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Renewable Eco-Friendly Activated Biochar from Tobacco: Chlorpyrifos Removal Studies

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Abstract - We evaluated the potential application of tobacco as a low-cost raw matter for the development of a new and ecological activated biochar, with the aim of chlorpyrifos adsorption. This was performed by means of characterization and testing the efficiency of the activated biochar based on tobacco from seized cigarettes. Chemically and thermally activated biochar were produced with diferent chemical modifying agents ($ZnCl_2$ and NaOH). The treatments improved the features of adsorbent structure, with an increas of 1775x in SSA of AB-$ZnCl_2$. The adsorption of chlorpyrifos by the activated biochar seems to occur partially by chemical and partially by physical interactions between the pesticide and the surface functional groups O-H, C-H, C=O, C-C, C-H, C-O. The good adjustments may indicate the adsorption of mono and multilayer. The materials show great results for removal of chlorpyrifos with an estimate q_m of 683.30 and 1602.40 µg g^{-1} for Langmuir, respectively found for AB and to AB-$ZnCl_2$. This way, the production of activated biochar can be an excellent alternative for the destination and use of tobacco deriving by seized cigarettes, allowing its use in remediation and decontamination of water.

Keywords: Organophosphates; Pesticides; Water Treatment; Adsorption; Smuggled Cigarettes.

1. Introduction

There is a worldwide interest in the maintenance of the environmental compartments quality, not only by environmentalist groups, but also by the productive systems, mainly due to the directly relation with these compartments to the global supply chain [1]. In this scenario, water resources have major importance, being specially linked to the Sustainable Development Goals proposed by the United Nations (United Nations, 2020), especially regarding goal #6 - Clean Water and Sanitation for all. In a recent investigation conducted in Brazil that aimed to identify pesticides in water supply chains found out that 91% of the samples contained some concentration of chlorpyrifos (CPF) [2]. Among the alternatives for the remediation of water compartments, the adsorption process is a promising option, since it is a technology with effectiveness and high efficiency in the removal of organic and inorganic pollutants, besides being environment-friendly [3]. A material that currently does not have adequate destination or economic value is the cigarette seized by the Federal Revenue of Brazil in border regions of Brazil-Paraguay. The transformation of a potentially toxic waste which causes numerous environmental problems - such seized cigarrets - into modified adsorbents for water decontamination, could allow this waste to have an environmentally appropriate destination [4].

2. Material and Methods

2.1 Adsorbents obtainment and preparation

The tobacco used in this study derived from the Federal Revenue of Brazil, through cigarette seizures in western regions of the State of Paraná, South of Brazil. The tobacco was sent to the Laboratory of Environmental and Instrumental Chemistry, at the State University of Western Paraná - State of Paraná, Brazil. The tobacco was standard in 14 and 54 mesh (0.212 and 1.400 mm). Two chemical activations (agents) were tested, a zinc chloride solution ($ZnCl_2$) (Anhydrous Zinc Chloride 97% P.A., NEON®) and a sodium hydroxide (NaOH) (Sodium Hidroxide in Micro Pearl P.A., NEON®).

After chemical activation, the materials were burned at a pre-set temperature (750 °C for 60 min, under nitrogen flow - N_2), in a FT 1200 1Z tubular oven, model FE50RPN (4000Watts - FORTELAB®). This procedure resulted in two thermally and chemically activated biochar, named AB-$ZnCl_2$ and AB-NaOH, and one thermally activated biochar (AB - thermally activated biochar), in addition to tobacco unmodified biomass (T *in natura*). Thus, the experiment consisted of four treatments: T *in natura*, AB, AB-$ZnCl_2$ and AB-NaOH. After obtaining all tobacco-based biochar, these were characterized and tested by means of adsorption studies with CPF.

2.2. Characterization of the adsorbents

The chemical elements (K, Ca, Mg, Cu, Fe, Mn, Zn, Zn, Cd, Pb and Cr) were determined by means of a nitroperchloric digestion followed by determination by atomic absorption spectrometry (FAAS), with certified standard curves for all metals (GBC 932 AA). Scanning electron microscopy (SEM), infrared (IR) spectroscopy were also performed.

For the determination of the zero load point (pHPCZ), 0.5 g of each material produced was weighed and 50 mL of 0.5 mol L-1 aqueous solution of potassium chloride (KCl) was added with pH values between 2.0 and 13.0 (pH adjusted with HCl and NaOH - 0.1 mol L-1). The pH variation (ΔpH) occurred during the process (final pH - initial pH) was then determined. When plotting the data, pHPCZ corresponded to the value at which the dependent variable (ΔpH) exceeded the value of the independent variable (initial pH) - adapted methodology [5].

