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Heavy Metals Removal in Aqueous Solution by two Delta-diketones

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Abstract: This research presents the elimination of lead, coppers, zinc and iron by complexation with δ -diketones particularly, 1, 3, 5-triphenylpentane-1,5-dione and 3-furyl-1,5-diphenylpentane-1, 5-dione in liquid biphasic system (water/dichloromethane). Various factors (pH, nature and concentration in metal ions, time of contact, chelating capacity and temperature) influencing this interaction were examined. The use of these molecules in the complexation optimal conditions (Temperature = 35°C, Mass ratio $C_{\text{metal}}/C_{\text{extractant}} = 4$, Contact time = 30 min and pH 4), led to the elimination of more than 70% of lead, iron, coppers and zinc.

Key words: Heavy metals uptake, delta-diketones, liquid liquid extraction, complexation

INTRODUCTION

The water pollution by heavy metals is nowadays one of the major environmental problems. Indeed, at least 20 metals are classified as toxic and half of these are emitted into the environment in quantities that pose risks to human health (Kortemkamp *et al.*, 1996). Current methods were developed in order to eliminate these toxic elements from water (Blais *et al.*, 1999) among those, liquid-liquid extraction. However, the choice of new ligands remains a challenge to develop this technology, although various molecules were reported (Kavalieratos *et al.*, 2005; Nigond, 1992; Yong *et al.*, 1999; Namor *et al.*, 2000, Yang *et al.*, 2004). This study examines the possibility of the use of delta-diketones, particularly 1,3,5-triphenylpentane-1,5-dione and 3-furyl-1,5-diphenylpentane-1,5-dione as ligand for heavy metals removal. In order to define optimal experimental conditions, the system 1,3,5-triphenylpentane-1,5-dione and Pb was considered and the effects of various physicochemical factors on their interaction (pH, concentration in metal ions, duration of agitation, chelating capacity and temperature) were studied. Then these conditions were applied to Cu, Zn, Fe and 3-furyl-1, 5-diphenylpentane-1, 5-dione.

MATERIALS AND METHODS

Equipment and reagents: Concentrations of metals ion in the synthetic aqueous phase were performed on atomic absorption apparatus (Varian AA 300).

General procedure: The solvent (dichloromethane) was distilled prior to use. Synthetic aqueous solution samples were prepared with double distilled water and metallic nitrate. The aqueous phase (20 mL; at desired pH) containing the metal ions and an organic phase (20 mL) containing the ligand were mixed by agitation at 600 rpm during desired time, at room temperature (30±1)°C, excluded the tests implying the temperature effect. The pH of the aqueous phase was adjusted by addition of nitric acid or sodium hydroxide. After a 30 min decantation, the phases were carefully separate and the residual concentration of metal ions in the aqueous one was determined.

RESULTS AND DISCUSSION

Effect of pH on the removal of lead: Figure 1 shows the removal of Pb versus pH over the range of 2 to 4. The extraction percentage of lead ion increased with further increase of pH. For a Pb concentration of 300 mg L⁻¹, the rates of extraction in the range of pH indicated pass from 22.83 to 53.15%. It is apparent that the increase of removal is very strong between pH 2 and 3 while it is rather weak between pH 3 and 4. This observation can be explained by the Pb speciation diagram on which the Pb²⁺ is the predominant specie of lead when pH ranges from 2 to 3. Above pH 3 precipitated species appear. Moreover, at lower pH, protonation of chelating groups takes place. So complexation with available ligands is reduced and hence the percentage uptake decreases. But at higher pH,

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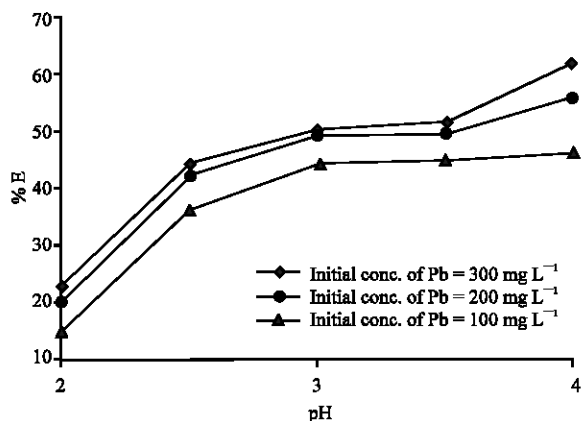


