

Remediation of contaminated waters with lead using activated carbon from tobacco seized in Brazilian border regions

Jéssica Manfrin. Author, M.Sc.,¹ Affonso Celso Gonçalves Jr. Author, Dr.,² Daniel Schwantes. Author, Dr.,³ Gabriel José Klassen. Author, Graduate student,⁴ Élio Conradi Junior. Author, M.Sc.,⁵ Juliano Zimmermann. Author, Graduate student,⁶ Ariane Bazzo Santorum. Author, Graduate student,⁷ Andréia da Paz Schiller. Author, M.Sc.⁸

¹Post Graduate Program in Agronomy, State University of Western Paraná (UNIOESTE), Marechal Cândido Rondon, State of Paraná, Brazil, Pernambuco Street, nº 1777; e-mail: jessicamanfrinn@gmail.com

²Center of Agrarian Sciences, State University of Western Paraná (UNIOESTE); e-mail: affonso133@hotmail.com

³Educational College of Medianeira, Department of Agronomy (UDC); e-mail: daniel_schwantes@hotmail.com

⁴Center of Agrarian Sciences, State University of Western Paraná (UNIOESTE); e-mail: gklassen86@gmail.com

⁵Post Graduate Program in Agronomy, State University of Western Paraná (UNIOESTE); e-mail: elio.conradi@outlook.com

⁶Center of Agrarian Sciences, State University of Western Paraná (UNIOESTE); e-mail: juliaanozimmermann@gmail.com

⁷Center of Agrarian Sciences, State University of Western Paraná (UNIOESTE); e-mail: arianesantorum@outlook.com

⁸Post Graduate Program in Agronomy, State University of Western Paraná (UNIOESTE); e-mail: andreia.schiller@hotmail.com

ABSTRACT

This work aimed to develop adsorbent materials from tobacco to remediate Pb^{2+} from contaminated water. Three materials were used: tobacco *in natura* and two chemically activated carbons (CT NaOH and CT $ZnCl_2$). The adsorbents studied were characterized by chemical composition, zero charge point, infrared spectra, scanning electron microscopy, and BET and BJH. Studies of relationship between pH, adsorbent doses and equilibrium were also conducted. The results showed that the lower adsorbent doses (0.200 mg i.e., 4 g L⁻¹) exhibit higher efficiency for Pb^{2+} removal. The results suggest the occurrence of adsorption in mono and multilayer. The highest adsorption rate was found for the adsorbent CT $ZnCl_2$ ($Q_m = 84.7458$ mg g⁻¹), with higher adsorption capacity when compared to the precursor material (T *in*

natura). It can be concluded that the remediation of water containing Pb^{2+} by activated carbon from tobacco have high efficiency.

INTRODUCTION

The quality of environmental compartments is a subject of great importance, which has been discussed globally in terms of its influence on the maintenance of life on earth. Among the environmental compartments, the water resources have received more attention due to the importance and concern for water quality. In 2015, the United Nations (UN) launched the 2030 Agenda and established a guarantee of drinking water and sanitation among the 17 Sustainable Development Goals (SDG's).

Water is a fundamental resource for the maintenance of life. Due to its great importance and in function of the increasing restriction of access to quality and abundant water, in the last decades many conflicts are observed (Schewe et al. 2014). However, water quality has been compromised over the years, especially in the last 50 years, in regions with industrial agglomeration and high population densities. After Second World War, there was an increase in problems related to water contamination as urbanization and industrialization intensification (Libânio 2010).

Currently, among the main anthropic activities that affect water resources, the most important are those related to the industrial and agricultural sectors. Among the contaminants released by these activities, which cause great impacts on water resources, toxic metals stand out, since these metals have the ability to persist in different environmental compartments as a function of bioaccumulation (Tural et al. 2016). Due to its high toxicity, lead (Pb^{2+}) is among the metals that cause great damage to humans and the environment (Souza et al. 2010).

The adsorption process is an alternative with great potential, since it can be used in the removal of pollutants that have both organic and inorganic composition (Gonçalves Jr., et al. 2016). There are many materials that can be used in the adsorption processes including the activated carbons, which have been shown high efficiency. They have been used in decontamination of water resources in several countries because they are an excellent option for the removal of contaminants due to their high surface and large porosity internal structure (Bhatnagar et al. 2013).

