

*Full Length Research Paper*

# Adsorption in column of Cu (II), Ni (II) and Pb (II) with XAD-7 resin impregnated with bis (2-ethylhexyl) ammonium bis (2-ethylhexyl) dithiocarbamate (BEABEDC) in aqueous solution

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The extraction of copper, nickel and lead in mini-column pack of resin XAD-7, impregnated with BEABEDC was realized by varying the concentration of metallic solution, flow rate of elution in the case of copper in order to carry out the kinetic exchanges which govern the system. These experiments were carried out in acidic region. Extraction chromatography is combined with the spectrometer of atomic absorption for analysis of solution collected after extraction. The experimental data have been integrated into Langmuir adsorption model. Cu (II) can be desorbed using H<sub>2</sub>SO<sub>4</sub> 4M when the temperature is elevated to 50 °C.

**Key words:** Extraction chromatography, Copper Lead, Nickel, mini-column, resin XAD-7 impregnated, langmuir adsorption model, BEABEDC.

## INTRODUCTION

The impact of heavy metals on environment due to development with industrial wastes resulting from human activities is a real problem that encourages national and international institutes to set requirements to industries whose influents contain heavy metals [Davis et al., 2001; Gove et al., 2001; Singh et al., 2005]. For example, in USA, the daily maximal concentrations of finishing metals discharged in municipal network sewer are in mg/L: Cd 0.69; Cr 2.77; Cu 3.38; Pb 0.69; Ni 3.98; Ag 0.43 and Zn 2.61. This strengthening of limits is essentially attributable to the continued progress of industrial production and to development of knowledge to heavy metals toxicity that integrates human food chain for accumulation in plants and animals. It is due essentially to their non-biodegradability [Blais et al., 1999; Sigg et al.,

2001; Fiset et al., 2000]. The characteristics and treatment of domestic effluents are well known, as industrial wastes pose a great problem because of their diversity and composition [Brooks, 1991]. Most technologies are available to remove metals from industrial waste including the following: precipitation (in hydroxide and sulfur form) [Alfassi, 1992], solvent extraction [Zolotov et al., 1986; Hayes, 1985], ion exchange [Walton and Rocklin, 1990; De Dardel, 1998; Hellerich, 1995], extraction chromatography [Braun and Ghersini, 1975], cementation [Doridot et al., 2006; Bramat, 2007; Passier et al., 1993; Ageledis et al., 1985], electrodepositing [Addach et al., 2006; Millon, 1985] and membrane separation technology [Crini and Badot, 2007]. In our works, extraction of heavy metals technology with impregnated resin has been used to extract copper and other metals in solution with macroporous support [Horwitz et al., 1997; Draa et al., 2004]. The resin is used as stationary phase in extraction chromatography and technology application [Braun and Ghersini, 1975; Horwitz et al., 1992; Menon and Agrawal, 1992]. The extraction of copper, lead and nickel in mini-column pack of resin XAD-7 impregnated with bis (2-ethylhexyl) ammonium, bis (2-ethylhexyl) dithiocarbamate

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**Abbreviations:** BEABEDC, Bis (2-ethylhexyl) ammonium bis (2-ethylhexyl) dithiocarbamate; H<sub>2</sub>SO<sub>4</sub>, Sulfuric acid.

(BEABEDC) was carried out by varying the metallic solution concentration for pH and flow rate constants. To carry out the kinetic exchange that governs the system, the flow rate effect of elution was studied in the case of copper only. The absorption isotherms of metals are plotted in using results of experiments previously cited. The objective of this study is to set up a method of extracting heavy metals from industrial wastes by using impregnated resin which can be regenerated for several uses.

## MATERIALS AND METHODS

### MATERIALS

The polymeric support used is Amberlite XAD-7 (Rohm and Haas Company), with acrylic resin slightly polar (20-60 mesh), having a specific area of 450 m<sup>2</sup>/g and 90 Å to pore diameter. It comes in the form of white ball with pH 7 to 8. It is stable in normal condition and its decomposition can generate vapor of monomers. It is used in process of ion exchange and in/or adsorption.

To purify, wash and impregnate the resin, we used acetone and prepared HNO<sub>3</sub> 0.1 M solution by dilution from a concentrate solution of 67.5%. The extractant BEABEDC, which is a new derivative to dithiocarbamate, is synthesized [Fall et al., 1999] in the laboratory.

