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Study of the Complexation of Some Heavy Metals in Sight of Their Elimination by Ultrafiltration

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Abstract: In Algeria, the water becomes more and more rare, more and more assaulted; this country suffers for several decades from the aridity and from the pollution, the industries directly throw out in the natural environment without a preliminary treatment their waste water that volume and degrees of concentration are very variable what disrupts ecological balance and returns the treatment of industrial refusals necessary. The objective that we had settled by beginning this study was to determine the best conditions of complication of heavy metals, namely the pH of environment the complexant power of some ligands, the temperature, the speed of agitation, etc., in order to have a better separation by ultrafiltration. The analysis of the various metals in solution was realized by the volumetric method (Titration by the EDTA, citric and nitric acid). The experimental study of the reaction of complexation of heavy metals by the EDTA allowed us to say that elimination will be more important for the group of cations (Ca^{2+}, Mg^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Cu^{2+}); If the concentration of the ligand increases $[Y^{4-}]_{opt} = 10^{-3}$M. If the speed of agitation increases $V_{agi\ (opt)} = 750$ tr min^{-1}. If the temperature of environment increases $T_{opt} = 50°C$. If the pH of environment increases $pH_{opt} = 7$ (neutral environment). In our team of search, we were interested to change the ligand (EDTA) by other ligands (citric acid and nitric acid), we can directly say that volumetric method does not give results because reaction environment becomes acid and the (Titling) EDTA reacts with protons and there will be also a destruction reaction of the least stable complex. We drew the curves of return on ultrafiltration according to the concentration of the perméat (free cation) supposing that the quantity of the complexed cation is retained with the membrane.

Key words: Heavy metals, environmental, ultra filtration, complexation, elimination, EDTA

INTRODUCTION

Industrial world is more and more confronted with the problem of the control of emissions, in particular under liquid shape, heavy metals in the environment.

Complexity and difficulty of the problem result from the variety from the sources of discharge, the quantitative importance of rejected quantities and, finally, from the variety of metals and their toxicity.

In Algeria, the water becomes more and more rare, more and more assaulted; this country suffers for several decades from the aridity and from the pollution, the industries directly reject in the natural environment without a preliminary treatment their waste water that volume and degrees of concentration are very variable what disrupts ecological balance and returns the treatment of industrial discharges imperative.

MATERIALS AND METHODS

The objective that we had settled in the beginning of this study was to determine the best conditions of complication of heavy metals, namely the pH of environment, the complexant power of some ligands, the temperature, the speed of agitation, etc., in order to have a better separation by ultra filtration (Edeline, 1993).

The analysis of the various metals in solution was realized by the volumetric method (Titration by the EDTA, citric and acid nitric).

The experimental study of the reaction of complexation of heavy metals by the EDTA allowed us to say that elimination will be more important for the group of cations (Ca^{2+}, Mg^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Cu^{2+}).

Except instrumental methods, one distinguishes the volumetric methods which possess a big advantage with regard to the other methods (especially in the gravimetric analysis) as regards the speed of execution (Rodier, 1996).

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The acceleration of the dosage is obtained in that case because instead of weighing the product of the reaction, we measure the volume of the solution of reagent used, concentration of which is exactly known about us. Besides the preparation and the normalization of the reagent, the main stages of a volumetric dosage are:

- The experimental measure of volumes (and sometimes of masses) of sample and of reagent,
- The determination of the equivalent point, which often requires the choice of an indicator,
- The calculations of the expression of results (in the different units of concentration) reflecting precision.

We began the analysis with the method of atomic merger (result of the influence of the pH on the reactions of complexation) but we realized according to the bibliography that this method gives the total concentration of the metal (under the free shape and complexed); for it, it is necessary to make an origin of the complex then to analyze, in spite of all that the variation of the concentration of the cation studied in that case (Cu^{2+}) according to the pH decrease considerably (in agreement with the theory).

Parameters varied for various reactions are:

- Influence of the initial concentration of the ligand on the reactions of complexation,
- Comparison of the ability to react of some metals according to the initial concentration of the ligand (EDTA),
- Influence of the variation of the nature of the ligand,
- Influence of the speed of agitation on the reactions of complexation,
- Influence of the temperature on the reactions of complexation,
- Influence of the pH on the reaction of complexation ions Cu^{2+},
- Influence of the perméat concentration on the return on the method of separation by ultrafiltration (Jean, 1989).