On the other hand, the use of commercial activated carbon demands a complex production process, which makes it costly. Given this, the development of alternative materials, with low added value becomes an attractive choice for the decontamination of water resources. Several authors have been researching alternative materials to obtain activated carbon for the removal of contaminants from water, such as *Ulva lactuca* (Ibrahim et al. 2012), bamboo and cattle bone (Lo et al. 2012), olive stone (Bohli et al. 2015), and orange peel (Foo and Hameed 2015).

Among the alternative materials that can be used is the tobacco from the seizure of smuggled cigarettes. There is no report of the adsorptive capacity of activated carbon from tobacco in the context of their use as

natural or chemical and physical modified adsorbents. However, it is important to evidence the presence of toxic compounds in the *in natura* cigarettes, such as carcinogenic compounds – arsenic, nickel, cadmium and many others (Goulart et al. 2010).

The amount of seized cigarettes is large and continues to grow every year, especially in Brazil. In the year of 2013 it was seized about 3.61 billions of cigarettes. The usual destination of these products has been the incineration of seized material, although this destination corroborates with soil contamination and atmospheric pollution and it is a major environmental concern (Jooseens et al. 2010; Silva et al. 2016).

In this way, this work aimed to develop a sustainable alternative for the destination of smuggled and seized cigarettes in Brazilian borders, through the development of activated carbons to remove Pb^{2+} from contaminated water through the adsorption process, being in this way a sustainable alternative for this residue and for the contaminated water treatment.

MATERIAL AND METHODS

The tobacco used in this study comes from seizures of smuggled cigarettes in the border region between Brazil and Paraguay. The tobacco was dried; in a forced air circulation oven at 65 °C for 24 hours, crushed and sieved for particle size standardization (14 and 65 mesh).

For chemical activation modifying chemical agents were added to the material, both solutions of $ZnCl_2$ and $NaOH$ were used a concentration of 1 mol L^{-1} . The mixture containing the chemical solution and the material to be activated remained in direct contact under constant stirring for 6 h at 45 °C. After 6 h, the material was filtered, washed; with ultrapure water, and then dried in an oven for 24 h at 65 °C. Then the carbonization in tubular furnace material (FT 1200 1Z, with internal dimension of 120 x 300 mm) was carried out, using the predetermined temperature of 750 °C, in which carbonization occurred only under continuous flow of inert gas N_2 and absence of O_2 to obtain the activated carbon. Then, the decanted material was washed with ultrapure water (to neutral pH) and then brought to the oven for drying for 4 h at 110 °C (Rocha et al. 2006), resulting: T *in natura* (unmodified), CT $ZnCl_2$ and CT $NaOH$.

The materials were submitted to chemical characterization by AOAC (2005) and subsequent determination of the concentrations of K, Ca, Mg, Cu, Fe, Mn, Zn, Cd, Pb and Cr by FAAS (Welz and Sperling 2008).

The adsorbents pH_{PZC} , which refers to the pH in which the resultant of adsorbent surface is null, was determined (Mimura et al. 2010). Vibrational spectroscopy in the infrared region was used to perform the characterization of the molecular structure of the material from the analysis of vibrational modes related to functional groups present in the adsorbent. The specters were obtained by transmittance using KBr pellets and analyzed using a Shimadzu 8300 spectrophotometer Infrared Spectrophotometer FTIR - Fourier Transform in the region between 400 and 4000 cm^{-1} with resolution of 4 cm^{-1} .

The morphology of all the materials was evaluated by electron scanning microscopy (SEM), using a microscope JEO JSM 6360-LV equipped with energy dispersive microscopy. For analysis, the samples were dispersed in double-sided tape coated with a thin layer of gold (30 nm) using Bal-Tec SDC Sputter Coater (New York, USA).

The surface, size and pore volume analysis were performed and the surface size and pore volume were calculated using the standard Brunauer, Emmett and Teller (BET) and a pore size was obtained using the method of Barrett – Joyner-Halenda (BJH) (Barret et al. 1951; Brunauer et al. 1938).

In order to evaluate the remediation capacity of the activated carbon, experiments were conducted in laboratory with contamination of water samples with lead, prepared from certified standards diluted in ultrapure water type I. Fortified solution with Pb^{2+} were prepared from salts of lead nitrate [$\text{Pb}(\text{NO}_3)_2$. P.A. $\geq 99\%$ Sigma-Aldrich]. The solution with the desired concentrations for each adsorption were prepared with mono-elementary solutions of 1000 mg L^{-1} , while pH rates were adjusted by adding $\text{NaOH } 0.1 \text{ mol L}^{-1}$ and $\text{HCl } 0.1 \text{ mol L}^{-1}$.