Metallic's solutions have been prepared with standard solutions to 1000 ppm: Copper ; 3.802g Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O /2 to 5% HNO<sub>3</sub>; Nickel ; 4.953 g Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O /2 to 5% HNO<sub>3</sub> and lead ; 1.599 g Pb(NO<sub>3</sub>)<sub>2</sub> /2 to 5% HNO<sub>3</sub>, from Spectro ECON.

The scale XS603S Mettler Toledo used for weighing the mass of resin, pH-meter PHM 210 to Meterlab™, was used for the measurement of pH. In these experiments, we used a column of glass from Omnifit of interior diameter (0.66 mm). Ismatec pump peristaltic, Redifrac collector fractions to Pharmacia Biotech and plastic tubes for connexion to the inlet and outlet of the column are also used. The spectrometer of atomic absorption used for analysis of collected fractions is from Thermo Electron Corporation.

### METHODS

#### Purification of the resin XAD-7

The resin is washed to remove all impurities. 400 g of commercial resin XAD-7 is immersed in one liter of acetone and left over night. The mixture is filtered and rinsed with acetone and then resin dried at rotary evaporator. It is again immersed in HNO<sub>3</sub> solution 0.1M and left over night. It is filtered and rinsed with distilled water and acetone, then dried at rotary evaporator. After dryness, resin is immersed once more in acetone for a whole night. We filtered, washed with acetone and dried at rotary evaporator. For removing acetone traces, we filtered under vacuum to be sure the resin is well dry. Thus we obtained a resin ready to be impregnated.

#### Impregnation of resin XAD-7

32 g of extractant BEABEDC were diluted in 200 cm<sup>3</sup> acetone. 80 g of washed resin is immersed in this solution and agitated with a magnetic agitator for at least three hours. We filtered and dried at rotary evaporator. The impregnated resin is dry and ready to be used.

#### Experimentation

The metallic solution of concentration 10<sup>-4</sup> to 10<sup>-5</sup> M has been

prepared with a metallic standard solution to 1000 ppm. The column was packed with impregnated resin that was immersed in nitric acid solution for three hours, just as pH to metallic solution to elute. The packing was realized so that cracking space for grains was minimized. In all experiments carried out, passing of metallic solution is done to pH 2 (acidic region) and flow rate elution at 150 mL/h. In the study of the kinetic of exchange, we varied the flow rate from 150 to 300 mL/h.

A fraction of 10 mL has been collected in glass tube and then analyzed with atomic absorption. If the analyzed solution is too concentrated, a dilution is realized so that this value could be located in calibrate curve.

## RESULTS AND DISCUSSION

### Effect of concentration in the amount of metal

The amount of metals varies from 1.7141 to 0.7453 mg; 6.1884 to 1.9707 mg and 0.5989 to 0.0848 mg for copper lead and nickel respectively when the concentration of metallic solution decreases. The study of the effect of concentration in the amount of metal is realized in using a column to little length comparable to micro-column. Figures 1 to 3 showed that a breakthrough curve (ions which entry has been preferred compared to the ion present in the column) has formed in this column during the passing of metallic solution. The integration of breakthrough curve determines the amount of metal not retained (outlet) q<sub>s</sub>. From the total volume and the concentration inlet of solution, the amount of metal introduced is then known as q<sub>i</sub>. The amount of metal retained by the resin is obtained with the difference between q<sub>i</sub> and q<sub>s</sub>.

All figures show that an ionic leak [Conference and Seminar Collection, 1972; Boumediene and Achour, 2004; Gressier, 2008] happened from the starting of passing on the residence time τ. This leakage is defined by the link between the concentration outlet of ion and the concentration inlet of the same ion that is written in this form:

$$F(t = \tau) = \frac{C_{A_s}(t = \tau)}{C_{A_0}}$$

Considering the column, the low concentrations of solution and higher flow rate, we can predict the fact that the step time of solution in column will be flash. The step time is insufficient so that ions cannot get over the film. One part of ions passes through the column "never has seen resin". A leakage was observed and is nearly constant for rather a long time. We have then a plateau called "leakage plateau". This leakage plateau is obviously more than copper and lead. This leakage plateau is observed too when As, Cd and Pb solutions have been passed in a column pack of resin XAD-7 impregnated with BEABEDC, but with a rather limit flow rate and a flow rate of 24 mL/h [14, Wakui et al., 1998].

