

REMOVAL OF COPPER IONS FROM AQUEOUS SOLUTIONS BY USING RESINS FROM *Pinus Radiata* BARK RESINS

FRANCISCA L. ARANDA ^{1*}, ALEXA GAYOSO ², VALERIA PALMA-ONETTO ³ AND BERNABÉ L. RIVAS ^{1*}

¹Departamento de Polímeros, Facultad de Ciencias Químicas, Universidad de Concepción, Concepción, Chile.

²Flamacar S.A. Planta Santa Fe, CMPC pulpa, Nacimiento, Chile.

³Centro de Investigación en Biodiversidad y Ambientes Sustentables (CIBAS). Universidad Católica de la Santísima Concepción, Concepción, Chile.

ABSTRACT

A large amount of copper ions are released into the environment, which significantly affects water resources. The reduction of copper contaminants and the potential reutilization of these ions are important issues for environmental and human health. Resin based on *Pinus radiata* tannin and its derivatives obtained via chemical modifications with three cyclic anhydrides (maleic, citraconic, and itaconic) adsorbed Cu(II) from aqueous solutions. It was carried out in order to incorporate functional groups able to interact with heavy metal ions. The effect of the pH on the adsorption, desorption, and maximum adsorption capacity for Cu(II) solutions was studied. The adsorption depends largely on the pH of the solution, and the highest adsorption was observed at pH 3. Modified tannins showed lower maximum adsorption values than the original tannin. However, tannins modified with maleic and citraconic anhydrides presented larger values than the unmodified tannin under high ion concentrations. The resin showed an adsorption capacity of Cu (II) of approximately 55 mmol g⁻¹ and a desorption capacity higher than 55%. It is the reason why it represents a complementary alternative, with respect to current treatments, for future use in the treatment of contaminated water.

Keywords: Tannin, adsorption, desorption, water pollution, metal ions.

1. INTRODUCTION

Water pollution is a severe problem around the world, as many pollutants are transferred to the aqueous environment due to industrial waste, agriculture, atmospheric deposition, and lixiviation from mining^[1,2,3]. Many of these pollutants are toxic and carcinogenic heavy metals^[4,5,6-9], which include Pb, Hg, Cr, Cu, and Cd^[10]. While organic pollutants can be easily biodegraded, most heavy metals accumulate in a variety of animals and plants and tend to persist for a long time in ecosystems and be difficult to eradicate. The removal of copper ions, which are the main waste product from Chilean mining is especially complex since they easily attach organic and inorganic substances depending on the solution pH^[11,12,14].

Water scarcity is the major problem that is faced all across the world. Although 70% of the world is covered with water, only 1% is fresh water, hence, it is necessary to recycle wastewater to satisfy the needs. Due to the negative effects of heavy metals, their removal from wastewater has become an important concern. Various physicochemical processes have been proposed for removing metal ions from water solutions, such as ion exchange processes, precipitation, carbon adsorption, membrane filtration, electrodeposition techniques, application of microorganisms and biomass^[15,16,17-22]. However, these methods are typically expensive and inefficient for treating water with low metal ion concentrations and may secondarily produce a large amount of waste. Hence, it is necessary to develop low-cost and environmentally friendly materials for treating large volumes of wastewater^[23,24].

Many adsorbent materials are of agricultural and forestry origin^[25] such as peanut waste^[26,27], onion skin^[28], bagasse pith^[29], cork wastes^[30], technical lignins^[31], coconut fibers^[25,32], conifer leaves^[33], and wood barks^[34,35,36]. Wood barks, especially those from pine have been studied over the past years for possible application in the removal of heavy metals from wastewater^[37,38,39] due to their high abundance and low cost.

Pine bark is a polyphenol-rich substrate (8-18 wt%), which has been found to be effective in removing copper metal ions from water solution. Among those polyphenols, tannins are one of the main components that enable effective removal^[10,13,40]. This is due to their multiple phenolic groups that have an elevated affinity for metal ions^[41]. Nevertheless, tannins are not ideal as they have a limited number of adsorption sites which show poor stability, exhibit low solubility in organic solvents and thermal instability, lack reactive functional groups beyond hydroxyl groups (-OH), and must be immobilized to avoid dissolution in water^[40,42,43]. In condensed tannin monomers there are three sites for derivatization. The A-rings can be derivatized at the C-5 or C-7 -OH group or at the C-6 position. On the B-ring, derivatization takes place mainly at the C-3' or C-4' -OH group (or additionally at the C-5' -OH group in case of delphinidins or gallo-pyrogallols). The C-ring can be modified at the C-3 -OH

