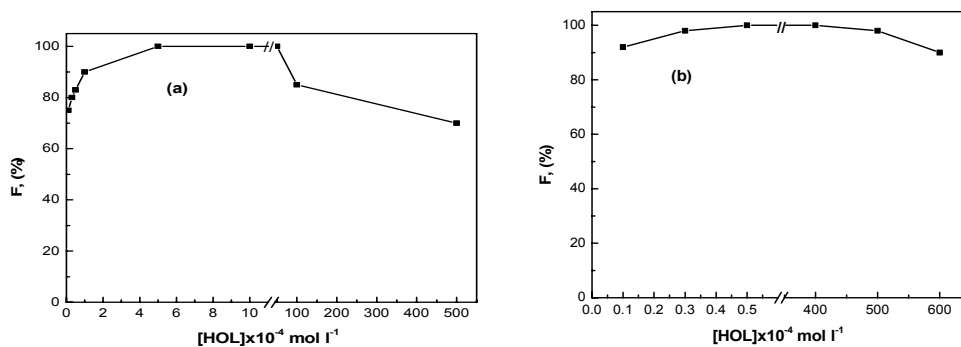


Figure 4. Floatability (%) of 1×10⁻⁴ mol l⁻¹ Cu²⁺ ions at pH 6 (a) or Pb²⁺ ions at pH 7 (b) using different concentrations of HOL and 2×10⁻³ mol l⁻¹ of HDPC.

Effect of the Ligand and Metal Ion Concentrations

Two parallel series of experiments were undertaken to study the influence of changing HDPC concentration Figure 2 (a and b) and changing copper and lead concentrations Figure 3 (a and b) on the floatability percentage of Cu²⁺ or Pb²⁺ ions from aqueous solutions at pHs 6 and 7, respectively using 1×10⁻³ mol l⁻¹ HOL. As can be seen from the figures, the removal percentage of Cu²⁺ or Pb²⁺ ions was directly proportional to HDPC concentration and maximum floatability (~ 100 %) was

achieved at 1 : 2 (M²⁺ : HDPC) ratio. These results agree well with those obtained in Figure 3 (a and b), where the floatability of metal ions decreased at their higher concentrations owing to the fact that there is no sufficient amount of HDPC for binding them. Also, these data are in accordance with the literature (Balt and Van Dalen, 1963; Steven, 1966; Trinder, 1966), where the divalent metal ions of Cu and Pb ions react with HDPC to form 1:2 neutral complexes according to the following equation:

$$M^{2+} + 2HDPC = M(HPDC)_2 + 2H^+ \quad (2)$$

* Corresponding author: Ghazy S. E.

Moreover, the excess of HDPC has no adverse effect on the flotation process which may find application for the removal of Cu^{2+} or Pb^{2+} ions from different samples and matrices. Accordingly, $2 \times 10^{-4} \text{ mol l}^{-1}$ of HDPC was used in the recommended procedure.

Effect of the Surfactant Concentration

Experiments were performed to float $1 \times 10^{-4} \text{ mol l}^{-1}$ Cu^{2+} ions at pH 6 (Figure 4a) or Pb^{2+} ions at pH 7 (Figure 4b) using $2 \times 10^{-4} \text{ mol.l}^{-1}$ of HDPC and different concentrations of HOL. It was observed that the maximum floatability ($\sim 100\%$) was attained in the HOL concentration ranges of $5 \times 10^{-4} - 5 \times 10^{-3} \text{ mol l}^{-1}$ for Cu^{2+} ions and $3 \times 10^{-5} - 4 \times 10^{-2} \text{ mol.l}^{-1}$ for Pb^{2+} ions, below which the flotation decreases. This may be attributed to the presence of insufficient amounts of surfactant required for complete flotation.

At higher surfactant concentration the poor flotation is caused by the formation on the air bubble surface of a stable, hydrated envelope of surfactant or, perhaps, by forming a miscelle (Ghazy et al., 2004). Therefore, $3 \times 10^{-3} \text{ mol.l}^{-1}$ of HOL was fixed throughout all the measurements for the removal of Cu(II) or Pb(II).

