

# HIGH MOLECULAR WEIGHT ORGANIC MATTER PRECIPITATION FROM KRAFT MILL EFFLUENTS: PROCESS DEVELOPMENT

M. C. Diez<sup>(\*)</sup>, O. Rubilar, M. Cea and R. Navia

*Chemical Engineering Department, University of La Frontera, P.O. Box 54-D, Temuco, Chile  
mcdiez@ufro.cl*

## Abstract

Kraft mill effluent is characterized by a high chemical oxygen demand (COD), constituted by a non-biodegradable fraction, which is mainly composed by lignin, tannins, wood extractive compounds, monomers and halogenated organic compounds (in the case of elemental chlorine free bleaching process).

The objective of this work was the development of a process for high molecular weight organic matter precipitation, present in these effluents. The used effluent was produced in a Chilean bleached Kraft mill plant that uses *Pinus radiata* as raw material. The effluent was concentrated and the organic matter was subsequently precipitated using cold methanol. Then, the effluent was centrifuged for organic matter separation. The obtained solid was redissolved and dialyzed for salts excess elimination. For this objective, membranes filters with a cut-off of 1,000 Da were used in a three-step process, until constant conductivity was obtained. A fraction of the non-permeated solution was diluted and purified through a cationic exchange Dowex 50-X8 column for mineral contaminants retention. Finally, both solid samples were lyophilized.

The results indicate that the treated effluent (without organic matter, after centrifugation) could be recovered and recycled to the bleaching process. In addition, the purified organic matter characterization indicates the presence of reactive groups, suggesting the possible use of these organic matter as a reactive adsorption material. BOD<sub>5</sub>, COD and color removal efficiency was 87%, 43% and 77%, respectively.

## 1. Introduction

World paper and pulp production is estimated at ca. 300 million ton/a (CEPI, 2002), while the Chilean production will reach about 3.5 million ton in 2006, with the start-up of new planned pulp plants. Considering 1 ton of final product, the wastewater generation for pulp production ranges between of 10 to 110 m<sup>3</sup>/ton (European Commission, 2001; CEPI, 2002) of a brown-colored effluent. This effluent is characterized by a high chemical oxygen demand (COD) constituted by a non-biodegradable fraction, which is mainly composed by lignin, tannins, wood extractive compounds, monomers and halogenated organic compounds (in the case of elemental chlorine free bleaching) (Vidal, 1999). Lignin and tannins are the main components of this non-biodegradable fraction. Particularly, lignin is a complex molecule with a high molecular weight, between 1100 and 24000, depending on its origin (Sun et al., 1997). Lignin is built from polyphenyl propane units with  $\beta$ -O-4 ether linkages, and -OH (phenolic groups), -O- (ether groups), -OCH<sub>3</sub> (methoxy groups), C-H (aromatic rings), -COOH (carboxylic groups) and C=O (carbonyl groups) have been detected in this polymer (Nada et al., 1998a; Nada et al., 1998b; Tan,

1998). Many of these groups are known to be reactive, like -OH phenolic groups and -COOH carboxylic groups in humus from soil for example, and capable to adsorb environmental pollutants (Mora & Canales, 1995a; Mora & Canales, 1995b).

Organic reactive compounds present in industrial wastewaters like olive oil mill can be recovered and used in agricultural, biotechnological, chemical and environmental processes (Capasso, 1997; Capasso et al., 2002a). Indeed, polyphenols recovered from these effluents have been evaluated as alternative antioxidants in agriculture (Capasso et al., 1995; Capasso et al., 1999). Moreover, polymeric compounds like humic acids have been evaluated as bioamendments for agricultural soils improvement (Capasso et al., 2002b). Finally, investigations done by Capasso et al. (2002a) and Capasso et al. (2003), have demonstrated that this organic polymer, recovered from olive oil mill wastewater, has a high capacity for heavy metals retention, which may be attributed to the functional negative groups of the polymer. In this sense, this polymer may be used in environmental technology as an adsorbent for heavy metals sorption (like Cr, Zn and Cu) from wastewater. The polymer ("polymerin") recovering process is based on the treatment of the wastewater using cold methanol at -20°C, obtaining a precipitated, which is centrifuged and dialyzed. The non-permeated fraction from the dialysis process is finally lyophilized (Capasso et al., 2002a). The recovered polymerin is mainly composed by carbohydrates (52%), melanin (26%) and proteins (10%), with their respective monosaccharides, phenols and amino acids content (Capasso et al., 2002a). Polymerin also contains heavy metals (11%), mainly K<sup>+</sup> and, to a lesser extent, Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Zn<sup>2+</sup>, Fe<sup>2+</sup> y Cu<sup>2+</sup>. The main functional groups detected by infrared spectroscopy in polymerin were -OH (phenolic), -NH (peptidic), -COOH (carboxylic), C-H (polysaccharide), C=O (esther and peptidic) y C=C (aromatic), (Capasso et al., 2002a). The main objective of this work is the recovery and characterization of a reactive polymer from Kraft mill wastewater

## 2. Materials and methods

### 2.1 Kraft mill wastewater

The used wastewater for organic polymer extraction is the wastewater produced in a bleached Kraft mill plant that uses *Pinus radiata* as raw material. The physicochemical characterization of this wastewater has been previously reported by Diez et al. (2001), and is presented in Table 1.

