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An Innovative Phenolic Resin and its Application to Paracetamol Removal

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Water scarcity has been a concern worldwide, especially since the presence of micropollutants in wastewater has increased. In this scenario, adsorption and advanced oxidative processes have gained increasing attention in environmental chemistry, emerging as promising alternatives for water decontamination. Drugs are a good example of those pollutants and, among all drugs, paracetamol is a widely used one and was used in the current study. Thus, alternative precursors of phenolic compounds, as a blend of Kraft black liquor and tannin, were used for an innovative activated phenolic resin (APR) production and investigated for paracetamol removal. When the APR was used in a photocatalytic process, the paracetamol removal mechanism was predominantly by adsorption rather than by photocatalysis. The paracetamol adsorption onto APR was almost 70 % higher than in the conventional thermally treated photocatalysts, encouraging a further assessment of paracetamol adsorption onto APR. The adsorption capacity reached a maximum value for an APR weight of 0.02 g, with an adsorption capacity of 19.43 mg g^{-1}. Moreover, the paracetamol solution pH did not show noteworthy effect on the adsorption capacity in the pH range evaluated. Chemical structure characterization pointed out a variety of functional groups on the APR surface, which are characteristic of bio-phenolic compounds structure. The drug adsorption onto APR may be explained by the adsorbent - adsorbate π-π interactions and hydrogen bonding. At the maximum adsorption capacity, the use of APR as adsorbent provided a paracetamol removal of about 45 %, which can be increased to greater than 90 % by increasing the adsorbent weight. This confirmed the resin's potential as an adsorbent for paracetamol removal.

1. Introduction

The population and industrial production have increased the contamination of aquatic environments by emerging pollutants, endangering water quality. Among all the emerging contaminants, drugs have been the focus of innumerous research studies, since their consumption has increased considerably in recent years. That increase is also a consequence of their indiscriminate use. After their therapeutic use, drugs are excreted by the human body in its original form and as metabolites. That way, they are frequently detected in surface and ground water, and even in drinking water as biologically active substances (Liu and Wong, 2013). Since these contaminants are not biodegradable, they are not effectively removed by the conventional wastewater treatments (Villaescusa et al., 2011). As a result, drugs are detected in aquatic systems, causing chronic effects and ecotoxicological impacts on ecosystems (Vaiano et al., 2018). Moreover, the harmful effects on human and animal health due to the presence of drugs in aquaculture are also known, such as endocrine disruption and increased resistance to pathogenic bacteria (Yang et al., 2008). Among all the drugs, paracetamol (N- (4-hydroxyphenyl) ethanamide)), also known as acetaminophen, is the most used analgesic and antipyretic drug (Leyva et al., 2018; Hernández et al., 2018), so that it is also part of countless formulations in medicines against cold and flu (Marques et al., 2017). According to Fent et al. (2006), paracetamol is classified as a Non-Steroidal Anti-Inflammatory Drugs (NSAID) and among all its adverse effects, the formation of hepatotoxic metabolites and the proliferation of cultured breast cancer cells are cited by the author. As a result, the search for efficient technologies to remove organic contaminants, especially

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drugs, has been challenging in recent years. In this scenario, adsorption and advanced oxidative processes have gained increasing attention in environmental chemistry, emerging as promising alternatives for water decontamination. The application of advanced oxidative processes in the treatment of water, such as heterogeneous photocatalysis using titanium dioxide and zinc oxide, have been well studied due to its high catalytic efficiency, low cost and its low environmental impact (Cantarella et al., 2018). Along with them, adsorption is another alternative process for wastewater pollutants removal and is also part of the heterogeneous photocatalysis fundamental mechanisms. While the pollutant is being degraded by photocatalysis, it is also being adsorbed within the catalyst. The contributions of these two processes are accounted for separately, being the adsorption the amount of pollutant removed in the absence of UV light. When compared to the total pollutant removal in the presence of the UV light, the photocatalysis efficiency is obtained. Several residues are produced by the pulp and paper industry, due to the process high chemicals demand and its recovery steps. Black liquor is one of the byproducts of the pulping process. In order to promote a sustainable environment, a fraction of the black liquor can be retrieved for an innovative application. Thus, alternative precursors of phenolic compounds, as a blend of Kraft black liquor and tannin, were used as raw materials for a condensation polymerization reaction in a basic medium, aiming the phenolic resin production. In the field of new materials and in line with the environmental protection and the concepts of sustainability, green chemistry and circular economy, this work aims to investigate the potential of an innovative phenolic resin in water treatment for removing drugs, being the paracetamol the molecular model studied.