2.3 Studies on the dose of adsorbent and ph effect on the adsorption process

In order to evaluate the possible interactions between the tobacco adsorbent doses and the pH of the solution on CPF adsorption, a Central Composite Design (CCD) was used [6]. Different adsorbent masses were evaluated ranging from 5.0 to 25.0 g L-1 while the pH was evaluated in the range on 3.0 a 7.0, as described by the matrix proposed by [7]. The results obtained in the aforementioned tests were tabulated and evaluated according to multivariate analysis by using the software Statistica 7® (StatSoft, 2004), which was used for Analysis of Variance (ANOVA) and the generation of response surface graphs. The mean values of CPF removal (qe and %) were also evaluated by using the software Sisvar 5.6 [8].

2.4 Kinetics, equilibrium and thermodynamics studies on chlorpyrifos adsorption process

Erlenmeyers flasks, 200 mg of the tobacco adsorbents were set in contact with 50 mL of CPF solution (1000 µg L-1) at pH 5.0 [both of these conditions were obtained in previously tests (item 2.6)]. In this study, each erlenmeyer corresponded to a specific time interval (10, 20, 30, 40, 50, 60, 80, 100, 120, 140 and 180 min). After stirring, samples were taken for liquid-liquid extraction (10:1) (previously described), and the remaining concentration (Ce) of CPF was determinated by GC-ECD. The obtained results were studied by using the models of pseudo-first order, pseudo-second order, Elovich and intraparticle diffusion.

Equilibrium isotherms were obtained by means of adsorption studies. For this purpose, 200 mg of adsorbent was added to 125 mL erlenmeyers flask together with 50 mL of CPF solution at pH 5.0, in increasing concentrations of CPF: 100, 300, 600, 900, 1200, 1500, 1800, 2100 and 2700 µg L-1. These flasks were stirred for 100 min at 200 rpm and 25 ºC. Then, samples were taken for liquid-liquid extraction (previously described) and further Ce determination by GC-ECD. From the obtained results, the adsorption isotherms were evaluated by using the nonlinear models of Langmuir [9], Freundlich [10], Dubinin-Radushkevich [11] Sips [12], Temkin [13] and Liu [14]. The adsorption isotherms were constructed in three temperature conditions, 25, 30 and 35 °C. The experimental conditions of this test were: adsorbent mass of 200 mg in 50 mL of CPF solution of 1000 µg L-1 at pH 5.0, 200 rpm, and 100 min of stirring. Then, samples were taken for liquid-liquid extraction (previously described) and further Ce determination by GC-ECD. The Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were calculated in order to evaluate the thermodynamics of CPF adsorption [15].

3. Results And Discussion

The AB-NaOH, obtained the highest pHPZC, the chemical activation (by a strong base) in addition to the thermal activation resulted in an even higher increase of the pHPZC value [6]. FT-IR shows that functional groups from macromolecules such as lignin, proteins, carboxyl, phenolic groups and aromatic modes (mainly skeleton of cellulose and lignin) are exposed in tobacco-based adsorbents (Figura 1). The characteristics observed from SEM might suggest that the

biochar materials developed from tobacco have enhanced characteristics of adsorption, which could be a good indicator for the adsorption of CPF [16]. The specific surface area (SSA) followed the order: AB-ZnCl2 > AB > AB-NaOH > T in natura, with following values: 479.4, 83.6, 76.61 and 0.27 m2 g-1, respectively.

According to the results found for the biochar from tobacco, none statistic influence for the CPF adsorption regarding the studied pH range, or the interaction between adsorbent doses and pH range were found. Thus, it can be concluded that the CPF adsorption process depends only on the adsorbent dose; the pH solution, in the studied range (3.0 to 7.0), do not influence CPF adsorption process. In genneral, the highest adsorbed amount (qe) as well as the highest removal of CPF, are found by using tobacco-based biochar in doses of around 4.0 g L-1. This can be considered a great advantage, i.e., using low doses of tobacco-adsorbent (4.0 g L-1) one liter of solution containing CPF can be decontaminated.