**Table 1.** Physicochemical characterization of bleached Kraft mill wastewater

Parameter	Unit	Range	Average ± STD
pH		3.5-10.6	5.1 ± 2.5
Color	mg/l	592-1400	951 ± 290
COD	mg/l	823-1942	1208 ± 415
BOD <sub>5</sub>	mg/l	242-513	319 ± 79
Suspended solids	mg/l	40-296	147 ± 99
TKN	mg/l	3.7-9.0	6.0 ± 1.5
Phosphor	mg/l	0.4-1.3	1.1 ± 0.3
Phenol	mg/l	0.9-1.2	1.2 ± 0.1
UV Phenol	mg/l	190-350	322 ± 52
Tannins & lignins	mg/l	44-64	52 ± 7

STD: Standard deviation

## 2.2 Polymer extraction and purification procedure

1 L sample was filtered through 1.2 and 0.2  $\mu\text{m}$  membranes and subsequently concentrated by vacuum evaporation for obtaining a final volume of 0.5 L. The obtained solution was treated with methanol at  $-20^{\circ}\text{C}$  using a 1:3 solution/methanol relationship, and left settling for 4 hours. The precipitated was separated by centrifugation at 8400 rpm for 30 minutes. Then, the obtained solid was redissolved in 50 mL distilled water and dialyzed for salts excess elimination. For this objective, membranes with a cut-off of 1,000 Da were used in a three-step process, until constant conductivity was obtained after about 3 hours of purification (Capasso *et al.*, 2002a). A fraction of the non-permeated solution was diluted in 200 mL distilled water and purified through a cationic exchange Dowex 50-X8 column (2.2 cm internal diameter and 37 cm long), for mineral contaminants retention. Finally, both samples were lyophilized.

## 2.3 Polymer characterization

The lyophilized polymer was characterized by evaluating total nitrogen (TN) using the Kjeldahl method, UV phenols, cations, total, carboxylic and phenolic acidity,  $E_4/E_6$  ratio and infrared Fourier transform spectroscopy (IFTS).

Total nitrogen (TN). The TN content was determined according to APHA (1989) dissolving 20 mg sample in 50 mL distilled water.

UV Phenols. As described by APHA (1989), a spectrometric method was used at a wavelength of 215 nm for UV phenols determination. For this objective, 20 mg sample were dissolved in 100 mL distilled water.

Protein determination. The used method is described by Bradford, 1976 dissolving 20 mg sample in 100 mL distilled water.

Heavy metals determination. Al, B, Ca, Cu, Fe, K, Mg, Na, P y Zn were determined by atomic absorption spectrometry using 0,5 g digested sample (Sadzawka, *et al.* 2001).

Total, carboxylic and phenolic acidity. Total polymer acidity was determined using the barium hydroxide method. The carboxylic acidity was measured using the calcium acetate method while the phenolic acidity was determined as the difference between total and carboxylic acidity (Tan, 1996). Each measurement was done using 20 mg samples.

$E_4/E_6$  ratio. Polymer condensation degree was evaluated using the  $E_4/E_6$  ratio. A 1 mg polymer sample was dissolved in 10 mL of a KOH 0,1 M solution, reading the absorbance at 440 y 640 nm according to Mora *et al.* (1995a).

Infrared Fourier transform spectroscopy (IFTS). 1 mg sample was mixed with 300 mg of KBr (infrared - IR- grade). Subsequently, a solid tablet was formed under pressure with the obtained mixture.

Operational conditions of the Brckner IFTS equipment used were the following:  $2\text{ cm}^{-1}$  resolution, 3.5 mm and 64 scan optic step. IFTS spectra were obtained in the medium IR region, i.e., between  $4000\text{-}600\text{ cm}^{-1}$ .

### 3. Results and discussion

#### 3.1 Polymer extraction and purification procedure

The organic polymer extraction and purification process developed is presented in Figure 1. Total polymer extraction yield was found to be 1.4 g per 1 L effluent sample. The dark brown color of the polymer was attributed to the presence of lignin and polymerized tannins that are present in Kraft mill effluents. The extracted polymer was purified using a dialysis procedure with a 1000 Da membrane, with the final objective of removing salts excess.