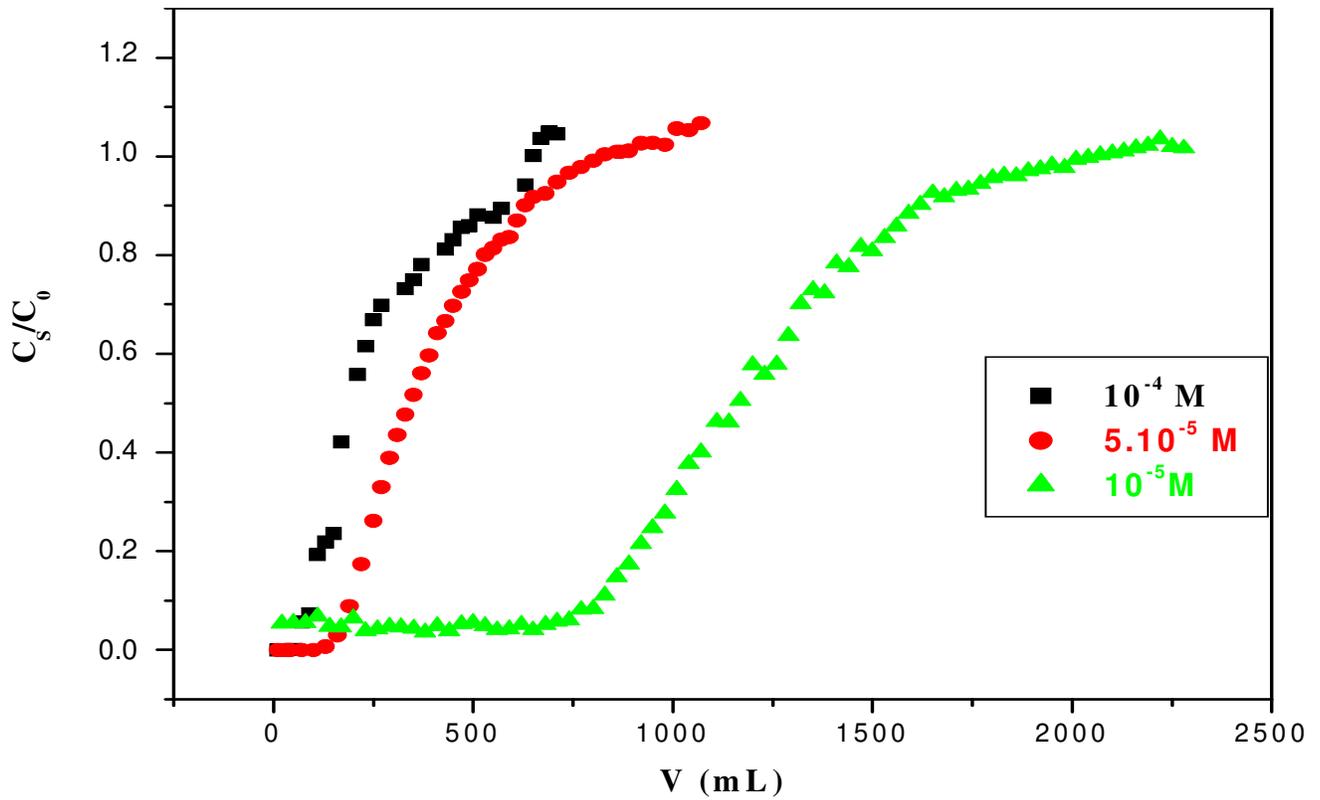


Figure 1. Breakthrough curve of Copper at various concentrations, pH = 2.1; Flowrate = 150 mL/h.