and at the C-4 inter C₁₅ linkage. In C₁₅ terminal units of condensed tannins, derivatization may occur at the C-8 position^[45]. Tannins' ability to adsorb metal ions is improved by chemical modifications, tailoring properties and diversifying their applications^[24,44]. Therefore, the derivatization is considered a useful method that allows the molecule to be given greater functionality. Derivatization has a series of advantages in terms of improving the properties of the molecules, among which they are providing higher or lesser reactivity, providing more active sites for the reaction, etc. A modification that provides advantages is the esterification of polyflavonoids and lignin with five-member unsaturated cyclic anhydrides (see Fig.1). In general, cyclic anhydrides such as maleic anhydride, itaconic anhydride, and citraconic anhydride have high reactivity and can be very useful agents for the synthesis of functional polymers. Since the process is free of side-chain products, cyclic anhydrides are more reactive than their linear-chain counterparts, which enables derivatization reactions at room temperature, and the unsaturated carboxylic chain is a desirable functional group for several types of polymerization pathways^[43]. The chemical combination of natural and synthetic polymers yields new materials that have desirable properties, such as biodegradability. Thus, the modification of natural polymers via graft copolymerization is anticipated to be a promising technique as it functionalizes these natural polymers to their potential uses and give desirable properties^[46].

In the present study, we aim to study the Cu(II) uptake and desorption capacity of tannins and their derivatives via reaction with three cyclic anhydrides (maleic, itaconic, and citraconic) to obtain new resins able to remove copper ions (see Fig. 1). We hypothesize that condensed tannins from *Pinus radiata* bark resins and their modified derivatives are polymeric building blocks with the capacity for cationic exchange of Cu(II). We addressed the following questions: (a) Is Cu(II) ion uptake realized by tannin-based resins? (b) What is the maximum uptake capacity (at which pH is it realized)? (c) Are tannin-based resins highly desorbed? (d) Do the tannin uptake and desorption capacities depend on the ligand (-OH vs chains from the remains of the reaction with anhydrides)?

MATERIALS AND METHODS

2.1 Adsorbents

The condensed tannins and semi-commercial modified condensed tannins, provided by the Technological Development Unit (UDT) of the Universidad de Concepción (UdeC), the significant characteristics of condensed tannins were described by García et al., 2015^[53]; 2016^[54]; 2017^[55]. CuSO₄ x 5H₂O (MERCK) was used to prepare the Cu (II) solution with milli-Q water, all the equipment used to carry out this research was provided by the Faculty of Sciences of the Universidad Católica de la Santísima Concepción.

The adsorption capacity of copper(II) by condensed tannins from radiata pine bark and their respective modifications with five-member anhydrides (maleic, citraconic, and itaconic) were considered to determine the effects of pH at various

exposure times and in consideration of ambient temperature. Subsequently, the maximum adsorption capacity was determined, and studies were conducted regarding FT-IR characterization. Finally, the metal desorption from each adsorbent was investigated.

2.2 Effect of pH on concentration

50 mg of condensed tannins and 100 mg of modified condensed tannins were dissolved in a 50 mL $\text{CuSO}_4 \times 5\text{H}_2\text{O}$ (2000 ppm) dissolution^[41] at pH range from 3 to 5. The residual dissolution was analyzed on a model 902 atomic absorption spectrophotometer (EAA) at 228.8 nm^[10]. Via this approach, the amount of adsorbed copper was calculated using the difference in concentration before versus after treatment.

2.3 Maximum adsorption capacity

Study of condensed tannins and modified condensed tannins in a $\text{CuSO}_4 \times 5\text{H}_2\text{O}$ solution at six concentrations (1000, 2000, 3000, 4000, 5000, and 6000 ppm)^[10] was carried out. Residual dissolution was conducted via the same process as in the previous stage, however, the remaining solid was reserved for subsequent characterization via FTIR spectroscopy.

2.4 FTIR spectroscopy analysis.

The characteristic absorption bands describe the metal-ligand interaction after the defined exposure time. For this, the Fourier-transformed infrared spectrometry (FTIR) Cary 630 model mode was used, which was configured at a resolution of 4 cm^{-1} with 32 scans per sample in the spectral region in the range of 4000 - 650 cm^{-1} ^[47].

2.5 Cu(II) desorption.

The use of 1 M and 2 M HCl as elution reagents was considered. The resins were poured into a defined amount of acid, where they were subjected to constant agitation for 24 h at 250 rpm. Next, they were analyzed using a GBC model 902 atomic absorption spectrophotometer (EAA)^[48].

3. RESULTS AND DISCUSSION

The condensed tannins and semi-commercial modified condensed tannins, provided by the Technological Development Unit (UDT) of the Universidad de Concepción (UdeC), the significant characteristics of condensed tannins were described by García et al., 2015^[53]; 2016^[54]; 2017^[55]. The modification and general structures are shown in figure 1.