Fig. 1: Effect of pH on the removal of Pb, Extractant Conc. = 50 mg L⁻¹; Temp. = 30°C; Contact time = 30 min

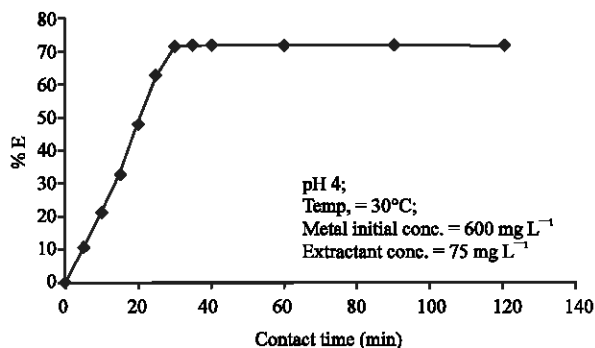


Fig. 2: Influence of contact time on the extraction of lead

deprotonation takes place and hence the percentage uptake increases. The optimal removal is obtained at pH 4, whatever the initial concentration of lead.

Effect of the time of contact (agitation duration): It is evident that the extraction increases with the contact time until 30 min. At this time 71.67 % of the lead is extracted. After this time, no extraction is observed (Fig. 2). The speed of the extraction can be explained by the presence of hydrophobic groups that present excellent complexants properties (Reddy and Reddy, 2003).

Effect of the initial concentration of lead: The effect of the initial concentration of lead (from 50 to 600 mg L⁻¹) on the extraction of the metal ion at pH 4 is given in Fig. 3. It appears a significant increase in the extraction of lead with an increase in the initial concentration of the metal ion from 50 to 300 mg L⁻¹. This observation is in accordance with the literature data (De le Chatelier, 1990). In a range of initial concentration from 300 to 600 mg L⁻¹ the increase in extraction is less significant. These observations are probably related to a saturation of the extractant. By

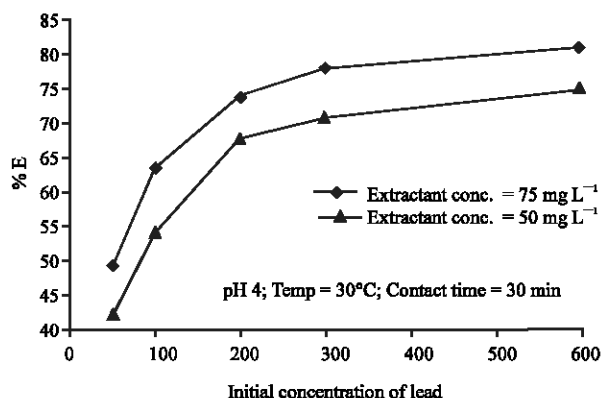


Fig. 3: Effect of the initial concentration of lead

considering the case of an initial metal concentration of 600 mg L⁻¹, the maximum rate of extraction is 80.91%. The residual metal concentration in the aqueous phase is then 114.54 mg L⁻¹. In the case of an initial metal concentration of 300 mg L⁻¹, the maximum extraction rate is 78.07%, that is to say a residual concentration in the aqueous phase of 65.79 mg L⁻¹. While taking into account, the total objective which is the maximum reduction of metals of the aqueous phase, it can be concluded that the extraction is better with 300 mg L⁻¹. Moreover, the extraction is better when the extractant concentration passes from 50 to 75 mg L⁻¹. It is thus important to study the impact of this parameter on the extraction.

Effect of extractant concentration: Figure 4 indicates an increase in the extraction of lead with concentration of extractant. Indeed, for values of concentrations ranging between 25 to 75 mg L⁻¹, the elimination of the metal ions varies from 53.65 to 78.07%. Beyond 75 mg L⁻¹, the rate of extraction decrease. All these observations seem logical. Indeed, the increase in the concentration involves an increase in the number of active sites and thus, the chelating capacity. The fall of the extraction with the high concentrations could be justified by an obstruction due to the great quantity of extractant molecules in the medium. The best results are obtained with 75 mg L⁻¹, corresponding to a mass ratio (metal/extractant) equal to 4.