RESULTS AND DISCUSSION

Influences the initial concentration of the ligand (Zinc case, calcium, cadmium, copper, mercury, magnisum): We can notice according to it Fig. 1 that the increase of the initial concentration of the ligand EDTA engenders the quantitative elimination of the cation Zn^{2+} until a value of 5×10^{-4}M, from this value the elimination (complexation) of Zn^{2+} is total (Alexeev, 1990).

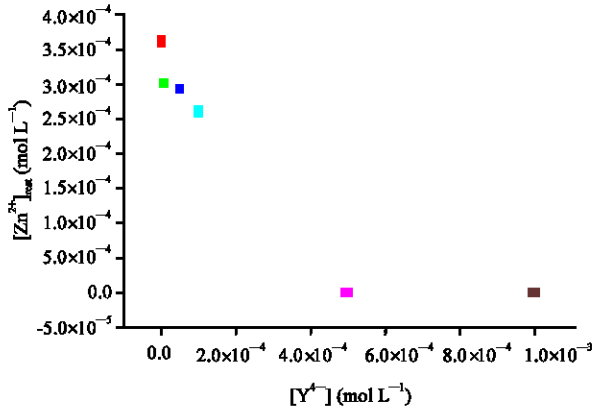

Fig. 1: Influence of the initial concentration of the ligand EDTA on ions Zn^{2+}

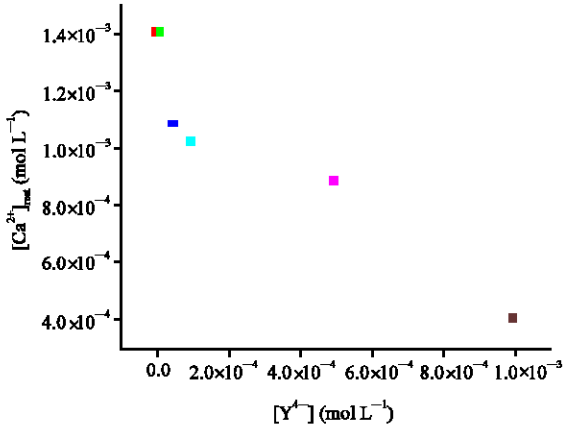

Fig. 2: Influence of the initial concentration of the ligand EDTA on ions Ca^{2+}

In the same way, we notice according to it Fig. 2 that the increase of the initial concentration of the ligand EDTA favors the quantitative elimination of the cation Ca^{2+}, in the concentration of EDTA of 2×10^{-3}M, the elimination of Ca^{2+} is total.

For the cation Cd^{2+} elimination is almost total in a concentration of the ligand EDTA of 1×10^{-3}M, Fig. 3 shows the variation of the concentration of Cd^{2+} with the increase of the initial concentration of the ligand EDTA which favors elimination quantitative of the cation Cd^{2+}. On the other hand, the Fig. 4 shows the variation of the concentration of the cation Cu^{2+} according to the concentration of the ligand Y^{4-} and we notice that for a concentration of this last is equal to 5.10^{-4}M, the elimination of the cation is total.

The same thing for the cation Hg^{2+}, we notice that the increase of the concentration of the ligand provokes the almost total elimination of the cation in a concentration of 5.10^{-4}M (Fig. 5).

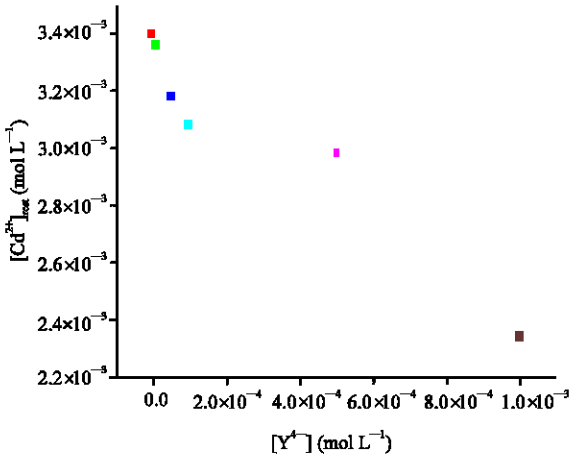

Fig. 3: Influence of the initial concentration of the ligand EDTA on ions Cd^{2+}

