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AMINO-FORMALDEHYDE RESINS. PROPERTIES AND APPLICATION TO REMOVE CONTAMINANT METAL IONS. AN OVERVIEW

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ABSTRACT

The global production of formaldehyde urea resins (UF) for 2019 was 6 million ton/year, being the largest use in the forestry industry in the production of MDP and MDF boards. It is in the resin industry's interest to develop other applications of these polymers.

The possible metal ion separation properties of commercial resins of the type urea-formaldehyde resins (UF), melamine-urea-formaldehyde resins (MUF), and formaldehyde melamine (MF) are achieved by modifying with functional groups.

The metal retention properties are determined by batch method in aqueous phase where the purified and sieved solid resin is put into contact with the metal ions at different pH, controlling temperature and ion force. The most studied metal ions are metal ions like Cu(II), Co(II), Cd(II), Zn(II), Cr(III), Hg(II) and Cr(VI).

The aim to contribute with this overview, is demonstrate the use of these modified resins to remove metal ions and also the potential application to use them as support to include new functional groups to increase the efficiency and affinity, Moreover, it is motivated by the production in our country of these resins and investigate possible applications in this research field.

Keywords: Amino-formaldehyde resins, separation process, environment, metal ions, removal.

1. INTRODUCTION

Eugenol is part of the family of allylbenzenes, which in turn are part of the Global production of formaldehyde urea resins (UF) for 2019 was estimated at 6 million ton/year, being the largest use in the forestry industry in the production of MDP and MDF boards, therefore the entire resin, logistics, production, R&D etc. Industry is oriented to the optimization of this type of products that are exported and that must constantly comply with environmental regulations especially after the formaldehyde was declared as cancerogenic. In recent years the forestry business in has stopped growing, in some cases some producers have disappeared because they have not been able to compete economically with higher volume producers that achieve better production costs, especially by having their inputs integrated into cellulose plants. That is why chemical resin plants have some production capacity that could meet some new need or requirement, but no longer of the forest area.

In 2014 the Innovation for Development Council (CNID) constituted the "Mining and Development Commission of Chile" developed the Technology Roadmap from 2015 to 2035[1] identifying five drive nuclei such as relays, smelting and mining, mining planning operations, mineral concentration and hydrometallurgy, which require enabling cores such as human capital, suppliers and innovation and intelligent mining, reaching the production of 8.5 million tonnes of copper in 2035.

Within the technological search of flotation were found 88 patents of which 2 of them are based on amino aldehyde resins used in the separation process. "Modified amine-aldehyde resins and uses thereof in separation processes” [2] and "Amine-aldehyde resins and uses thereof in separation processes" [3]. They describe the removal of a variety of solids and/or ionic species from liquids that are suspended or dissolved. These resins are especially useful as depressants in foam flotation processes for the benefit of obtaining materials valued as (bitumen, coal, kaolin clay) of impurities such as sand. Resins are also used in the treatment of aqueous suspensions to remove solid particles or to remove metal ions in water purification.

Currently in flotation processes are commonly used as depressant agents the cyanide-zinc complex that depresses copper sulfides (calcosite), ferrocyanide, and Nokes reagents, sodium hydroxide plus phosphorus pentasulfide that depresses copper sulfides, fluorosilicate, and ion fluoride to depress quartz and silicates. Organic depressants are commonly used in the flotation of non-metallic minerals and can be categorized as polyglycol ether, polysaccharides (starch, carboxymethyl cellulose, dextrin, and rubber), and polyphenols (tannin, crack and mimosa). The greatest application is in the depression of calcite, dolomite, talc, and pyrophyte, although starch and dextrin are used to depress galena, pyrite, and molybdenite. The main process of adsorption is hydrogen bond although polysaccharides seem to react especially with iron minerals, thus favoring their use for flocculation and depression of these minerals.

In the copper mining industry in the flotation process stage several reagents with foaming functions, collectors, depressants and pH modifiers are used, commonly the depressant reagents used are sodium sulfide (Na_2S), NaHS sodium sulfidrate, NaCN sodium cyanide, lime, and chromates and dichromates, $K_2Cr_2O_7$.

2. CONTAMINATION BY METALS

The presence of a large number of chemical and biological pollutants is expected in drinking water. This pollution of water resources caused by an increasing population occurs via the use and disposal of chemical, agricultural, animal products, and industrial waste.

The major percentage of inorganic substances found in groundwater is derived from natural origins. However, significant amounts are also a result of the human activities. Thus, the removal/remediation of these substances is necessary. Over the last few years, discarding solid and/or liquid waste products containing heavy metals emanating from industrial processes has received much attention, and consequently, legislation for the protection of the environment has gradually become more strict [4,5]. Contamination of the environment by heavy metals is a growing concern because are highly toxic at low concentrations and can accumulate in living organisms, causing several disorders and diseases. According to the World Organization of Health (WHO), the cationic metals of most immediate concern are aluminum, cadmium, chromium, cobalt, copper, iron, lead, magnesium, nickel, and zinc, whereas arsenic and hexavalent chromium as anionic pollutants [4].

