Chapter 5

Structure-performance relationship in metal ion uptake of chemically modified alternating aliphatic polyketones

Abstract

Four novel types of cross-linked beads were synthesized by using functional polymers bearing primary, secondary and tertiary amines or amino-carboxylic groups as pendant moieties. The synthesis was carried out by Paal-Knorr chemical modification of aliphatic polyketones. Different cross-linking protocols were implemented for the four polymer resins, all involving formation of imine and/or pyrrolic bridges between the macromolecules.

Three cross-linked beads bearing piperazine (X-PKpip), primary amine (X-PKDap) or glycine-type functional groups as pendant moieties (X-PKlys) were used for the first part of the study, in which the role of each functional group of the crosslinked beads in the interaction with different metal ions (i.e. Cu(II), Ni(II), Co(II), Fe(III) Cr(III), Ag(I) and Hg(II)) was qualitatively assessed by FT-IR studies. The results of the FT-IR study were then related with the metal ion uptake in aqueous solution of the three crosslinked beads at different contact times and temperatures. The three cross-linked beads showed an excellent adsorption for four metal ions (i.e. Cu(II), Ni(II), Ag(I) and Cr(III)).

For the second part of the study, selectivity measurements were carried out by evaluating the single adsorption of the supra-mentioned four metal ions. X-PKpip, X-PKDap and cross-linked beads bearing tertiary amines (X-PKDeae) showed different affinity for the supra-mentioned metal ions, thus demonstrating that the metal ion uptake can be influenced by systematically changing the chemical structure of the amino groups (i.e. primary, secondary and tertiary). Preliminary continuous experiments have been carried out (for Cu(II) only) to assess the feasibility of the proposed approach at industrial scale.
5.1 Introduction

Many separation techniques (i.e. liquid–liquid extraction [1], bulk-liquid membrane systems [2], sorption, precipitation, coagulation and flocculation processes [3] as well as electrochemical treatment [4]) have been employed and described in literature for metal ion removal from wastewater. However, membrane saturation/deactivation, long residence times and/or use of toxic chemicals (e.g. bases used for precipitation of metal ions as hydroxides) render up-scaling and application at industrial level at least questionable from a technological as well as economic point of view.

The use of functional polymers may represent a solution in this respect since these materials have the ability to chelate or exchange metal ions by establishing coordinative and/or electrostatic interactions [5]. These are usually due to the presence of functional groups along the backbone, which are able to chelate and withhold the metal ion center. Upon addition of such polymers (as water soluble materials), a colloidal dispersion is usually generated, which can be isolated by ultra-filtration. However, this technique cannot be up-scaled because it does not support a stable out-stream of the purified solution. The use of the same materials in the form of cross-linked insoluble resins represents the most popular choice in order to overcome such restriction. Moreover, the resins can be re-used for the same adsorption process by regeneration under acidic pH or temperature [6]. If this is not possible, the exhausted metal-rich polymer network can still be re-used as hybrid catalyst, in electric devices or as added-value fillers for engineering plastics [7-9].

Against this backdrop, the use of polymeric networks containing N-substituted functional groups represent a clear advantage because of their high chelating ability towards most of the d-transition metal ions. The chelation of a metal center by functional groups was firstly described by Pearson [10], who defined metal and ligands in hard and soft depending on their electronic structure. This is usually reflected by the charge-radius ratio for a given metal ion. Examples of soft metal ions are represented by Ag(I), Hg(II), Cr(III), Fe(II). Hard metal ions, on the other hand, are for example Cr(VI) and Fe(III), while “borderline” ones are Cu(II), Co(II) and Ni(II) [10].

If the same concept is applied to functional polymers, soft pendent groups, such as secondary and tertiary amines [11-13], pyrrole and pyridine [14], preferably interact with soft metal ions while hard pendent groups, such as primary amines [15] and imines, chelate with hard metal ions. As a consequence, depending on the nature of the metal ion to be preferentially removed, the corresponding functional polymer can in principle be appropriately designed [16]. In particular, primary amino groups, such as those present in poly(vinyl)amine, showed a wide affinity for all the supra-mentioned metal, which render them particularly attractive as universal adsorbents. However, the synthesis of polymeric materials bearing such groups is often cumbersome and costly, since it typically involves the use of solvents, different expensive reactants and multiple reaction steps [17].

From a scientific point of view, it is also worth noticing how the current systems, as described in the open literature, offer little versatility in terms of amount and kind of amino groups present along the backbone, thus hindering the study of a reliable structure-property relationship.
Chemically modified polyketones represent a valid alternative for obtaining polyamines with tunable amine concentration and cross-linking degree [18]. Indeed, perfectly alternating aliphatic polyketones (PK) copolymers produced by carbon monoxide and unsaturated hydrocarbon monomers (e.g. olefins), react, through the Paal-Knorr mechanism, with N-functionalized amines and form pyrrolic moieties with the functional group pendant as in a comb-like polymer [19]. The versatility of this reaction for 1,4-dicarbonyl polymers, such as aliphatic polyketones, has already been proven in several publications of our group [20-22], demonstrating the possibilities to incorporate several kinds of functional groups (with tunable concentration) and combinations thereof along the polymeric backbone. Furthermore, the simultaneous presence of pyrrolic rings linked by an aliphatic spacer with a functional group might increase their affinity towards the supra-mentioned set of metal ions (i.e. Ag(I), Hg(II), Cu(II), Ni(II), Co(I), Cr(III), Fe(III)).

In the present chapter, we aim at studying the metal uptake behavior of several different functional polymers (derived from polyketones) bearing amines and glycine-type (i.e. amino-carboxylic) groups along the backbone. Indeed, four polyamines were synthesized by reaction of aliphatic polyketones (PK) with 1,2 diaminopropane (PKDap), with 1-aminoethylpiperazine (PKPip), N, N-Diethylethylamine (PKDeaea), L-Lysine (PKLys) (Figure 5.1).

![Figure 5.1. Paal-Knorr reaction of aliphatic polyketones (PK) with several N-substituted amines: 1-aminoethylpiperazine (I), N-diethylethylamine (II), 1,2-diaminopropane (III) and L-lysine (IV)](image)

The structure of the four polymers (PKDap, PKLys, PKPip and PKDeaea) was established by $^1$H-NMR and FT-IR and the carbonyl conversion was calculated by elemental analysis. Four cross-linked polymers (X-PKDap, X-PKLys, X-PKPip and X-PKDeaea) were synthesized by formation of either pyrrolic or amines bridges and their structure was elucidated by FT-IR spectroscopy. Such polymers were then used in batch uptake experiments in the presence of water solutions of the metal ions described above (i.e. Cu(II), Co(II), Ni(II), Cr(III), Fe(III), Hg(II) and Ag(I)). The uptake kinetics as well as its dependence on temperature was then evaluated and tentatively explained on the basis of parallel FT-IR studies able to qualitatively identify the functional groups involved in the chelation of the metal ions.
In the second part of the study, selectivity measurements for the same polymers were carried out in the presence, simultaneously, of the four metal ions that showed the best affinity during the previous study. Finally, uptake studies in preliminary continuous experiments were carried out in order to evaluate the performance of PK-Dap and compare it to literature data for a single metal ion, Cu(II).