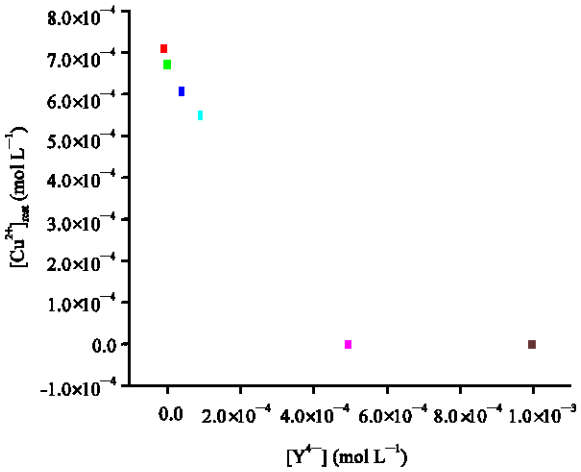

Fig. 4: Influence of the initial concentration of the ligand EDTA on ions Cu^{2+}

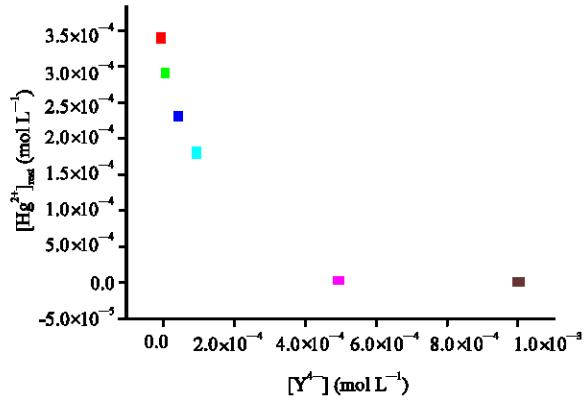

Fig. 5: Influence of the initial concentration of the ligand EDTA on ions Hg^{2+}

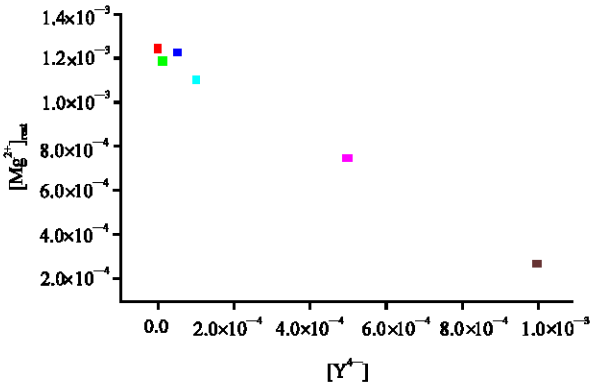

Fig. 6: Influence of the initial concentration of the ligand EDTA on ions Mg^{2+}

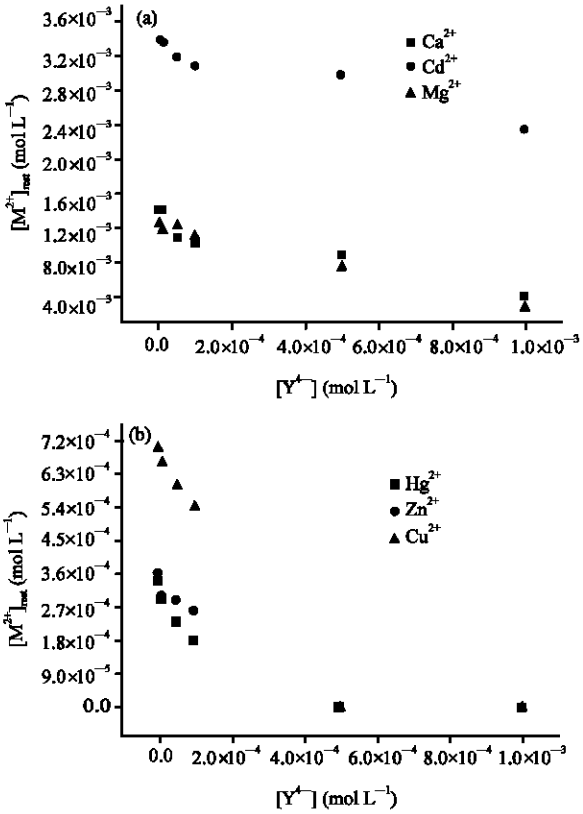

Fig. 7a, b: Comparison of the ability to react (complexation) of some cations with the various initial concentrations of the EDTA

According to Fig. 6, we notice that the total elimination of the cation Mg^{2+} is equivalent to the concentration of the ligand Y^{4-}de 1.10^{-3}M.