2. Material and Methodology

2.1 Material

The chemicals used were: Tannin (SETA S/A), Industrial Kraft Black Liquor, Formaldehyde 37 % (Synth) and NaOH (Vetec). Thermal treatment (TT) was performed on ZnO (Sigma-Aldrich) and TiO_2 (Kronus) by keeping them at 550 °C for 2 hours.

2.2 Phenolic resin preparation

In order to produce the phenolic resin (APR), a blend of 70 g of *Kraft* black liquor and 1.5 g of tannin was first hydroxymethylated with 16 g of aqueous formaldehyde 37 % (w/w) at 70 °C, for 2 hours, under reflux. Then, the blend was crosslinked and cured at 90 °C. The cured material was washed with 2:1 ethanol:acetone solution and dried at room temperature. Afterwards, the resin was also subjected to a heat treatment by means of a ramp starting at 100 °C for 30 minutes, followed by another at 170 °C for 2 hours, both at a rate of 5 °C min^{-1}.

2.3 Photocatalysis tests

The photocatalytic tests were carried out in a sludge-type batch reactor, under four 15 W germicidal UV lamps. The reactor was equipped with a magnetic stirrer to ensure catalyst suspension during reaction and a thermostat bath at 30 °C. The tests were performed in triplicate by using 250 mL of a 50 mg L^{-1} paracetamol aqueous solution either with a catalyst concentration of 2 g L^{-1} or in the absence of catalyst to evaluate the degradation only by the UV light. Aliquots were collected after 2 hours and filtered with 0.22 µm nylon membrane. The absorbance of each aliquot was measured at 243 nm for evaluation of the catalytic activity. For each experiment conditions, the adsorption was also assessed after repeating the stated procedure without the UV light. In order to evaluate color change and chemicals release, a control test was also performed for each catalyst by replacing the paracetamol solution by distilled water. The paracetamol removal was calculated by Eq. (1):

$$\%R = \frac{C_o - C_t}{C_o} x100 \quad (1)$$

Where:
%R: Paracetamol removal (%);
C_0: Paracetamol concentration ($mg.L^{-1}$) at t=0h;
C_t: Paracetamol concentration ($mg.L^{-1}$) at time t.

2.4 Adsorption tests

The adsorption tests were carried out batchwise. For that, given amounts of the adsorbent (10, 20, 40, 50, 80 or 160 mg) were mixed with 20 mL of 50 mg L^{-1} paracetamol solution at different pH (5, 6, 7, 8, 9 or 10). The adsorbate-adsorbent solution was continuously stirred in an orbital shaker at 150 rpm and 30 °C for 24 hours.

Prior to analysis, the samples were filtered with 0.22 μm nylon membrane. The paracetamol removal was calculated by Eq. (1) and the adsorption capacity (q_t) by Eq. (2):

$$q_t = \frac{(C_o - C_t).V}{\mathrm{m}} \quad (2)$$

Where:
q_t: Adsorption capacity (mg g^{-1}) at t=24h;
C_0: Paracetamol concentration (mg L^{-1}) at t=0h;
C_t: Paracetamol concentration (mg L^{-1}) at t=24h;
V: Paracetamol solution volume (L);
m: Adsorbent weight (g).

2.5 Characterization

The paracetamol concentration after the photocatalysis and adsorption experiments was measured in an UV HACH DR5000 spectrophotometer, at a wavelength of 243 nm. Moreover, the materials specific surface area (BET), total pore volume (at (P/P_0 = 0.95) and the pore size distribution (BJH) data were obtained in a Quantachrome NOVA-1200. Their pH point of zero charge evaluations were performed in terms of the pH of the suspension according to the 11-points methodology described by Regalbuto & Robles (2004). The catalysts (TiO_2 and ZnO) were characterized by X-Ray Fluorescence (XRF) in a Rigaku ZSX Mini II and the activated phenolic resin (APR) by Fourier-transform infrared spectroscopy (FTIR) in a Bruker VERTEX 70V equipment.

