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Extraction of anions from pyrolytic bio-oil by Liquid-Phase Polymer-Based Retention

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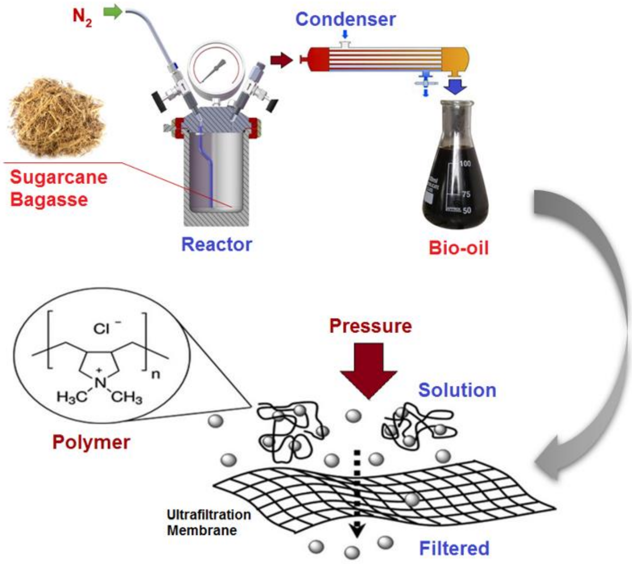
Graphical Abstract



Abstract. The development of techniques that allow the separation of organic compounds present in the bio-oil of the pyrolysis of biomass is of great interest for using this technology to generate chemical products with added value. Thus, this work aimed to evaluate the extraction of the organic anions acetate and sulfonate from pyrolytic bio-oil of sugarcane bagasse (SCB) by means of Liquid-phase Polymer-based Retention (LPR). For this, the SCB was characterized using elementary analysis, thermogravimetric analysis, and differential thermal analysis. Subsequently, the pyrolysis of the SCB was performed, and the liquid fraction was analyzed by GC/MS. Finally, the synthesis and characterization of sodium *p*-toluenesulfonate (*p*-TsNa) was carried out, and retention and release tests of the acetate and sulfonate anions were carried out with the poly (diallyldimethylammonium chloride) (pDADMAC). The model solutions show the highest retention is obtained at pH 9.0 and the ionic strength of 0.01 molal of NaCl for the acetate anion.

In contrast, for the sulfonate anion, the best retention was obtained at low ionic strength (without adding NaCl). In contrast, the lowest retentions were obtained at pH 4.0 with an ionic strength of 0.01 molal of NaCl for both cases. On the other hand, removing the *p*-TsNa anion in the bio-oil showed that it is possible to recover 237.3 mg of *p*-TsNa per gram of pDADMAC. It was concluded that the LPR technique using pDADMAC can be used to separate anions, acetate, and sulfonate in the pyrolytic bio-oil of SCB.

Keywords: Sugarcane bagasse, bio-oil, ultrafiltration, water soluble polymer.

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1. Introduction: An overview of microplastic pollution

In Colombia, the thirteen sugar mills currently have approximately 232.070 hectares planted in sugarcane (*Saccharum officinarum*), mainly destined for the production of carbohydrates and carburant alcohol by processes based on the extraction of sucrose from the fibrous part of this tropical grass (1). As a result of the methodology used in this process, more than 5 million tons of organic byproduct known as sugarcane bagasse (SCB) are generated per year, and the remaining fiber of the entire juice extraction process is enriched in sucrose (2).

The SCB presents a disadvantage in that its degradation by the action of microorganisms occurs very slowly concerning the large quantities generated annually. Consequently, the sugar industry has developed as its primary method for employing this by-product, its use as fuel to produce the heat and mechanical (or electrical) energy necessary for the different industrial operations (3). However, the direct combustion of SCB produces ash accumulation and undesirable toxic gases that can contaminate air, soil, adjacent waters, and groundwater, negatively affecting human health; this represents a significant disadvantage of this process (4,5).