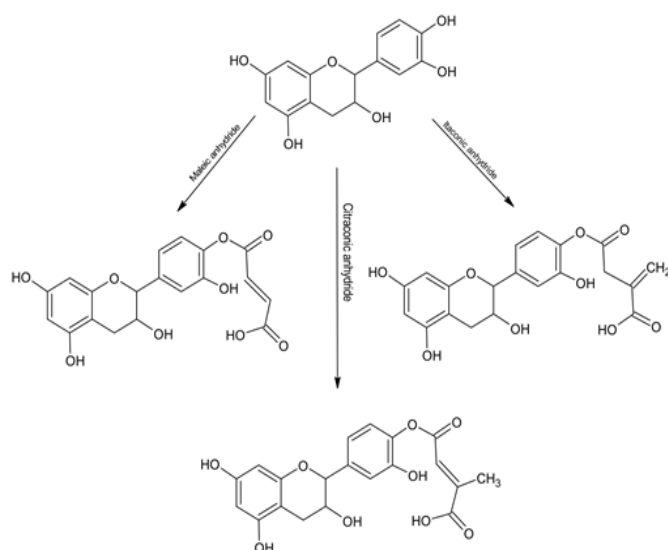


Figure 1. Modification of the tannin condensate with five-member anhydrides (maleic, citraconic, and itaconic).

The modified tannins were characterized by FT IR spectra. The most characteristic absorption bands are summarized in table 1. These corroborate that the functional groups were present at the structure.

Table 1. FTIR characteristic absorption bands of modified tannins.

Absorption band (cm^{-1})	Appearance	Group
3200 - 3600	Stretching vibration	O - H
2850 - 2980	Stretching	C - H
1700	Stretching (C-O bond)	C-O carbonyl group
1400 - 1450	Anti - voltage stress deformation or deformation vibrations	C - H in CH_3 or C - H in CH_2
1000 - 1200	voltage vibrations	C - O
700 - 900	push-up off the plane and in the plane	C - H cis alkenes and C-H trans alkenes

3.1 Influence of pH on Cu(II) adsorption.

It was determined that Cu(II) adsorption occurs more efficiently at higher acidity (considering pH values of 3.0, 4.0, and 5.0), and it is best suited for unchanged condensed tannin with a stabilization period that ranges from 2 up to 24 h (see figure 2a, 2b, 2c).

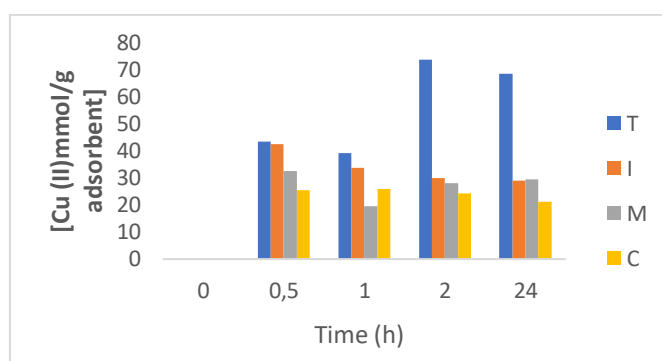


Figure 2a. Copper (II) adsorption by unmodified condensed tannin and cyclic anhydride modified tannins at various exposure times and pH 3. Unmodified tannin (T); tannin modified with maleic anhydride (M), tannin modified with itaconic anhydride (I), and tannin modified with citraconic anhydride (C).

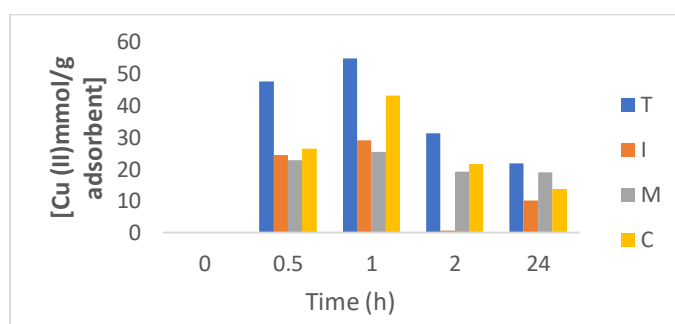


Figure 2b. Copper(II) adsorption by unmodified condensed tannin and cyclic anhydride modified tannins at various exposure times and pH 4.

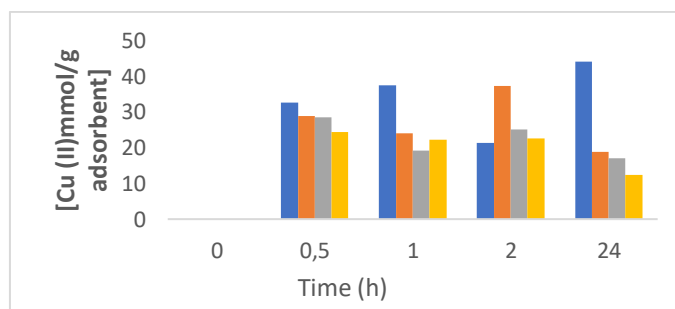


Figure 2c. Copper(II) adsorption by unmodified condensed tannin and cyclic anhydride modified tannins at various exposure times and pH 5.