5.2 Experimental

5.2.1 Materials
Alternating polyketones with 30 wt % ethene and 70 wt % propene (PK30, M_w-3970 g/mol) based on the total olefin content were synthesized according to a reported procedure [23]. 1,2-Diaminopropane (1,2-Dap, Acros, >99%), L-Lysine ((C_6H_{14}N_2O_2), Sigma-Aldrich 99%), 1-Amino-ethylpiperazine (C_6H_{15}N_3, Sigma Aldrich 99%), 2,2-Diethylaminoethylamine (DAEA, Sigma-Aldrich 99%), Hexamethylenediamine (HDA, Sigma-Aldrich 98%), Chromium nitrate (Cr(NO_3)_3.9H_2O, Sigma-Aldrich 99%), Cobalt (II) nitrate (Co(NO_3)_2.6H_2O, Sigma-Aldrich 99%), Iron(III) nitrate (Fe(NO_3)_3.9H_2O, Sigma Aldrich 99%), Nickel (II) chloride (NiCl_2, Sigma Aldrich 99%), Copper (II) sulfate (CuSO_4.5H_2O, Merck 99%), Silver (I) nitrate (AgNO_3, Merck 99%), Mercury chloride (HgCl_2, Baker 99%), Chloroform (Acros) and Tetrahydrofuran (THF, Acros) were purchased and used as received. De-ionized Milli-Q water has been used.

5.2.2 Chemical modification of polyketones (synthesis of PKDap, PKPip, PKDeaea)
The chemical modifications were carried out in a sealed 250 ml round bottom glass reactor with a reflux condenser, a U-type anchor impeller placed in an oil bath for heating. After pre-heating the polyketones to the liquid state at the employed reaction temperature (110 °C), the di-amine (i.e. 1,2-diaminopropane, 1-aminoethylpiperazine or 2,2-diethylaminoethylamine), at a molar ratio 0.7 between 1,4-dicarbonyl groups in polyketone and the amino compound, were added drop-wise into the reactor during the first 20 min. The stirring speed was set at a constant value of 500 rpm for each reaction [19]. During the reaction, the reactants mixture typically changed from slight yellowish, low viscous fluids into highly viscous dark brown homogeneous paste. At the end of the reaction (after 4 hrs), the resulting products were cooled to room temperature. After grinding into small particles, the resulting polyamines were washed several times with de-ionized Milli-Q water to remove, if any, unreacted amine. After filtering and freeze-drying, light brown polymers were obtained as the final products.

In order to calculate the conversion of reacted 1,4-dicarbonyl units (y) (Figure 5.1), elemental analysis was performed using a Euro EA elemental analyzer. The results of this analysis are linked to the conversion by the following formula:
Metal ion uptake modified polyketones

\[ N = \frac{M_N n_1}{M_{w1}(1-y)+M_{w2}y} \]

where \( M_N \) represents the atomic mass of nitrogen, \( n_1 \) is the number of nitrogen atoms in the repetitive unit of the reacted polyketone, \( N \) is the nitrogen content per gram calculated by elemental analysis, \( M_{w1} \) is the molecular weight of a non-converted 1,4-dicarbonyl segment (131.6 g/mol) of PK30 and \( M_{w2} \) is the molecular weight of converted 1,4-dicarbonyl segment (169.7 g/mol for PKDap, 225.7 g/mol for PKDeaea and 223.6 g/mol for PKPip) (Figure 5.1). \( M_{w1} \) and \( M_{w2} \) are calculated by taking into account the presence of 30 wt % ethylene and 70 wt % propylene in the copolymers.

From that, the conversion \( y \) can be calculated by:

\[ y = \frac{N_M w_1}{M_N n_1 + N (M_{w1} - M_{w2})} \]

The 1,4-dicarbonyl yields for each modified polyketone (X-PKlys, X-PKDap, X-PKLys and X-PKPip) were calculated on the basis of elemental analysis data (Table 5.1).

<table>
<thead>
<tr>
<th></th>
<th>Carbonyl conversion (%)</th>
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<tbody>
<tr>
<td>PKLys</td>
<td>47%</td>
</tr>
<tr>
<td>PKDap</td>
<td>65%</td>
</tr>
<tr>
<td>PKPip</td>
<td>47%</td>
</tr>
<tr>
<td>PKDeaea</td>
<td>68%</td>
</tr>
</tbody>
</table>

Table 5.1. Conversion of carbonyl groups

5.2.3 Synthesis of cross-linked PK-Lys (X-PKLys)

The synthesis of PK-Lys was carried out in microwave oven and thus deviates from the procedure described above. The reason behind the use of microwave is mainly linked to the faster kinetics. Moreover, the chemical modification and the cross-linking occur in one-pot reaction by reaction of both amine groups of the used amino-acid, L-lysine.

The reaction was performed in a glass flask (100 ml) equipped with a magnetic stirrer and a reflux condenser. First, the polyketone (3.0 g, 0.023 mol di-carbonyl units in PK30) was dissolved in methanol (30 g) upon stirring. Subsequently, the amino acid (0.011 mol, ratio 0.47 between the amino groups of L-lysine and 1,4-dicarbonyl groups of PK30) and the catalyst (TEA) (3 g, 0.029 mol) were added to the mixture and transferred to the microwave apparatus (CEM Discover). The reactions were carried out for 60 minutes with stirring. The microwave power was kept at 250 W and the temperature was set at 60 °C controlled by a thermocouple insert within the reaction media. The color of the
reaction mixture typically changed from slightly yellowish to dark brown or dark orange (Figure 5.2).

![Diagram of Paal-Knorr reaction](image)

**Figure 5.2.** Paal-Knorr reaction of PK30 with L-Lysine in microwave. Production of pyrrole-amino/carboxylic units (y), imino pyrrole units (z1) and carboxylic-pyrole moieties (z2)

After 60 minutes, microwave heating was ceased and the solvent removed by using rotary evaporation under vacuum (100 mbar) at 40 °C. The product (X-PKLys) was dried at 40 °C and 100 mbar in a vacuum oven until constant weight (typically for 12 h). The product was further purified by dispersing the samples in water at a pH of about 2 (obtained by using 1.0 M HCl for gross and 0.1 M HCl for fine adjustment) to remove the un-reacted amino acid and the catalyst. The desired product, precipitated as a solid, was separated by centrifugation and further dried in a vacuum oven (100 mbar) at 40°C until constant weight [24].

### 5.2.4 Cross-linking of PKDap

PKDap was cross-linked via thermal heating for 10 minutes at 150°C. In this case, the network formation has been shown [25] to proceed via reaction of the PKDap free amino groups with the free carbonyls on other chains to mainly yield a Schiff base.

### 5.2.5 Cross-linking of PKPip and PKDeae

Immediately, after the Paal-Knorr modification, PKDeaea and PKPip were cross-linked by addition of hexamethylenediamine (HDA) solution in methanol (0.04 equivalent with the respect of total amount of 1,4-dicarbonyl group present in the polyketone precursor) drop-wise for 10 minutes at a reactor stirring speed of 500 rpm and at a temperature of 110°C. After a total reaction time of 100 min, the suspension was kept at 110°C without cooler in order to evaporate the residual methanol. The resulting solid was a rubbery, dark brown material that was washed several times with de-ionized Milli-Q water to remove unreacted di-amine. However, in all cases, GC/MS analysis of the water solution after evaporation used to wash the polymer yielded only traces of unreacted di-amine. This suggests a quantitative conversion of the hexamethylenediamine.
5.2.6 Characterization
Atomic Absorption Spectroscopy (AAS) measurements were carried out by using an AAnalyst 200 device interfaced with Perkin-Elmer software 5.0.0.1. All solutions, both before or after adsorption, were filtered and diluted till the respective linearity range for the detecting element.
IR spectra were recorded using a Perkin Elmer Spectrum 2000 FT-IR apparatus. \(^1\)H-NMR spectra were recorded on a Varian Mercury Plus 400 MHz NMR apparatus using CDCl\(_3\) as solvents.