Effect of the temperature: The results indicate that a rise in the temperature involves the increase in the extraction of the lead from 54.95 to 75%. This shows that the process of extraction is endothermic. However beyond 35°C, a fall of the extraction is observed (Fig. 5).

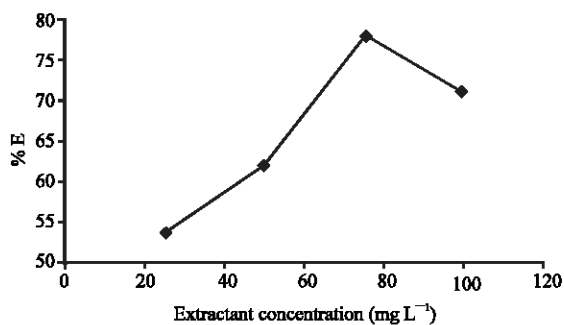


Fig. 4: Effect of extractant concentration of lead, pH 4; Temp. = 30°C; contact time = 30 min, Metal initial Conc. = 300 mg L⁻¹

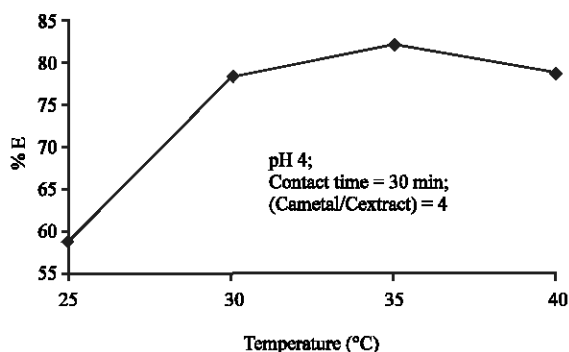


Fig. 5: Effect of the temperature on the extraction of lead

APPLICATION

According to the previous results the optimal conditions for the lead removal are defined:

- Temperature = 35°C,
- Mass ratio $\frac{C_{\text{metal}}}{C_{\text{extractant}}} = 4$
- Contact time = 30 min

The application of these conditions to various metals such as zinc, iron and copper gives the results in Fig. 6. It appears that, the eliminations rates are, respectively, 72.08, 71.23 and 69.41% for iron, copper and zinc. These values are lower than that obtained with lead. This observation can be explained by the ionic radii of the metal ions. Indeed it is reported that, the amount of uptake of the cations was related to the ionic radii (Tobin *et al.*, 1984). That is confirmed by Fig. 7 which presents a correlation coefficient (R^2) equal to 0.9237. That Fig. 7 shows that, when the ionic radius increases (or the hydrated radius decreases), the extraction increases. For example, lead (ionic radius = 122 pm; hydrated radius = 261 pm) shows a extraction rate