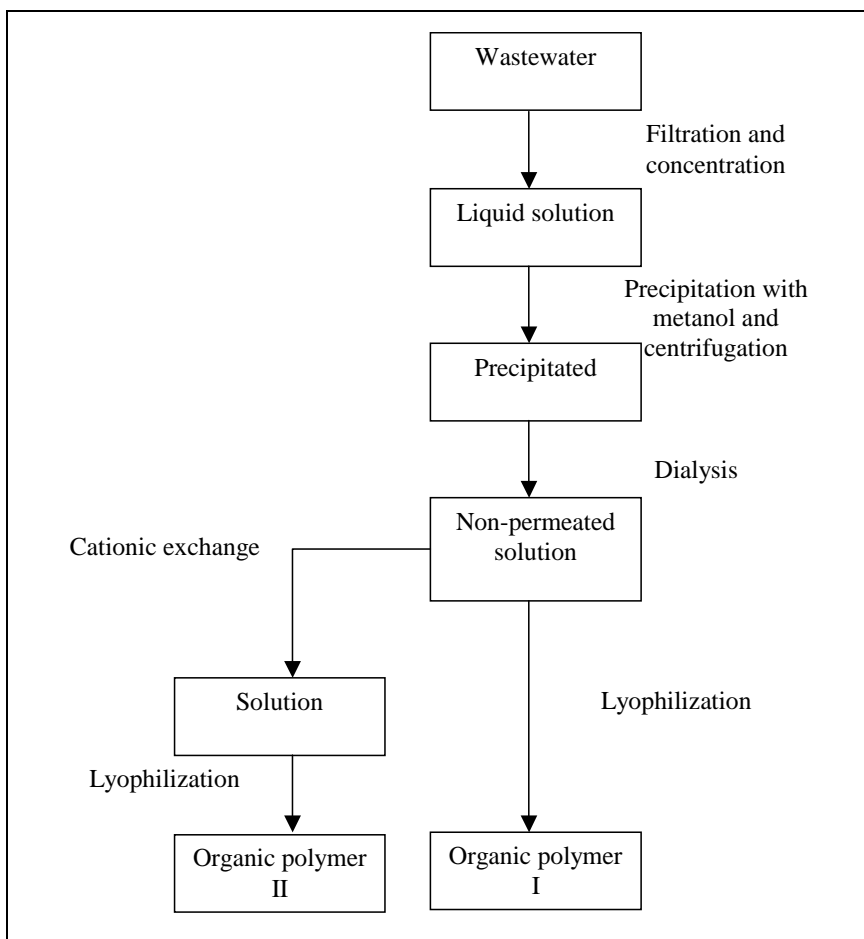


Figure 1. Polymer extraction and purification procedure

For polymer cations purification and retention, a Dowex 50-X8 cationic exchange column was used. The resin has the capacity to exchange metals like Fe and to protonate the polymer sample. Previous to the cationic exchange purification procedure, the polymer showed a pH value around 7, and after

the cationic exchange process the polymer was found to have a pH value of 3.3, clearly indicating the resin effect.

### *3.2 Treated effluent quality*

The quality of the treated effluent indicates a final BOD<sub>5</sub>, COD and color content of 435, 302 and 64 mg/L, respectively, with overall removal efficiencies of 87%, 43% and 77%, respectively. This results were found to be very interesting, as they are very similar to those of the normal biological process existing in the plant, except for color removal, which is almost not removed in biological processes. It seems that optimizing the treatment process, the quality of the treated effluent could reach the appropriate standard for its reuse in the process, at the digestion or bleaching stage.

### *3.3 Polymer characterization*

The UV phenols concentration in polymer I reached 57% (weight) of the sample. Proteins reached 7,4% (weight) of the sample, mainly attributed to wood as raw material. Total Kjeldahl nitrogen was found to be a 6,7% (weight) of the sample. Nitrogen is generally associated with the presence of proteins and sugars in polymer matrix, which also account for the presence of oxygen and carbon. Heavy metals content in polymers I and II, was 6,9 y 1,6% respectively, demonstrating that the Dowex 50-X8 cationic exchange process was very efficient in the removal of these metals. Total, carboxylic and phenolic acidity is a measure of these reactive sites in both polymers. On one hand, total acidity in polymer I was found to be 7,7 meq total acidity/g, value that is comparable to that of humic acids from soil of Southern Chile. On the other hand, the humification degree ( $E_4/E_6$ ) of polymer II was 6,72, indicating a low condensation degree and high reactivity. Finally, IFTS analyses shows the presence of alcoholic OH groups, phenolic groups, and C=O linkages from cetones, esters, quinones and carboxylic acids. However, polymer I did also present carboxylic acid salts vibrations, confirming low carboxylic acidity.