5.2.7 Batch experiments
For all batch experiments, 0.15 g (corresponding to X-PKDap: 0.570 mmol, X-PKLys: 0.315 mmol and X-PKPip: 0.630 mmol of amino groups) of polymer was poured in a beaker at different temperatures (e.g. 35, 50, 60, 70 and 80°C) in the presence of 20 ml of the selected metal ion (i.e. Ag(I), Hg(II), Cu(II), Ni(II), Co(I), Cr(III), Fe(III)) solution at equimolar ratio with the total nitrogen intake (i.e. taking into account also the pyrrole groups along the modified polyketones backbone). Upon reaching the desired contact time (e.g. 10, 20, 30 and 40 minutes), the solution was filtered off under vacuum and the filtrate was analyzed by AAS (using AAnalyst 200 atomic adsorption spectroscopy interfaced with Perkin-Elmer software 5.0.0.1). For all the experiments, the pH values were fixed in the range between 4 and 5 (thus avoiding the formation of any precipitate), i.e. at their natural value depending on the chemical composition. The use of a buffer for finer pH adjustments has been considered but discarded in order to ensure a proper comparison with similar studies described in the literature [29].

5.2.8 Selectivity batch experiment
To evaluate the selectivity of the cross-linked polymers (X-PKDap, X-PKPip and X-PKLys) for copper(II), chromium(III), nickel(II) and silver(I), the metal ions in solution were mixed in a beaker (80 mL). The metal ion content (for each single metal) of the solution was equimolar to the total nitrogen equivalent calculated by elemental analysis for 0.15 g of resin. The polymer was stirred for 40 minutes in the presence of the metal solution. The solution was then filtered off and analyzed by inductively coupled plasma (ICP) equipped with a Perkin-Elmer interface. The metal ion uptake selectivity has been calculated according to the equation:

\[
M_{\text{ratio}} = \frac{M_{\text{ads}}}{N}
\]

Where \(M_{\text{ratio}}\) is the metal ion uptake selectivity calculated for each couple metal ion/cross-linked resin, \(M_{\text{ads}}\) is the total amount in mol of adsorbed metal per gram of resin and \(N\) is the total amount of nitrogen equivalent per gram of resin.
5.3 Results and discussion

In the following paragraphs, firstly polymer structures, as determined by $^1$H-NMR, FT-IR and elemental analysis (5.3.1), are discussed for the three un-crosslinked resins (PKDap, PKPip and PKDeaea) while the four crosslinked ones (X-PKDap, X-PKLys, X-PKPip and X-PKDeaea) are characterized by FT-IR and elemental analysis (5.3.2). Uptake measurements for the binary mixtures (resin in the presence of one kind of metal ion) are then described and the data tentatively explained on the basis of parallel FT-IR measurements (5.3.3). From the supra-mentioned metal ions, four of them (Ag(I), Cu(II), Ni(II) and Cr(III)), displaying the best performance in the previous study, are chosen for selectivity measurements (5.3.4).

Finally, a comparison with literature data for the batch experiments as well as continuous ones is carried out by taking Cu(II) as reference system (5.3.5).

5.3.1 Synthesis of chemically modified polyketones (PKDap, PKPip, PKDeaea)

The Paal-Knorr reaction of 1,2-diaminopropane (PKDap), 1-Aminoethylpiperazine (PKPip) and N,N-diethylethylamine with PK30 has been carried out for four hours. The elemental analysis (Table 5.1) confirmed the fixation of nitrogen on the backbone of the polymer and the 1,4-dicarbonyl conversion resulted to be 64.7% for PKDap (4.3 mmol/g resin of amino groups), 47.0% for PKPip (4.2 mmol/g resin of secondary and tertiary amino groups) and 68% for PKDeaea (4.3 mmol/g resin). IR and $^1$H-NMR spectra have been recorded after functionalization and will be briefly discussed in the following (details are reported in Section 5.5.1). The FT-IR spectrum of PK30 and PKDap showed the appearance of two peaks at 3300-3340 cm$^{-1}$ (N-H stretching of free amine groups), 1625 cm$^{-1}$ (N-H scissoring primary amines), 1076 cm$^{-1}$ (pyrrole ring mode), 1033 cm$^{-1}$ (C-N aliphatic stretching), 750 cm$^{-1}$ (N-H wagging) which confirmed the presence of free amine ring and pyrrole ring [26]. On the other hand, the drop in intensity of the peak at 1705 cm$^{-1}$ (stretching C=O) is in agreement with the reaction of carbonyl groups to form pyrrolic moieties along the backbone. Furthermore, $^1$H-NMR spectrum of PKDap and PKPip displays, in comparison with the one of PK30, the appearance of a peak at around 5.5-6.0 ppm and at 130 ppm in the $^{13}$C-NMR, assigned to the pyrrole group in agreement with previous studies [19]. The complicated and random structure of the polymer (i.e. ethylene/propylene distribution along the backbone) resulted in relatively broad peaks, which hinders a more detailed interpretation of the peaks at high field (low δ).

Moreover, for PKPip a shift of the peaks of PK30 from the region 3.2-2.2 ppm (CH and CH$_2$ in α to carbonyl moieties) towards lower ppm (i.e. 2.9-2.0) is observed and one strong peak appears at 2.2 ppm (attributed to the CH$_2$ of the piperazine group [27]). FT-IR spectra of the latter showed, with respect to PK30, a new broad peak at 3448 cm$^{-1}$ (N-H aromatic and aliphatic stretching) and weaker C=O stretch adsorption at 1705 cm$^{-1}$.

PKDeaea has been already fully characterized in a previous publication [19] of our group and
elemental analysis data used in this chapter are available in the Appendix 5.5.1.

5.3.2 Synthesis of cross-linked modified polyketones (X-PKlys, X-PKpip, X-PKDap, X-PKDeaea)

The reaction of PK30 with L-Lysine was carried out in a microwave at 60°C for 1 hr and resulted in a conversion of 1,4-dicarbonyl groups to L-lysine derivatives of 47%.

A broad peak at 3434 cm\(^{-1}\) (N-H and O-H stretching) appears in X-PKlys FT-IR spectra (details are to be found in Section 5.5.1) and confirmed the presence of amine and carboxylic groups. Furthermore, the peak at 1705 cm\(^{-1}\) (C=O stretching) decreased in intensity and became a shoulder of the one set at 1647 cm\(^{-1}\) (C=N imine stretching) thus suggesting, as expected, a simultaneous cross-linking reaction. The peaks at 1455 cm\(^{-1}\) (C=C pyrrole stretching) and 1398 cm\(^{-1}\) (C-N pyrrole stretching) indicate the increased aromaticity of the polymer backbone [28].

A comparison between the FT-IR spectra of PKDap before and after cross-linking for 15 minutes at 150°C (reaction of the remaining carbonyl moieties with the pendent primary amine groups) showed the appearance of a peak at 1669 cm\(^{-1}\) (C=N stretching) as well as a decreasing of the shoulder at 1705 cm\(^{-1}\) (C=O stretching) after cross-linking.

