Conversion of solid waste into nitrogen-rich biochar using aromatic amine amine

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Aromatic amines have been applied in many industrial processes, including industrial pesticides manufacturing, drugs, dyestuffs, polymers, surfactants, cosmetics, and corrosion inhibitors, textile processing (Erdemir et al, 2009)1. As these amines could be discharged into the atmosphere and water, they constitute an important class of environmental pollutants due to their toxic nature and potential carcinogenic properties (Pacheco et al, 2011), especially the aromatic sulfonated amines, since they are very soluble in water and many of them are resistant to microbial degradation (Pacheco et al, 2011). Several treatments have been reported to reduce the concentration of these compounds in effluents. The most used treatment is based on the oxidation of these compounds or adsorption on several material types. Recently, some new treatments have been proposed combining a strong oxidant with ultrasound process (Liang et al,2016) or the electrochemical process(Pacheco et al, 2011).

New biobased materials have been reported with several applications and properties including solid antioxidants (Jesus et al, 2017), supercapacitors (Huang et al, 2016), CO2 adsorbents (Zhao et al, 2010). One large number of the carbon-based new materials are doped with nitrogen. The N-doped materials are produced using polymers with high nitrogen content as melamine, chitosan, or biological rich nitrogen materials as a precursor and thermal treatment (pyrolysis or hidrocarbonization).

In this work, we analyze the stabilization of aromatic amine compounds into biochar structure using the co-pyrolysis of waste biomass and aromatic solutions. We used the N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine (figure 1) also known by the commercial name santoflex as a molecular model. Santoflex is widely used as rubber additive but it can be also used as biodiesel marker or antiozonant compound. Santoflex has large molecular mass and high-temperature stability both important characteristics to be applied in pyrolysis.

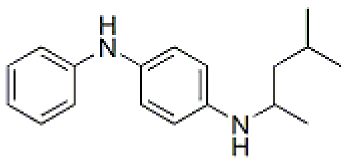

Figure 1 - N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine

100 mL of a hexane solution of aromatic amines with several concentrations was added into a beaker having 20 g of sugarcane residual biomass with granulometry between 80 and 32mesh. The mixture was agitated for 24h at room temperature and dried at 100 °C by 5h. The sample with 20 g of sugarcane bagasse adsorbed with santoflex was pyrolyzed for 2 h at 500 °C under dynamical N2 atmosphere with a flux of 600 mL/h. The final product was analyzed by elementary analysis, thermal analysis, scanning electronic microscopy, and XPS. Using these conditions, the yields of pyrolysis were about 25 %, for any concentration of santoflex or with pure biomass. But, surprisingly, the carbon content of biochar produced with diamines was higher (~70%) than the biochar produced only with biomass (60%).

The results showed that nitrogen from santoflex was incorporated in biochar structure with good yield. Figure 2 presents the nitrogen incorporation for several diamine concentrations. These results were obtained by elementary analysis.

The thermogravimetric analysis result does not show any meaningful difference for sample with or without diamine incorporation, although the differential scanning calorimetry shows a small increase at energy content of biochar with diamine incorporation. Probably it was caused by higher value of C content.

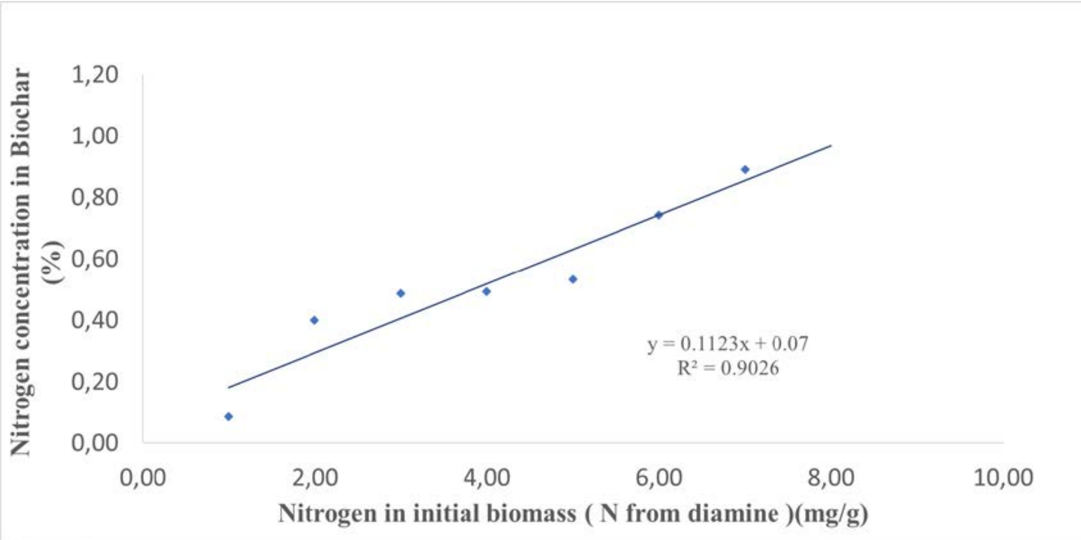

Figure 2 – Nitrogen incorporation from diamine on biochar.

X-Rays photoelectron spectroscopy showed two different nitrogen groups for biochar com diamines, while the biochar from pure biomass just one type of nitrogen bond was detected. Thus, the work shows that is possible to insert the diamine group into solid biochar. This process can be used to stabilize the diamines into solid waste, avoiding the liquid discharged and reducing the risk of a leak in water bodies.

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