

COMPARATIVE STUDY OF ION-EXCHANGE AND FLOTATION PROCESSES FOR THE REMOVAL OF Cu^{2+} AND Pb^{2+} IONS FROM NATURAL WATERS

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ABSTRACT

In the present work, a method has been described for the determination of copper and lead by flame atomic absorption spectrometry (FAAS) after preconcentration and separation in water by ion exchange resin and coflotation.

Purolite S-940, that is a strong cation exchanger, was used for preconcentration and separation of the trace metals as the first method. Optimum metal uptake conditions were investigated using batch systems. These optimum conditions are: pH, contact time, the initial metal concentration and the amount of resin. Using results obtained from experiments of optimum conditions, Cu and Pb in water samples which were taken from ISKI (Water Authority for İstanbul) Kağıthane and ISKI Büyükçekmece were enriched and determined by FAAS.

The second method is a preconcentration and separation using hexamethylenedithiocarbamate as a chelating agent for colloid flotation Cu and Pb from water. The influences arising from pH, nitric acid concentration, amount of analytes, and sample volume on the recoveries were assessed. Cu and Pb in water samples which were taken from ISKI Kağıthane and ISKI Büyükçekmece were enriched and determined by FAAS.

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Results of these two methods are compared. Our results showed that two methods were very effective but flotation results higher than ion exchange.

Keywords: Ion-exchange, flotation, resin, preconcentration, separation, copper, lead, water, AAS

1. INTRODUCTION

The tremendous increase in the use of heavy metals over the past few decades has inevitably resulted in an increased flux of metallic substances in the environment. There is a critical need for preconcentration and separation of trace metals from matrices prior to their determination, due to their frequent presence in environmental samples and higher matrix interferences /1/.

More than 75% of copper that is mined is used in the electrical industries. Other applications include household, metallic blends and pigments. It is an essential element for enzymes, but over a healthy limit it accumulates in the liver, causing dizziness, vomiting, diarrhea, transpiration and, depending on its concentration, can lead to death /2/.

In natural water and biological samples the level of copper is low, and previous steps of separation and enrichment are usually required /3/.

Lead occurs naturally mainly as PbS and it is widely distributed all over the world. It is used in accumulators, to produce tetraethyl lead, guns, solders and X-ray equipment, among other uses. This metal inhibits biosynthesis and affects the kidneys, brain cells and liver membrane permeability, reducing some of their functions /2/.

The allowance of lead concentration recommended by the WHO is less than 0.01 ppm for drinking water. Thus, separation and removal of lead (Pb(II)) from industrial effluent and water systems has become of great importance /4/.

Hence, many preconcentration procedures for copper and lead determination /5-14/ have been developed and they involve different analytical techniques and several materials. Flotation technique is much simpler than conventional preconcentration and separation techniques such as liquid-liquid extraction, sorption, etc. /15/. Flotation is an accurate, fast, and inexpensive procedure /16/.

In the present work, a method has been described for the determination of copper and lead by flame atomic absorption spectrometry (FAAS) after preconcentration and separation in water by ion exchange resin and co-floitation. Results of these two methods are compared. Analytical parameters such as precision and accuracy of method have also been studied. The equilibrium experimental results of Cu and Pb ions exchanged have been fitted by Langmuir-Freundlich adsorption isotherm models.

2. EXPERIMENTAL

2.1. Reagents

2.1.1. Ion Exchange

All solutions were prepared with deionised water. Unless stated, analytical-grade acids and other chemicals used in this study were obtained from Merck, Darmstadt, Germany. Synthetic Purolite Aminophosphonic S-940 hydrogen form was obtained from Purolite Intl. The properties are given in Purolite Aminophosphonic S-940, Table 1. Stock solutions 1000 mg/L of Cu(II), Pb(II) were prepared by dissolving appropriate amounts of CuCl₂ (Merck) ve PbCl₂ (Merck). Working standard solutions of the metal ions were prepared by a suitable dilution with a stock solution with double distilled water.