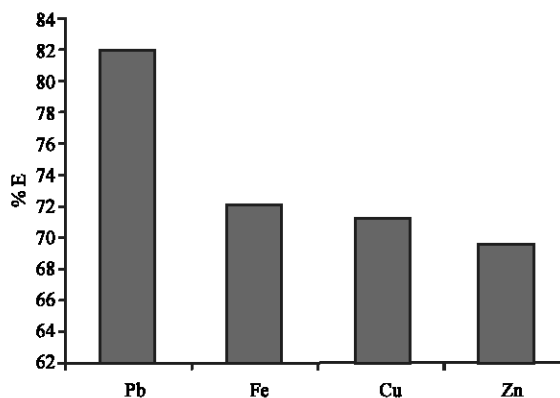


Fig. 6: Application of the optimal condition to various metals

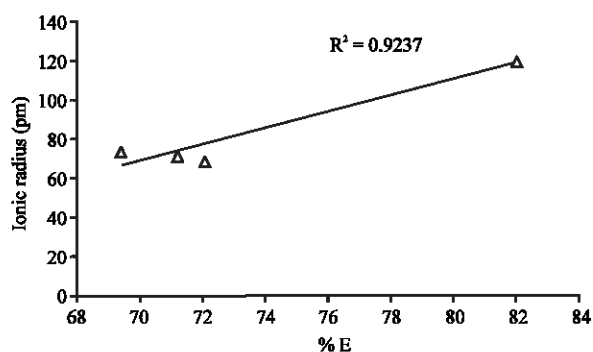


Fig. 7: Relationship between ionic radii and selectivity of ligand

of 82%, while copper (ionic radius = 72 pm; hydrated radius = 295 pm) is extracted with a rate of 71.23%. Other metals whose ionic radii are practically identical, do not present a significant difference in extraction rate. So, the smaller the hydrated radius of a metal, the better its complexation (Canet and Seta, 2001; Kaoser *et al.*, 2005).

Competition between metal ions: Let us note that this simultaneous presence involves a competition. It appears globally a decrease of the removal of each metal (20.26, 15.49, 13.55 and 11.34, respectively for Pb, Fe, Zn and Cu). Pb is the least supported by the presence of the other metal (Fig. 8). These observations are in agreement with those mentioned previously and confirm the relation between hydrated ionic ray and selectivity. It is however notable that in spite of this competition, all metal are nevertheless satisfactory complexed since the removal of each one of them is higher than 60%.

Comparative study of two ligands: The 1,3,5-triphenylpentane-1,5-dione (Compound I) and the 3-furyl-1,5-diphenylpentane-1,5-dione (Compound II). It appears generally that compound II presents an activity slightly

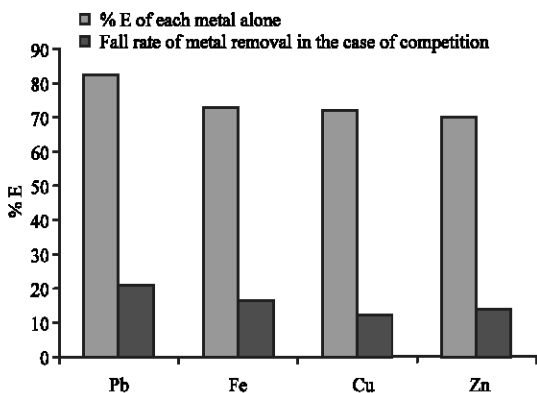


Fig. 8: Competitive extraction study of different metals ions

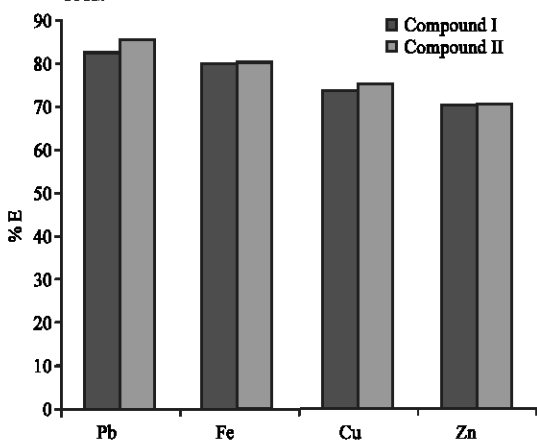


Fig. 9: %E as a function of ligands

better than compound I. Indeed in the first case, the rates of extraction vary from 85.05 to 70.15%, while in the second case; these rates vary from 82 to 69.14% Fig. 9. This observation is probably due to the presence in compound II of additional oxygen brought by the furyl group. This oxygen would be probably a site of coordination in the mechanisms of metal ions complexation. It thus seems that a way of improvement of the uptake capacity of these molecules would be to modify their structure, by fixing groups containing several heteroatoms such as carboxylic acid, hydroxyl or amino groups in 3-position.

CONCLUSIONS

In conclusion, it has been shown that the use of 1,3,5-triphenylpentane-1,5-dione and 3-furyl-1,5-diphenylpentane-1,5-dione for heavy metals removal from aqueous solution appears to be technically feasible with high efficacy. Although the tests were carried out on synthetic solutions, these molecules can be good candidates for treatment of wastewaters contaminated by heavy metals.

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