At higher pH values, there is a lower adsorption due to factors such as (i) the three-dimensional conformations of the biopolymers and (ii) the formation of hydrated species of Cu(II) showing a lower affinity at higher pH values. Thus, variations in the acidity of the dissolution have an important effect on copper adsorption, namely, the adsorption capacity for metal cations depends on the pH for both the unmodified tannin and its modified counterparts. The acidity significantly affects the degrees of dissociation of the acidic and basic groups of tannins to promote the processing of active groups with bivalent metals^[41].

However, as the pH dissolution increases, more carboxylic acid groups are deprotonated, thereby, favoring the metal-ligand interaction through carboxylate ions. In addition to the deprotonation capacity of the active groups, other factors may influence the metal-ligand interaction, such as the supramolecular interactions between polymeric chains^[48]. In addition, under acidic conditions two competing reactions occur: (1) the polymeric or oligomeric chains can be degraded to their monomers and (2) the flavonoid units can condense^[45].

3.2 Maximum adsorption capacity of Cu(II).

Regarding the adsorption capacity (see Table 2), the condensed tannin had more stable values. However, as the Cu(II) concentration increases, the values begin to decrease substantially. Hence, at high concentrations, the structure of the polymer is saturated due to the structure characteristics of oligomers^[24]. In addition, the competitive effect between phenolic groups that belong to rings A and B of condensed tannins provides destabilization during the process of interaction with bivalent metals in aqueous solutions^[49]. However, the condensed tannin chemistry is dominated by the presence of multiple -OH groups with narrow but varying dissociation constants. In consequence, acid and base catalyzed rearrangements, nucleophilic substitutions, and electrophilic aromatic substitutions are common reactions^[45].

Table 2. Maximum copper(II) adsorption (Molarity) of the condensed tannin and its modified derivatives at pH 3.

Copper(II) adsorption of tannins [mmol Cu(II)/g adsorbent]				
Molarity	T	C	I	M
0	0	0	0	0
0.07	3.59	0.44	0.38	1.86
0.14	26.22	12.37	0.60	11.47
0.20	23.00	12.75	3.00	6.26
0.24	21.21	15.0	42.99	4.00
0.35	23.54	17.55	39.00	2.00
0.45	3.59	17.00	31.64	0
0.5	1.2	16.50	30.40	0

Although the tannin that was modified with citraconic anhydride had a low adsorption capacity compared to the unmodified condensed tannin, it demonstrated a stable adsorption capacity under increasing concentration values, while for the other two modifications, unstable adsorptions were observed.

Accordingly, with the behavior and relationships from a molecular perspective, to propose a couple of factors that are closely related to the adsorption capacity of each tannin, which affects the selectivity: (i) the molecular structure of the ligand and (ii) the stability of the three-dimensional structure of the ligand.

Thus, for unmodified condensed tannins, the hydroxyl group is the only chelating reagent, in contrast to modified tannins, in which the chelating reagent is in addition to the remaining hydroxyl groups in all three cases and the terminal carboxyl group that results from the modification may interact with Cu(II). These modifications can generate various degrees of rigidity, which depend on the characteristics of the modifying agent. Thus, the vibrational movements and the rotations on the axes of these molecules could be factors to consider during the coupling of Cu(II) in the active adsorption sites for each type of tannin.

The unmodified tannin exhibits the most rigid structure, which is followed by the unsaturated derivatives in the lateral chain (double-link C-C-type endo) of the maleic and cyclical anhydrides and, finally, the double bond C-C exo type that possesses the itaconic anhydride, which endows it with a higher degree of rotation release. When we consider the sp² hybridizations of the carbons that belong to the tannins that are based on citraconic anhydride and maleic anhydride, in comparison with the hybridization of the itaconic anhydrous-based derivative, these hybridizations are identified as factors that influenced the adsorption and molecular stability^[50].

3.3 Metal ion interaction– linking via FT-IR spectroscopy.

All tannins showed similar FT-IR spectra. However, differences are observed between the modified and unmodified tannin spectra, which demonstrate that the esterification reaction was successful. For the unmodified tannin, wideband and intense characteristics of the absorption of the O-H bonds are recorded, which are highly sensitive to the structure of the compound and to the conditions under which the spectrum was obtained. Although this functional group is involved in the formation of intermolecular hydrogen bridges, these interactions are more significant in primary alcohols and less significant in secondary. These absorption bands in the intervals of 3200-3600 cm⁻¹ correspond to the stretching vibrations of -OH^[50,51].

The O-H absorption band differs between the untreated condensed tannin and the condensed tannins that were treated with Cu(II). For most of the treatments, less data were obtained compared to the untreated tannin, and a weak stretching C-H band that absorbs in the interval of 2850 – 2980 cm⁻¹ was identified^[43]. The difference is observed with more detail in the spectrum that corresponds to the tannin that was treated with Cu(II) at a concentration of 0.452 M. However, no major band changes/deformations are observed in the spectra.