In this sense, obtaining organic products from sugarcane bagasse, raw material, or biomass of lignocellulosic type that is highly available offers an option for its use and additionally allows for increasing its added value. However, its employment is difficult due to its complex structure, so it must be refined in more convenient ways (6). In this way, thermochemical conversion is a favorable alternative for this purpose since heat and catalysts are used to transform natural polymers into biofuels and/or other useful chemical products in a manner analogous to natural or biochemical degradation processes with the main difference that in thermochemical processes the degradation takes place more quickly, in a matter of a few minutes or hours, and also a source of thermal energy is required (7).

Pyrolysis is one of the most investigated thermochemical processes for biomass conversion because organic macromolecules can be broken down into smaller fragments by rapid heating without oxygen. This method allows condensing the gases generated to produce a liquid product called bio-oil, which is easy to store and transport (8). The bio-oil produced from lignocellulosic material typically contains organic compounds of variable polarity (approximately 70-80 % by weight) and water (approximately 20-30 % by weight) (9,10). Organic compounds include acids (formic, acetic, propanoic), aldehydes (acetaldehyde, hydroxy acetaldehyde), ketones (acetone, hydroxyacetone, hydroxy butanone), sugars (glucose, xylose, fructose), alcohols, esters, furans, furfural derivatives, guaiacols, and some particles of carbon with micrometer size (6). On the other hand, the low cost of producing bio-oil by pyrolysis makes it a competitive technology compared to other processes, such as gasification and cellulosic ethanol (11). However, the direct use of this substance as a replacement for liquid petroleum fuel is limited due to its insolubility in this mixture, corrosiveness, phase instability, high viscosity, and high carbon content. In addition, the acidity of bio-oil is relatively high (pH ~ 2.5) due to the presence of organic acids, which can cause corrosion in the equipment used (12-15). However, organic acids, especially acetic acid, are valuable byproducts if they can be efficiently separated from bio-oil. Therefore, its elimination is essential for the use of bio-oil as an intermediary in the production of fuels and for the generation of value-added chemical products.

There are several possible techniques for the elimination of bio-oil acids. However, they are constrained because they have some drawbacks related to bio-oil's properties and physical and chemical characteristics. Also, some have high solvent consumption, temperature dependence, long implementation times, and high costs (16,17). Despite this, the removal of loaded species in the bio-oil is possible through the use of pressure-driven separation processes using liquid phase membranes in combination with functionalized water-soluble polymers; this is because this method does not require the use of organic solvents, the separation occurs through the affinity of the species of interest for the interaction sites that the water-soluble polymer possesses, besides this type of separation techniques are generally more efficient in terms of capital, energy, and ease of operation compared to traditional separation processes such as distillation, adsorption, and absorption (18-20). In this sense, the main objective of this research is to extract, by retention technique in the liquid phase assisted by polymers, anionic organic compounds (acetate and sulfonate) present in the bio-oil obtained by the pyrolysis of sugarcane bagasse.

2. Methodology

2.1. Characterization of sugarcane bagasse

The sugarcane bagasse of the variety CC 01-1940 was provided by the Ingenio del Occidente and subjected to heating at 85 °C until obtaining a constant weight. Subsequently, it was sieved until achieving a particle size of less than 0.33 mm. Elemental analysis was carried out using Flash EA model 1112 of the Thermo brand as a quantifier of carbon, hydrogen, nitrogen, and sulfur (CHNS) elements. Finally, a thermal characterization was made by Thermogravimetric analysis (TGA) and Differential Thermal Analysis (DTA). Thermograms were purchased with the Perkin Elmer model TGA Q50 V20.13 Build 39, 140 µL alumina crucibles were used to contain the sample, and a non-oxidizing atmosphere was used with nitrogen at a flow rate of 20 ml/min. The temperature range studied was from 40 ºC to 550 ºC with a heating rate of 10 ºC min.

2.2. Pyrolysis of sugarcane bagasse

10.0 g of sugarcane bagasse was subjected to pyrolysis by using a stainless steel batch pilot reactor equipped with external tubular resistance, a dielectric, a metal shell, a thermocouple, a continuous power regulator, a power source, a PVC box that has a digital panel for programming the equipment and three valves incorporated in part higher; where one of them works as a device that allows evacuating excess fluid in case of overpressure in the reactor, the second allows to supply the purge gas (N_2) inside the device. The third evacuates the gases generated during the process of pyrolysis. This procedure was carried out by heating the reactor at a rate of 5 °C min-1 up to 350 °C and 200 kPa. Subsequently, the pyrolytic gas flow condensation was carried out by means of a flash separator system equipped with two stainless steel containers with a cylindrical shape, coupled in series to a gas collection tube with a capacity of 500 mL. Once the condensable and non-condensable gaseous fractions were obtained separately, the yield of the condensable fraction was determined and characterized by gas chromatography coupled to mass spectrometry (GC-MS).