Table 1
Characteristic Data of Tested Purolite S-940

Polymer Structure	Macroporous crosslinked polymer
Appearance	Spherical beads
Functional Group	-CH ₂ NHCH ₂ PO ₃ Na Aminophosphonic
Ionic form	Na ⁺
Moisture Retention (Na)	55-65 %
Mean Size Typical	0.55-0.75 mm
Temp Limit	90°C
Total exchange capacity	20 g Ca/L (pH: 9,5)
pH Limits	0-14 (Stability)

2.1.2. Flotation

All chemicals used were of the highest grade available except for surfactants sodium dodecyl benzene sulfonate stock solutions (1 mg/mL) of Cu and Pb served for preparation of standards by a suitable daily dilution before each investigation. Stock solution of Co(II) (10 mg/mL) was prepared by dissolving an appropriate amount of Co(NO₃)₂ · 6H₂O (Merck) in deionized redistilled water. The 0.1 mol/L solution of HMDTC was prepared by dissolving an appropriate amount of home-synthesized crystalline hexamethylenammonium hexamethylenedithiocarbamate /15,16,17/ in 96% ethanol.

The pH was adjusted by solutions of KOH (1.25%, 2.5%, and 10%) and HNO₃ (0.1 mol/L). Ionic strength (Ic) was regulated with saturated solution of KNO₃. 0.1 mol/L NH₄NO₃ solution served to transfer the contents of the beaker into the flotation cell.

2.2. Apparatus

2.2.1. Ion Exchange

A Varian Spectra AA-20 Model atomic absorption spectrometer (AAS) equipped with deuterium lamp, background correction, a hollow cathode lamp, and an air-acetylene burner was used for quantitative determination of Cu(II) and Pb(II), under the following conditions: wavelength, 324.8 nm, 283.3 nm ; spectral bandwidth, 0.5 nm, 0.7 nm. All pH measurements were performed with Metrohm Herisau E 510 Model pH meter. An electrical temperature-controlled shaker was used for shaking.

2.2.2. Flotation

The flotation cell, was a glass cylinder (4 x 105cm) with a sintered glass bottom (porosity no. 4) to produce air bubbles as described before /16/. A Varian Spectra AA-20 Model atomic absorption spectrometer (AAS) was used for determination. All pH measurements were performed with Metrohm Herisau E 510 Model pH meter.

2.2.3. Ion Exchange Procedure

2.2.3.1. Water washing of resin

The hydrogen form of the ion exchange resin was washed with double distilled water to remove all the excess acid. It was dried at 110 °C for 1 h and stored in a desiccator until use.

2.2.3.2. General studying procedure

The metal ions were preconcentrated by batch methods.

2.2.3.3. Batch method

10 ml of solution containing Cu(II), Pb(II), in the concentration range of 5-1000 mg/L were taken in a stoppered glass bottle after adjusting their pH to an optimum value 5-1000 mg of resin in H^+ form was taken in different stoppered conical flasks containing varying amounts of pure metal solution and the volume was adjusted to 50 ml with double-distilled water. The flasks were shaken thoroughly in a temperature-controlled shaker for 1 h at room temperature. The resin was filtered from quantitative filter paper, washed with double distilled water, shaken with 10 ml of 0,1 M HNO_3 for 60 min and filtered. After filtration, the concentration of the metal ions in the eluate was determined by atomic absorption spectrometry; if dilution was necessary it was diluted.

The optimum amount of resin was contacted with 50 ml of solution containing 10 mg 1-1copper (II) and lead (II) at the optimum time. All the operations were conducted at room temperature. After filtration of resin, the amounts of copper and lead in the liquid phase were determined by atomic absorption spectrometry.