In order to evaluate the influence of the modified adsorbent dose and the pH of the solutions, a central composite design (multivariable study) was carried out. Studies were carried out in relation to the adsorbent dose, as well as pH variation. For this, a rotational composite central design was used with mass values studied from 396 to 1250 mg (ratio of adsorbent mass/volume of solution from 7.9 g L^{-1} to 25 g L^{-1}) while the pH was evaluated in the range 3.00 to 7.00. Experimentally, 50 mL of Pb^{2+} solution was added to erlenmeyers with the doses of adsorbent, which were then arranged in a thermostated Dubnoff system with constant stirring at 200 rpm.

The samples were then filtered and aliquots removed for the determination of the metals by flame atomic absorption spectrometry (FAAS) (Welz and Sperling 2008).

In order to evaluate the removal of lead in higher concentrations, equilibrium studies were developed. For that, the ideal adsorbent dose found in previous tests were disposed in 125 mL erlenmeyers and added with 50 mL of the solutions in increasing concentrations of Pb^{2+} . The experimental conditions for this study also include pH of the contaminating solution at ideal pH found in the previous tests, system temperature at $25 \text{ }^\circ\text{C}$ and contact time between adsorbent and adsorbate of 45 minutes.

In the above aforementioned physical and chemical conditions, the adsorption process was evaluated by following concentrations of Pb^{2+} : 5, 30, 60, 90, 120, 150, 180, 210, 240, 270, 300 mg L^{-1} . The obtained results were linearized by the models of Langmuir, Freundlich and Dubinin-Radushkevich (D-R) (Langmuir 1916; Freundlich 1906; Dubinin and Radushkevich 1947).

RESULTS AND DISCUSSION

The chemical composition of the adsorbents were determined by nitroperchloric digestion (AOAC 2005) followed by the determination of metal concentration by FAAS (Welz and Sperling 2008). Table 1 exhibit the

average contents of the chemical compounds of *T in natura* and after chemical activation with NaOH and ZnCl₂.

Table 1: Result of the chemical analysis carried out on adsorbents *T in natura* and activated carbons CT NaOH and CT ZnCl₂

| Adsorbents | P | K | Ca | Mg | Cu | Zn | Fe | Mn | Cd | Pb | Cr |
|----------------------|-------------------------------|-------|------|------|----|-----|---------------------------------|--------|-----|-------|-----|
| | -----g Kg ⁻¹ ----- | | | | | | ----- mg kg ⁻¹ ----- | | | | |
| <i>T in natura</i> | 5.92 | 44.8 | 26.1 | 5.88 | 10 | 19 | 283 | 175.67 | <LQ | 26.67 | <LQ |
| CT NaOH | 7.67 | 14.65 | 61.7 | 7.2 | 11 | 5 | 626 | 317 | 3 | 97 | <LQ |
| CT ZnCl ₂ | 13.54 | 4.68 | 14 | 5.4 | 3 | 319 | 25 | 304 | 0 | 43 | <LQ |

LQ (limits of quantification): K = 0.01; Ca = 0.005; Mg = 0.005; Cu = 0.005; Fe = 0.01; Mn = 0.01; Zn = 0.005; Cd = 0.005; Pb = 0.01; Cr = 0.01 (mg kg⁻¹).

A change in metals concentration in the activated carbon is observed. An increase of P, Ca, Mg, Cu, Fe, Mn, Pb content, and a reduction of Zn and K is observed when the tobacco is activated with NaOH. On the other hand, when activated with ZnCl₂, it is possible to verify an increase in the concentration of P, Zn, Pb and a reduction of K, Ca, Mg, Cu and Fe.

Changes in the composition of the adsorbents were also observed in the literature when the chemical modifications were made (Schwantes et al. 2018). The concentrations were changed by the activity of the modifying chemical solutions. The extraction of these elements occurs because solutions function as chemical modifiers of the biomass by extracting a certain amount of its constituent elements. Significant parts of the elements were lost during the washing as well after the chemical activation and carbonization of precursor material, what can promote greater availability of other elements (Schwantes et al. 2018; Nacke et al. 2017).