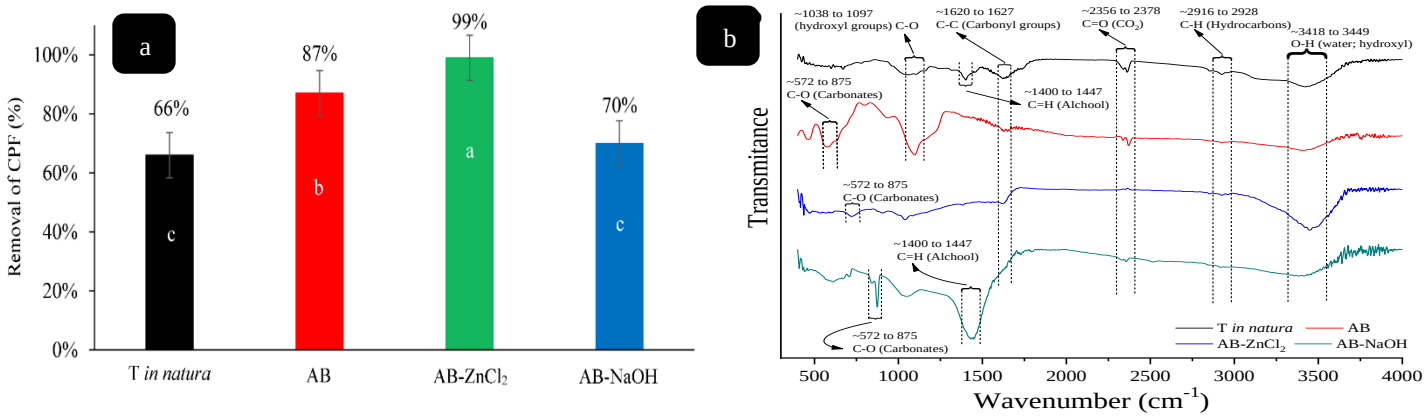

Fig. 1: Means obtained for the removal of CPF in the CCD experiment (a) and infrared spectrum analysis from 4000 to 500 cm^{-1} for the adsorbents T *in natura*, AB, AB-$ZnCl_2$ and AB-NaOH (b). Notes: Different letters inside the bars indicate statistical difference among treatments at 5% by Tukey test.

It is important to stand out the results obtained for AB-$ZnCl_2$, with a fast adsorption of CPF, with more than 95% of CPF removal ocurring within 10 min. A similar performance is also observed for AB-NaOH, with the equilibrium being reach in about 80 min. In contrast, for T *in natura* and AB the equilibrium is not established even after 180 min, with very low adsorption rates being observed.

It is observed that the adsorption of CPF is exothermic for T in natura and for AB, in function to the negative values of ΔHo (ΔHo T in natura = -684 kJ mol-1; ΔHo AB = -859 kJ mol-1); for AB-NaOH are observed positive values of ΔHo (ΔHo AB- NaOH = 993 kJ mol-1) indicating an endotermic process [17]. The values of ΔGo < 0, indicate that the adsorption of CPF onto T in natura, AB-NaOH and AB is a spontaneous process (Hamid et al., 2014). The negative values found for Gibbs free energy, i.e., ΔGo > 0, suggest that regarding this parameter, CPF adsorption was energetically favourable and spontaneous at the studied range of temperatures (25 to 35 oC) for T in natura, AB-NaOH and AB.

The goodness of the fit found for Langmuir, Freundlich and Sips for AB, AB-ZnCl2 and AB-NaOH, could suggest that these materials pass through cooperative adsorption where initially adsorption occurs in monolayers (in high affinity sites), with the interaction between CPF molecules and the surface of the tobacco activated biochar and, in a second moment, with the formation of multilayers, from the interactions between adsorbate-adsorbent and absorbate-adsorbate. The materials show great results for removal of chlorpyrifos with an estimate qm of 683.30 and 1602.40 µg g-1 for Langmuir, respectively found for AB and to AB-ZnCl2. The values of sorption energy (E) for all studied adsorbents are higher than 8 kJ mol-1, with a predominance of high energy bonds due to chemical forces, suggesting chemical sorption [18]. The best ajustment for Liu was observed for AB, with adj-R2 of 0.981 and with low values for σ in all parameters. In this specific case, the values of qmax reached 913 µg g-1, followed by AB-NaOH, with qmax reaching 689 µg g-1, indicating the great potential of tobacco biochar for CPF removal.

4. Conclusion

The proposed procedure for thermal and chemical modification of tobacco biomass successfully generated activated biochar with excellent characteristics for the removal of chlorpyrifos from waters. The use of 4 g of adsorbent is sufficient to remediate 1 L of water contaminated by chlorpyrifos. The adsorption of chlorpyrifos seems to occur by physical and chemical bonds, in a favourable and spontaneous process. This statement is due to the excellent fits found by the following models: pseudo-first, pseudo-second order, Langmuir, Freundlich, Sips, Dubinin-Radushkevich, Temkin and Liu. Also, it is evidenced the formation of mono and multilayers of chlorpyrifos in the adsorbents surface.

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