Effect of Temperature

To study the effect of temperature on the flotation efficiency, the Cu^{2+} or Pb^{2+} ions and HDPC as a first solution and HOL as a second solution were either heated or cooled to the same temperature in a water bath. Both solutions were quickly poured at a time zero into the flotation cell jacketed with 1 cm thick fiberglass insulation. The flotation procedure was then followed over the range 10-80°C. It was found that the floatability of the systems Cu^{2+} -HDPC and Pb^{2+} -HDPC was not markedly affected by raising the temperature in this range; it just made an acceleration of the flotation process. Since most industrial influents are usually hot, the simple procedure presented here may find its application in the removal of Cu^{2+} or Pb^{2+} 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

Table 1 shows the effect of ionic strength on the floatability of $1 \times 10^{-4} \text{ mol l}^{-1}$ Cu^{2+} ions at pH 6 or $1 \times 10^{-4} \text{ mol l}^{-1}$ Pb^{2+} ions at pH 7 using $2 \times 10^{-4} \text{ mol.l}^{-1}$ of HDPC and $3 \times 10^{-3} \text{ mol l}^{-1}$ HOL. The cations and

anions which nearly resemble that present in natural waters are taken into consideration. The data are given in Table 1. As can be seen, all the salts added to the floating medium have no effect on flotation efficiency. Only CaCl_2 and 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 CaCl_2 and MgCl_2 can be overcome by adding slight excess of oleic acid surfactant.

Table 1 Effect of ionic strength on the floatability (%), of $1 \times 10^{-4} \text{ mol l}^{-1}$ Cu^{2+} ions at pH 6 and $1 \times 10^{-4} \text{ mol l}^{-1}$ Pb^{2+} ions at pH 7 from aqueous solutions using $3 \times 10^{-3} \text{ mol l}^{-1}$ HOL and $2 \times 10^{-4} \text{ mol l}^{-1}$ HDPC.

Salt	Concentration, mol l^{-1}	Cu^{2+} floatability (%)	Pb^{2+} floatability (%)
NaCl	0.1	100.0	100.0
	0.5	100.0	100.0
KCl	0.1	100.0	100.0
	0.5	98.0	100.0
Na_2SO_4	0.1	100.0	100.0
	0.5	98.0	98.0
MgCl_2	0.1	100.0	100.0
	0.5	96.0	94.0
CaCl_2	0.1	98.0	98.5
	0.5	93.0	95.0

Effect of Some Foreign Ions

Under the optimized conditions determined, the percentage removal of $1 \times 10^{-4} \text{ mol l}^{-1}$ Cu^{2+} at pH 6 and $1 \times 10^{-4} \text{ mol l}^{-1}$ Pb^{2+} at pH 7 using $2 \times 10^{-4} \text{ mol l}^{-1}$ of HDPC and $3 \times 10^{-3} \text{ mol l}^{-1}$ HOL was studied. High concentrations of various cations and anions usually found in some water samples were investigated. All cations were used as their nitrates whereas the anions were used as their sodium salts. The tolerable amounts of each ion giving a maximum error of $\pm 2\%$ in the flotation efficiency are summarized in Table (2). It can be seen that most of the investigated ions did not interfere. Only Pb^{2+} interferes in the flotation of Cu(II) while Cd^{2+} , Co^{2+} , Ni^{2+} , Ag^+ , Cu^{2+} and Al^{3+} ions interfere in the flotation of Pb(II) which may be due to a competition between these ions and Cu(II) and Pb(II) towards HDPC. This effect could be overcome by increasing the HDPC concentration. Thus, the recommended procedure could be fairly employed for the removal of Cu^{2+} and Pb^{2+} ions from various complex water samples.

Table 2: Effect of some foreign ions on the floatability (%) of 1×10^{-4} mol l Cu^{2+} at pH 6 and 1×10^{-4} mol l Pb^{2+} at pH 7 from aqueous solutions using 3×10^{-3} mol l⁻¹ HOL and 2×10^{-4} mol l HDPC.