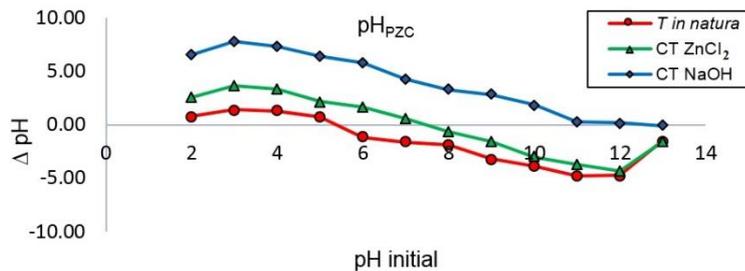
The following pHPZC's were found for the adsorbents: 5.40 *T in natura*, 7.47 CT ZnCl₂ and 12.84 CT NaOH, showed in Figure 1. Anion adsorption is favored when the surface of the adsorbent is predominantly charged with positive charges, this occurs in the condition of pH_{solution} is lower than pHPZC. Otherwise, when the surface of the adsorbent has a predominance of negative charges, i.e., when pH_{solution} is greater than pHPZC cation adsorption is predominant (Mimura et al. 2010; Tagliaferro et al. 2011). Since this, both the *T in natura* and the activated carbon possibly have preference in the adsorption of anions, since they exhibited higher pHPZC than the pH of the solution (pH: 5.0).

It is worth mentioning that pHPZC determination allows a prediction of the adsorption capacity as a function of the surface characteristics of the material (Pintor et al. 2013). However, other factors may also influence the adsorption process, such as porosimetry and the presence of functional groups on the surface of the adsorbent and the ionic radius of the contaminant.

It is important to point out that the development of activated carbon by different chemical caused a great change in the pHPZC when compared to the precursor material *T in natura*. In the literature, it is verified that the differences between pHPZC of the activated and the precursor material is common (Nacke et al. 2017; Dovbeshko et al. 2002). In the case of Bohli et al. (2015) when producing activated carbon from olive stone, obtained pHPZC

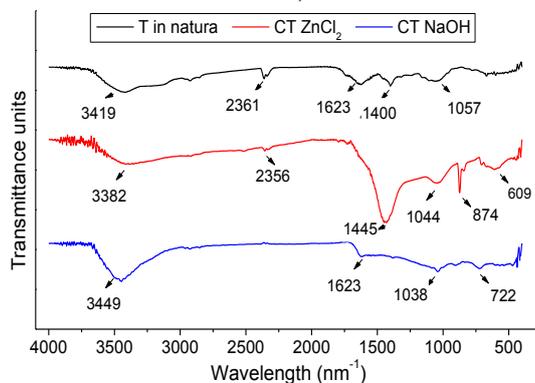
much lower than that found in the present study. It is important to emphasize that the pH_{PZC} is related to the chemical activation process and, consequently, to the chemical compound used in the activation. In this sense, the chemical characteristics of activated carbons and the pH_{PZC} are determined by surface chemical heterogeneity, i.e. that substances in the structure that are not carbon, like hydrogen, nitrogen, oxygen among others can influence in the process e consequently in the determination (Shafeeyan and Daua 2010).

Figure 1: pH_{PZC} for adsorbents *T in natura*, CT ZnCl₂, CT NaOH.



By means of infrared spectra (Figure 2) for the *T in natura* and activated carbons CT ZnCl₂ and CT NaOH, it is possible to observe vibrational stretching in 3449 at 3382 nm⁻¹, 2361 to 2356 nm⁻¹, 1623 to 1400 nm⁻¹, 1057 to 1038 nm⁻¹ and 874 to 609 nm⁻¹.

Figure 2: Infrared spectrum analysis from 4000 at 400 nm⁻¹ for the adsorbents *T in natura*, CT ZnCl₂ e CT NaOH.



The bands found near 3400 nm⁻¹ suggest the presence of (OH) stretching vibrations due to the presence of hydroxyl groups. The bands with values between 2361 and 2356 found for adsorbents *T in natura* and CT ZnCl₂ indicate C-H vibrational stretching, suggesting the existence of alkyl groups. In materials *T in natura* and CT NaOH it is possible to observe vibrational stretch C=C and C=N with the presence of bands at 1623 nm⁻¹, which can be attributed to the presence of olefins and in aromatic groups. Differing from CT NaOH, the adsorbents *T in natura* and CT ZnCl₂ have bands between 1445 and 1400 nm⁻¹, suggesting the presence of vibrational C=C and CH stretches, suggesting the existence of aromatic structures and ester groups (Bouchelta et al. 2008).