Various pollutants such as organic compounds, heavy metals, and oxyanions emerge as a result of industrial applications. Especially organic pollution combining with heavy metals should be taken into consideration as an important problem in terms of environment. Since these pollutants and their derivatives are carcinogenic and have toxic effect on humans, animals as well as aquatic plants and animals, they should be removed via wastewater treatment methods. According to that, several methods and materials have been developed for environmental clean-up and remediation of metal ions from wastewater and synthetic wastewater, such as adsorption, also by using biomaterials, nanocomposites, ion exchange, membrane separation, solvent extraction [4-17]. All methods have advantages and disadvantages, however, ion exchange and adsorption are well studied since they are efficient for heavy metal recovery and water deep purification. Thus, removal of heavy metals from aqueous solutions by using adsorption method with low-cost adsorbents might be both economic and effective adsorption is considered to be one of the most efficient techniques because of its good operational flexibility, high efficiency, and excellent reusability [20-22, 22.a, 22.b, 22.c]. During the adsorption, heavy metals are transferred from wastewater and adhered to the surface of the adsorbent by the physical and/or chemical interactions between them.

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In recent years, the researchers have tried various composite production methods in order to activate the adsorbents. It was observed that formation of different composites from natural adsorbents activated them and their adsorption capacities increased [23–24].

3. REMOVAL BY AMINO-FORMALDEHYDE RESINS

Modified resins [24-26] to improve mechanical properties, but other applications are also described to remove a wide variety of solids and / or ionic species from the liquids in which they are suspended and / or dissolved. These modified resins are especially useful as foam buoyancy depressants, to treat aqueous liquid suspensions to facilitate the removal of solid particles, as well as the removal of metal ions in water purification. Modified resins comprise a base resin that is modified with a coupling agent, which is highly selective for binding to metal ions.

3.1 Urea formaldehyde Resins. UF Resins

3.1.1 UF resins modified with thiourea for separation Au(III), Cu(II), and Zn(II).[27]

In this research proceed to synthesize two resins, one totally urea-formaldehyde and another totally thiourea formaldehyde. The resins are carried up to 100% conversion or gelled. Resins were characterized by elemental analysis and FT-IR spectroscopy. The metal ion retention capacity was studied through a column with resin to which Au(III), Cu(II), and Zn(II) solutions are passed on to constant flow pump. The concentrations of the metals in solution are determined by atomic absorption spectroscopy (AAS). Studies are carried out at different pH and the metal retention capacity of both resins is determined.

Figure 1 represents the general mechanism for obtaining a UF, MUF or MF resin. It shows the following: (1) the methylolation reaction of urea with formaldehyde in acidic or basic medium is carried out, and then in (2) and (3) begin the condensation reaction. Side reactions that generate rearrangement are explained in eqs. (4) and (5).