The synthesis of X-PKpip and X-PKDeaea has been carried out by cross-linking of the respective polymer with 1,6-hexamethylene diamine (HDA). Firstly, the cross-linking reaction of PKpip is qualitatively confirmed by the appearance of a strong peak at 1670 cm\(^{-1}\) (C=N stretching) simultaneously with weaker ones at 1013 cm\(^{-1}\) (C-N imine stretching). Along the same line, the decreasing of carbonyls groups intake (decrease of the C=O absorption at 1705 cm\(^{-1}\)) and formation of imine and pyrrole rings as cross-linked bridges were registered through FT-IR at the same frequencies (vide supra), e.g. 1013 cm\(^{-1}\) for C=N imine stretching.

5.3.3 Metal uptake studies in batch experiments

All prepared resins in their cross-linked form (i.e. X-PKlys, X-PKpip and X-PKDap) were used for uptake studies in batch experiments. In contrast to the majority of the works present in the open literature often using an excess of metal ion, such experiments were carried out according to an equimolar ratio between the metal ion and the N-functional groups on the polymer. This choice can result in relatively lower uptakes (with respect to literature data), but it allows a more rational comparison of the different polymeric materials, since the latter display significantly different carbonyl conversion values (vide supra).

For every combination resin/metal ion 40 minutes of contact time was enough to reach equilibrium in the system, this being confirmed by experiments (not shown for brevity) of metal uptake as function of the contact time. The obtained results (Figure 5.3) clearly show the different behavior of the different metal ions and resins.
Chapter 5

Figure 5.3. Metal ion (i.e. Cu(II), Ni(II), Co(II), Cr(III), Fe(III), Ag(I) and Hg(II)) uptake of X-PKDap, X-PKLys and X-PKPip after 40 minutes of contact time at room temperature.

In order to rationalize the different uptakes for every polymeric material employed, an FT-IR study has been performed by recording the spectra of the used polymer before and after being in contact with the metal ion solution for the same amount of time (i.e. 40 minutes). FT-IR vibrational shifts and/or changes in adsorption have already been proposed by B.L. Rivas et al. [29] as proof of chelation between poly(vinyl)amine and several different metal ions. Such changes in the wavelength as well as in the absorbance can be used as a kind of fingerprints for the interaction of the corresponding group with the metal ion. Therefore, a larger variation in the wavelength (i.e. red or blue shift) or decrease in transmittance of a vibrational peak related to a given functional group in the presence of an ion can be interpreted as a higher affinity of the latter for the employed functional group. As an example, FT-IR spectra (Figure 5.4) for the X-PKPip/Cu(II) binary mixture (b in the figure) and X-PKPip (a in the figure) are shown and discussed.

Figure 5.4. FT-IR of X-PKPip before (a) and after 40 minutes mixing (b) of equimolar amounts between amine groups and copper(II) ions. Spectra have been normalized by considering the –CH₃ peak at 2873 cm⁻¹.
The spectra of X-PKPip before and after mixing with copper showed increased intensity and a shift towards lower wavelength for the broad band at 3450 cm\(^{-1}\) (N-H stretching) as well as for the peaks at 1713 cm\(^{-1}\) (C=O stretching) and 1654 cm\(^{-1}\) (C=N stretching) 1464 cm\(^{-1}\) (N-H bending piperazine ring) and 1123 cm\(^{-1}\) (C-N aliphatic stretching piperazine ring). This suggests, on a qualitative level, the involvement of such functional groups in the chelation of Cu(II).

The same analysis has been carried out for every possible combination of resin and metal ion (see Appendix 5.5.2), which allows defining a qualitative rank of affinity for every functional group/metal ion couple (Table 5.2). The obtained results clearly show relevant differences in the affinity of the metal ions towards specific functional groups. It must be noticed how a quantitative analysis of the data is factually hindered by the fact that the three resins show different carbonyl conversions and thus different amounts of functional groups along the backbone. Moreover, the different hydrophilic character of the three resins and their cross-linking method have an influence on the beads swelling, thus on the accessibility of the chelating center for the metal ion. By making allowances for the factors outlined above, one is able to use the observed affinity ranking in order to explain the uptake data, although only at a qualitative level.
Table 5.2. Specific affinity of the functional groups (e.g. pyrrole, amine, carboxyl, carbonyl, imine) contained in X-PKDap, X-PKLys and X-PKPip towards seven metal ions (e.g. Cu(II), Co(II), Ni(II), Fe(III), Cr(III), Ag(I) and Hg(II)). In case a functional group is not present in the table, it means that it display no (or negligible) vibrational changes upon contact of the polymer with the metal ion solution.

Based on Pearson’s theory [10] and for the sake of a more rational discussion, three groups of metal ions can be outlined in order to simplify the observed metal ion affinity. The following sections will thus discuss the observed uptake (Figure 5.3) on the basis of FT-IR analysis (Table 5.2) according to a classification of the employed metal ions into borderline (Cu(II), Ni(II) and Co(II)), hard (Cr(III), Fe(III)) and soft metal ions (Ag(I), Hg(II)).
5.3.3.1 Cu(II), Ni(II) and Co(II)

For all three resins it is possible to rank the metal ions according to their uptake into the following:

- **PK-Dap**
  - Cu>Ni>Co

- **PK-Pip**
  - Ni>Co>Cu

- **PK-Lys**
  - Ni>Co>Cu

The affinity rank for PK-Dap is in agreement with the FT-IR data and the expected behavior according to the Irving-Williams theory, which ranks the complex stability for primary amino groups and divalent cations of the first transition series in the following way: Mn<Fe<Co<Zn<Ni<Cu [30]. However, such theoretical predictions are clearly not respected for the affinity ranks of PK-Pip and PK-Lys. This can be explained by the specific interactions of the Ni and Co for other functional groups present in the polymeric materials. The fact that the Co uptake is higher than that of Cu is probably related to its specific interactions with imines (see FT-IR data). This is in agreement with other studies [31, 32] and indirectly confirms the restively strong character of such affinity when taking into account the fact that Co does not display any relevant affinity for carbonyl groups [33] (which should result indeed in the reverse order, i.e. Cu>Co). This observation is probably valid also for Ni, which shows an affinity towards imine groups (Table 5.2) only in PK-Pip and PK-Lys. However, the observed deviations in metal uptake for Ni are also probably related to the geometry of the formed complex [29] and might explain the better performance (Figure 5.3) of PK-Pip with respect to the other two polymers. Indeed, Ni(II) exhibited highest affinity for pyrrole rings exclusively with PK-Pip as chelating resin. This might be related to a cooperative bonding between the metal ion and the pyrrolic groups and one of the N-atoms of piperazine rings. In particular, the flexible ethylene bridge between pyrrole and the piperazine ring could help in folding them in order to create a “sandwich” complexation. A direct proof of such statement (beyond the scope of this work) could be obtained with appropriate model systems. However, an indirect proof is obtained by studying the uptake behavior of the complex as function of temperature (Figure 5.5) under the assumption, corroborated by literature [29], that such “sandwich complex” should display a relatively high thermal stability.
It is clear that a restively higher thermal stability is displayed by PK-Pip, for which the Ni uptake is factually stable up to 70°C. This behavior is less prominent for PK-Lys and factually absent (differences are within the experimental error range) for PK-Dap.

