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ORIGINAL ARTICLE

Competitive extraction of Cu(II), Zn(II), Ni(II), and Mn(II) cations using acetyl acetone and benzoyl acetone as carriers

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Abstract The competitive metal ion extraction of Cu(II), Ni(II), Zn(II) and Mn(II) with acetyl acetone and benzoyl acetone were examined and compared with each other. The experiments were buffered (acetic acid/sodium acetate and formic acid/sodium formate) at pH 3–7. The extraction behaviors for Cu(II), using both acetyl acetone and benzoyl acetone are similar. In fact the extraction behavior for Cu(II) is much better than the other cations. The extraction results are closely parallel for the other cations using the present ligands. The concentration in extraction experiments for the cations and ligands used was 10 mM and 1.0 mM, respectively.

1. Introduction

Solvent extraction has been widely used as a pre-concentration method for analytical applications. Also, conventional solvent extraction involving chelating extractants (or ionophores) dissolved either in organic solvents or in water, is an important industrial technique for the recovery and refining of metals from dilute solutions (Brooks, 1993; Ismael and Tondre, 1994; Benedetto et al., 1995; Matsuyama et al., 1996; Seddon, 1997; Earle and Seddon, 2000). Solvent extraction processes based on simple organic complexing extractants are often used commercially for the recovery and purification of metal ions. Metal ion extraction depends on ligand structure, pH of solution, type of solvent, temperature and time of extraction. The requirement to limit industrial waste in the natural environment is responsible for the increase in the number of research programs devoted to the improvement of technical processes for the separation and recuperation of valuable and/or toxic species (Canet and Seta, 2001). There have now been a considerable number of investigations of the competitive transport and solvent extraction of transition metal cations through bulk liquids using a wide range of synthetic macrocyclic or acyclic derivatives ionophores (Lee et al., 2002; Kim et al., 2000; Fainerman-Melnikova et al., 2004; Nezhadali, 2006, 2010).

The main aim of the present research is to investigate the competitive extraction of Cu(II), Zn(II), Ni(II) and Mn(II) cations. We used acetyl acetone and benzoyl acetone as carrier agent for the competitive metal ion extraction of Cu(II),

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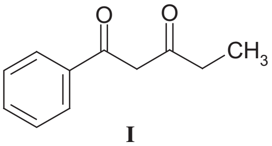
Ni(II), Zn(II) and Mn(II). The structure of benzoyl acetone and acetyl acetone is shown in **I** and **II**, respectively.



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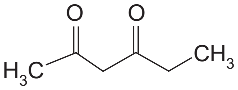

II

2. Experimental

2.1. Materials and solutions

All reagents were of analytical grade and used without further purification. All aqueous solutions were prepared with double distilled deionized water. The standard stock solution of Cu(II), Mn(II), Zn(II), and Ni(II) was prepared by dissolving nitrate salts of them. A 1.0 mM stock solution of acetyl acetone and benzoyl acetone was prepared in dichloromethane.

2.2. Instrumental

Concentrations of cations were obtained using a Philips PU9100X atomic absorption spectrometer. The extraction samples were shaken on an IKA-WERKE shaker. All of the pH measurements were carried out by 741 Metrohm pH meter.

2.3. Procedure

The competitive metal ion extraction from an aqueous phase into a dichloromethane phase was employed. The aqueous phase was buffered at pH 3.5–7.0 using sodium acetate/acetic acid and sodium formate/formic acid. The metal ions present were Cu(II), Mn(II), Zn(II) and Ni(II) as their nitrate salts at a concentration of 10 mM. The extractions were carried out in sealed flasks (25 ml). The flasks were shaken for 24 h on a mechanical shaker (at 25 °C). The metal ion concentrations were determined after each extraction experiment, using atomic absorption spectrophotometer. Each experiment was performed in triplicate runs and the reported value is the average of them.

The optimal value for pH was used to optimize ligands concentration. Alternatively, the obtained values were used in the optimizations of time and finally, all these values were used to optimize the rate of shaking on the extraction experiments.

3. Results and discussion

3.1. Extraction with benzoyl acetone

To obtain optimum conditions with the ligand, effects of pH, time, rate of shaking and concentration of the ligand was investigated.

3.1.1. pH effect

Most chelating ligands are conjugate bases of weak acid groups and, accordingly, have a very strong affinity for hydrogen ions. The pH, therefore, will be a very important factor in the separation of metal ions by chelating, because it will determine the values of the conditional stability constants of the metal complexes on the surface of the sorbent. The extraction experiments of Cu(II), Mn(II), Zn(II), and Ni(II) using the ligand in different pH have been done. Data given in Table 1 shows that best pH for extraction is 6.5 and for the other cations, extraction percent is zero.

3.1.2. Time effect

The effect of time on the extraction experiments of Cu(II), Mn(II), Zn(II), and Ni(II) with benzoyl acetone in different times has been done. As shown in Fig. 1 the extraction of Cu(II) from the aqueous feed phase into the organic phase occurs very rapidly and after 1 h is constant. It means after this time extraction% do not have variation.

3.1.3. Effect of shaking rate

The competitive extraction experiments of Cu(II), Mn(II), Zn(II), and Ni(II) with benzoyl acetone in different rate of shaking has been done. In order to explore the effect of stirring speed, the extraction experiments were performed at five different speeds, 0, 100, 150, 300, 500 and 700 rpm. As shown in Fig. 2 the convenient results are found with 100 rpm. It means, the shaking rate over this amount, does not have any effect on extraction percent. So, this shaking rate was used for the experiments.

3.1.4. Effect of the ligand concentration

The extraction experiments of Cu(II), Mn(II), Zn(II), and Ni(II) with benzoyl acetone in different concentration of

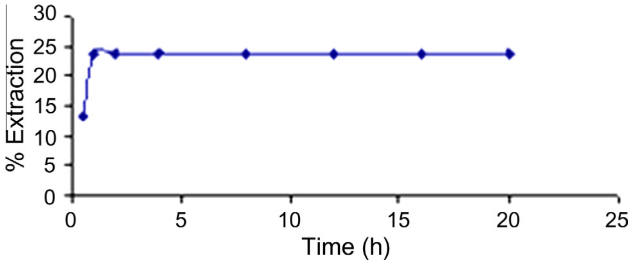

Figure 1 The effect of extraction time on the competitive extraction of Cu(II). Conditions: Initial concentration of [Cu(II), Mn(II), Zn(II) and Ni(II)] 10 mM, pH 6.5, benzoyl acetone in dichloromethane 5 mM, shaking rate 300 rpm.

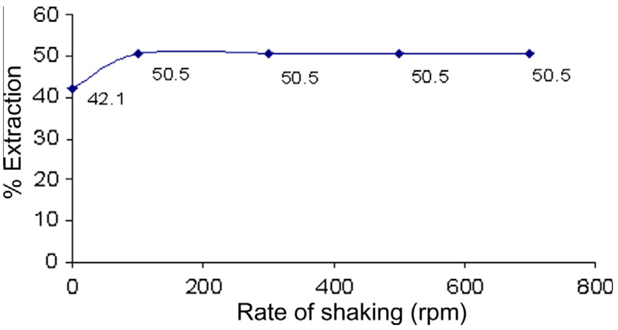

Figure 2 The effect of shaking rate on the competitive extraction of Cu(II). Conditions: Initial concentration of [Cu(II), Mn(II), Zn(II) and Ni(II)] 10 mM, pH 6.5, benzoyl acetone in dichloromethane 5 mM and extraction time 1 h.