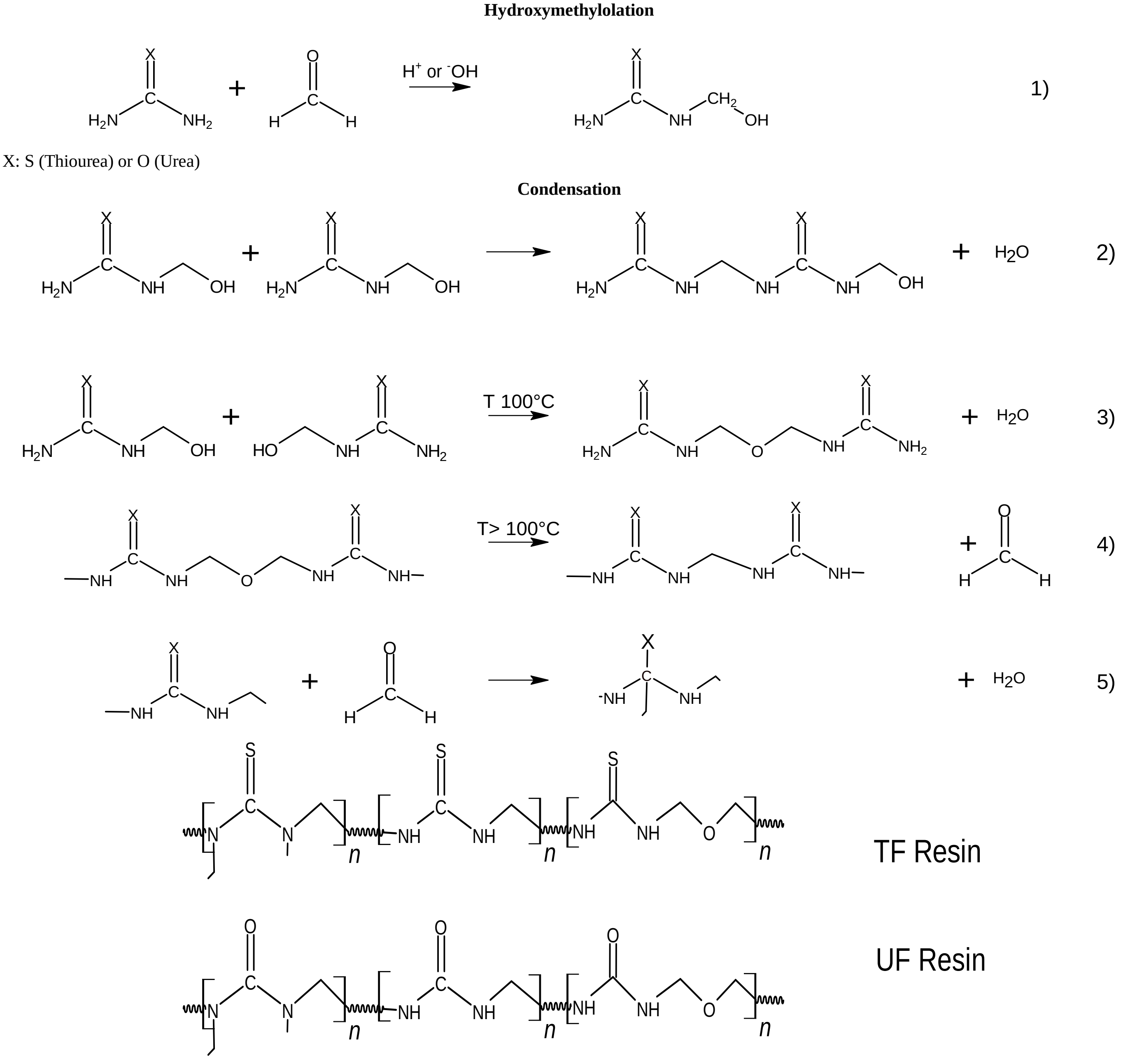

Figure 1. General scheme of UF resin reaction mechanism and comparison of the general structures [27].

Figure 2 shows adsorption curves for Au(II), Cu(II), and Zn(II) obtained for TF resin and UF. 1 g of resin at a flow of 0.74 BV/min. They see a noticeable effect on the substitution of a functional group.

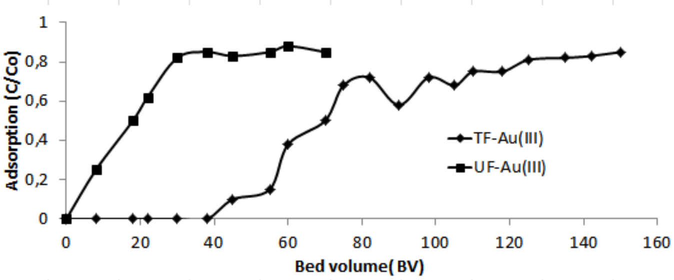

Figure 2. Adsorption curves for Au(II), Cu(II), and Zn(II) obtained for TF and UF resin. [27].

3.1.2 Foamed urea-formaldehyde microspheres for removal of heavy metals from aqueous solutions [28]

Because a high degree of crosslinking can make it difficult for ions to penetrate the chelating surface of the resins. The other authors [28] modified the gelling mechanism, achieving microspheres.

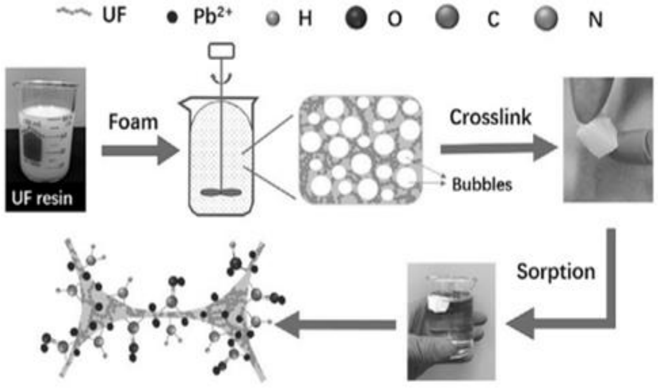

Figure 3. Foamig method to fabricate UF resins microspheres.[30].

A simple foaming method (see Fig 3) was applied to fabricate urea formaldehyde (UF) microspheres with crosslinked porous structures for environmental remediation of heavy metals. The specific surface area and average pore radius of the resultant foamed UF microspheres were 11 - 29 m^2 /g and 11-25 nm, respectively, which increased with the increasing molar ratio of formaldehyde to urea. All the foamed UF microspheres showed good removal of heavy metals ions (Pb(II), Cu(II), and Cd(II)) in both single- and mixed-metal solutions. Further investigations of Pb(II) adsorption on a selected UF microspheres showed fast kinetics and relatively high adsorption capacity (21.5 mg g^{-1}), which can be attributed to the mesoporous structure and abundance of oxygen surface functional groups of the microspheres.

Both experimental and model results showed that chelation or complexation interactions between Pb(II) and the surface functional groups were responsible to the strong adsorption of the heavy metal ions on the microspheres. Hydrochloric acid (0.05 M) successfully desorbed Pb(II) from the post-adsorption microspheres for multiple times and the regenerated microspheres showed high Pb(II) removal rates (>96%) in five adsorption-desorption cycles. With many promising advantages, foamed UF microspheres show great potential as a wastewater treatment agent for heavy metal removal. In table 1, a summary of their adsorption capacity and a comparison with similar adsorbents is made.

Table 1. Summary of the Pb(II) adsorption capacity of various adsorbents. [28]

Adsorbent	Pb(II) sorption capacity (mg g^{-1})	Reference
Melamin-Formaldehyde resin microspheres	4.9	[29]
Betonite/Thiourea-formaldehyde composite	13.38	[30]
Poly(Anthranilic acid-2-aminopyridine-formaldehyde)	6.54	[31]
Foamed Urea Formaldehyde	21.5	[28]

3.1.3 Synthesis and Characterization of Antibacterial Polychelates of Urea–Formaldehyde Resin with Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II) Metal Ions.[32]

Uses and applications of UF resins already formed as polyquelates have also been reported as for example in antibacterial activity. This research studies the reaction between urea and formaldehyde with the aim of preparing polyquelates of Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II) as shown in Figure 4. The compounds were characterized by elemental analysis, FT-IR, ^{1}H-NMR, XPS, TGA, and magnetic susceptibility. A ratio (metal/ligand) 1:1.15 was found, and greater thermal stability to complexes versus UF resin, the congenital susceptibility allows to confirm the geometry of the complexes. The bactericide activity of polychelates is investigated with diffusion methods in agar, found similar to stable drugs such as ciprofluoxacin or ampicillin (see Table 2).