For the modified tannins, the esterification reactions resulted in a deformation in the absorption band near 1700 cm⁻¹, which corresponds to the carbonyl group (stretching of the C-O bond). Thus, the formation of carboxylic acids occurred through the replacement of hydrogen atoms in the hydroxyl groups of the modified tannins^[43]. The absorption bands that are discussed above suffered a series of deformations, of the modified tannins that were treated with various concentrations of Cu(II), because after adsorption by these polymers, the C-O absorption band suffered substantial deformation, which caused the weak intensity of the signal. The O-H absorption band that corresponds to carboxylic acid deforms such that it coincides with the absorption band of the -OH groups in the free state. In addition, to show the adsorption of Cu(II), the absorption band of the carbon-carbon double bond (C=C) that corresponds to aromatic compounds is considered. This absorption band presents readily observable deformations with respect to the band of the modified tannin without treatment, hence, the interaction of Cu(II) with the polymers occurred both with the -OH groups of the tannin and with those derivatives^[24,52]. The absorption bands between 1400 – 1450 cm⁻¹, anti-voltage stress deformations (C-H in CH₃) or deformation vibrations (C-H in CH₂) are observed. However, these absorption bands are contiguous with the absorption bands of the C-O group. Hence, they more likely correspond to a deformation vibration (C-H). At values that were recorded at 1000 – 1200 cm⁻¹, we can assign voltage vibrations C-O, namely, ν(C-O). Finally, there are absorption bands that range from 700 – 900 cm⁻¹ and correspond to C-H push-ups off the plane, which are characteristic of *cis* alkenes, and C-H push-ups that are characteristic of *trans* alkenes.

3.4 Desorption of Cu(II)

The metal ion desorption after the treatment of tannins with 1 M and 2 M hydrochloric acid are used to evaluate the recovery. Similar to adsorption, this stage is fundamental for the manufacture of ion-exchange resins, thus, the effectiveness of tannins as materials to remove metal ions was determined^[48].

According to Figure 3, 1 M hydrochloric acid was more efficient as a desorbing reagent, which is because the higher concentrations of acid damage the structure of the adsorbent such that the desorption capacity is affected by a possible mass loss of the polymer or by irreversible chemical modification^[48]. The derivative that was obtained with maleic anhydride performed better in terms of metal recovery with a recovery of 55% with 1 M HCl, and although it was the most efficient, compared to the other derivatives, it is high unstable, which suggests that the higher chelating power influences the strength of the interaction substantially during the desorption process.

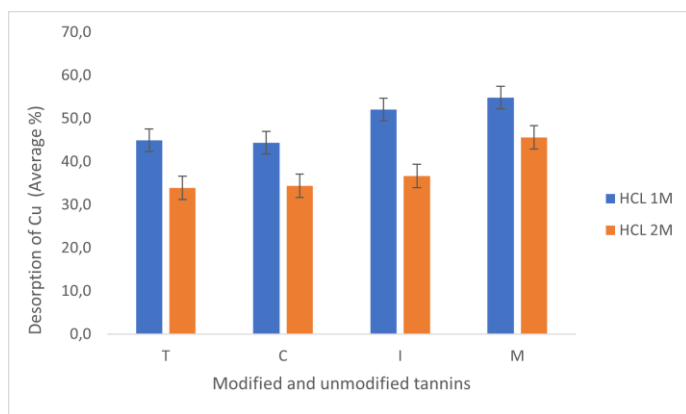


Figure 3. Weighted overall average desorption of Cu(II) according to the experimental results and the concentrations that were tested with the tannins under study.

The desorption percentage for resin containing itaconic anhydride (53% Cu(II) with 1 M HCl) is lower than that of the maleic anhydride derivative. However, the derivative with itaconic anhydride has a higher adsorption capacity (35 – 40 mmol of Cu(II)/g adsorbent), therefore, it was recovered higher Cu(II) than that other polymer adsorbents. The unmodified condensed tannin and the citraconic-anhydride-modified tannin yielded similar results under both acid concentrations.

Although the tannins realized acceptable values for the adsorption capacity, chelation with Cu(II) can be classified as satisfactory in quantitative terms. In contrast, the process of desorption was not sufficiently efficient, which could be related to the characteristics of the previous adsorption in each case

CONCLUSIONS

The Cu(II) adsorption and desorption capacities of pine bark polyphenols resins (condensed tannins) were determined from the maximum adsorption capacity, the desorption via acid-base behavior, and the FT-IR spectroscopy results, which demonstrated that modification (esterification) was an important factor for ion desorption. However, the modification of polyphenol with cyclic anhydrides substantially affected the ion uptake compared to unmodified polyphenol.