2.3. Synthesis of sodium *p*-toluenesulfonate

To carry out the synthesis of sodium *p*-toluenesulfonate (*p*-TsNa), 32 mL of toluene (Merck, 99.9 %) were mixed with 19 mL of H_2SO_4 (Merck, 95.0 %) and subjected to reflux for 20 min at 165 °C. This mixture was cooled after adding 100 mL of boiling water, 15 g of $NaHCO_3$ (commercial), and 40 g of NaCl (commercial). After cooling, the mixture was filtered and washed with 20 mL of saturated NaCl solution. Subsequently, the resulting solid was mixed with 100 mL of boiling water and 15 g of NaCl. Finally, *p*-TsNa was obtained by slow and constant cooling. The white crystals thus formed were filtered and washed with methanol (Merck) (21). The percentage of yield was determined, and crystals were characterized by ^{1}H-NMR.

2.4. Acetic acid and *p*-TsNa retention experiments in aqueous solution

A solution of 50 mL of acetic acid (Merck) at 0.01 mmol / mL and pH four was contacted for 2 hours under constant stirring with a 50 mL pDADMAC (SIGMA®) at 0.01 mmol / mL in the same pH conditions. From the above mixture, 55 mL was added to the 8050 ultrafiltration cell of Amicon®, equipped with a regenerated cellulose membrane of 10,000 MWCO. The system was subjected to a pressure of 400 kPa until five permeates of 10 mL were collected. Subsequently, the concentration of acetic acid in the permeate was measured by titration with NaOH. The same procedure was repeated for the other possible combinations of ionic strength (without adding NaCl, 0.0025 m of NaCl, 0.0050 m of NaCl, 0.0100 m of NaCl) with the pH values of 4, 5, 7, and 9. An analogous experiment was carried out in the absence of pDADMAC. For the *p*-TsNa, the same procedure was applied for the acetic acid retention experiment in aqueous solution, with the difference that the organic anion studied was *p*-TsNa and the quantification method used was UV-Vis at a length of 261 nm wave. Additionally, a blank of the experiment was made.

2.5. Acetic acid and *p*-TsNa retention experiments in bio-oil

0.3 mL of bio-oil was diluted in 250 mL of distilled water, then an aliquot of 50 mL was taken, the pH was set to nine, and the ionic strength was 0.0100 m of NaCl. The solution obtained was put in contact for 2 hours with 50 mL at 0.01 mmol / mL of pDADMAC at the same pH and ionic strength conditions as the previous solution. Then, 55 mL of the final mixture was subjected to the LPR technique at 400 kPa until five permeates of 10 mL each. Finally, the concentration of acetic acid in the permeate was measured by titration with $NaHCO_3$ (commercial). An experiment blank was also run, and the polymer discharge was performed, considering the conditions of lower retention for acetic acid.

Table 1. Elemental analysis of sugarcane bagasse.

Element	Percentage
Nitrogen	0.06
Carbon	39.85
Hydrogen	5.28
Sulfur	0.31

About the *p*-TsNa, 0.5 mL bio-oil was diluted to 250 mL with distilled water, and then an aliquot of 50 mL was fixed at pH nine without adding NaCl. The solution obtained was contacted for 2 hours with 50 mL of pDADMAC at 1.5 × 10-3 mol/L, which replicated the same pH and ionic strength conditions of the previous solution. Then, 55 mL of the final mixture was subjected to the LPR technique at 400 kPa until five permeates of 10 mL each. Finally, the absorbance of the samples was measured by UV-Vis at 261 nm. An experiment was also run as an experimental blank, and the polymer discharge was performed, considering the conditions of lower retention for the *p*-TsNa.