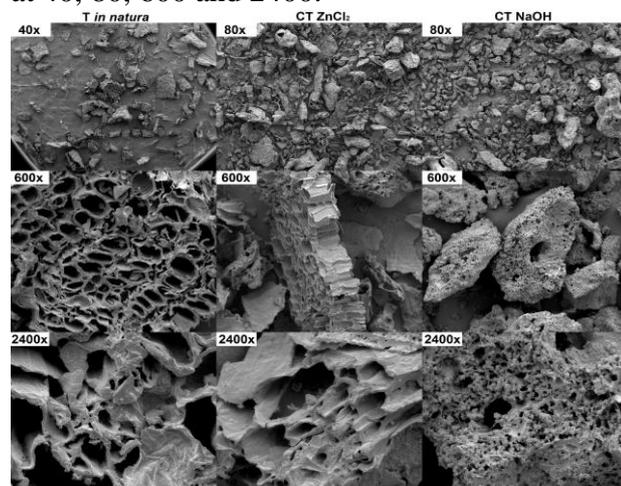
It is possible to observe in all adsorbents, bands between 1038 and 1057 nm⁻¹ referring to the vibrational stretches C-O-C and C=C, which can

be attributed to pyranose ring skeletal or aromatic ring. The degradation found at 874 nm^{-1} in the adsorbent CT ZnCl₂ and 722 nm^{-1} CT NaOH, may evidences C-H links, suggesting hydroxyl groups (Bouchelta et al. 2008; Smidt and Meissl 2007).

It was observed (Figure 2) the disappearance of bands when comparing the infrared spectra of the *in natura* material (T *in natura*) with activated carbons (CT ZnCl₂ and CT NaOH), and emergence of others smaller than 1057 nm^{-1} . This fact suggest that the aromaticity of the material increases during the activation (Bouchelta et al. 2008; Yang et al. 2007). Many of the clusters in the precursor material are also in the activated carbon, demonstrating that the modified material has many of the same functional groups of its precursor; except for the formation of carbonates exclusively in activated carbons (Bouchelta et al. 2008; Schulz and Baranska 2007). In this way, the obtained results corroborate with the hypothesis that the transformation of the tobacco *in natura* into activated carbon was effective in the modification of the material, suggesting the formation of new active sites (Shafeeyan and Daa 2010; Feng et al. 2011); Wan Ngah and Hanafiah 2008).

Figure 3 shows the scanning electron micrographs for the *in natura* adsorbents and activated carbons in different approaches.

Figure 3: SEM images for adsorbents T *in natura*, CT ZnCl₂ and CT NaOH at 40, 80, 600 and 2400.



The visualization of SEM exhibit great variations on the adsorbents surface morphology. The adsorbents T *in natura* and CT ZnCl₂ exhibit tubular structures with a certain regular aspect, with asymmetric cavities, similar to that observed by Ibrahim et al. (2016) in activated carbon modified originated from aquatic plants biomass (*Ulva lactuca*) modified with KOH.

In addition, the CT NaOH exhibited irregular and heterogenic structures, also presenting spongy appearance, being the same by Bouchelta et al. (2008) in date stones. According to Nacke et al. (2017) such a characteristic may indicate good adsorption capacity of the material.

The surface area found for T *in natura* ($0.27\text{ m}^2\text{ g}^{-1}$) exhibit similar value to other studied biosorbents, as found by Penha et al. (2016) ($1.13\text{ m}^2\text{ g}^{-1}$) in

rice hulls. Schwantes et al. (2018) in studies with chemically modified plant biomass, found values similar to T *in natura* in biosorbents of *Pinus* bark modified with H₂SO₄ (0.33 m² g⁻¹) and NaOH (0.48 m² g⁻¹), *cassava* barks modified with H₂SO₄ (0.4637 m² g⁻¹).

On the other hand, it is possible to observe the increase in the surface area in activated carbons (Table 2). Both materials, CT NaOH (76.61 m² g⁻¹) and CT ZnCl₂ (479.40 m² g⁻¹) had higher Specific Surface Area (SSA) than the T *in natura*, with CT NaOH and CT ZnCl₂ respectively 283 times and 1775 times higher SSA than the precursor material.