Ion	[Ion]/[Cu^{2+}]	F (%) of Cu^{2+}	[Ion]/[Pb^{2+}]	F (%) of Pb^{2+}
K^+	10000.0	99.9	20000.0	99.9
Na^+	10000.0	100.0	5000.0	100.0
Ba^{2+}	5000.0	100.0	500.0	100.0
Ag^+	50.0	99.7	2.0	99.7
Sr^{2+}	100.0	100.0	200.0	100.0
Mg^{2+}	5000.0	100.0	2500.0	100.0
Ni^{2+}	900.0	99.9	0.5	99.7
Co^{2+}	900.0	99.8	0.5	99.9
Mn^{2+}	800.0	99.7	500.0	99.9
Cd^{2+}	100.0	99.8	0.1	99.9
Ca^{2+}	10000.0	99.9	1000.0	99.8
NH_4^+	10000.0	99.7	635.3	99.7
Hg^{2+}	100.0	99.9	50.0	99.7
Zn^{2+}	70.0	100.0	20.0	100.0
Cu^{2+}	-	-	5.0	99.9
Al^{3+}	50.0	99.5	5.0	99.7
Pb^{2+}	5.0	99.2	-	-
SO_4^{2-}	5000.0	99.8	5000.0	99.8
NO_3^-	10000.0	100.0	5000.0	100.0
Cl^-	9100.0	100.0	5000.0	100.0
H_2PO_4^-	1200.0	99.9	1200.0	99.8
$\text{S}_2\text{O}_3^{2-}$	10000.0	100.0	500.0	100.0
CH_3COO^-	1000.0	100.0	500.0	100.0
HCOO^-	10000.0	100.0	700.0	100.0
$\text{C}_2\text{O}_4^{2-}$	500.0	99.9	250.0	99.9

Table 3: Floatability of different concentrations of Cu^{2+} or Pb^{2+} ions added to 1l of various water samples using 10 ml of 3×10^{-3} mol l⁻¹ HOL and 2×10^{-4} mol l⁻¹ of HDPC at pHs 6 for Cu^{2+} and 7 for Pb^{2+} ions.

Sample (Location)	Cu(II) or Pb(II) added (mg)	Cu(II) found (mg)	F (%) Cu^{2+}	Pb(II) found (mg)	F (%) Pb^{2+}
Distilled water	6.5	6.494	99.9	6.480	99.7
	9.5	9.490	99.9	9.480	99.8
Tap water (our- lab.)	6.5	6.435	99.0	5.435	99.0
	9.5	9.31	98.0	9.329	98.2
Nile water (Mansoura City)	6.5	5.859	90.0	5.859	90.0
	9.5	8.075	85.0	8.265	87.0
Sea water (Gamasah)	6.5	6.494	99.9	6.494	98.9
	9.5	9.315	98.0	9.329	98.0
Lake water (El-Manzalah)	6.5	6.494	99.9	6.494	97.9
	9.5	9.490	99.9	9.480	98.9
Underground water (Salka)	6.5	6.494	99.8	6.422	98.8
	9.5	9.405	99.0	9.405	99.0

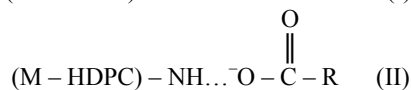
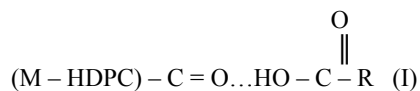
Application

To investigate the applicability of the recommended procedure, a series of experiments was performed to recover 6.5 and 9.6 mg of Cu(II) or Pb(II) spiked to 1l of tap and some natural water samples. The flotation experiments were carried out using clear, filtered through 0.45 μm filters, uncontaminated sample solutions after adjusting their pH values to 6 for Cu^{2+} and 7 for Pb^{2+} ions. The results obtained are listed in Table 3. Recovery data indicated that the method could be successfully applied for the separation of Cu^{2+} and Pb^{2+} at mean levels of 6.4 and 9.5 mg l⁻¹ from natural water samples containing large amounts of salt matrix under the recommended conditions. Moreover, the recovery was satisfactory and quantitative (~ 100 %).

Flotation mechanism

The proposed flotation mechanism for Cu^{2+} and Pb^{2+} ions, in the present work, is based upon the following bases:

- Cu^{2+} and Pb^{2+} ions react with HDPC to give (1:2) complexes as given by Equation (2), which have many sites containing electronegative atoms, such as oxygen and nitrogen, capable of forming hydrogen bonds.
- Oleic acid begins to dissociated at $\text{pH} \geq 5$ (Ghazy et al., 2004) and the presence of different forms of oleic acid determined by IR analysis at pH 9 (adjusted by NaOH) are 13.2 % oleic acid, 68.2 % oleate and 18.2 % sodium oleate, in the form of soap [38]. Therefore, oleic acid can interact with the above complex systems (through hydrogen bonds, either by its un-dissociated or dissociated forms depending on the pH of the medium) according to the following schemes:



where M is Cu^{2+} or Pb^{2+} ion.