2.2.3.4. Analysis of the water samples

The water sample analysed included drinking waters; treated waters and filtered raw waters. The pHs of the samples were adjusted 5 with buffer solution. Then the separation and preconcentration method given was applied. The concentration of the investigated analyte ions in final solution was determined by atomic absorption spectrometer. Results are shown in Table 2.

2.3.2. Flotation Procedure

Flotation procedure was applied as previously described [16]. The flotation procedure consisted of two steps: Coprecipitation and air bubble separation.

Table 2
Metal determination in natural water samples

Sample	Raw Water		Treated Water		Raw Water		Treated Water	
	Ion Ex.	Flo.	Ion Ex.	Flo.	Ion Ex.	Flo.	Ion Ex.	Flo.
K.H. Spring	88.3±1.5	99.3±0.5	91.4±1.0	100.4±1.0	86.3±0.6	99.4±1.1	90.1±1.3	102.2±0.5
K.H. Summer	90.5±1.1	100.1±1.4	93.3±1.1	102.1±1.2	84.5±1.4	99.6±0.9	87.2±2.0	100.3±1.0
B.Ç Spring	93.6±2.0	102.3±2.1	95.2±0.9	105.1±1.5	92.3±1.7	100.3±0.5	94.4±2.3	105.3±1.4
B.Ç Summer	95.1±1.3	101.3±1.0	97.3±2.3	105.4±1.7	85.3±1.0	99.5±1.0	88.1±1.2	100.4±1.2
<i>K.H.: Kağıthane, B. Ç.: Büyükdere</i>								
<i>Ion Ex.: Ion Exchange, Flo. Flotation</i>								

2.3.2.1. Coprecipitation

A combined glass pH electrode was immersed into water sample. 6 ml of saturated KNO_3 solution and 1.5 mg of Co(II) as nitrate solution was introduced. The pH was carefully raised to 6.0 by KOH solutions and adjusted by HNO_3 solution (0.1 mol/L). When 3mL 0.1 mol/L solution of HMDTC- was introduced, the desired pH was established again with a few milliliters of 0.1 mol/L HNO_3 . During 15 min of stirring, Co(II) oxidized to Co(III), and a green precipitate of $\text{Co}(\text{HMDTC})_3$ occurs that act as collector for our metals./16/.

During this process, analytes were taken up in this collector. At the end of stirring, 1ml of sodium dodecyl benzene sulfonate solution was added. The combined glass electrode was washed by the electrolyte NH_4NO_3 (0.1 mol/L), which served to transfer the contents of the beaker into the flotation cell so the medium Ic was not changed.

2.3.2.2. Separation by Air Bubbles

A stream of air bubbles (50ml/min) was passed from the bottom of the cell for 1 min, raising the precipitate flakes of the system to the water surface. The glass pipette tube was immersed into the cell through the froth layer and the liquid phase was sucked off. The water phase was drawn out and the solid phase left in the cell was decomposed by 5ml hot 65% HNO_3 . The clear red solution was sucked off through the sintered bottom of the cell and collected in a 25-ml flask. The flotation cell and a glass pipette tube were washed twice by 5mL of hot 4 mol/L HNO_3 solution. At the end, the flask was filled up to the mark by redistilled water and the sample was ready for AAS /16/.

3. RESULTS AND DISCUSSION

3.1. Ion Exchange Results

The effects of pH, Purolite Aminophosponic S-940 dosage, initial metal concentration and contact time were investigated for determination of optimum conditions and adsorption isotherms.

3.1.1. Effect of pH

The sorption of metal ion on the Purolite Aminophosponic S-940 resin was studied at pH range of 1.0-7.0. Buffer solutions of potassium hydrogen

phthalate–HCl and potassium dihydrogen phosphate–NaOH were used for pH adjustment. As seen in Fig. 1, quantitative retention was obtained at the pH 5.0 for copper and lead. Experimental conditions showed concentration of metals 10 mg/l-1, resin amount 500 mg and contact time 60 min. At pH 5.0 the highest retention of copper and lead was seen.