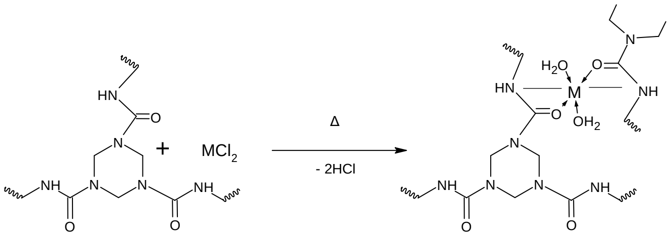

Figure 4. Scheme of obtaining polychelates from a UF resin, where M = Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) [32].

Table 2. Antibacterial activity ligand UFR and its polychelates with metal ions Mn(II), Fe(III), Co(II), Ni(II), and Cu(II) obtained from UF resins [32].

Compound	**Antibacterial activity**[a]				
	E.Coli	***S. aureus***	***B. megaterium***	***P.vulgaris***	***B.Subtilis***
$C_8H_{11}N_4O_2$	5	8	7	6	10
$(C_8H_9N_4O_2Mn\cdot 2H_2O)_n$	12	11	14	13	11
$(C_8H_9N_4O_2Fe\cdot 2H_2O)_n\cdot{}_nCl$	10	15	12	12	14
$(C_8H_9N_4O_2Co\cdot 2H_2O)n$	18	10	9	14	13
$(C_8H_9N_4O_2Ni\cdot 2H_2O)_n$	13	17	11	12	15
$(C_8H_9N_4O_2Cu\cdot 2H_2O)_n$	16	14	13	14	19
DMSO	-	-	-	-	-
Ciprofloxin	25	24	20	22	22
Ampicillin	18	22	15	20	20
Kanamycin	26	25	22	26	25

0-5 = Inactive; 5-10 = mildly active ; 10-15 = moderately active; >15 = highly active. Ciprofloxacin, ampicilin,and kanamycin were udes as standard drugs. DMSO was udes as a control.

a Zone of inhibition in 0 -25 mm at a concentration of 25 μg mL -1

3.2. Melamine Urea Formaldehyde Resins. MUF Resins

An example of separation of Cr((III) and Cr(IV) using MUF resin [33] which can be considered as a UF resin modified with melamine to be converted into MUF resin. In this work it is used to preconcentrate and separate these ions.

3.2.1 Speciation of Cr(III) and Cr(VI) using melamine-urea-formaldehyde resins and FAAS. [33]

A method is described for the quantitative preconcentration and separation of trace chromium in water by adsorption on melamine-urea-formaldehyde resin. Cr(VI) is enriched from aqueous solutions on the resin. After elution the Cr(VI) is determined by Flame atomic absorption spectroscopy (FAAS). The capacity of the resin is maximal at pH 2. Total chromium can be determined by the method after oxidation of Cr(III) to Cr(VI) by hydrogen peroxide. The relative standard deviations (10 replicate analyses) for 10 mg L^{-1} levels of Cr(VI), Cr(III, and total chromium were 1.5, 3.5, and 2.8% respectively. The procedure has been applied to the determination and speciation of chromium in lake water, tap water, and chromium-plating baths.

The preparation of MUF resin is described [34] 1 mol melamine, 1 mol of urea, and 6.5 mole formaldehyde (35% solution) in a ball, being mixed to reflux for 15 min with magnetic agitation until a transparent gel is achieved, NaOH is added to 10% slowly until the gel is white and insoluble at pH 10. The resin is washed and dried sifted at 350-853 um and characterized by FT-IR spectroscopy.

The tests are performed in column and procedure for speciation of Cr(III) and Cr(VI). Selection of optimal pH of preconcentration portions (25 mL) of 10 mg L^{-1} Cr(VI) solution, at pH ranging from 1 to 9 were shaken with 0.5 g of resin for 2 h. After filtration, the chromium adsorbed on the resin was eluted with 0.1 M sodium hydroxide, and determined by AAS. At pH 2-2.5 was found optimum for the selective sorption of Cr(VI) (see Fig. 5).

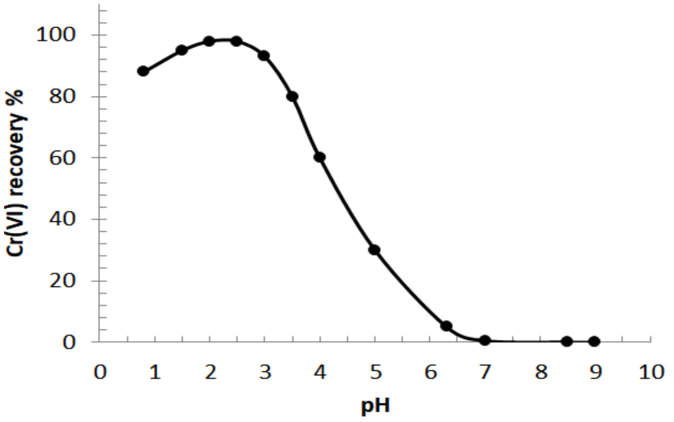

Figure 5. Recovery of chromium as a funtion of pH [33].