3. Results and Discussion

3.1. Characterization of sugarcane bagasse

The properties obtained concerning the elemental analysis of the BCA are shown in **Table 1**. This result allows to observe that the content of S and N is shallow, so this biomass produces a low amount of SO_X and NO_X during the pyrolysis; this result is consistent with that observed by Varma and Mondal, where it is shown that the content of N and S is 0.24 and 0.06 % (22). In addition, Asadullah and collaborators indicate that, given the low content of precursor species of poisonous components, such as sulfur, the SCB can be considered biomass suitable for low-temperature pyrolysis to produce bio-oil (23). On the other hand, the behavior of sugarcane bagasse was analyzed by pyrolyzing it with thermal analysis and differential thermal analysis in the temperature range of 40 to 550 ° C, as shown in **Figure 1**. A weight loss was observed characterized by four stages; the initial stage (< 200 °C) describes a loss of approximately 6 % of the weight of the sample, which can be attributed to the process of drying the bagasse by vaporizing water absorbed on the surface or physically adhered to the pores of the material (24). The second and third stages take place between 200 and 340 ° C, where an approximate weight loss of 20 % is observed, referring to the elimination of a significant amount of volatile matter by the release of hydrocarbons from the thermal

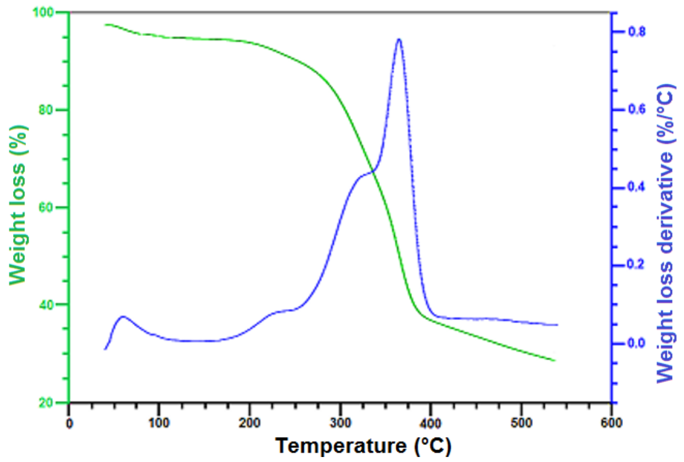

Figure 1. Thermogravimetric analysis and differential thermogravimetric analysis of sugarcane bagasse.

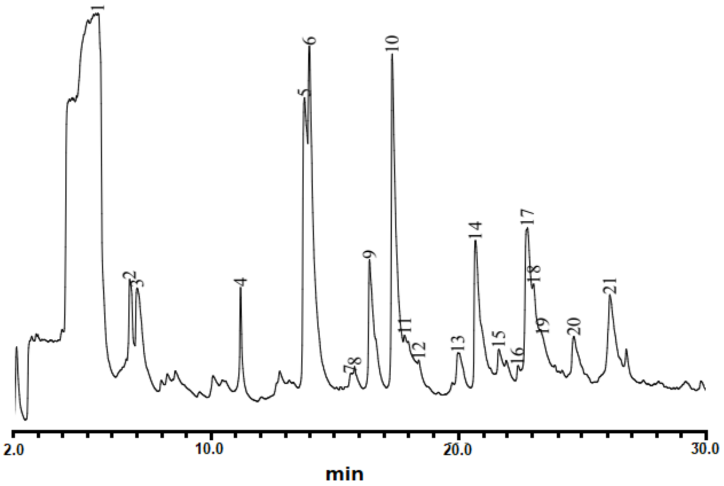

Figure 2. GC-MS chromatogram of bio-oil.

degradation of the hemicellulose and cellulose; The DTG curve shows two peaks at 249 °C and 335 °C which shows that these are shoulders corresponding to the degradation of hemicellulose and cellulose, respectively (25).

The fourth stage of the process describes a total weight loss of approximately 48 % of the sample. It is related to the partial degradation of the lignin with its corresponding visible shoulder at 365 °C. It is observed that above 390 ºC, lignin degradation occurs very slowly.