Comparaison of reactivity (ability to react) of some metals: In seen to compare the quantity of cations complexed by the EDTA we have to draw the Fig. 7

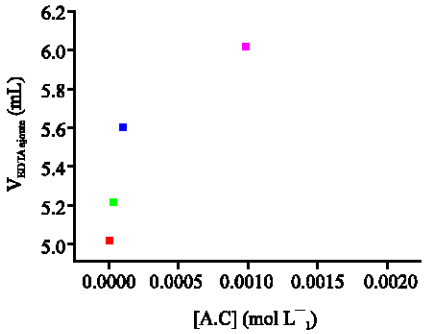

Fig. 8: Influence of the initial concentration of the nitric acid ligand on the volume of added EDTA

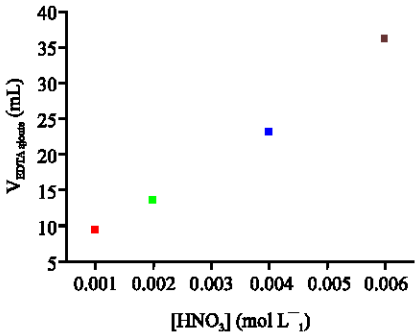

Fig. 9: Influence of the initial concentration of the citric acid ligand on the volume of added EDTA

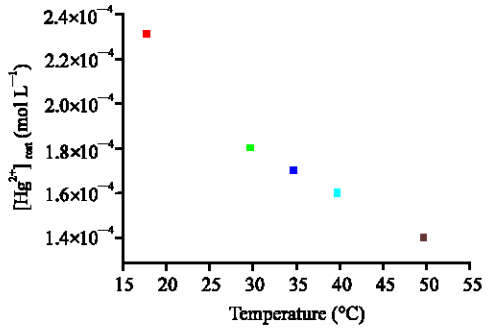

Fig. 10: Influence of the agitation on forming of complex

which present free cations (not complexed) according to the various concentrations of EDTA, we can notice that cation least complexed is Cd^{2+} (Bregeault, 1992).

Influence of the nature of the ligand: In these experiences, we were expecting that the EDTA's volume (of the titration) decreases if the concentration of the nitric Acid ligand increases, obtained result is against what it is supposed, it can be explained by secondary reactions which take place, they are reactions of protonation of the EDTA and as the complexométrique

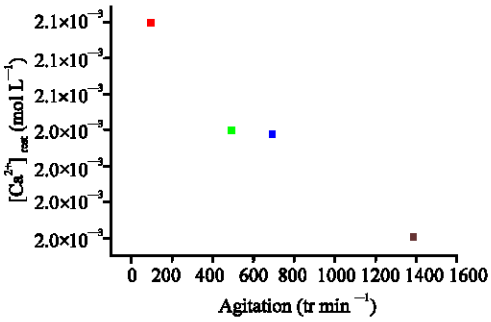

Fig. 11: Influence of the temperature on forming of complex

titration by the EDTA is favored in alkaline environment, so the capacity of the complexometry by the EDTA decreases in the acid circles.

In the same way, we notice according to the Fig. 8 that the increase of the concentration of the citric acid provokes an increase of EDTA's volume.

To title, what is not waited; and that returns of same reason by contribution has the nitric acid, (Fig. 9) in spite of the citric acid is weaker than this last one. pKc (citric acid) = 8, 9.

Influence of the agitation: Figure 10 shows the variation of the concentration of the cation Hg^{2+} with the temperature; we notice that the increase of this last one favors the elimination of the mercury. The same thing for the agitation (excitement) (Fig. 11).

Influence the concentration of the permeat on the return on the ultrafiltration: We supposed that the complexed quantity of the cation is retained with the membrane of the ultrafiltration, the concentration of the permeat is so the concentration of the free cation (not complexed). We have to draw curves showing the influence of the permeat concentration on the ultrafiltration return which must be calculated with the following formula:

$$R = (1 - \frac{C_1}{C_0}).100$$

With: C_0 = Concentration in solution in the solution.
C_1 = Concentration in solution in the permeat.