As shown in Fig. 5, optimum efficiency of enrichment was obtained at pH 2±2.5. There was no interference by the diverse ions which were examined (see Table 3).

Table 3. Effect of foreing ions (all 100 mg L^{-1}) on the adsorption of Cr(VI) (20 mg L^{-1}) [33].

Foreing ion	Recovery of Cr(VI) (%)
Fe^{3+}	100
Zn^{2+}	99.8
Cr^{3+}	99.5
Cl^{-}	100
SO_4^{2-}	100
NO^{3-}	99.5
PO_4^{3-}	98.5
Cd^{2+}	99.9
Ni^{2+}	99.7

It was shown that good sensitivity and selectivity for the determination of chromium can be attained by using preconcentration with melamine-urea-formaldehyde resin and subsequent determination of chromium in the eluate. This resin has some advantages, its low toxicity and low cost relative to melamine-formaldehyde resin [37]. Known extraction methods are frequently very slow and tedious and moreover are less sensitive than the proposed method. Other pre-concentration methods such as co-precipitation, use of chelating agents and electrodeposition on a graphite tube are also complicated and do not give an improvement in sensitivity. The method studied in this work has good precision and accuracy and matrix effects are absent. It can be concluded that the speciation of chromium is possible by use of the proposed pre-concentration method.

3.3 Melamine Formaldehyde Resins. MF Resins

The main applications in the wood industry for melamine formaldehyde resins is in the production of impregnating papers, whose paper is adhered to the surface of the wood board with beautiful finishes in different colors. This type of resins have limited solubility and are mostly colorless.

3.3.1 Melamine–formaldehyde–NTA chelating gel resin: Synthesis, characterization and application for copper(II) ion removal from synthetic wastewater. [36]

Selective removal of Cu(II) from wash water using melamine-formaldehyde MF resins modified with triethic nitrile acid (NTA) has been reported [39]. The effect of preparation conditions such as (temperature, acidity, water content) and resin characteristics (water recovery, stiffness, NTA functionality and porosity) was studied. It was found that at pH 1.3 and 150°C are the best resin preparation conditions. The resins were characterized by FT-IR spectroscopy, CHNO elemental analysis, and nitrogen adsorption (BET), and scanning electron microscopy (SEM), surfaces of 159 $m^2 g^{-1}$ were achieved.

The simultaneous adsorption of Co(II), Cd(II), Zn(II), and Cu(II) from synthetic washwater solutions were determined by batch process and quantified their content by atomic absorption spectroscopy, a selective adsorption of ion Cu(II) was observed between Co(II), Cd(II), Zn(II), thermodynamic properties were calculated finding that for Cu(II) it is spontaneous (ΔGads <0), exothermal (ΔHads > 0), and reversible (ΔSads < 0), and reversible (ΔSads < 0). Kinetically, the reaction is reversible kinetics of the first order, according to the Langmiur isotherm model the capacity of Cu(II) is 52.6 mg g^{-1} (0.083 mmol g^{-1}. Using an EDTA solution, the resin can be regenerated by metal ions. After regeneration it is observed that the capacity decreases due to partial hydrolysis of the functional active groups NTA.

Other chelating groups [44] have been studied in this same type of resins, such as dietary-minopentatic acid (MF-DTPA) (see Fig. 8) in the removal of heavy metals such as Co(II), Cd(II), Zn (II), and Cu(II) and nitro acetic acid (NTA) [43] during the ratio of melamine-formaldehyde resin in the presence of water using acetone and guaicol as a porogenic mixture in removing Cu(II) from synthetic wash water. Fig 6 proposes a possible structure of MF-NTA resin. It is also of interest to determine the optimal pH adsorption since at pH greater than 6 copper hydroxide is formed.

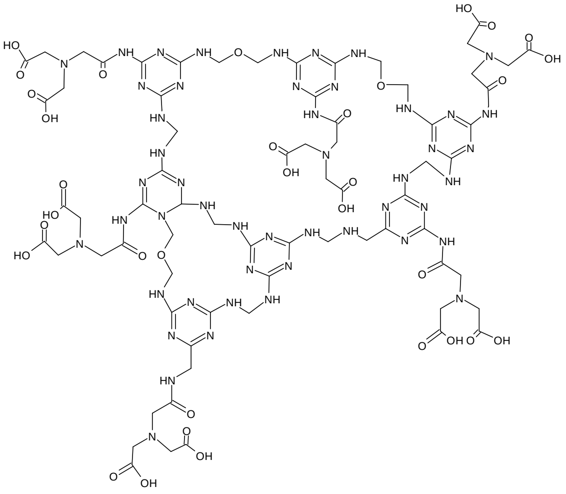

Figure 6. Possible structure of MF-NTA resin [36].