### 5.3.3.2 Cr(III) and Fe(III)

For all three employed polymers the uptake for Cr(III) is significantly higher than the one for Fe(III) (Figure 5.3). Moreover, for every metal PK-Dap shows the best uptake followed by PK-Pip and PK-Lys. Moreover, the FT-IR study clearly shows pyrrole, amine and imine groups to be chelating towards Cr(III) and Fe(III) (Table 5.2)

The highest uptake of Cr(III) with respect to Fe(III) is most probably related, as already suggested in the literature, to its relatively high affinity for pyrrole [34, 35] and amine groups [36]. However, primary amines do participate in the chelation of Cr(III) when they are included in a glycine-type ligand, such as amino-carboxylic group. Also in this case, as for Ni (vide supra), the formation a sandwich complex might be inferred. Uptake studies as function of temperature (Figure 5.6) corroborate in an indirect way such assumption.

![Figure 5.5. Uptake metal ion ratio for Ni(II) in the presence of X-PKDap (A), X-PKLys (B) and X-PKPip (C) as chelating resins at five different temperatures.](image-url)
Figure 5.6. Uptake metal ion ratio for Cr(III) in the presence of X-PKDap (A), X-PKLys (B) and X-PKPip (C) as chelating resins at five different temperatures (e.g. 35, 50, 60, 70 and 80°C).

The deviation of PK-Pip from this general trend (it shows a decrease of the uptake with temperature) is most probably related to the absence of primary amino groups in this polymer. Indeed, in general terms, the kind of amine group used (primary, secondary and tertiary) has relevant influence on the uptake behavior (see section 5.5.3).

5.3.3.3 Ag(I) and Hg(II)

In general the uptake for Ag(I) is higher (PK-Pip and PK-Dap) or equal (PK-Lys) than the one for Hg(II). The high affinity of Ag(I) for amino as well as pyrrole groups, corroborated by data on similar systems [37, 38], is probably the reason behind the observed behavior. It must be noticed, however, how the absorption of Ag(I) on the different polymers is in this case not governed by the same mechanism. Indeed, upon complexation with Ag(I), PKPip, as only functional polymer in the group, showed the formation of a translucent metallized surface (Figure 5.7).

Figure 5.7. Silver metal particles after mixing with X-PKPip for 40 minutes at room temperature.

This is most probably related to the in situ electro-reduction of Ag(I) by the piperazine rings with precipitation of macro-particulate Ag(0) [39]. Although the presence of such different absorption
mechanism factually hinders a rational comparison between the polymers (in terms of Ag absorption), it might represent a breakthrough in a closely related field. If one takes into account the easiness of the chemical modification as well as the possibility (in general for polyamines derived from polyketones [25]) for dispersion in water, PK-Pip might be employed as relatively cheap and easily available driving agent for the assembling of Ag(0) nanoparticles in a one-step process. Since the latter show optical, electrical, and thermal properties when nano-dispersed in a polymeric media, their dispersions are particularly interesting for applications as photonic device and antimicrobial coatings [40].

5.3.4 Selectivity of the cross-linked modified polyketones towards specific metal ions

In order to obtain preliminary information regarding the selectivity of the resin, the same three polymers presented above have been also investigated in the simultaneous presence of four different metal ions (i.e. Cu (II), Ni(II), Cr(III) and Ag(I)). The choice is not random: indeed, two metal ions, copper and nickel, belong to the divalent cations of the first transition series as well as chromium, but with different oxidations states. Finally silver is representative of a soft metal ion at lower oxidation state.

The three modified resins show remarkable differences in metal uptake when in the presence of different metal ions (Figure 5.8).

![Graph showing selectivity batch at equimolar ratio between amine groups and the total amount of metal ion of X-PKDap, X-PKPip and X-PKLys.](image)

In first instance it is worth noticing the lack of any Cr(III) adsorption by X-PKDap and Ni(II) by X-PKLys. The Cr/PK-Dap behavior can be easily explained when one takes into account that Cr(III) is...
considered as a hard metal ion [10] and thus with low affinity for amine groups unless upon cooperation with other ligands (vide supra). The reasons behind lack of affinity of Ni(II) with X-PKLys have yet to be found.

From a scientific perspective, the presence of several different factors (e.g. diffusivity, kind and accessibility of functional groups, swelling degree…) seriously hinders a deeper analysis of the obtained results. However, from an applicative point of view, one must notice that the maximum selectivity has been reached by silver for X-PKDap, nickel and copper for X-PKPip and chromium for X-PKLys. This confirms the versatility of the proposed approach (Paal-Knorr modification of aliphatic polyketones) in the preparation of functional polymers with tailored complexation abilities towards different metal ions (simultaneously) present in water solution.

The uptake capacity of such materials with other described in the literature needs to be assessed in order to fully evaluate the potentiality of the latter. This constitutes the objective of the following paragraph.

### 5.3.5 Comparison with literature for Cu(II), Ni(II) and Co(II)

The exceptional uptake (during batch experiments) shown by the three modified polyketones towards the selected metal ions is clearly shown when comparing data from published sources (Table 5.3).
<table>
<thead>
<tr>
<th>Metal</th>
<th>Polymer</th>
<th>Ligand</th>
<th>N content (mmol/g)</th>
<th>Retention (mmol/g)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(II)</td>
<td>Modified polystyrene</td>
<td>Diethylentriamine</td>
<td>1.3-3.0</td>
<td>2.9</td>
<td>[41]</td>
</tr>
<tr>
<td></td>
<td>Modified polystyrene</td>
<td>Phenylendiamine hydrochloride</td>
<td>0.6</td>
<td>0.4</td>
<td>[42]</td>
</tr>
<tr>
<td></td>
<td>Chitosan</td>
<td>Primary amines</td>
<td>n.a.</td>
<td>1.3</td>
<td>[43]</td>
</tr>
<tr>
<td></td>
<td>Chitosan-epichlorohydrin</td>
<td>Primary amines</td>
<td>n.a.</td>
<td>1.0</td>
<td>[43]</td>
</tr>
<tr>
<td></td>
<td>PEI/biomass modified</td>
<td>Primary, secondary and tertiary Amines</td>
<td>2.0</td>
<td>0.9</td>
<td>[44]</td>
</tr>
<tr>
<td></td>
<td>poly(iminoethylene) dithiocarbamate</td>
<td>Carbammatae</td>
<td>7.6</td>
<td>3.4</td>
<td>[45]</td>
</tr>
<tr>
<td></td>
<td>X-PKDaP</td>
<td>Primary and pyrrole amine</td>
<td>4.3</td>
<td>4.3</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>X-PKLys</td>
<td>Primary amine with carboxylic acid</td>
<td>2.1</td>
<td>0.6</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>X-PKPip</td>
<td>Secondary and tertiary amines</td>
<td>4.2</td>
<td>1.7</td>
<td>This work</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>Chitosan</td>
<td>Primary amines</td>
<td>n.a.</td>
<td>2.0</td>
<td>[43]</td>
</tr>
<tr>
<td></td>
<td>Modified polystyrene</td>
<td>diethylentriamine</td>
<td>1.3-3.0</td>
<td>1.0</td>
<td>[41]</td>
</tr>
<tr>
<td></td>
<td>PEI/biomass modified</td>
<td>Primary, secondary and tertiary amines</td>
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<td>0.5</td>
<td>[44]</td>
</tr>
<tr>
<td></td>
<td>poly(iminoethylene) dithiocarbamate</td>
<td>Carbammatae</td>
<td>7.6</td>
<td>0.7</td>
<td>[45]</td>
</tr>
<tr>
<td></td>
<td>X-PKDaP</td>
<td>Primary and pyrrole amine</td>
<td>4.3</td>
<td>1.8</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>X-PKLys</td>
<td>Primary amine with carboxylic acid</td>
<td>2.1</td>
<td>1.5</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>X-PKPip</td>
<td>Secondary and tertiary amines</td>
<td>4.2</td>
<td>2.6</td>
<td>This work</td>
</tr>
<tr>
<td>Co(II)</td>
<td>poly(iminoethylene) dithiocarbamate</td>
<td>Carbammatae</td>
<td>7.6</td>
<td>2.2</td>
<td>[45]</td>
</tr>
<tr>
<td></td>
<td>X-PKDaP</td>
<td>Primary and pyrrole amine</td>
<td>4.3</td>
<td>0.7</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>X-PKLys</td>
<td>Primary amine with carboxylic acid</td>
<td>2.1</td>
<td>1.3</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>X-PKPip</td>
<td>Secondary and tertiary amines</td>
<td>4.2</td>
<td>2.0</td>
<td>This work</td>
</tr>
</tbody>
</table>