3. Result and Discussion

The photocatalysis process was evaluated by the degradation of paracetamol in wastewater, as well as the APR performance in that process. For that, TiO_2 and ZnO, with and without thermal treatment, were used as photocatalysts for comparison and reference purposes. The thermal treatment was performed aiming to improve the photocatalyst activity, once their size and morphology are parameters of great impact on the photocatalytic process (Teixeira & Jardim, 2004). According to Abdullah et al. (2017) and Zulkiflee et al. (2016), calcination increases the material textural properties, i.e., particle size, porosity and specific surface increase. Moreover, the authors also claim that the thermal treatment controls the materials crystalline phase to a more stable structure with a homogeneous and smooth surface.

Table 1: A comparison between photocatalysis and adsorption upon paracetamol removal

CATALYST	$\%R_{ADSORPTION}$ [a]	$\%R_{TOTAL\ (ADSORPTION+PHOTOCATALYSIS\ -2h)}$ [a]
Photolysis	-	3.25 ± 2.18
APR	22.02 ± 0.36	24.04 ± 0.36
TiO_2	4.52 ± 2.65	15.90 ± 2.95
TiO_2 - TT	13.69 ± 6.96	23.40 ± 6.83
ZnO	3.52 ± 2.46	12.58 ± 4.92
ZnO - TT	13.02 ± 3.92	22.70 ± 1.39

[a]Paracetamol concentration: 50 mg L^{-1}; Volume: 250 mL; Catalyst weight: 50 mg; pH: 7.

The results in Table 1 show that the catalysts played an important role on the photocatalysis, given that the photolysis (without the catalyst) accounted only for 3.25 % of paracetamol removal. However, when catalysts were used, the $\%R_{TOTAL}$ went up to an average of 14 and 23 % for the catalysts without and with thermal treatment, respectively. As assumed earlier, thermal treatment improved the photocatalyst activity, providing a process improvement of about 47 and 80 % for TiO_2 and ZnO, respectively. Moreover, it also increased the adsorption by 3 and 3.7 times for TiO_2 and ZnO respectively. Between the photocatalyst, TiO_2 stands for its photoactivity and, without TT, the paracetamol removal was 26 % higher when compared to ZnO. However, when the thermal treatment was performed, their photoactivity became nearly even, being the TiO_2 only 3% better than ZnO. A comparison between the catalysts highlights that the APR has no photoactivity, once the paracetamol removal occurred predominantly by adsorption. The paracetamol removal by adsorption onto APR was about 60 and 70% greater than the adsorption onto thermal treated TiO_2 and ZnO, respectively.
The very good performance of APR in paracetamol removal by adsorption led to a more in-depth study of this process. As all processes, the adsorption also has some limiting factors that need to be investigated in order to understand the process behavior, the type of interactions and the adsorption mechanisms.
First, APR, ZnO and TiO_2 were characterized by investigating their textural properties (Table 2), and chemical structure (Figure 1). For assessing the photocatalysts, XRF spectroscopy was used, as shown in Figure 1 (a)

and (b). Once XRF cannot identify C, N and O elements, which are predominant in organic materials, such as the APR, its chemical structure was identified by FTIR spectroscopy, Figure 1 (c).

Table 2: APR, TiO_2, ZnO and Paracetamol characteristics

	APR	TiO_2	ZnO
S_{BET} ($m^2 g^{-1}$)	5.759	44.347	11.314
V_{TOTAL} ($cm^3 g^{-1}$)	0.011	0.182	0.064
$D_{AVERAGE}$ (Å)	45.85	82.25	41.32
pH POINT OF ZERO CHARGE (pH_{PZC})	8.6	6.1	7.9
	PARACETAMOL		
Dimensions (Å)	4.6 x 7.5 x 11.9 (monomer) - 11.9 x 6.6 x 15.6 (dimer) [a]		
pK_a	9.38[b]		

[a] Galhetas et al. (2014) [b] Villaescusa et al. (2011)

APR textural characterization revealed the polymer lower specific surface area when compared to commercial adsorbents, such as the activated carbons (García-Mateos et al., 2015; Marques et al., 2017). Its pH_{PZC} value of 8.6 means that the material assumes a positive surface when suspended in a medium with pH < 8.6, a negative surface in a medium with pH > 8.6 and the electrical surface charges are cancelled, becoming neutral, at pH = 8.6. Thus, when materials are suspended in a medium with pH different from its pH_{PZC}, a surface charge instability occurs, favoring the adsorption by electrostatic forces.