Finally, copper adsorption through the use of condensed tannins and modified condensed tannins is considered a viable technique for the recovery of bivalent ions such as Cu(II), however, it is suggested to continue future research to obtain, greater and better results that allow the recovery of metal ions more efficiently and sustainably.

CONFLICTS OF INTEREST.

The authors declare that there is no conflict of interest regarding the publication of this paper.

REFERENCES

- M.C.S. Minello, A. L. Paço, R. S. D. Castro, L. Caetano, P. M. Padilha, G. Ferreira, M. A. U. Martines & G. R. Castro, "Evaluation of heavy metal availability in contaminated sediments from the Ilha Solteira hydroelectric dam on the Paraná River at Ilha Solteira, SP, BRAZIL," *Fresenius Environmental Bulletin*, 19, 2210-2214, 2010.
- Q. Wang & Z. Yang, "Industrial water pollution, water environment treatment, and health risks in China," *Environmental Pollution*, 218, 358-365, 2016.
- A. E. Evans, J. Mateo-Sagasta, M. Qadir, E. Boelee & A. Ippolito, "Agricultural water pollution: key knowledge gaps and research needs," *Current Opinion in Environmental Sustainability*, 36, 20-27, 2019.
- S. Hokkanen, E. Repo, T. Suopajarvi, H. Liimatainen, J. Niinimaa & M. Sillanpaa, "Adsorption of Ni(II), Cu(II) and Cd(II) from aqueous solutions by amino modified nanostructured microfibrillated cellulose," *Cellulose*, 21, 1471-1487, 2014.
- G. Z. Kyzas, G. Bomis, R. I. Kosheleva, E. K. Efthimiadou, E. P. Favvas, M. Kostoglou, & A. C. Mitropoulos, "Nanobubbles effect on heavy metal ions adsorption by activated carbon," *Chemical Engineering Journal*, 356, 91-97, 2019.

- A. Piccolo, R. Spaccini, A. De Martino, F. Scognamiglio, & V. di Meo, "Soil washing with solutions of humic substances from manure compost removes heavy metal contaminants as a function of humic molecular composition," *Chemosphere*, 225, 150-156, 2019.
- Y. L. Xu, S. Y. Song, J. D. Chen, R. A. Chi & J. X. Yu, "Simultaneous recovery of Cu²⁺ and Pb²⁺ from metallurgical wastewater by two tandem columns fixed respectively with tetraethylenepentamine and phosphoric acid modified bagasse," *Journal of the Taiwan Institute of Chemical Engineers*, 99, 132-141, 2019.
- J. Yuan, Y. Yang, X. H. Zhou, Y. C. Ge & Q. R. Zeng, "A new method for simultaneous removal of heavy metals and harmful organics from rape seed meal from metal-contaminated farmland," *Separation and Purification Technology*, 210, 1001-1007, 2019.
- Q. Zhou, B. Liao, L. Lin, Z. Song, Z. H. Khan & M. Lei, "Characteristic of adsorption cadmium of red soil amended with a ferromanganese oxide-biochar composite," *Environmental Science and Pollution Research*, 26(5), 5155-5163, 2019.
- G. Palma, J. Freer & J. Baeza, "Removal of metal ions by modified *Pinus radiata* bark and tannins from water solutions," *Water Research*, 37, 3974-3980, 2003.
- S. Hasan, T. K. Ghosh, D. S. Viswanath, & V. M. Boddu, "Dispersion of chitosan on perlite for enhancement of copper (II) adsorption capacity," *Journal of Hazardous Materials*, 152(2), 826-837, 2008.