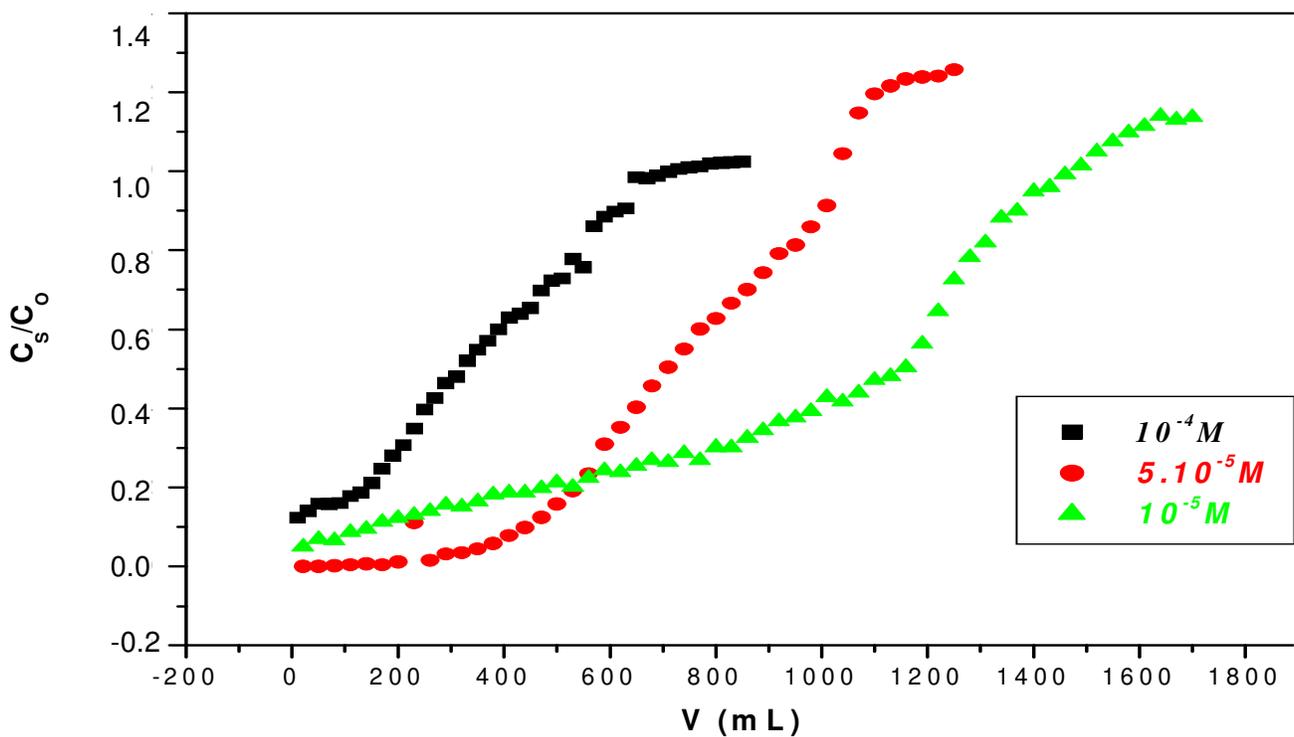


Figure 2. Breakthrough curve of lead at various concentrations; pH = 2.1; Flow rate = 150 mL/h.

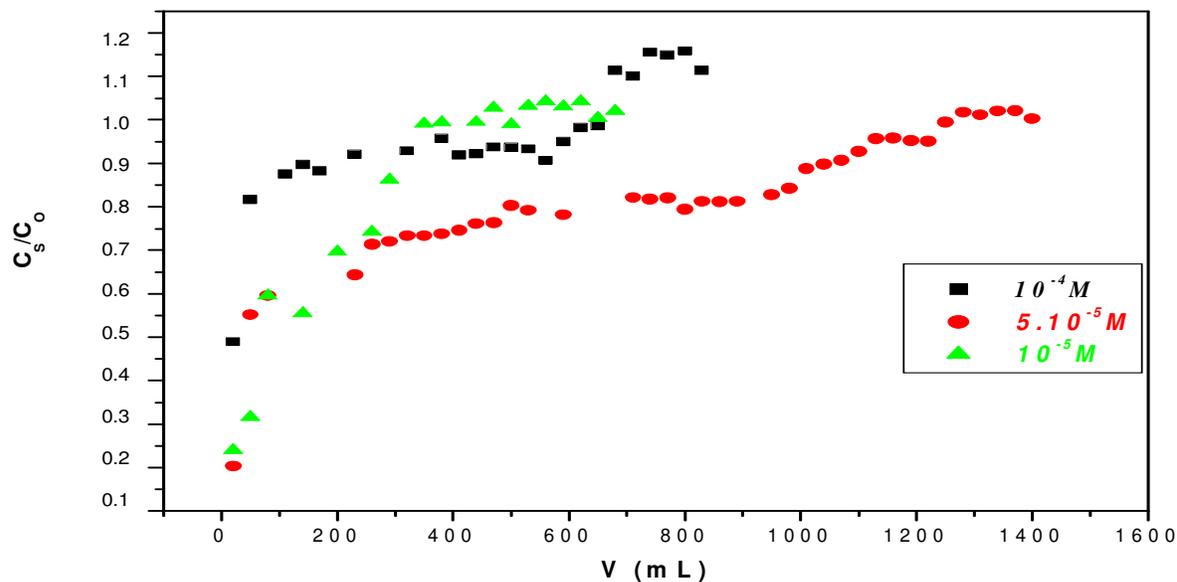


Figure 3. Breakthrough curve of Nickel at various concentrations, pH = 2.1; Flow rate = 150 mL/h.