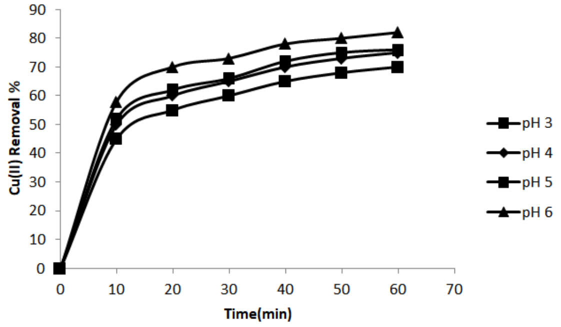

Figure 7. Example of kinetic study [8] of metal retention Cu(II) at 25 °C, 150 rpm, initial concentration 100 mg L^{-1} ppm, volume 30 mL, adsorbent gel 0.3 g, pH values 3, 4.5, and 6.[36].

Comparison of the adsorption capacity of MF-NTA resin is shown in Table 4. These are moderate compared to those materials.

Table 4. Comparison of adsorption property, Qo of Cu(II) MF-NTA. [36]

Material	Qo (mg g^{-1})	Reference
Spirogyra (biomass)	133.3	[37]
Raw Kaolinite	10.78	[38]
AMA	7.09	[39]
PMA	8.55	[39]
Chitasan-Cellulose beads	53.2	[40]
P(HEMA-*co*-MAH)	122.7	[41]
Polydithiocarbamate(synthetic resin)	35	[42]
MF-NTA	29.7	[36]

3.3.2 . Preparation and characterization of melamine–formaldehyde–DTPA chelating resin and its use as an adsorbent for heavy metals removal from wastewater [44] .

Melamine–formaldehyde–diethylenetriaminepentaacetic acid (MF–DTPA) resin was prepared as a new adsorbent for removing heavy metals from wastewater effluents. The resin was synthesised by anchoring the chelating agent diethylenetriaminepentaacetic acid (DTPA) to melamine via amide covalent bond during melamine–formaldehyde condensation reaction in an acidic aqueous medium. The effects of reaction parameters (temperature, acidity, and water content) on resin characteristics (water regain, rigidity, DTPA functionality, and porosity) were monitored to specify the best synthesis conditions. The resin was chemically characterized using infrared spectroscopy (FTIR), elemental analysis (EA), thermal programmed decomposition-mass spectrometry (TPD-MS), solid-state ^{13}C-NMR and ^{15}N-NMR spectroscopy, and was morphologically characterized using N_2 gas adsorption/desorption (BET analysis) and field emission-scanning electron microscopy (FESEM).

The water regain factor was also calculated to determine hydrophilic character of the resin. The simultaneous adsorption performance of MF–DTPA resin towards selected heavy metals, Co(II), Cd(II), Zn(II), and Cu(II), was discussed. (see figure 8). Quantitative analysis for adsorption was conducted using atomic absorption to investigate the kinetics, adsorption isotherm and thermodynamics of the removal process considering pH, initial concentration, temperature, and contact time as controlling parameters. The mechanism of adsorption was suggested based on experimental results. This work shows the potential application of the MF–DTPA.

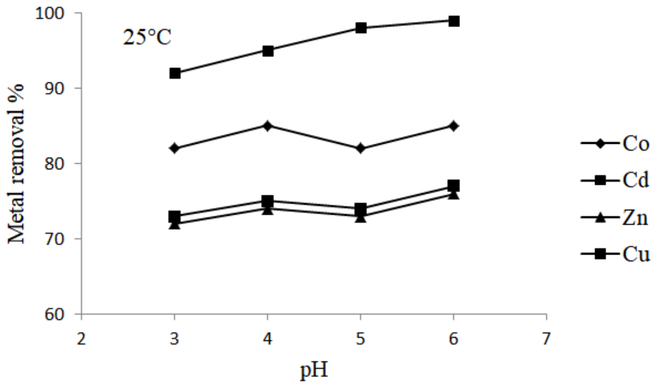

Figure 8. Example of kinetic study of metal retention at different pH (top) and lower, study of metal removal in a mixture at different pH. [44]

In the figure 9 is suggested the formation mechanism of MF-DTPA resin from melamine, formaldehyde and DTPA.

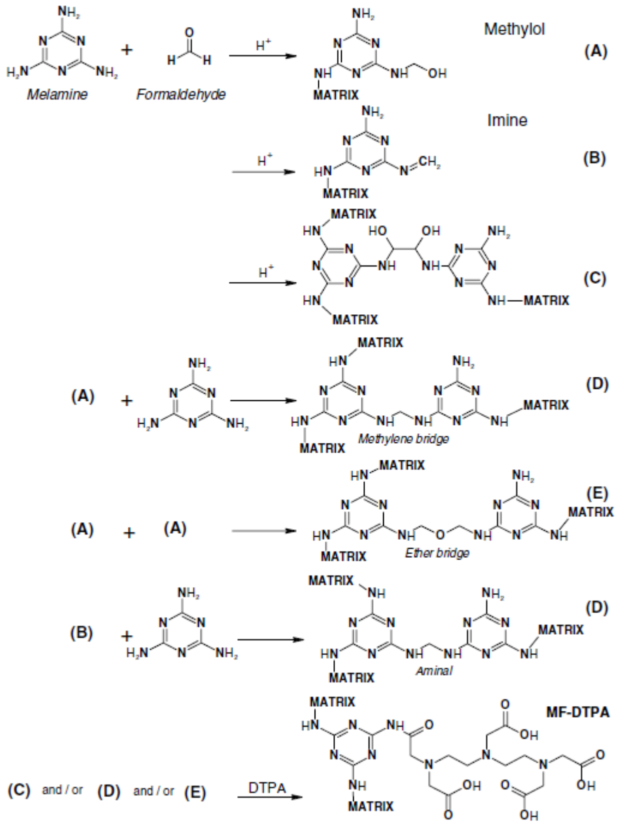

Figure 9. Suggested formation mechanism of MF-DTPA resin from melamine, formaldehyde, and DTPA precursors under acid conditions [44].