Table 2: Porosimetry of adsorbents by BET and BJH models

| Parameters | T <i>in natura</i> | CT NaOH | CT ZnCl ₂ |
|---|--------------------|---------|----------------------|
| Specific Surface Area (m ² g ⁻¹) | 0.27 | 76.61 | 479.40 |
| Pore volume (cm ³ g ⁻¹) | 0.0008 | 0.0525 | 0.06012 |
| Pore diameter (nm) | 2.18 | 1.90 | 1.67 |

Ibrahim et al. (2016) obtained values similar to those found for CT ZnCl₂ when producing activated carbon produced from the aquatic plant *Ulva lactuca* (345.40 m² g⁻¹). It is worth mentioning that these values are lower when compared to the obtained for commercial activated carbon (894.00 m² g⁻¹) (Merk®). However, Bohli et al. (2015) found the SSA for activated carbon developed from olive stone was even higher than commercial carbon (1194 m² g⁻¹).

With regard to pore volume, it is possible to observe a significant increase for activated carbons. The adsorbent T *in natura* (0.0008 cm³ g⁻¹) exhibited pore volume similar to Penha et al. (2016) in rice hulls (0.0019 cm³ g⁻¹) and Schwantes et al. (2018) in *cassava* bark modified with NaOH (0.00146 cm³ g⁻¹).

In contrast, the number of pore volumes of the NaOH (0.0525 cm³ g⁻¹) and CT ZnCl₂ (0.06012 cm³ g⁻¹) was lower than Ibrahim et al. (2016) (0.320 cm³ g⁻¹) for *Ulva lactuca* activated carbon and (0.108 cm³ g⁻¹) for *Ulva lactuca* as biosorbent.

As for the pore diameter, it is observed a reduction in the activated carbon. It is also important to note that the pore diameter of precursor material T *in natura* (2.18 nm) is higher than other biosorbents studied.

Schwantes et al. (2018) found pore diameter for *cassava* barks modified with H₂O₂ (1,732 nm) and NaOH (1,924 nm). However, Ibrahim et al. (2016) found pore diameter of (1.11 nm) and (1.85 nm) for *Ulva lactuca* as biosorbent and activated carbon, respectively. However, the values found for the activated carbons CT NaOH (1.90 nm) and CT ZnCl₂ (1.67 nm) have lower values than the tobacco *in natura* material.

Gao et al. (2015) when producing activated carbon from *Enteromorpha prolifera* using K₂CO₃ found pore diameter of 2,976 nm. Ramos et al. (2009) studied the activated carbon produced from the black, green, burned defect of the coffee, which is mainly composed of micropores with a diameter of (1,1 to 1,7 nm).

The obtained results indicate that the activation process caused a decrease in pore diameter and consequent increase in surface area, besides the increase of the pore volume, allowing the production of activated carbons

with texture predominantly microporous, since the pore diameter found is lower than 2.0 nm (El-Sadaawy and Abdelwahab 2014), characteristic that can significantly favor the adsorption process.

Considering the analysis of variance (Anova) for adsorbent doses and pH of the solution for Pb^{2+} removal, it was observed statistical difference at the 5% level of significance was found for adsorbent doses (mass factor), in both linear and quadratic models. It demonstrates that the adsorption process of Pb^{2+} by the materials: *T. in natura*, CT NaOH and CT $ZnCl_2$ depends intimately on the amount of adsorbent, however it does not depend on the pH of the solution in the studied range.

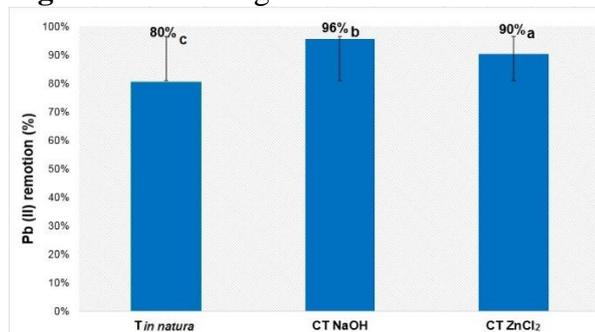
For all evaluated adsorbents, the pH studied range did not influence the adsorption process of Pb^{2+} . This is a very positive result, since it allows the use of modified adsorbents based on tobacco in the treatment of water contaminated with Pb^{2+} at different pH values, reducing limitations or loss of efficiency.

It is also observed that the adsorbents evaluated have a higher capacity of removal lead using small doses of adsorbent material, that is, four grams of the adsorbent were needed to decontaminate one liter of solution (4 g L^{-1}). Schwantes et al. (2018) also observed that *Pinus* biosorbents were more effective in the removal of Pb^{2+} when using 4.0 g L^{-1} .