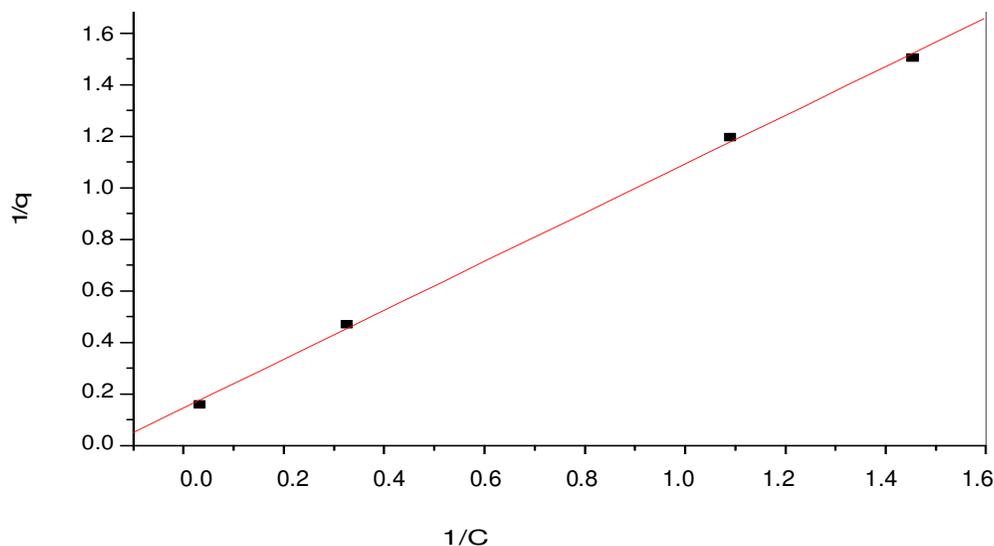


Figure 4. Adsorption isotherm of copper.

### Adsorption isotherm

The adsorption technology is based on a selective adsorption (thermodynamic or kinetic) of various constituents and fluid (gas or liquid) by adsorbents. This is possible through specific interactions between the adsorbents areas and adsorbed molecular. One of the essential characteristics of the adsorption technology is functioning in the transitory; being cyclic generally, in which after an adsorption phase, the adsorbents are regenerated partially or totality for another use [Meunier and Sun, 2003; Meunier et al., 2005].

In this study, Vander Waals's forces and probably other forces due to polarization essentially lead to the fixation of metals in adsorbent molecular. The Van der Waals's interactions are naturally electrostatic, quite weak and the released energy when a molecular is physically adsorbed is the same size with that of the enthalpy [Gubbins et al., 1997].

The curve can be plotted with  $1/q = f(1/C)$  of copper and lead (Figures 4 and 5), which are characteristic of linear representation to Langmuir isotherm in general form  $Y = A + B.X$ . The common two-parameter Langmuir equation is given by:

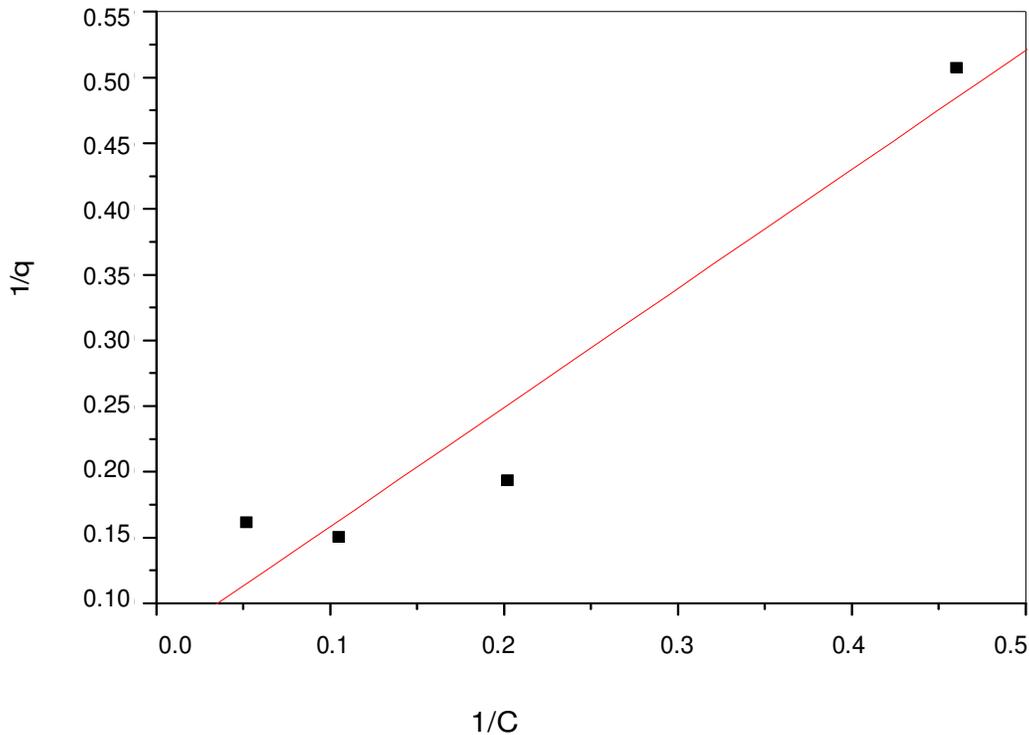


Figure 5. Adsorption isotherm of lead.

Table 1. Isotherm parameters.

| Isotherm parameter    | Copper | Lead   | Nickel  |
|-----------------------|--------|--------|---------|
| Q <sub>0</sub> (mg/g) | 6.806  | 14.738 | - 5.969 |
| b (L/mg)              | 0.155  | 0.075  | -0.0254 |
| R                     | 0.9994 | 0.9642 | 0.9907  |

$$\frac{1}{q} = \frac{1}{q_0 K_L C_e} + \frac{1}{q_0} \quad (I) \quad \text{With} \quad A = \frac{1}{q_0} \quad (III) \quad \text{and} \quad B = \frac{1}{q_0 K_L} \quad (IV)$$

according to equation of Langmuir isotherm

With the software used, the various parameters, A (origin ordinate) and B (gradient) permit us to deduce the maximal adsorption capacities  $q_0$  and Langmuir constants  $K_L$ . A, B and the correlation coefficient R are the characteristics of Langmuir isotherm.

The correlation coefficients are close to 1, particularly of copper.

Table 1 showed that experimental data are therefore in correlation with Langmuir isotherm equation. Nature of ion (average, charge, etc.) plays an important part in the retention of metallic species for impregnated resin. Indeed, maximal adsorption capacity of lead is higher than those of copper but comparing the values of Langmuir constant of two ions, we can say that resin has a highest affinity for copper than lead and nickel.

### Kinetic of exchange

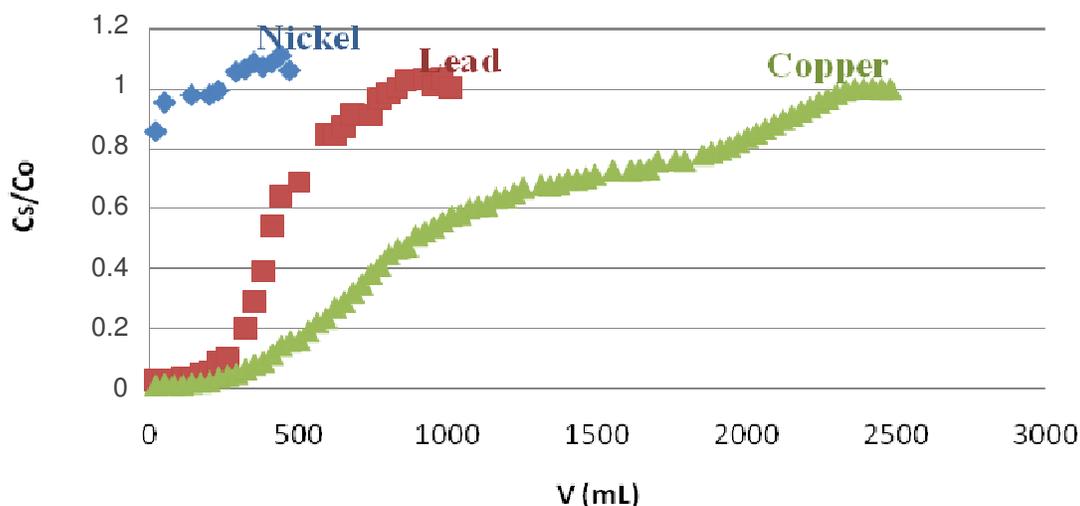
The study of influence of flow rate is carried out in passing a metallic solution to copper at concentration of  $10^{-5}M$  at various flow rates of 150 at 300 mL/h. We have calculated parameters  $\tau$  and  $t_e$  which are respectively residence time for the solution in column and external transfer time to the solution in resin. For each flow rate, we can calculate the leakage average concentration for a number of volumes and concentration input. From the leakage and  $\tau$ , we can deduce the value of  $t_e$ . The leakage is given by the following expression [Meunier and Sun, 2003]:

$$F = \frac{C_{output}}{C_{input}} = \left[ 1 + \frac{\tau (1 - \epsilon)}{J} \frac{6}{\epsilon t_e} \right]^{-J} \quad (III)$$

From this expression, external transfer time  $t_e$  is deduced:

**Table 2.** Variation of flow rate.

| Flow rate                   | 300 mL/H | 200 mL/H | 150 mL/H |
|-----------------------------|----------|----------|----------|
| $C_0$ (mg/L)                | 0.6354   | 0.6354   | 0.6647   |
| $C_{\text{average}}$ (mg/L) | 0.0622   | 0.0379   | 0.0304   |
| J (Number of mixers)        | 94       | 94       | 94       |
| $\tau$ (s)                  | 18.63    | 27.61    | 36.82    |
| $t_e$ (s)                   | 71.2     | 86.8     | 105.64   |
| F (Leakage)                 | 0.0979   | 0.0596   | 0.0457   |

**Figure 6.** Breakthrough curve of mixture of Copper, lead and nickel.

$$t_e = 6 \frac{1 - \varepsilon}{\varepsilon} \frac{\tau}{J} \frac{1}{\left[ \exp\left(\frac{\ln F}{J}\right) - 1 \right]} \quad (IV)$$

$\tau$ , J and  $V_b$  are respectively step time, number of mixers and volume in bed of resin which are given by the following expressions:

$$\tau = \frac{\varepsilon \times V_b}{W} \quad (V)$$

$$J = \frac{h}{4 \times d_g} \quad (VI)$$

$$V_b = h \times S = \frac{\pi h d^2}{4} \quad (VII)$$

$\varepsilon = 0.4$  ; is porosity of bed resin, h corresponds to the level of bed resin in cm,  $d_g$  diameter of resin in cm,  $V_b$

volume of bed resin in mL, W flow rate in mL/s.

The decreases of flow rate leads to the increasing of step time in column like external transfer time of ion in resin. The results in Table 2 are in accordance with those funded by Monzie et al. [2002, 2001] who had studied influence of flow rate on  $t_e$  for extra pure water production by ion exchange. Indeed, when the flow decreases, cracking speed decreases. The thickness of limit layer  $\delta$  increases and therefore  $t_e$  increases too.

### Chromatographic separation

The separation of heavy metals is carried out in draining off a solution containing simultaneous copper, lead and nickel at concentration of  $1.5 \cdot 10^{-5} M$  with pH 2.1 and a flow rate of 150 mL/h.

Figure 6 shows clearly that in acidic region, a separation is quite possible. After flowing 500 mL of solution, the resin is already saturated in nickel; until 1000 mL resin is saturated in lead and hereafter resins retain only copper until 2500 mL. Then, we can conclude that resin impregnated prefer ions  $Cu^{2+}$  more than ions

Pb<sup>2+</sup> and Ni<sup>2+</sup>.

## Regeneration of resin

Most of ion exchanger resin used in scientific studies is regenerated using basics or acids solutions as NaOH, KOH, HCl, H<sub>2</sub>SO<sub>4</sub>, sodium citrate, EDTA (Burghoff et al., 2009). Then, we have realized a test for regenerating resin which retains copper.

The resin that has retained copper solution at concentration of 10<sup>-4</sup>M has been eluted with H<sub>2</sub>SO<sub>4</sub> 4M solutions. When elution is realized in batch, at high temperature (50°C), 25.26% of metal is eluted. With agitation for 8 h, 10.13% of metal is eluted.

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