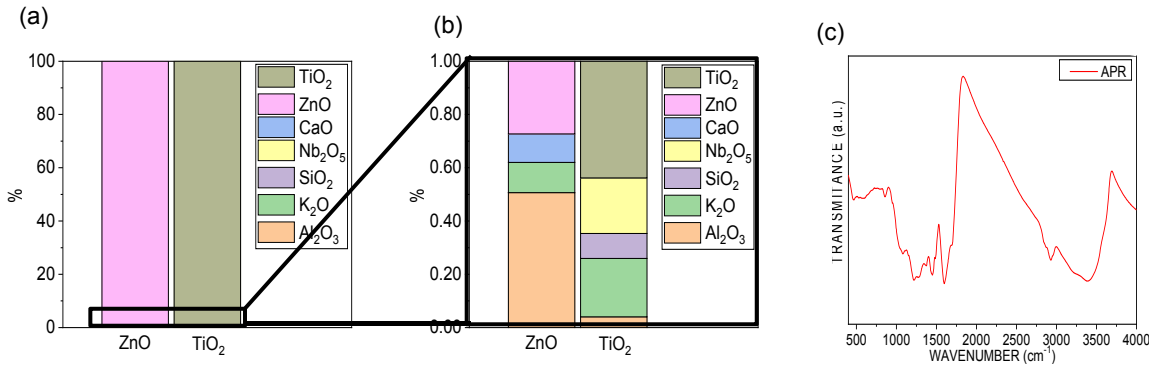

Figure 1: (a) XRF of ZnO and TiO_2 on a scale of 0-100 %; (b) Magnification of the region 0-1 % of the ZnO and TiO_2 XRF; (c) APR FTIR spectrum.

The material chemical structure analyses proved the inorganic nature of ZnO and TiO_2, with linkages between metals and oxygen. XRF analysis also gives ZnO and TiO_2 purities, which are 99.3 and 99.5 %, respectively. The organic nature of APR is noticeable by looking at the FTIR spectrum, which shows diversified organic functional groups on materials surface. Moreover, the resin FTIR analysis revealed the presence of hydroxyl (-OH) groups by the peak 3400 cm^{-1}, the APR aromatic nature (C=C) is represented by the peaks at 1496 and 1593 cm^{-1}, and the polymer methylene (C-H) and ether-methylene (C-H and C-O) bridges through the peaks at 2937, 1463 and 1037 cm^{-1} (Martínez et al., 2016). Despite the APR low specific surface area, its diversified surface functional groups have a positive impact on the adsorption, showing its potential for the drug removal from wastewater.

The influence of the solution pH on the paracetamol removal is illustrated in Figure 2. The APR adsorption capacity did not show noteworthy changes in the pH's range assessed, remaining constant at an average value of 12 mg g^{-1}. Since the paracetamol pK_a is 9.38, as shown in Table 2, at pH below its pK_a the drug molecules are found deprotonated, i.e., in their molecular form. As a result, the adsorption is not dictated by the electrostatic interactions between the APR and paracetamol. Moreover, the APR has a variety of surface functional groups, Figure 1 (c), including aromatic rings and hydroxyl groups. Those groups are characteristic of bio-phenolic compounds structure, such as tannin and lignin. As a result, the adsorption mechanisms are related to the π-π interactions between the aromatic rings from the APR and paracetamol. Moreover, the phenolic hydroxyl groups on the APR surface can make hydrogen bonds with the O-H and N-H linkages of the paracetamol molecule, which justifies the adsorption capacity achieved (Rivera-Utrilla & Sánchez-Polo, 2011; Villaescusa et al., 2011).

