

Communication: The synthesis of poly(*N*-acryloylpiperazine) was carried out by radical polymerization giving a yield of 90%. The polymer was soluble in water and was characterized by FTIR, ¹H NMR, ¹³C NMR spectroscopy, and TGA. The metal ability binding properties for the Ag(I), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Pb(II), and

Cr(III) metal ions in the aqueous phase were investigated using the liquid-phase polymer-based retention (LPR) method. The metal ion interactions with the hydrophilic polymers were determined as a function of pH and filtration factor.

Chelating properties of poly(*N*-acryloyl piperazine) by liquid-phase polymer-based retention (LPR) technique

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Introduction

Polymeric supports with complexing groups are widely investigated and applied for the metal recovery from a dilute solution, such as industrial fluids and waste water. Apart from insoluble, crosslinked polymer reagents containing ligands, e.g. amino, ammonium, phosphoric acid, carboxylic acid, amidoxime,^[1–7] water-soluble functional polymers have been investigated for the removal of metals in the homogenous phase.^[8–13]

Membrane filtration processes are among the most promising technologies for enrichment of various species from solutions and for separation. However to date, membrane separation has been relatively seldom used in analytical chemistry, particularly in inorganic analysis.

The water-soluble chelating polymers, termed polychelators, have been prepared by functionalizing various basic polymers. By using these polychelators in combination with membrane filtration, higher efficiency and selectivity of membrane separations can be achieved. This method, based on the retention of certain metal ions by a membrane which separates low molecular mass compounds from macromolecular complexes of the ions, is called liquid-phase polymer-based retention (LPR).^[10]

Application in the recovery of metals from dilute solutions both on an analytical and technical scale has already been reported.^[10] However, no study on the influence of different variables in the retention properties has yet been done.

The aim of this paper is to investigate the metal ion binding ability of a polymer containing tertiary amino groups as ligand groups with a cyclic spacer group. The metal ion binding ability to Ag(I), Co(II), Ni(II), Cu(II),

Zn(II), Cd(II), Pb(II), and Cr(III) through the LPR technique varying the pH and the filtration factor was investigated.

Experimental part

Reagents

N-methyl piperazine (Aldrich) and acryloyl chloride (Merck) were distilled. *N*-acryloyl-*N*-methyl piperazine (AP) was synthesized according to the literature.^[14] Yield: 65%.

The metal salts (Merck, analytical grade) were used as received.

Polymerization

Homopolymerization reaction was carried out in water by using ammonium persulfate (APS) (2 mol-%) as initiator reagent. The reaction mixture was kept at 60 °C for 24 h. The polymer was purified by ultrafiltration membranes with a cut off of 50000 and 100000 Daltons. Yield: 90%. Molecular weight: 303000 g mol⁻¹ determined by light scattering. TDT_{50%} 428 °C.

(C₈H₁₄ON₂)_n (154)_n Calc. C 62.30 H 9.08 N 18.17
Found C 62.21 H 9.11 N 18.10

FT-IR (KBr pellets): 2820 (s N—CH₃), 1630 (s C=O, amide), 1360 cm⁻¹ (s C—N, tertiary amine).

¹H NMR (D₂O, TMS as reference): δ = 3.50 (CH₂—N—C=O), 2.56 (CH—C=O), 2.37 (CH₂—N(CH₃)—CH₂), 2.27 ppm (CH₃).

¹³C NMR (D₂O, TMS as reference, in ppm): δ = 175 (C=O, amide), 57 (CH₂—N(CH₃)—CH₂), 45 ppm (CH₃).

Characterization

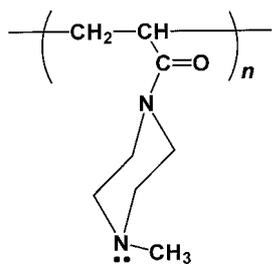
The FT-IR, ^1H NMR, and ^{13}C NMR spectra were recorded on a Magna Nicolet 550 spectrophotometer and Bruker AC 250 P Multinucleous spectrometer respectively. The molecular weight was determined in water at room temperature ($\sim 20^\circ\text{C}$) with a Wyatt/Optilab 903 Interferometric refractometer and Dawn DSP-F Laser photometer. This measurement was taken in UNED, Spain. The thermal stability of the polymers was studied under N_2 using a thermoanalyzer Polymer Laboratories STA 625. The pH was determined with a Metrohm pH-meter E 512. For the LPR technique, a membrane filtration system was employed to test the coordinating properties of the polychelators. A Perkin Elmer 1100 Atomic Absorption Spectrometer was used for the determination of the metal ion concentrations in the filtrate.