It is found that in higher adsorbent amounts, particle aggregation occurs, resulting in a decrease in the total free surface area and in an increase in the length of the diffusion path (El-Sadaawy and Abdelwahab 2014; Rodriguez et al. 2018). This aggregation phenomenon is possibly influenced by the nature of the adsorbent (Rodriguez et al. 2018).

The percentage of Pb^{2+} removal is exhibited in Figure 4. It is noteworthy that, although in a preliminary study, it is observed that independently of the condition, the chemically activated materials CT NaOH and CT $ZnCl_2$ exhibit higher percentage of contaminant removal. The adsorbent CT NaOH, even in this preliminary study, exhibit superior values to the tobacco *in natura*, being the values of Q_{eq} (adsorbed amount of Pb^{2+}) for the CT NaOH 16 % points higher and 6 % points higher than CT $ZnCl_2$.

Figure 4: Percentage of Pb^{2+} removal for studied adsorbents.



**Averages followed by the same letter in the column do not differ from each other to a 5% probability by the Tukey test.

In Table 3 are exhibited the parameters for linear equilibrium models of Langmuir, Freundlich and Dubinin-Radushkevich (D-R) for the removal of Pb^{2+} by *T in natura*, CT NaOH and CT $ZnCl_2$.

The results obtained (Table 3), show that the Langmuir model presented satisfactory adjustments (R^2), with values close to 1, demonstrating that the results obtained for this model satisfactorily represent the experimentally obtained data, suggesting the occurrence of lead adsorption in monolayers.

In relation to the Langmuir parameters (Table 8), the maximum amount of adsorption (Q_m) exhibited high values for all studied adsorbents. However, CT adsorbent $ZnCl_2$ (84.74 mg g^{-1}) exhibited the higher values.

Table 3: Adsorption equilibrium linear parameters for Langmuir, Freundlich and D-R models for Pb^{2+} removal by T *in natura*, CT NaOH and CT $ZnCl_2$

| Parameters / Adsorbents | T <i>in natura</i> | CT NaOH | CT $ZnCl_2$ |
|-------------------------------------|--------------------|---------|-------------|
| Langmuir | | | |
| Q_m (mg g^{-1}) | 56.8182 | 34.3600 | 84.7458 |
| b ou K_L (L mg^{-1}) | 0.0183 | 0.0128 | 0.0181 |
| R_L | 0.1592 | 0.1028 | 0.2203 |
| R^2 | 0.9843 | 0.9300 | 0.9793 |
| Freundlich | | | |
| K_f (mg g^{-1}) | 1.4798 | 4.2700 | 7.1598 |
| n | 1.3029 | 1.7300 | 2.3063 |
| R^2 | 0.9913 | 0.9400 | 0.9908 |
| D-R | | | |
| Q_d (mol g^{-1}) | 0.0090 | 0.0004 | 0.0035 |
| E (KJ mol^{-1}) | 7.1796 | 10.0000 | 8.5749 |
| R^2 | 0.9902 | 0.9000 | 0.9941 |

Q_m (mg g^{-1}): maximum adsorption capacity; K_L ou b (L mg^{-1}): constant related to the adsorbent / adsorbate interaction forces; R_L : Langmuir constant; R^2 : determination coefficient; K_f (L mg g^{-1}): related to adsorption capacity; n : related to the heterogeneity of the solid; Q_d : maximum adsorption capacity; E : mean sorption energy.

The adsorbent CT $ZnCl_2$ exhibited 2.4 times better removal capacity of Pb^{2+} in relation to CT NaOH and 1.5 times in relation to T *in natura*.

In Table 4, it is possible to observe the great Pb^{2+} removal potential of T *in natura*, CT NaOH and CT $ZnCl_2$ when compared to other adsorbent materials.