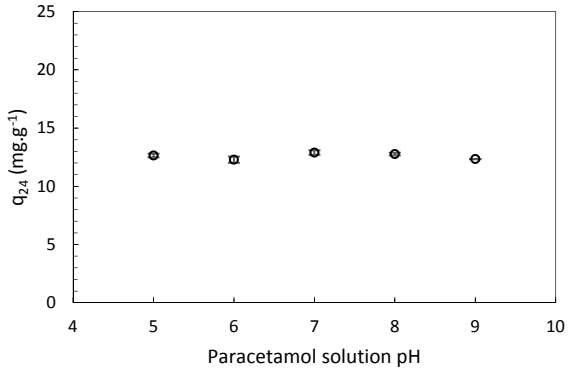

Figure 2: Paracetamol solution pH effect on adsorption capacity. Paracetamol concentration: 50 mg L^{-1}; Volume: 20 mL; APR weight: 50 mg; pH: 5-9.

As the adsorption capacity was not dependent on the paracetamol solution pH (Figure 2), the APR dosage influence on the paracetamol adsorption was evaluated at a neutral pH by varying the APR weight from 0.01 to 0.16 g, as shown in Figure 3. Paracetamol removal efficiency increased with the APR dosage. This increase can be attributed to more active sites available for the mass transfer. The highest paracetamol removal was achieved for an APR weight of 0.16 g, with a removal of 90%. In order to maximize the amount of paracetamol adsorbed by APR weight, the adsorption capacity was evaluated according to Eq. (2). The maximum adsorption capacity (q_{max} = 19.43 mg g^{-1}) was achieved for an APR weight of 0.02 g. As the amount of APR increased, the adsorption capacity decreased. That behavior may be a consequence of the possible aggregation of APR particles, limiting the diffusion rate and making difficult the adsorbate access to the active sites.

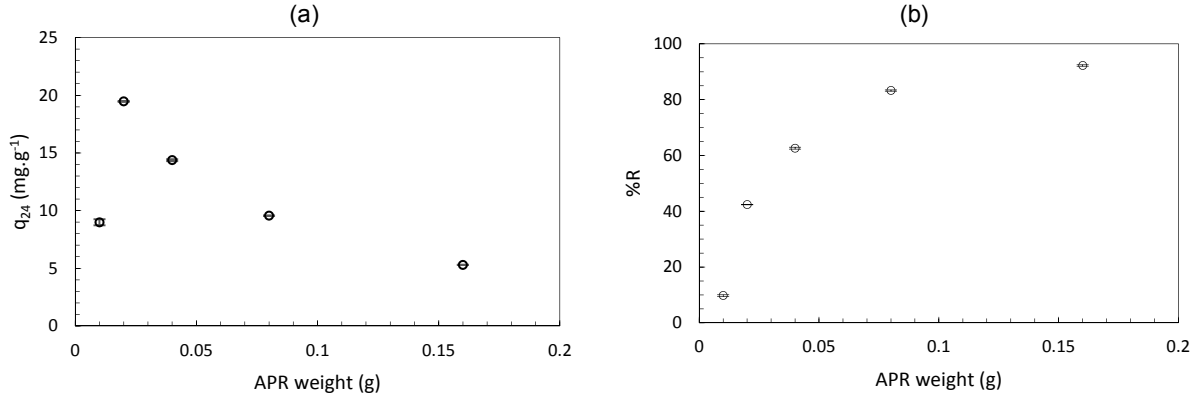

Figure 3: (a) APR dosage effect on adsorption capacity; (b) APR dosage effect on paracetamol removal. Paracetamol concentration: 50 mg L^{-1}; Volume: 20 mL; APR weight: 10 – 160 mg; pH: 7.

4. Conclusion

An innovative phenolic resin has been prepared by the polycondensation reaction of a blend of Kraft black liquor and tannin with a thermal treatment at 170 °C (APR). Then, the material was evaluated for paracetamol removal from wastewater. When compared to the conventional photocatalysis process, the resin stands for its adsorption capacity rather than for its photoactivity. The resin great potential for the adsorption may be related to its diversified surface groups, a characteristic of bio-phenolic compounds. The adsorption capacity reached a maximum value of 19.43 mg g^{-1} for an APR weight of 0.02g. Moreover, the influence of the pH of paracetamol solution on the adsorption capacity was also assessed and no significant changes occurred in the pH range evaluated, remaining close to 12 mg g^{-1}. At its highest adsorption capacity (0.02 g), the use of APR as adsorbent achieved a paracetamol removal of about 45 %. However, by increasing the adsorbent weight, it will be possible to improve paracetamol removal to values greater than 90 %.

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