Procedure

The aqueous solutions of polychelator (0.0002 M) and metal nitrates or chlorides (0.00005 M) were placed into the filtration cell. The total volume in the cell was kept constant 20 mL. The reservoir contained water adjusted at the same pH as the cell solution. A membrane with an exclusion limit of 10000 g mol^{-1} (Filtron) was used. The system was pressurized (300 Kpa) and the cell solution was stirred and then washed with the reservoir fluid. The study was carried out at constant temperature, 20°C in a clean room. The filtration fractions ($Z = 1-10$) were collected and the concentrations of metal ions in the filtrate were determined by atomic absorption spectroscopy.

Results and discussion

The poly(*N*-acryloylpiperazine), PAP, was synthesized to achieve a ligand polymer containing a tertiary amine coordinating group as part of the cycle spacer group to improve the efficiency and/or the selectivity to metal ion retention. The complexing behavior of the polymers was investigated with seven different metal ions (Ag(I), Co(II), Cu(II), Ni(II), Cd(II), Zn(II), Pb(II), and Cr(III)) which are of interest from an environmental point of view.



A typical retention profile shows the metal ion retention (R) versus filtration factor (Z). Z is defined as the ratio volume of the filtrate (V_f) versus volume in the cell (V_0) and R is the fraction per unit of metal ions remaining in the cell (see Fig. 1).

The polymer metal ion interaction is pH-dependent. In strongly acidic solutions no complexation takes place, and protonated PAP and aqua-metal complexes co-exist in solution. In alkaline solutions, hydroxo complexes are formed, or at least there is competition between HO- and tertiary amine groups for metal coordination and the formation of mixed complexes cannot be ruled out. Therefore, the intermediate pH range ($3 > \text{pH} < 8$) is the most appropriate for the formation of "single" PAP metal complexes for the majority of metal ions.

In general, there is not an important effect of the ionic radius of the metal ion on the metal ion retention. Ag(I) is poorly retained ($< 20\%$) in the pH range tested. At pH 3, Cr(III) is retained by about 50%. It is necessary consider that at this pH chromium basically exists as Cr^{3+} which co-exist with basic species such as $\text{Cr}(\text{OH})_2^+$ and CrOH^{2+} .

At pH 1 the retention is very low but as the pH increases, the metal ion retention increases. The highest values ($> 90\%$ at $Z = 1$) are achieved at pH 5 which is attributed to the electrons of nitrogen atom available to coordinate with the metal ions.

Ni(II), Co(II), Cd(II), and Zn(II) ions interact relatively strongly with the amino groups during the filtration, which is in agreement with the literature data.^[15]

At $Z = 10$ the retention remained above 47% for Cd(II), but the highest retention behavior was observed for Ni(II) at 66%. This is shown in Fig. 2.

At pH 5, $Z = 10$, the retention of Co(II) (62%) is higher than that of aliphatic amines such as branched poly(ethyleneimine), BPEI, and poly(*N*-hydroxyethyl)ethyleneimine, PHEA. Both polyamines contain the amino groups on the main chain, except BPEI where 30% corresponds to primary amino groups. The retention of Zn(II) ions by PAP is higher than that of PHEA but lower than that of BPEI.^[16]

Copper(II) was not studied above pH 5 to avoid the precipitation of $\text{Cu}(\text{OH})_2$.

In conclusion, the new polychelator containing piperazine ring showed interesting metal ion binding properties forming stable complexes with Co(II), Ni(II), Cd(II), and Zn(II) ions depending on the pH. The complexation of metal ions with PAP yielded water soluble products, probably due to intramolecular formation of chelates.