3.3.3 Extraction and separation studies of silver (I) and copper (II) from their aqueous solution using chemically modified melamine resins. [45]

Two modified melamine resins has been prepared and investigated, the modification process took place through the treatment with thiourea to produce R1 or tetraoxalyl ethylenediamine to produce R2. The adsorption behaviour of the obtained resins towards Ag(I) and Cu(II) from their aqueous solutions has been studied using batch method.

The experimental part was done *:* the resins was prepared from the reaction of melamine, thiourea (or tetraoxalylethylenediamine) and formaldehyde at molar ratio of (1.5: 1:1) respectively and aqueous media at pH 9. The mixture was heated at 75-90 °C for 6 h, the precipitate or gel particles is washed, and dried. Both resins were characterized using, water regain, surface area, pore size, FT-IR spectra, and elemental analysis. The structures proposed are shown in figure 10.

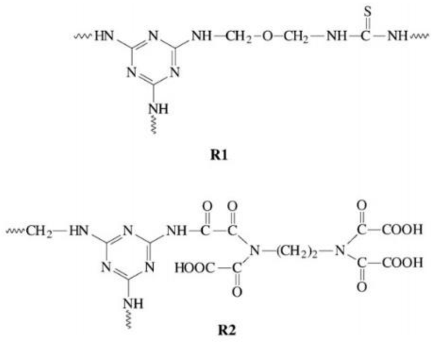

Figure 10. Proposed structures of the studied chelating resins. [45]

Uptake measurements was done, studyng de effect of equilibruim pH on the uptake, selectivity studies, kinetic, adsoprtion isotherms, column equilibrium procedure, and elution. The main adsorption results for different metal ions and conditions are summarized in figure 11.

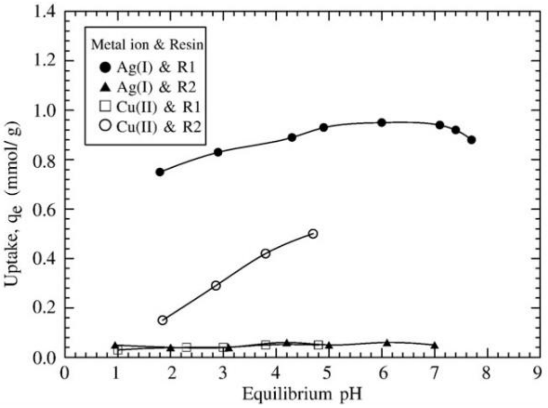

Figure 11. Effect of pH on the uptake of Ag(I) by R1 and Cu(II) by R2 from initial concentration $1x10^{-2}$ M at 25°C [45].

The obtained resins were tested for selective separation between Cu(II) and Ag(I) from their binary mixtures. The figure 11 showed a Resin R1 has a high selectivity towards Ag(I) from Cu(II) solution, while R2 gave promising results for the selective separation of Cu(II) from Ag(I) solution.

The explanation of the mechanism of adsorption of Ag(I) of R1 is shown in the figure 12 using the theory of Hard and Soft Acid and Bases (HSAB) [46]. The sulphur and the nitrogen atoms in thiourea moiety have an easily polarizable lone pairs of electrons and is considered as a ‘soft base’’, which would have a tendency to create complex with silver ions (considered ‘‘soft acids’’). HSAB theory confirms that, the selective resins containing N or S donor atoms interact strongly with soft acids like Ag(I) even in the presence of high concentration of protons. The observed decrease in the uptake of Ag(I) prior to initial pH 8 may be due to the masking of Ag(I) ions in the form of soluble anions. At pH >8, almost all of the Ag(I) ions are precipitated in the form of AgOH [47]. It is also worth mentioning that the equilibrium pH is lower than initial pH in all studied rang. The released H^+ can be attributed to the deprotonation of thiol form of thiourea moiety at the end of reaction as shown in fig 12.

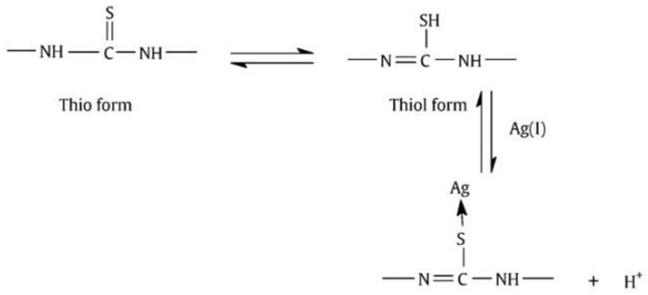

Figure 12. Released H^+ can be attributed to the deprotonation of thiol form of thiourea [45].