3.2. Pyrolysis of sugarcane bagasse

The yields of the fractions obtained when carrying out the pyrolysis process were: 17,6 % liquid, 81,1 % solid, and 1,3 % gas, which it is observed that the liquid fraction presents a low value compared with the results reported in the literature (23, 26-29), it is because there is a close dependence between the yields of the pyrolysis products (bio-oil, bio-carbon, and biogas) with the effect of the operating parameters, such as temperature, heating rate, the flow of nitrogen and the particle size of the biomass (22,23). In addition, some of the mentioned parameters could not be controlled due to the limitations of the pilot equipment used to perform the pyrolysis of the SCB. Despite this, these parameters are not relevant to the interests of this work.

Figure 2 shows the GC-MS spectrum of the bio-oil, and **Table 2** represents the list of components present in the bio-oil that has a peak-area percentage more significant than 5.0 %, with their retention time (RT), percentage area-peak, name of the compound, and molecular formula.

The most significant volatile compounds present in the SCB bio-oil are phenol, 4-methylphenol, 4-ethylphenol, acetic acid, 1,2-benzenediol, *p*-toluenesulfonic acid, and furfural with a relative percentage area of 15.861 %, 13,172 %, 11.744 %, 11.671 %, 11.374 %, and 9.813 %, respectively. The range of carbon distribution of the volatile compounds in the bio-oil is C_2-C_8, similar to the other petroleum products. The presence of alcohols, aldehydes, ketones, acetic acid, furfural, and furan in the bio-oil is due to cellulose decomposition and the biomass's hemicellulose fraction (30).

The presence of aromatics, creosol, and phenolic derivatives in the bio-oil is due to the degradation of lignin (31). Acetic acid is an important chemical compound for producing various valuable products. The main uses of acetic acid are the manufacture of vinyl acetate, acetic anhydride, acetate esters, monochloroacetic acid, and the application as a solvent in the production of dimethyl terephthalate and terephthalic acid (32). Vinyl acetate produces latex emulsion resins for applications in paints, adhesives, paper coatings, and textile treatments. Acetic anhydride is used to manufacture textile fibers such as cellulose acetate, cigarette filter cable, and cellulose plastic (33).

3.3. Characterization of sodium *p*-toluenesulfonate

Sodium *p*-toluenesulfonate is a toluenesulfonate ester used in organic chemical reactions as an alkylating agent, a non-oxidizing catalyst, an intermediate for the synthesis of biologically active compounds, and a supporting electrolyte for depositing polypyrrole membranes (34-36). As a result of the synthesis, a crystalline, white, flaky solid with a percentage yield of 36.52 % was obtained. The low yield of the product is a consequence of the conditions and the reaction time, which were adapted in such a way that the *para* isomer was obtained quickly and disulfonation was avoided. On the other hand, ^{1}H-NMR was used for structural elucidation (see **Figure 3**).

The peak labeled "A" appears at 2.31 ppm and belongs to the hydrogens located in the methyl group. The peak labeled "B" at 7.13 ppm corresponds to the hydrogens in the *ortho* position concerning the methyl group in the aromatic ring. The peak at 7.49 ppm labeled "C" corresponds to the hydrogens in the *ortho* position relative to the methyl group.

Table 2. Compounds identified in the bio-oil of sugarcane bagasse pyrolysis.

Compound	Relative area > 5 %	Orden	RT (min)	Molecular formula
Phenol	15.861	5	13.774	C_6H_6O
4-methilphenol	13.172	10	17.318	C_7H_8O
4-ethylphenol	11.744	14	20.704	$C_8H_{10}O$
Acetic acid	11.671	1	5.447	$C_2H_4O_2$
1,2-benzenediol	11.374	17	22.783	$C_6H_6O_2$
p-toluenesulfonic acid	9.813	6	13.968	$C_7H_8O_3S$
Furfural	5.811	3	7.069	$C_5H_4O_2$

3.4. Acetic acid and *p*-TsNa retention experiments in aqueous solution

The results of the retained organic anions are presented systematically as the percentage of retention, R (%), against the pH factor. For a species of interest (X), its retention (Rx) is defined in Equation 1 as:

$$R_x = \left(1 - \left[\left(C_{x,p}\right)C_{x,R^{-1}}\right]\right) x\ 100\ \% \qquad [1]$$