Table 5.3. Retention properties of amine chelating resins known in literature

The versatility of the PK-modified polymers must be stressed here. From one single precursor, PK30, and through easy chemical modification (*vide supra*), it is possible to prepare chelating resins that consistently outscore (X-PKDaP for Cu(II) and X-PKPip for Ni(II)) other synthetic polymers. However, when evaluating application at industrial level, the use of continuous processes instead of
batch ones is of crucial importance. In this context we chose the Cu(II)/PK-Dap system to generate preliminary data and compare the obtained uptake (see Appendix 5.5.4 for details) with literature data. The obtained results (Table 5.4) clearly show the potentiality of the proposed materials.

<table>
<thead>
<tr>
<th>Polymer or biosorbent</th>
<th>Performance</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PK-Dap</td>
<td>196 mg/g</td>
<td>This work</td>
</tr>
<tr>
<td>Chitosan</td>
<td>222 mg/g</td>
<td>[46]</td>
</tr>
<tr>
<td><em>Aspergillus niger</em></td>
<td>4.9 mg/g</td>
<td>[47]</td>
</tr>
<tr>
<td>jute fiber</td>
<td>4.2 mg/g</td>
<td>[48]</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>1.9 mg/g</td>
<td>[49]</td>
</tr>
<tr>
<td>Clinoptilolite</td>
<td>1.6-3.8 mg/g</td>
<td>[50, 51]</td>
</tr>
<tr>
<td>fly ash</td>
<td>1.18-1.39 mg/g</td>
<td>[52]</td>
</tr>
<tr>
<td>oak sawdust</td>
<td>3.6 mg/g</td>
<td>[53]</td>
</tr>
<tr>
<td>seaweed biomass</td>
<td>52-114 mg/g</td>
<td>[54-56]</td>
</tr>
<tr>
<td><em>Thiobacillus thiooxidans</em></td>
<td>30.8 mg/g</td>
<td>[57]</td>
</tr>
<tr>
<td>Alfalfa</td>
<td>20 mg/g</td>
<td>[58]</td>
</tr>
<tr>
<td>carrot residues</td>
<td>32.7 mg/g</td>
<td>[59]</td>
</tr>
<tr>
<td>Palygorskite</td>
<td>30.7 mg/g</td>
<td>[60]</td>
</tr>
<tr>
<td>Clinoptilolite</td>
<td>25.7 mg/g</td>
<td>[61]</td>
</tr>
</tbody>
</table>

Table 5.4. Comparison of performance for Copper uptake (continuous experiments) with other different (bio)sorbents

Indeed, with the exception of chitosan, PK-Dap systematically and largely outscores all other proposed materials. Systematic studies on the resin regeneration possibilities as well as an economic feasibility study are needed for more complete comparison.
5.4 Conclusions

Four functional polymers were synthesized by Paal-Knorr reaction of aliphatic polyketones and successively cross-linked in different ways. These involved thermal heating by reaction of the pendent primary amino group, microwave technology (functionalization and cross-linking in one-step) and reaction with 1,6-hexamethyldiamine (HDA). In all these cases, the cross-linking reaction formed pyrrolic and imine bridges. These polymers bear as pendant groups: primary amines (X-PKDap), amino-carboxylic units (X-PKLys), secondary and tertiary amines (X-PKPip) and only tertiary ones (X-PKDeaea).

Three cross-linked resins (X-PKDap, X-PKLys and X-PKPip) were selected for batch uptake studies (Cu(II), Ni(II), Co(II), Cr(III), Fe(III), Ag(I) and Hg(II)). The measured uptake values could be tentatively explained on the basis of qualitative FT-IR studies and known theories described in the literature. Selectivity experiments clearly show that it is possible to tailor the chemical structure of the polymer (including the kind of amino group) towards specific interactions with a given metal ion. A comparison with other materials presented in the literature (for both batch and continuous experiments) highlights the outstanding performance of the proposed materials.
5.5 Appendices

5.5.1 FT-IR and elemental analysis characterization data

<table>
<thead>
<tr>
<th>Polymer and elemental analysis</th>
<th>FT-IR (KBr)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PKDap</strong></td>
<td></td>
</tr>
<tr>
<td>EA: Calcd. N 12.38; C 72.02; H 9.54; O 6.06.</td>
<td>3300-3340 cm(^{-1}) (m, N-H stretching of primary amine groups)</td>
</tr>
<tr>
<td>Found N 12.24; C 71.96; H 9.53; O 6.27.</td>
<td>1705 cm(^{-1}) (m, stretching C=O)</td>
</tr>
<tr>
<td></td>
<td>1625 cm(^{-1}) (m, N-H scissoring primary amines)</td>
</tr>
<tr>
<td></td>
<td>1373 cm(^{-1}) (s, C-N pyrrole stretching)</td>
</tr>
<tr>
<td></td>
<td>750 cm(^{-1}) (m, N-H wagging)</td>
</tr>
<tr>
<td><strong>PKPip</strong></td>
<td></td>
</tr>
<tr>
<td>EA: Calcd. N 9.85; C 68.98; H 9.92; O 11.25.</td>
<td>3448 cm(^{-1}) (m, N-H stretching of secondary amine groups)</td>
</tr>
<tr>
<td>Found N 11.13; C 69.18; H 10.14; O 9.56.</td>
<td>1705 cm(^{-1}) (m, stretching C=O),</td>
</tr>
<tr>
<td></td>
<td>1373 cm(^{-1}) (s, C-N stretching pyrrole),</td>
</tr>
<tr>
<td></td>
<td>663 cm(^{-1}) (N-H wagging)</td>
</tr>
<tr>
<td><strong>X-PKLy5s</strong></td>
<td></td>
</tr>
<tr>
<td>EA: Calcd. N 8.34; C 66.66; H 7.138; O 17.88.</td>
<td>3434 cm(^{-1}) (m, N-H and O-H stretching)</td>
</tr>
<tr>
<td>Found N 8.63; C 68.06; H 8.47; O 14.84.</td>
<td>1705 cm(^{-1}) (sh, stretching C=O)</td>
</tr>
<tr>
<td></td>
<td>1640 cm(^{-1}) (s, C=N stretching)</td>
</tr>
<tr>
<td></td>
<td>1390 cm(^{-1}) (s, C-OH bending)</td>
</tr>
<tr>
<td></td>
<td>663 (w, N-H wagging)</td>
</tr>
<tr>
<td><strong>X-PKDap</strong></td>
<td></td>
</tr>
<tr>
<td>EA: Calcd. N 12.36; C 71.86; H 9.86; O 5.92.</td>
<td>3358 cm(^{-1}) (m, N-H stretching of free amine groups)</td>
</tr>
<tr>
<td>Found N 12.12; C 72.35; H 9.5; O 6.04.</td>
<td>1705 cm(^{-1}) (m, stretching C=O)</td>
</tr>
<tr>
<td></td>
<td>1669 cm(^{-1}) (m, C=N stretching)</td>
</tr>
<tr>
<td></td>
<td>1458 cm(^{-1}) (m, scissoring of CH(_2) units)</td>
</tr>
<tr>
<td></td>
<td>1368 cm(^{-1}) (m, C-N pyrrole stretching)</td>
</tr>
<tr>
<td></td>
<td>1029 cm(^{-1}) (m, pyrrole ring breathing)</td>
</tr>
<tr>
<td></td>
<td>750 cm(^{-1}) (w, N-H wagging)</td>
</tr>
<tr>
<td><strong>X-PKPip</strong></td>
<td></td>
</tr>
<tr>
<td>EA: Calcd. N 13.09; C 70.29; H 12.63; O 3.99.</td>
<td>3430 (s, N-H stretching of secondary amine groups)</td>
</tr>
<tr>
<td>Found N 12.68; C 70.81; H 10.48; O 6.04.</td>
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</tr>
<tr>
<td></td>
<td>1670 (m, stretching C=N)</td>
</tr>
<tr>
<td></td>
<td>1464 (N-H piperazine ring bending)</td>
</tr>
<tr>
<td></td>
<td>1013 (m, pyrrole ring breathing)</td>
</tr>
</tbody>
</table>