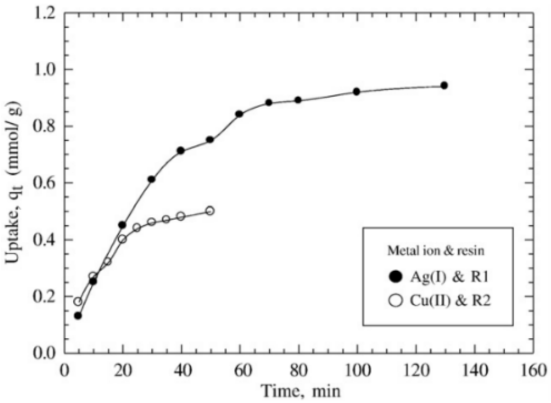

Figure 13. Effect of time on the uptake of Ag(I) by R1 and Cu(II) by R2 frrom initial concentration $1x10^{-2}$ M at normal pH and 25°C [45].

The figure 13 showed an effect of time on the uptake. Both kinetic and thermodynamic parameters of the adsorption process were obtained. Thermodynamic data indicated that the adsorption process is an endothermic spontaneous reaction. Kinetic analysis showed also that the adsorption of Ag(I) on R1 is perfectly fit pseudo-first order model; while the adsorption of Cu(II) on R2 is perfectly fit pseudo-second order one. The interaction mechanism between metal ion and active sites has been interpreted as chelation. Durability of resins was estimated from column studies. These parameters indicated that the prepared resins have a good efficiency for repeated use.

3.3.4 Synthesis and application of ion-imprinted resin based on modified melamine–thiourea for selective removal of Hg (II). [48]

A novel Hg(II) ion-imprinted resin based on thiourea-modified melamine was manufactured for selective elimination of Hg^{2+} from aqueous solutions.

The synthesis of Hg-PMTF is carried out using KSCN in an aqueous and acidic medium, it is refluxed in the presence of melamine at 90 °C for 1 h, to then cool and purify. The ligand obtained is used to form the complex with Hg(II) by dissolving the ligand in MeOH at 80 ° C for 2 h in the presence of the metal ion. The complex obtained is cross-linked with formaldehyde in a basic medium for 2 h at 90 ° C. The gel obtained is purified and dried. The Hg^{2+} is removed from the gel in an acid medium. Figure 14 summarizes the stages described.

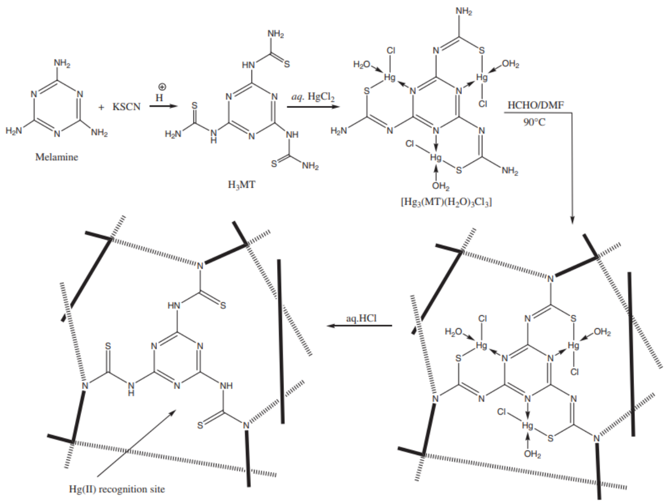

Figure 14. Synthesis of Hg(II) ion-imprinted resin (Hg-PMTF). [48]

The potential of the prepared resin for selective separation of Hg(II) ions from aqueous solutions was then evaluated by performing a series of batch experiments, studying in the adsorption the effect of pH, the thermodynamics, kinetics and isotherm, they are also carried out selectivity and reusability study.

Hg-PMTF displayed an obvious rapid removal of Hg(II) ions with a pseudo-second-order kinetic pattern. In addition, the Langmuir adsorption isotherm model exhibited the best fit with the experimental data with comparatively high maximum adsorption capacity (360.5 mg g^{-1}).

In general, the prepared resin shows a high adsorption capacity when compared to the other recently studied adsorbents (see Table 5).

Table 5. Maximum adsorption capacities for adsorption of Hg(II) onto various adsorbents. [48]

Adsorbent	**q_{max} (mg g^{-1})**	**Reference**
Polyamine chelating resins	340	[49]
Fe_3O_4/rhodamine/hydrazide	7.7	[50]
Thiol-modified ion exchanger	207	[51]
Chitosan-phenylthiourea	135.5	[52]
Chitosan-thioglyceraldehyde	98.7	[53]
Hg(II) ion-imprinted poly(ethylene terephthalate) fibres	77.51	[54]
2-Mercaptopyridine-modified silica	120	[55]
Ion-imprinted Hg-PMTF (present study)	340	[48]

CONCLUSIONS

Amino resins modifying the amino part by thiourea, NTA, DTPA, are capable to remove metal ions such as Au(II), Co(II), Cd(II), Ni(II), Mn(II), Fe(III) Cr(VI) Hg(II), Cu(II), Zn(II), and Pb(II) in solution. Foam or printed resins achieve better results by achieving greater contact surface and in turn can make several loading and unloading cycles when changing the pH of the solution. There are greater studies of melamine resins given their better resistance to hydrolysis than urea-based resins that can release formaldehyde, especially since they are resins with an interest in decontaminating. Melamine resins manage to form metal complexes, which have interesting antibacterial properties, which may be of interest in the application as an adhesive in the industry.

Is important conclude that these resins have good properties to modify by other different functional groups in order to remove water-contaminants in order to increase not only the efficiency but the selectivity and to reuse it. It would be important as a new potential applications at world level for these resins which are produced in Chile, particularly in Biobio Region.

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