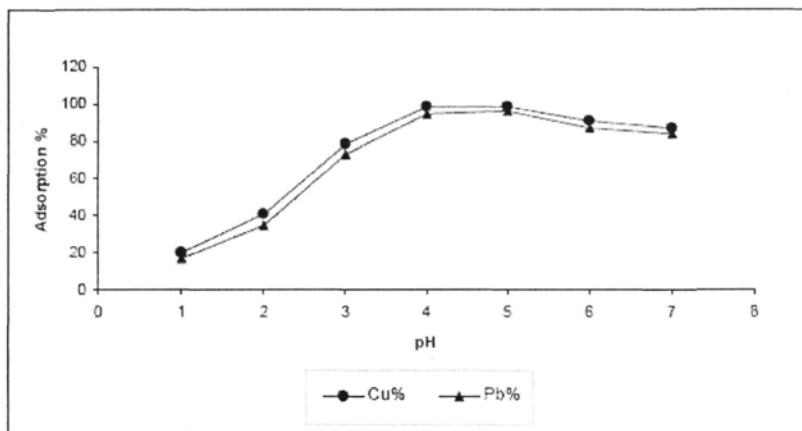


Fig 1: The effect of pH on the retention of metals on Puro-lite S-940

3.1.2. Effect of resin amount on metal adsorption

The resin amount is the other important parameter for obtaining quantitative recovery. Thus, the effect of amount of resin on the sorption concentration of metals 10 mg l-1, contact time 60 min., at pH 5 for copper and lead were examined in the range 5 - 1100 mg of resin. The results in Figure 2 give the effect of resin amount on metal adsorption. The results demonstrated that metals were quantitatively recovered by 400- 600 mg. Therefore, in subsequent experiments, 500 mg of resin was used.

3.1.3. Effect of contact time

The effect of time on the adsorption of metal ions by the resin was studied by taking 0.5 g Puro-lite Aminophosphonic S-940 hydrogen form with 10.0 ml of a metal salt solution of a metal ion in different stoppered flasks. The flasks were shaken for different time intervals. The effect of contact time on adsorption of Cu(II), Pb(II) using Puro-lite Aminophosphonic S- 940 resin are shown in Fig. 3. The results show that the percentage of metal ions and Puro-lite Aminophosphonic S-940 resin sorption increased with increasing time

of equilibration and it reached the plateau value at 60 min for Cu(II) and Pb(II).