Table 5.5. Elemental analysis and spectroscopic data for the two un-cross-linked (i.e. PKDap and PKPip) and three cross-linked resins (i.e. X-PKDap, X-PKLy5s and X-PKPip)
PKDeaea
EA: Calcd. N 10.87; C 74.60; H 10.39; O 4.14.
Found N 10.33; C 74.08; H 10.28; O 5.30.

X-PKDeaea
EA: Calcd. N 11.12; C 73.84; H 9.62; O 5.42.
Found N 10.87; C 74.60; H 10.39; O 4.14.

Figure 5.9. $^1$H-NMR (left) and FT-IR (right) spectra of PKDap

Figure 5.10. $^1$H-NMR (left) and FT-IR (right) spectra of PKPip
Figure 5.11. FT-IR spectra of PK30 and X-PKlys (a), PKPip and X-PKPip (b) and PKDap and X-PKDap (c)
### 5.5.2 FT-IR evaluation of metal complexes

<table>
<thead>
<tr>
<th></th>
<th>Stretching C=O carbonyl/ carboxyl</th>
<th>Stretching C=N imine</th>
<th>Bending N-H piperazine</th>
<th>Stretching C-N pyrrole</th>
<th>Stretching C-N pyp</th>
<th>Pyrrole ring breathing</th>
<th>Wagging N-H amine</th>
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<tr>
<td><strong>resins</strong></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>CK-PKDap</td>
<td>1705 sh</td>
<td>1669 s</td>
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<td>N/A</td>
<td>1029 s</td>
<td>750 w</td>
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<td>N/A</td>
<td>1074 w</td>
<td></td>
</tr>
<tr>
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<td>1720 s</td>
<td>1670 m</td>
<td>1464 m</td>
<td>1390 m</td>
<td>1141 m</td>
<td>1000 w</td>
<td>861 m</td>
</tr>
<tr>
<td><strong>Co</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CK-PKDap</td>
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<td>1684 s</td>
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<td>1342 m</td>
<td>N/A</td>
<td>X</td>
<td>X</td>
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<td>1647 s</td>
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<td>1386 m</td>
<td>N/A</td>
<td>X</td>
<td>669 m</td>
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<tr>
<td>CK-PKPip</td>
<td>X</td>
<td>1658 s</td>
<td>X</td>
<td>X</td>
<td>1176 vs</td>
<td>X</td>
<td>671 m</td>
</tr>
<tr>
<td><strong>Ni</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>1646 s</td>
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<td>N/A</td>
<td>X</td>
<td>843 w</td>
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<tr>
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<td>X</td>
<td>1657s</td>
<td>X</td>
<td>1386 vs</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td><strong>Cu</strong></td>
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<td></td>
<td></td>
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<td></td>
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</tr>
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<td>CK-PKDap</td>
<td>1700 vs</td>
<td>1684 s</td>
<td>N/A</td>
<td>X</td>
<td>N/A</td>
<td>1082 s</td>
<td>600 s</td>
</tr>
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<td>X</td>
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<td>1654 s</td>
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<td>621 m</td>
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<td>Stretch C=O carbonyl/ carboxyl</td>
<td>Stretch C=N imine</td>
<td>Bend N-H piperazine</td>
<td>Stretch C=N pyrrole</td>
<td>Stretch C-N pyp</td>
<td>Pyrrole ring breathing</td>
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<td>1639 vs</td>
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<td>N/A</td>
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<td>1385 vs</td>
<td>N/A</td>
<td>X</td>
</tr>
<tr>
<td></td>
<td>CK-PKPip</td>
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<td>1658 s</td>
<td>X</td>
<td>1386 vs</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Fe</td>
<td>CK-PKDap</td>
<td>1715 s</td>
<td>1686 s</td>
<td>N/A</td>
<td>1350 s</td>
<td>N/A</td>
<td>1080 m</td>
</tr>
<tr>
<td></td>
<td>CK-PKLys</td>
<td>X</td>
<td>1654 s</td>
<td>N/A</td>
<td>1388 vs</td>
<td>N/A</td>
<td>X</td>
</tr>
<tr>
<td></td>
<td>CK-PKPip</td>
<td>1723 vs</td>
<td>1685 s</td>
<td>X</td>
<td>1389 vs</td>
<td>1124 s</td>
<td>X</td>
</tr>
<tr>
<td>Cr</td>
<td>CK-PKDap</td>
<td>1706 s</td>
<td>1689 s</td>
<td>N/A</td>
<td>1375 s</td>
<td>N/A</td>
<td>1075 s</td>
</tr>
<tr>
<td></td>
<td>CK-PKLys</td>
<td>X</td>
<td>X</td>
<td>N/A</td>
<td>1386 vs</td>
<td>N/A</td>
<td>X</td>
</tr>
<tr>
<td></td>
<td>CK-PKPip</td>
<td>X</td>
<td>1659 s</td>
<td>X</td>
<td>1389 vs</td>
<td>X</td>
<td>X</td>
</tr>
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</table>

Table 5.6. Specific adsorption peak frequency and relative adsorption strength (medium (m), strong(s), shoulder (sh) and very strong (vs) of binary mixtures between seven metal ions (i.e. Cu(II), Ni(II), Co(II), Cr(III), Fe(III), Ag(I) and Hg(II)) and X-PKDap, X-PKLys and X-PKPip.
5.5.3 Influence of the kind of amino group on metal uptake behavior

In order to check the uptake behavior as function of the kind of amine group, i.e. primary secondary and tertiary, we selected three polymers (X-PKDap, X-PKPip and X-PKDeaea) and carried out the same study discussed during Section 5.3.3 (Figure 5.12). X-PKDap shows the presence of primary amine groups. X-PKDeaea of tertiary ones while X-PKPip displays one secondary and one tertiary amine enclose in a 6-member ring structure.