Cx, P, and Cx, R are the concentrations of the species of interest in the permeate and the retentate, respectively (17). On the other hand, the polycations (R^+) interact with organic anions (R^-) according to the following equations:

$$R^+Cl^- \leftrightarrow R^+ + Cl^- \qquad [2]$$

$$R^+ + R^- \leftrightarrow RR \qquad [3]$$

The retaining profile for acetate and sulfonate anions as a function of pH at different ionic strength values in the presence of pDADMAC as a polymeric binding agent is illustrated in **Figure 4**, and the data is presented in **Table 3**. In the pH range of 3 to 9, the degree of binding and retention of organic ions differ significantly; observing as a result that the highest retention is obtained at pH nine and an ionic strength of 0.01 molal for the acetate anion, while for the sulfonate anion, the best retention was obtained at low ionic strength (without the addition of NaCl). On the contrary, both cases obtained the lowest retentions at pH 4 with an ionic strength of 0.01 molal. This behavior is explained by the fact that for acetic acid, the degree of dissociation is appreciably more significant in a solution of sodium chloride than in pure water because, in the saline solution, both the acetate ions and the hydronium ions are found, surrounded by a layer of charged particles of opposite sign; this electrical density makes the reassociation of the two species less likely, forming the undissociated molecule of the acid, resulting from equilibrium effects in a greater degree of dissociation (37). The increase in the retention percentage as a function of the pH for both species is because the increase of the latter parameter by the addition of NaOH produces the deprotonation of the acetate and sulphonate groups, that is, they are positively charged and, therefore, they are more available to interact with the effective binding sites of pDADMAC (38). On the other hand, it was observed that the retention percentage of the sulfonate anion is greater when the ionic strength of the medium is low (without the addition of NaCl), being explained by the idea that when the *p*-TsNa is in the anionic feed solution in combination of NaCl its retention can be affected due to possible competition for the interaction sites with the polymer (39-41), it is also possible that the precipitation of *p*-TsNa can also occur as the ionic strength of the medium increases, since NaCl reduces the solubility in aqueous medium.

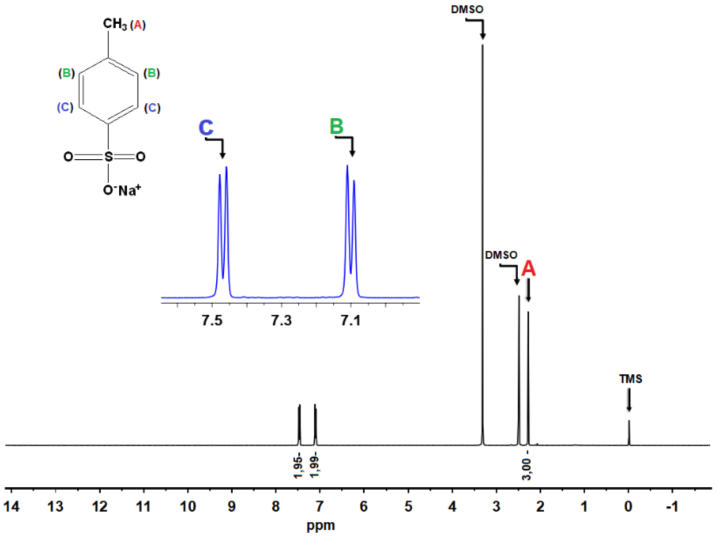

Figure 3. The ^{1}H-RMN spectrum of the p-TsNa.

3.5. Acetic acid and *p*-TsNa retention experiments in bio-oil

For these experiments, the maximum retention conditions for the organic anion *p*-TsNa in the bio-oil were implemented, and the retention was 30 ± 2 % at pH nine and had low ionic strength; which is equivalent to 395.5 mg of pTsNa retained per gram of pDADMAC . This is attributed to the fact that the nitrogen atom has the electrons available to interact with the *p*-TsNa. On the other hand, the discharge of the polymer was carried out under conditions of lower retention, achieving a retention of 40 ± 9 %, which is equivalent to 157.8 mg of pTsNa retained per gram of pDADMAC; this result is explained by the fact that at this pH value, the quaternary ammonium groups still have strong interactions with the *p*-TsNa anion, i.e., given the conditions of the medium the