Results presented in Fig. 12 show that if the concentration of the permeat decreases the return on separation by ultrafiltration increases, it means that a good return on separation is deducted by a big complexed part from the cation (Gal, 1980).

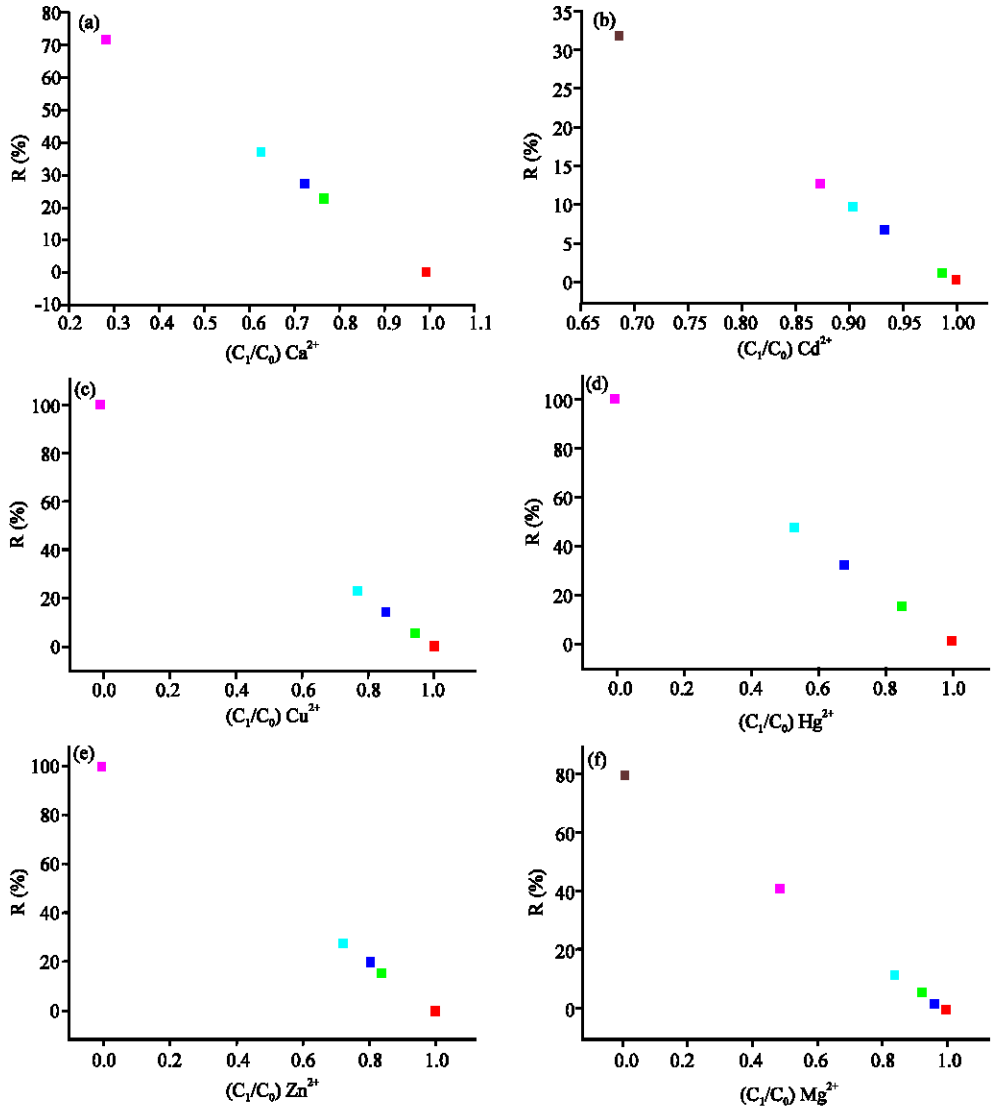

Fig. 12a-f: Influence of concentration of free metal (permeat) on the return of membrane

Rest to be madem: It would be interesting to improve this study to finalize a program of calculation which leads the modeling of curves giving the variation of the concentration of the free cation according to the pH, according to the initial concentration of the ligand, etc. …

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