![Figure 5.12. Metal ion uptake (%) of Ni(II), Cu(II) and Ag(I) at 35 °C for X-PKDap, X-PKDeaea and X-PKPip](image)

The results show a clear preference by Ag(I) and Ni(II) for X-PKPip and a substantial invariance of the Cu(II) uptake. This might suggest that secondary amine groups (as in X-PKPip) might outperform primary and tertiary ones. This is in agreement with other studies and can be explained on the basis of two opposing effects [63]. On one side more substituted amino groups display higher electron density and can be expected to make the nitrogen lone pair electrons more available for metal ion complexation. On the other hand, this is counteracted by the higher steric hindrance and the higher solvation energy (the latter hindering the solvation of the chelant group on the surface).
5.5.4. Details of continuous absorption experiments

Experimental part
In order to check the potential use of the cross-linked modified polyketones, we reported the use of X-PKDap as column adsorbent for a Cu(II)-enriched solution, being this binary mixture the best uptake out of the four resins.

Column experiments were operated with a 10 mm diameter and 159.2 mm length stainless steel column. At both ends of the column, a porous ring was placed to keep the polymer inside the column. All experiments were carried out at room temperature (293 K). A flux of 3.9 ml/min and 30% in volume column packing were applied at a constant concentration of 0.16 mmol/L Cu²⁺ solution. The Cu²⁺ solution was fed to the column in a downflow direction by a centrifugal pump (Verder VG 1000 BASIC). Effluent concentration was measured online by a conductivity probe (MRD 299 VernierSoftware&Technology).

After calibrating the column in the presence of X-PKDap with a salt-free solution as eluent, the influent concentration was measured by the same conductivity probe and the effluent samples were recorded each hour. The Conductivity Probe MRD 299 VernierSoftware&Technology interfaced with CoachLab II MRD 291 analysis software were used to measure indirectly metal concentrations.

Model fitting for continuous experiment
Two models have been employed in order to compare to the absorption profile of X-PKDap with the use of Cu(II) aqueous solution as eluent.

The BDST model [64] correlates the service time (i.e. i.e. how long a column can be used before saturation) with the packed bed depth of the column, according to the equation:

BDST model:

\[ C_0 \cdot t = \frac{N_0 h}{u} \cdot 1 - \frac{k}{k} \cdot \ln \left( \frac{C_0}{C_t} \right) - 1 \]

with \( C_0 \) being the influent concentration (mmol/L), \( t \) the service time to breakthrough (min), \( N_0 \) the adsorption capacity (mmol metal ion/L), \( h \) the bed depth (cm), \( u \) the linear flow rate (cm/min), \( k \) the adsorption rate constant (L/(mmol min)), \( C_t \) the effluent concentration at time \( t \) (mmol/L).

On the other hand, the Thomas model [66] determines the maximum solid phase concentration of solute on the adsorbent and the adsorption rate constant for an adsorption column as in the equation below:

Thomas model:

\[ \ln \left( \frac{C_0}{C_t} \right) = \frac{K_{th} q_0 m}{Q} - \frac{K_{th} C_0 V_{eff}}{Q} \]
where $K_{th}$ is the Thomas rate constant (mL/(min mmol)), $q_0$ the equilibrium Cu$^{2+}$ uptake (mmol/g), $m$ the amount of resin in the column (g), $V_{eff}$ the effluent volume, $Q$ the volumetric flow rate (mL/min).

Since $V_{eff}/Q$ is dimensionally a time as physical quantity, one single fitting equation can be obtained from both model equations:

$$\begin{align*}
\ln \left( \frac{C_0}{C_t} - 1 \right) &= A - Bt \\
A &= \frac{k_0 h}{u} \quad \text{(BDST model)} \quad \text{and} \quad A = \frac{K_{th} q_0 m}{Q} \quad \text{(Thomas model)}, \\
B &= k \cdot C_0 \quad \text{(BDST model)}, \\
B &= K_{th} \cdot C_0 \quad \text{(Thomas model)}. 
\end{align*}$$

The evaluation of the kinetic adsorption rate, the maximum adsorption capacity and the time service to breakthrough are indispensable parameters to evaluate a possible up-scaling of this technology.

**Results**

In order to check through continuous experiments the industrial applicability and feasibility of metal adsorption, a column filled for 30 vol % with X-PKDap has been assembled and a Cu(II) solution has been poured through at a fixed flow of 3.9 ml/min. The results have been discussed on the basis of two known physical models for continuous adsorption: the Bed Depth Service Time (BDST) and the Thomas model [64]. These two models are used to determine the adsorption rate constant ($K$), adsorption capacity ($N_0$ and $Q_0$ respectively), Thomas rate constant ($k_{th}$). The breakthrough point $t_b$ is defined as the point when the effluent concentration is approximately 5% of the starting concentration. The breakthrough curves showed steep slopes and almost a vertical mass transfer zone (MTZ), indicating fast diffusion between solid surface and the adsorbate, which in turn implies that the resistance to mass transfer was controlled by external diffusion in the boundary layer of the particles (Figure 5.13).
Subject: Metal ion uptake modified polyketones

Figure 5.13. Breakthrough curve of X-PKDap in the presence of Cu$^{2+}$ ions and its data fitting with Thomas and BDST model

The validity of the above-mentioned models has been confirmed by the high values of $R^2$ values (Table 5.7), with the Thomas model displaying a better fitting.

<table>
<thead>
<tr>
<th>Model</th>
<th>K (L/mmol*min)</th>
<th>$N_0$ (mmol/L)</th>
<th>$R^2$</th>
<th>$Q_0$ (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDST</td>
<td>0.008005</td>
<td>858.0</td>
<td>0.95846</td>
<td></td>
</tr>
<tr>
<td>Thomas</td>
<td>8.9121</td>
<td></td>
<td>0.97782</td>
<td>1.0165</td>
</tr>
</tbody>
</table>

Table 5.7. BDST and Thomas fitting models for binary system X-PKDap/Cu$^{2+}$

Higher values of K indicate a faster adsorption kinetics, while higher $N_0$ values mean that the sorbent or the ion-exchange resin has a longer time to respond to the in-feed of copper ion solution. A computed $N_0$ value of 40.5 mmol/L has been found for copper adsorption with a rate constant K of $1.65 \times 10^{-5}$ L/mmol min by using U. reticulata biomass [65] while a $K_{th}$ of 0.117-0.331 L/mmol min and a $Q_0$ of 55.7-59.5 mg/g depending of the flow rate has been calculated for the same system by using Thomas model. It is evident, by comparing the experimental $Q_0$ values, that the model overestimated the metal uptake capacity of X-PKDap. Similarly, Yan et al. [66] reported that Thomas model overestimated $Q_0$ values of cadmium, lead and zinc biosorption by immobilized Mucor rouxii.

The total amount of copper adsorbed per gram of resin in continuous studies can be extrapolated by calculating the integral of the breakthrough curve and subtracting it from the area in case of maximum adsorption for copper. This amount is equal to 193 mg/g resin and it correspond to a ratio [NH$_2$]/[Cu]= 1.5:1. By considering that Copper has been found usually as a complex with amine in coordination four [29], beside confirming the excellent adsorption uptake of Cu(II) (see main text for a detailed
comparison), this result proved that pyrrole plays an active role in copper adsorption.
5.6 References


[38] Choi, M.; Jang, J. *J. of Col. & Int.Sci.* **2008**, *325*, 287.