## **4. Conclusions**

The application the developed high molecular weight organic matter precipitation process to the Kraft mill effluent, suggests that the treated effluent (without organic matter, after centrifugation) could be recovered and recycled to the bleaching process, reaching removal efficiencies for BOD<sub>5</sub>, COD and color of 87%, 43% and 77%, respectively. In addition, the recovered polymer characterization indicates the presence of reactive groups, suggesting its possible use as a reactive adsorption material or as soil ammendment.

**Acknowledgment:** This work was supported by FONDECYT 1050614.

## **References**

APHA AWA WPCF. (1989). Métodos normalizados para el análisis de aguas potables y residuales. 17 ed. Dása de Santos. Madrid.

Bradford, M. (1976). A rapid and sensitive method for the quantification of microgram quantities of protein utilizing the principle of protein-dye binding. *Analytical Biochem.* 72, 248-258.

Capasso, R., Evidente, A., Schivo, L., Orru, G., Marcialis, M. A. & Cristinzio, G. (1995). Antibacterial polyphenols from olive oil mill waste waters. *J. App. Bacteriol.* 79, 393-398.

Capasso, R. (1997). The chemistry, biotechnology and ecotoxicology of the polyphenols naturally occurring in vegetable wastes. *Curr. Topics Phytochem.* 1, 145-156.

Capasso, R., Evidente, A., Avolio, A & Solla, F. (1999). A highly convenient synthesis of hydroxytyrosol and its recovery from agricultural waste waters. *J. Agric. Food Chem.* 47(4), 1745-1748.

Capasso, R., de Martino, A. & Arienzo, M. (2002a). Recovery and characterization of the metal polymeric organic fraction (polymerin) from olive oil mill wastewaters. *J. Agric. Food Chem.* 50(10), 2846-2855.

Capasso, R., de Martino, A. & Cristinzio, G. (2002b). Production, characterization, and effects on tomato of humic acid-like polymerin metal derivatives from olive oil mill waste waters. *J. Agric. Food Chem.* 50(14), 4018-4024.

Capasso, R., de Martino, A., Pigna, M., Pucci, M., Sannino, F. & Violante, A. (2003). Recovery of polymerin from olive oil mill wastewaters. Its potential utilization in environmental technologies and industry. *RICHMAC Magazine* 85, 1-7.

CEPI (2002). Annual Report. Confederation of European Paper Industries, Brussels.

Diez M. C., Castillo G., Aguilar L., Vidal G. and Mora M. L. (2001). Operation factors and nutrient affects on activated sludge treatment of *Pinus radiata* mill wastewater. *Bioresource Technology* 83, 131-138.

European Commission (2001). Integrated pollution prevention and control (IPPC). Reference Document on Best Available Techniques in the Pulp and Paper Industry.

Mora M. L. y Canales J. (1995a). Interactions of humic substances with allophanic compounds. *Commun. Soil Sci. Plant Anal.* 26, 2805-2817.

Mora, M.L. & Canales, J. (1995b). Humin-clay interactions on surface reactivity in Chilean andisols. *Comm. Soil Sci. and Plant Anal.* 26(17/18), 2819-2828.

Nada, A. M. A., Yousef, M. A., Shaffei, K. A. & Salah, A. M. (1998a). Infrared spectroscopy of some treated lignins. *Polym. Degrad. Sabil.* 62, 157-163.

Nada, A. M. A., El-Sakhawy, M. & Kamel, S. M. (1998b). Infra-red spectroscopy study of lignins. *Polym. Degrad. Sabil.* 60, 247-251.

Sadzawka A., Gerez R., Mora M. L., Saavedra N. y Carrasco M. A. (2001). Métodos de análisis de tejidos vegetales. Comisión de Normalización y Acreditación, Chile.

Sun, R., Lawther, J. M., Banks, W. B. & Xiao, B. (1997). Effect of extraction procedure on the molecular weight of wheat straw lignins. *Ind. Crops Prod.* 6, 97-106.

Tan, K. H. (1996). *Soil Sampling, Preparation, and Analysis*. Marcel Dekker Inc., New York.

Tan K. H. (1998). *Principles of soil chemistry*. Marcel Dekker Inc. New York.

Vidal, G. (1999). Revisión bibliográfica sobre los compuestos orgánicos producidos en la industria de la pasta y papel: incidencia en la toxicidad y biodegradabilidad anaerobia de sus efluentes. *Afinidad* LVI(481), 152-160.