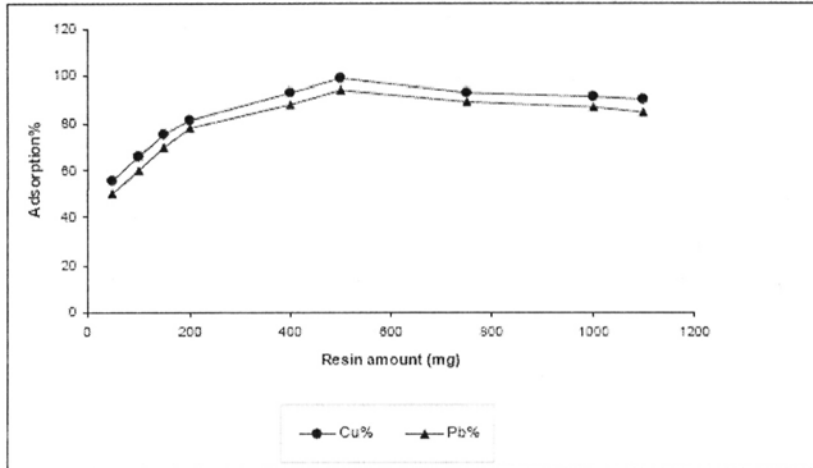


Fig.2: The effect of resin amount on the retention of metals

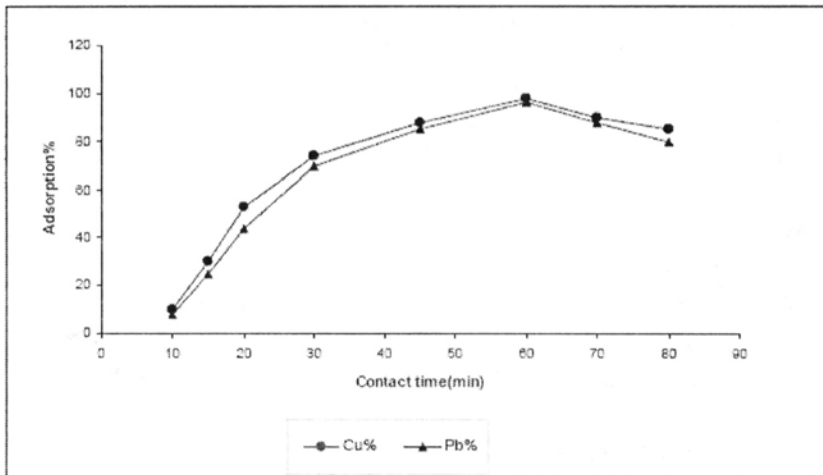


Fig.3: The effect of contact time on the recovery of metals

3.1.4. Effect of initial metal concentration

The effect of initial concentration on the capacity of sorption is shown in Figure 4 where the data obtained at the end of the experiment are given. Percent removal of Cu(II), Pb(II) ions determined at given contact times in

the range of between 5 and 1000 mg l⁻¹ concentrations of metals. The pHs of the solutions were adjusted to 5 with acetate buffer solution for Cu, and Pb, respectively.

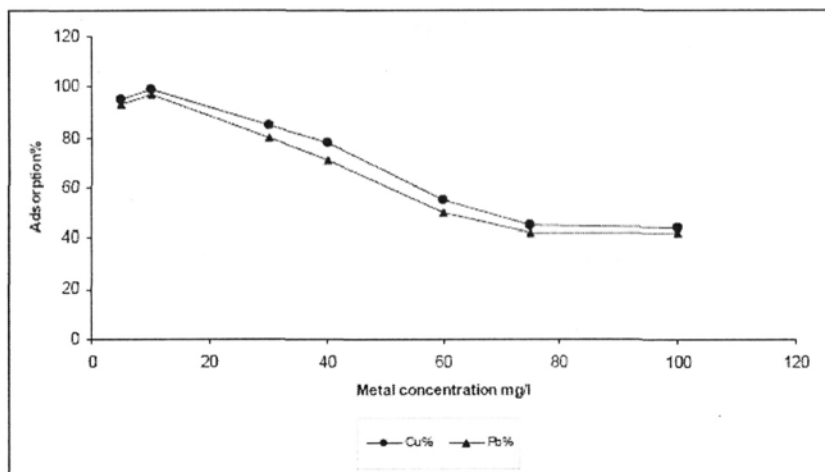


Fig. 4: The effect of initial metal concentration

3.1.5. Eluent type and eluent volume for desorption of Cu and Pb Ions

Desorption of Cu, and Pb ions from resin was investigated by using various eluting agents. The effects of 10 ml of various eluents on the recoveries of Cu and Pb on Purolite Aminophosphonic S-940 resin were studied at the model solutions containing 10 mg l⁻¹ of metal ions. The recovery values for metal ions by using 1 M HCl, 1M HNO₃, 2M HNO₃, 3M HNO₃, and 4M HNO₃ were 90±1, 92±2, 95±2, 98±2, and 101±1, respectively. The quantitative recoveries of metals were obtained by using 4M HNO₃ as an eluent. Quantitative recovery values for analytes were obtained using 10.0 ml of 4 M HNO₃.