- Y. Sun, K. J. Shah, W. Sun & H. Zheng, "Performance evaluation of chitosan-based flocculants with good pH resistance and high heavy metals removal capacity," *Separation and Purification Technology*, 215, 208-216, 2019.
- H. Sun, N. Xia, Z. Liu, F. Kong & S. Wang, "Removal of copper and cadmium ions from alkaline solutions using chitosan-tannin functional paper materials as adsorbent," *Chemosphere*, 236, 124370, 2019.
- B.L. Rivas, I. Moreno-Villoslada, "Evaluation of the Counterion Condensation Theory from the Metal Ion Distributions obtained by Ultrafiltration of a System Poly(Sodium 4 Styrene Sulfonate)/Cd²⁺/Na⁺," *Journal of Physical Chemistry, B* 102, 11024-11028, 1998.
- B.L. Rivas, H.A. Maturana, R.E. Catalán & I. M. Perich, "Branched and linear polyethyleneimine supports for resins with retention properties for copper and uranium. VII", *Journal of Applied Polymer Science*, 38(5), 801-807, 1989.
- B.L. Rivas, E. Pereira, "Obtention of Poly(allylamine)-Metal Complexes through Liquid Phase Polymer Based Retention (LPR) Technique". *Boletín de la Sociedad Chilena de Química*, 45, 165-171 (2000)
- B.L. Rivas, S.A. Pooley, G. Canessa, "Spontaneous Copolymerization via Zwitterion. 1.2 Methyl-2-oxazoline and Succinic Anhydride", *Polymer Bulletin* 9, 417-422 (1983).
- J. A. Sánchez, B. L. Rivas, S. A. Pooley, L. Basaez, E. Pereira, I. Pignot-Paintrand & J. C. Moutet, "Electrocatalytic oxidation of As (III) to As (V) using noble metal-polymer nanocomposites," *Electrochimica Acta*, 55(17), 4876-4882, 2010.
- W. W. Ngah, L. C. Teong & M. A. K. M. Hanafiah, "Adsorption of dyes and heavy metal ions by chitosan composites: A review," *Carbohydrate Polymers*, 83(4), 1446-1456, 2011.
- B. L. Rivas, E. D. Pereira, M. Palencia & J. Sánchez, "Water-soluble functional polymers in conjunction with membranes to remove pollutant ions from aqueous solutions" *Progress in Polymer Science*, 36(2), 294-322, 2011.
- J. Sánchez, L. Riffo, P. Salazar & B. L. Rivas, "Removal of molybdate and vanadate ions by a copolymer adsorbent in a ultrafiltration system," *Journal of Applied Polymer Science*, 136(45), 48184, 2019.
- D. V. Morales, O. Kusku, B. L. Rivas, M. Arda, N. Kabay, & M. Bryjak, "Removal of Cr(VI) by stabilized solvent impregnated resin (sir) prepared by using a hydrophilic polymer adsorbent and aliquat 336," *Journal of the Chilean Chemical Society*, 64(2), 4432-4436, 2019.
- D. Sud, G. Mahajan & M. P. Kaur, "Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions-A review," *Bioresource Technology*, 99(14), 6017-6027, 2008.
- D. E. García, W. Glasser, A. Pizzi, C. Lacoste, M. P. Laborie, "Polyphenolic resins prepared with maritime pine bark tannin and bulky-aldehydes," *Industrial Crops and Products*, 62, 84-93, 2014.
- A. P. Lim & A. Z. Aris, "A review on economically adsorbents on heavy metals removal in water and wastewater," *Reviews in Environmental Science and Bio/Technology*, 13(2), 163-181, 2014.
- W. Wafwoyo, C. W. Seo & W. E. Marshall, "Utilization of peanut shells as adsorbents for selected metals," *Journal of Chemical Technology & Biotechnology: International Research in Process, Environmental & Clean Technology*, 74(11), 1117-1121, 1999.