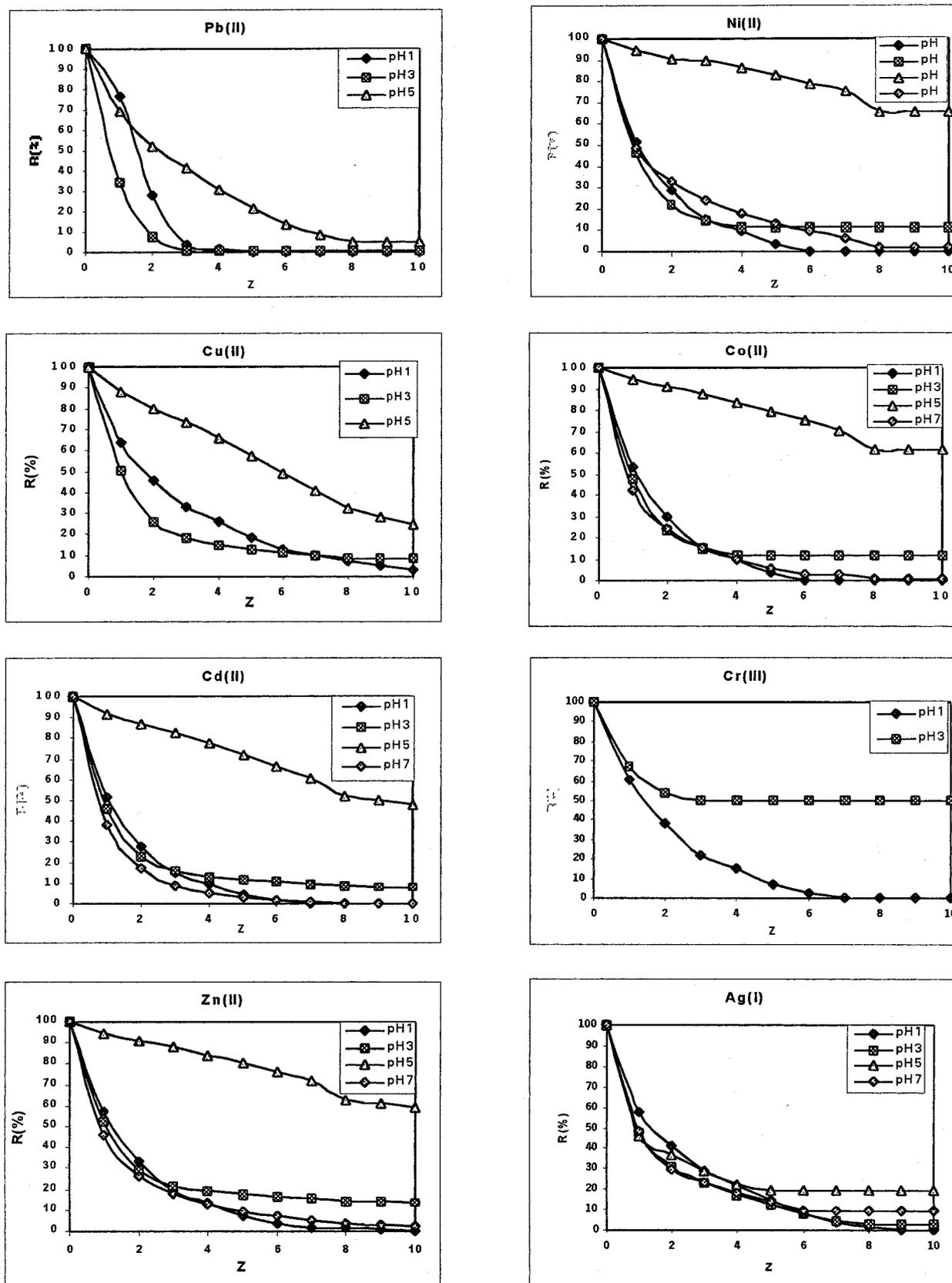


Fig. 1. Retention profiles of Cu(II), Cd(II), Co(II), Ni(II), Cd(II), Zn(II), Pb(II), and Cr(III) (0.2 mM) using PAP (0.00005 M) at different pH and Z values

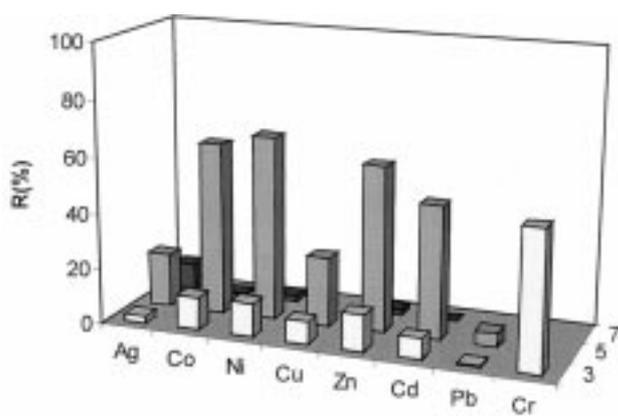


Fig. 2. Comparison of the retention values of PAP at different pH values where $Z = 10$

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