3.1.6. Adsorption Isotherms

The Langmuir model can be explained as follows [18]:

$$q = (q_{\max} \times b \times C_e) (1 + b \times C_e)^{-1} \quad (1)$$

where q is milligrams of metal accumulated per gram of the adsorbent material; C_e (mg l⁻¹) is the metal residual concentration in solution; q_{\max}

(mgg^{-1}) is the maximum specific uptake corresponding to the site saturation and b is the ratio of adsorption and desorption rates or related to the affinity between sorbent and sorbate. This is a theoretical model for monolayer adsorption. For the fitting of experimental data, the model was linearized as follows:

$$\frac{1}{q} = (q_{\max} \times b)^{-1} \times (C_e)^{-1} + (q_{\max})^{-1} \quad (2)$$

Another empirical model for monolayer adsorption is Freundlich equation which deals with heterogenous surface adsorption and can be explained:

$$q = K \times C_e^{\frac{1}{n}} \quad (3)$$

where K and n are Freundlich constants. This equation is easily linearized by plotting it in a log-log format.

$$\log q = \log K + \frac{1}{n} \times \log C_e \quad (4)$$

The Langmuir Model and the Freundlich Model were applied to experimental data. The correlation coefficients obtained from the Langmuir and Freundlich equations were for Cu 0.995 and 851 for Pb 0.991 and 955.

The Langmuir adsorption model was in correlation with the experimental data for copper and lead experimental data. Langmuir and Freundlich equation parameters are shown in Table 3.

The fitness of the Langmuir model for this system indicates that the monolayer coverage of metals on the outer surface occurred uniformly on the active part of the surface.

Table 3
Values of Constans of the Langmuir and Freundlich Models

METALS	LANGMUIR			FREUNDLICH		
	q_{max} mg/g	B l/mg	R ²	K L/g	n	R ²
Cu	20.00	1.21	0.995	0.34	0.642	0.851
Pb	11.92	1.47	0.991	1.18	0.416	0.955

3.2. Flotation Results

Flotation method was applied with Co(HMDTC)₃ for heavy metal separation and analyses including drinking waters; treated waters and filtered raw waters from Turkey. Water samples were floated, 40-fold concentrated, and tested by FAAS Results are shown in Table 2. The recoveries show the successfulness of the preconcentration and separation of Cu and Pb by the recommended procedure. The recommended preconcentration procedure is rapid (about 25 min) and extends the range of conventional AAS determination of heavy metals. The necessary equipment for flotation is simple and inexpensive. The use of a small amount of surfactant and tiny air bubbles necessary to perform the proper flotation cannot permit some serious contamination risks, which could be manifested by the high blank values.

4. CONCLUSION

Two methods; ion exchange and flotation, were used for the preconcentration of Cu(II), and Pb(II) ions in natural water. The ion exchanger resin as Purolite Aminophosponic S-940 examined in this paper provides a simple, rapid, accurate and reliable technique for the preconcentration of metals separation from water samples. The recovery yields obtained with standard metal solutions in deionized water were 95% for Cu 90% for Pb and the lowest detection limit for Cu(II) and Pb(II) based on three times the standard deviations of the blank (k=3, N=21) was 0.010 µg/l respectively. Detection limit can be improved by larger volumes of

sample. Flotation technique with $\text{Co}(\text{HMDTC})_3$ as collector can be used for the successful determination of trace elements. The flotation recoveries achieved were higher than 99%. The benefit of this method is the elimination of matrix interferences on Cu and Pb ions determination. Flotation procedure is rapid and extends the range of conventional AAS determination of heavy metals. Flotation equipment is simple and inexpensive.

Symbols

- AAS: Atomic Absorption Spectrometry
FAAS: Flame Atomic Absorption Spectrometry
ISKI : Water Authority for Istanbul
q: milligrams of metal accumulated per gram of the adsorbent material
 C_e : metal residual concentration in solution
qmax : maximum specific uptake corresponding to the site saturation
K and n : Freundlich constants
b: ratio of adsorption and desorption rates
Ic: Ionic Strength
HMDTC: Hexa methylene di thio carbamate

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