27. S. Chamrathy, C. W. Seo, & W. E. Marshall, "Adsorption of selected toxic metals by modified peanut shells," *Journal of Chemical Technology & Biotechnology: International Research in Process, Environmental & Clean Technology*, 76(6), 593-597, 2001.
28. P. Kumar & S. S. Dara, "Binding heavy metal ions with polymerized onion skin" *Journal of Polymer Science: Polymer Chemistry Edition*, 19(2), 397-402, 1981.
29. J. M. Rodríguez-Díaz, J. O. P. García, L. R. B. Sánchez, M. G. C. da Silva, V. L. da Silva & L. E. Arteaga-Pérez, "Comprehensive characterization of sugarcane bagasse ash for its use as an adsorbent," *Bioenergy Research*, 8(4), 1885-1895, 2015.
30. A. M. Pintor, C. I. Ferreira, J. C. Pereira, P. Correia, S. P. Silva, V. J. Vilar & R. A. Boaventura, "Use of cork powder and granules for the adsorption of pollutants: a review," *Water Research*, 46(10), 3152-3166, 2012.
31. S. K. Srivastava, A. K. Singh & A. Sharma, "Studies on the uptake of lead and zinc by lignin obtained from black liquor—a paper industry waste material," *Environmental Technology*, 15(4), 353-361, 1994.
32. F. H. Luzardo, F. G. Velasco, C. P. Alves, I. K. D. S. Correia & L. L. Cazorla, "Chemical characterization of agroforestry solid residues aiming its utilization as adsorbents for metals in water," *Revista Brasileira de Engenharia Agrícola e Ambiental*, 19(1), 77-83, 2015.
33. K. Seki, N. Saito & M. Aoyama, "Removal of heavy metal ions from solutions by coniferous barks," *Wood Science and Technology*, 31(6), 441-447, 1997.
34. V. Gloaguen, & H. Morvan, "Removal of heavy metal ions from aqueous solution by modified barks," *Journal of Environmental Science & Health Part A*, 32(4), 901-912, 1997.
35. I. Gaballah & G. Kilbertus, "Recovery of heavy metal ions through decontamination of synthetic solutions and industrial effluents using modified barks," *Journal of Geochemical Exploration*, 62(1-3), 241-286, 1998.
36. A. Şen, H. Pereira, M. A. Olivella, & I. Villaescusa, "Heavy metals removal in aqueous environments using bark as a biosorbent," *International Journal of Environmental Science and Technology*, 12(1), 391-404, 2015.
37. C. W. Kim, D. S. Kim, S. Y. Kang, M. Marquez & Y. L. Joo, "Structural studies of electrospun cellulose nanofibers," *Polymer*, 47(14), 5097-5107, 2006.
38. P. Kumararaja, K. M. Manjaiah, S. C. Datta, T. A. Shabeer & B. Sarkar, "Chitosan-g-poly (acrylic acid)-bentonite composite: a potential immobilizing agent of heavy metals in soil," *Cellulose*, 25(7), 3985-3999, 2018.
39. M. Stephen, N. Catherine, M. Brenda, K. Andrew, P. Leslie & G. Corrine, "Oxolane-2, 5-dione modified electrospun cellulose nanofibers for heavy metals adsorption," *Journal of Hazardous Materials*, 192(2), 922-927, 2011.
40. F. H. Luzardo, F. G. Velasco, I. K. Correia, P. M. Silva & L. C. Salay, "Removal of lead ions from water using a resin of mimosa tannin and carbon nanotubes," *Environmental Technology & Innovation*, 7, 219-228, 2017.
41. X. Sun, X. Huang, X. P. Liao & B. Shi, "Adsorptive removal of Cu (II) from aqueous solutions using collagen-tannin resin," *Journal of Hazardous Materials*, 186(2-3), 1058-1063, 2011.
42. J. Freer, J. Baeza, H. Maturana, G. Palma & N. Durán, "Removal and recovery of uranium by modified *Pinus radiata* D. Don bark," *Journal of Chemical Technology & Biotechnology*, 46(1), 41-48, 1989.
43. D. E. García, N. Delgado, F. L. Aranda, M. A. Toledo, G. Cabrera-Barjas, E. M. Sintjago & S. Paczkowski, "Synthesis of maleilated polyflavonoids and lignin as functional bio-based building-blocks," *Industrial Crops and Products*, 123, 154-163, 2018.
44. D. E. García, W. G. Glasser, A. Pizzi, S. Paczkowski & M. P. Laborie, "Hydroxypropyl tannin from *Pinus pinaster* bark as polyol source in urethane chemistry," *European Polymer Journal*, 67, 152-165, 2015.
45. D. E. Garcia, W. G. Glasser, A. Pizzi, S. P. Paczkowski & M. P. Laborie, "Modification of condensed tannins: from polyphenol chemistry to materials engineering," *New Journal of Chemistry*, 40(1), 36-49, 2015.
46. P. Das & J. P. Claverie, "Synthesis of single-core and multiple-core core-shell nanoparticles by RAFT emulsion polymerization: Lead sulfide-copolymer nanocomposites," *Journal of Polymer Science Part A: Polymer Chemistry*, 50(14), 2802-2808, 2012.
47. D. E. García, P. A. Medina & V. I. Zúñiga, "Toxicological features of maleilated polyflavonoids from *Pinus radiata* (D. Don.) as potential functional additives for biomaterials design," *Food and Chemical Toxicology*, 109, 1069-1078, 2017.
48. D. Kołodyńska, J. A. Krukowska & P. Thomas, "Comparison of sorption and desorption studies of heavy metal ions from biochar and commercial active carbon," *Chemical Engineering Journal*, 307, 353-363, 2017.
49. K. G. Nierop, C. M. Preston & J. M. Verstraten, "Linking the B ring hydroxylation pattern of condensed tannins to C, N and P mineralization. A case study using four tannins," *Soil Biology and Biochemistry*, 38(9), 2794-2802, 2006.
50. R. T. Morrison & R. N. Boyd. "Química Orgánica" 1998.
51. C. Christou, A. Agapiou & R. Kokkinofa, "Use of FTIR spectroscopy and chemometrics for the classification of carobs origin," *Journal of Advanced Research*, 10, 1-8, 2018.
52. R. Fessenden & J. Fessenden, "Química Orgánica," 1983.
53. D. E. García, W. Glasser, A. Pizzi Pizzi, S. Paczkowski & M. Pierre Laborie, "Modification of Condensed Tannins: From Polyphenol Chemistry to Material Engineering." *New Journal of Chemistry*, 40 (1), 36-49, 2015.
54. D. E. García, J. C. Carrasco, J. P. Salazar, M. A. Pérez, R. A. Cancino & S. A. Riquelme, "Bark polyflavonoids from *Pinus radiata* as functional building – blocks for polylactic acid (PLA) – based green composites." *EXPRESS Polymer Letters* 10(10), 835 – 848, 2016.
55. D. E. García, J. Gavino, D. Escobar-Avello & R. A. Cancino, "Maleinated polyflavonoids and lignin as functional additives for three kinds of thermoplastics". *Iranian Polymer Journal*. 26(4), 295-304, 2017.