3. The combination of oleic acid surfactant with copper-HDPC or Pb-HDPC systems give hydrophobic sublates which float with the aid of air bubbles (created inside the flotation cell by shaking) to the solution surface solution (Ghazy et al., 2004).

Conclusion: Diphenylcarbazone (HDPC) was used in this study as a good complexing agent for the heavy meals copper and lead. 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 Cu(II) and Pb(II) at pHs 6 and 7, respectively attained ~100% in the presence of HDPC and oleic acid as a cheap surfactant. Moreover, the recommended procedure was successfully applied to some natural water samples and was nearly free from interferences of some selected foreign ions.

REFERENCES

- Agency for Toxic Substances and Disease Registry (ATSDR), 1999. Toxicological Profiles, U.S. Department of Health and Human Services, Public Health Service, Atlanta.
- Al-Asheh, S. and Duvnjak, Z., 1997. Binary metal sorption by pine bark, study of equilibria and mechanisms. *Sep. Sci. Technol.*, 33: 1303-1329.
- Balt, S. and Van Dalen E., 1963. The reactions of diphenylcarbazide and diphenylcarbazone with cations. *Anal. Chim. Acta*, 29: 466-471.
- Blöcher, C., Dorda, J., Mavrov, V., Chmiel, H., Lazaridis, N.K. and Matis K.A., 2003. Hybrid flotation-membrane filtration process for the removal of heavy metal ions from wastewater. *Water Res.*, 37: 4018-4026.
- Doyle, F.M., 2003. Ion flotation-its potential for hydrometallurgical operations. *Int. J. Miner. Process.*, 72: 387-399.
- Doyle, F.M. and Liu Z., 2003. The effect of triethylenetetraamine (Trien) on the ion flotation of Cu^{2+} and Ni^{2+} . *J. Colloid Interface Sci.*, 258: 396-403.
- Freedman, R., Olson, L. and Hoffer, B.G., 1990. Toxic effects of lead on neuronal development and function. *Environ. Health Perspect.*, 89: 27-34.
- Freemattle, M.H., 1989. *Chemistry in Action*. Macmillan Education Ltd., London.
- Ghazy, S.E., 1995. Removal of cadmium, lead, mercury, tin, antimony, and arsenic from drinking and seawaters by colloid precipitate flotation. *Sep. Sci. Technol.*, 30, 933-947.
- Ghazy, S.E., El-Shazly, R.M., El-Shahawi, M.S., Al-Hazmi, G.A.A. and El-Asmy, A.A., 2006. Spectrophotometric determination of copper(II) in natural waters, vitamins and certified steel scrap samples using acetophenone-*p*-chlorophenylthiosemicarbazide. *J. Iranian Chem. Soc.*, 3: 140-150.
- Ghazy, S.E. and Kabil, M.A., 1994. Determination of trace copper in natural waters after selective separation by flotation. *Bull. Chem. Soc. Jpn.*, 67: 474-478.
- Ghazy, S.E., Mostafa, H.A., El-Farra, S.A. and Fouda A.S., 2004. Flotation-separation of nickel from aqueous media using some hydrazone derivatives as organic collectors and oleic acid as surfactant. *Indian J. Chem. Technol.*, 11, 787-792.
- Ghazy, S.E., Samra, S.E. and El-Morsy S.M., 2001. Removal of copper(II) from aqueous solutions using limestone fines as the sorbent and oleic acid as the surfactant. *Adsorp. Sci. Technol.*, 19: 175-185.
- Girek, T., Kozłowski, C.A., Koziol, J.J. and Walkowiak W., 2004. Polymerization of β -cyclodextrin with succinic anhydride. Synthesis, characterization and ion flotation of transition metals. *Carbohydrate Polymers*, 59: 211-215.
- Gksungure, Y., Uren, S. and Güvenc, U., 2005. Biosorption of cadmium and lead ions by ethanol treated waste baker's yeast biomass. *Bioresource Technol.*, 96: 103-109.
- Goldstein, G.W., 1990. Lead poisoning and brain cell function. *Environ. Health Perspect.*, 89: 91-94.
- Hasar, H., 2003. Adsorption of nickel(II) from aqueous solution onto activated carbon prepared from almond husk. *J. Hazard. Mater.*, 97: 49-57.