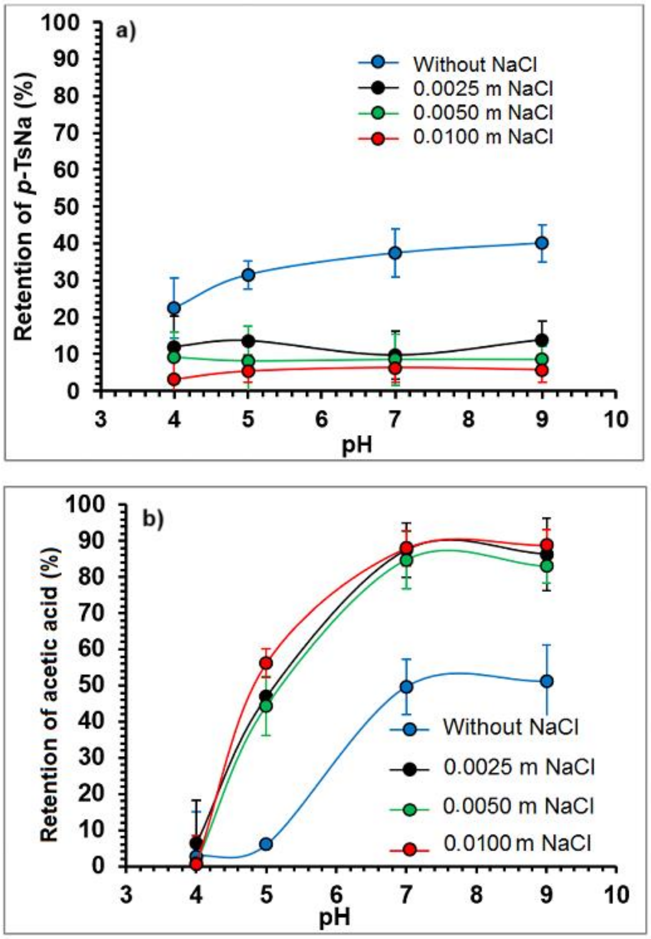

Figure 4. Retention profiles for a) *p*-TsNa at different ionic strength in pDADMAC aqueous solution, and b) for acetic acid at different ionic strength in pDADMAC aqueous solution.

pDADMAC has a relatively high capacity to bind or retain the negative ions of *p*-TsNa. *p*-TsNa and the protons in the middle must compete with the *p*-TsNa to free it from the interaction site.

Table 3. Retention values for acetic acid and p-TsNa at different pH.

pH	Acetate	*p*-TsNa
without addition of NaCl		
4	2.75 ± 0.12	22.38 ± 0.12
5	5.86 ± 0.01	31.41 ± 0.01
7	49.63 ± 0.08	37.34 ± 0.08
9	51.13 ± 0.10	40.03 ±0.10
with 0.0050 m of NaCl		
4	6.26 ± 0.03	12.01 ± 0.03
5	46.77 ± 0.04	12.59 ± 0.04
7	87.46 ± 0.01	9.80 ± 0.01
9	86.32 ± 0.02	13.83 ± 0.02
with 0.0075 m of NaCl		
4	0.86 ± 0.08	9.13 ± 0.08
5	44.31 ± 0.08	8.21 ±0.08
7	84.72 ± 0.08	8.57 ± 0.08
9	82.85 ± 0.05	8.57 ± 0.05
with 0.0100 m of NaCl		
4	57.56 ± 0.08	3.22 ± 0.08
5	56.12 ± 0.04	5.36 ± 0.04
7	87.94 ± 0.05	6.32 ± 0.05
9	88.79 ± 0.04	5.72 ± 0.04

4. Conclusions

The methodology described above shows that the LPR technique using pDADMAC as a polymer can be used to separate organic anions, acetate, and sulfonate in an aqueous solution. The results show that the highest retention is obtained at pH nine and an ionic strength of 0.01 m for the acetate anion. In contrast, for the sulfonate anion, the best retention was obtained at low ionic strength (without adding NaCl). On the contrary, the smallest retentions were obtained at pH 4 with an ionic strength of 0.0100 m for both cases. On the other hand, the loading and unloading experiments for the *p*-TsNa showed that its removal from the bio-oil is possible, recovering 237.3 mg of *p*-TsNa per gram of pDADMAC.

Conflict interest. The authors declare that there is no conflict of interest.

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