- Ho, Y.S., Ng, J.C.Y. and McKay, G., 2001. Removal of lead(II) from effluents by sorption on peat using second-order kinetics. *Sep. Sci. Technol.*, 36: 241-261.
- Kadirvelu, K., Thamaraislvi, K. and Namasivayam C., 2001. Adsorption of nickel(II) from aqueous solution onto activated carbon prepared from coirpith. *Sep. Purif. Technol.*, 24: 497-505.
- Khalifa, M.E., Akl, M.A. and Ghazy S.E., 2001. Selective flotation-spectrophotometric determination of trace copper(II) in natural waters, human blood and drug samples using phenanthraquinone monophenylthiosemicarbazone. *Chem. Pharm. Bull.*, 49: 664-668.
- Kim, J.S., Akeprathumchia, S. and Wickrasinghe S., 2001. Flocculation to enhance microflotation. *J. Member. Sci.*, 182: 161-172.
- Lazaridis, N.K., Peleka, E.N., Karapantsios, Th.D. and Matis K.A., 2004. Copper removal from effluents by various separation techniques. *Hydrometallurgy*, 74: 149-156.
- Leyden, D.E. and Wegscheider, W., 1981. Preconcentration for trace element determination in aqueous samples. *Anal. Chem.*, 53: 1059A-1065A.
- Liu, Z. and Doyle, F.M., 2001a. A thermodynamic approach to ion flotation. I. Kinetics of cupric ion flotation with alkylsulfates. *Colloids and Surfaces A*, 178, 79-92.
- Liu Z. and Doyle F.M., 2001b. Modeling metal ion removal in alkylsulfate ion flotation system. *Minerals Metallurgical Processing*, 18: 167-171.
- Matis, K.A. and Mavros P., 1991. Recovery of metals by ion flotation from dilute aqueous solutions. *Sep. Purif. Methods*, 20: 1-48.
- Meunier, N., Laroulandie, J. Blais, J.F., Tyagi, R.D., 2003. Coca shells for heavy metal removal from acidic solutions. *Bioresource Technol.*, 90: 255 – 263.
- Rubio, J., Souza, M.L. and Smith R.W., 2002. Overview of flotation as a wastewater treatment technique. *Minerals Eng.*, 15: 139-155.
- Sheng, P.X., Ting, Y-P., Chen, J.P. and Hong, L., 2004. Sorption of lead, copper, cadmium, zinc and nickel by marine algal biomass: characterization of biosorptive capacity and investigation of mechanisms. *J. Colloid Interface Science*, 275: 131-141.
- Sitting, M., 1981. *Hand Book of Toxic and Hazardous Chemicals*. Noyes Publications, Park Ridge, NJ.
- Sorensen, E.M.B., 1991. *Metal Poisoning in Fish*. CRC Press, Boston, MA, USA.
- Stalidis, G.A., Matis, K.A. and Lazaridis, N.K., 1989. Selective separation of Cu, Zn and As from solutions by flotation techniques. *Sep. Sci. Technol.*, 24: 97-109.
- Steven, W.I., 1966. Extraction and stability of copper complexes of 1,5-diphenylcarbazone. *Anal. Chim. Acta*, 36: 537-540.
- Stoica, L., Constantin, C., Meghea, A. and Micu, O., 2001. Alkylhydroxamic acids with Cu(II) and Co(II) interaction in metallic ion flotation. *Environ. Protect. Ecol.*, 2, 1015-1019.
- Stoica, L., Dinculescu, M. and Plapcianu C.G., 1998. Mn(II) recovery from aqueous systems by flotation. *Water Res.*, 32: 3021-3030.
- Trinder, N., 1966. The use of diphenylcarbazone for the determination of microgram amounts of lead. *Analyst*, 91: 587-590.
- Yan, G. and Viraraghavan, T., 2003. Heavy-metal removal from aqueous solution by fungus *Mucor rouxii*. *Water Res.*, 37: 4446 – 4496.
- Zouboulis, A.I., Lazaridis, N.K., Zamboulis, D., 1994. Powdered activated carbon separation from water by foam flotation. *Sep. Sci. Technol.*, 29: 385-400.