Table 4: T *in natura*, CT NaOH and CT $ZnCl_2$ capacity to remove contaminants compared to other adsorbent materials.

| Adsorbent | Langmuir adsorption capacity (mg g^{-1}) | Contaminant | Reference |
|-------------------------------------|---|-------------|-----------------------|
| <i>Ulva lactuca</i> (Biosorbent) | 68.90 | Pb^{2+} | Ibrahim et al. [7] |
| <i>Ulva lactuca</i> (AC) | 83.30 | Pb^{2+} | Ibrahim et al. [7] |
| Bamboo (AC) | 0.67 | Pb^{2+} | Lo et al. [8] |
| Oak wood (Biosorbent) | 3.03 | Cr^{3+} | Mohan et al. [51] |
| Olive stone (AC) | 147.52 | Pb^{2+} | Bohli et al. [9] |
| <i>Jatropha curcas</i> (Biosorbent) | 22.90 | Pb^{2+} | Nacke et al. [26] |
| <i>Cassava</i> barks (Biosorbent) | 42.46 | Pb^{2+} | Schwantes et al. [40] |
| Cattle bone (AC) | 32.10 | Pb^{2+} | Lo et al. [8] |
| T <i>in natura</i> (Biosorbent) | 56.81 | Pb^{2+} | Present study |
| CT NaOH (AC) | 34.36 | Pb^{2+} | Present study |
| CT $ZnCl_2$ (AC) | 84.74 | Pb^{2+} | Present study |

*Note: Activated Carbon (AC).

It is observed that even the biosorbent T *in natura* exhibit a great capacity of removal of Pb²⁺ 56.81 mg g⁻¹, being superior to other biosorbents as obtained by Schwantes et al. (2018) from *cassava* peel 42.46 mg g⁻¹ and Nacke et al. (2017) using *jatropha* 22.90 mg g⁻¹.

It is important to emphasize that the material *in natura* is compound for many toxic compounds. According to Goulart et al. (2010) *in natura* cigarettes have in their composition toxic and carcinogenic compounds, such as arsenic, nickel, cadmium. In addition, it is possible to observe in the chromatograms shown in Figure 6 the presence of various possibly toxic organic compounds in the T *in natura*. Compounds such as hydrocarbons, aromatic hydrocarbons (Eldridge et al. 2015; Novotny and Slaughter 2014) besides pesticides may be present in this material.

However, when the material is submitted into thermal activation (high temperature) these compounds are lost in the process, evidence in this way the benefits of the thermal activation, what can be seen in the Figure 6.

The adsorbent CT ZnCl₂ exhibited the highest capacity of Pb²⁺ removal. By contrasting the result obtained with others from literature (Table 9), it was observed that CT ZnCl₂ was superior in the removal of Pb²⁺ in relation to all the other, only lower than the activated carbon produced from olive seed 147.526 mg g⁻¹ studied by Bohli et al. (2015).

On the other hand, CT NaOH 34.36 mg g⁻¹, despite the reduced Pb²⁺ removal capacity in relation to CT ZnCl₂ and T *in natura*, still has a superior ability to remove contaminants when compared to other activated carbons produced from alternative materials as studied by Lo et al. (2012) using bovine bones 32.10 mg g⁻¹ and bamboo 0.67 mg g⁻¹.

It is also possible to observe that, when evaluating the R_L values (Table 8), the process was favorable for all the adsorbents, since the values found are between 0 and 1 (Lin and Juang 2002). The K_L values observed in Table 8 are low, indicating that the interaction forces between adsorbent/adsorbate are not strong.

The values obtained for the Freundlich models also showed good adjustments (R²), suggesting the occurrence of adsorption of Pb²⁺ also in multilayers. However, reduced adsorption values (K_f) of the adsorbents were observed, and the adsorbent CT ZnCl₂ 7.15 mg g⁻¹ exhibited the highest Pb²⁺ removal capacity.

The values of "n" observed in Table 8 are higher than "1" and this is a strong indicative of good reactivity of the active sites of the adsorbents with the Pb²⁺ present in the solution (Gao et al. 2015).

The D-R model also showed good adjustments for the adsorption of Pb²⁺ to adsorbents T *in natura*, CT NaOH and CT ZnCl₂. The parameter "E" refers to the adsorbate-adsorbate binding energy, and when E assumes values lower than 8 KJ mol⁻¹, the DR model suggests the occurrence of low-energy binding bonds. In this sense, suggesting occurrence of physical and reversible forces in the sorption process (Ramos et al 1985).

As observed in Table 8, for the adsorption of Pb²⁺ by the adsorbents CT NaOH and CT ZnCl₂, the values of E > 8 KJ mol⁻¹ suggesting the occurrence of chemisorption, whereas for T *in natura* physical sorption of lead appears

to predominate (Gao et al.2015; Ramos et al. 1985). Therefore, the adsorption of Pb^{2+} can be better explained by the Langmuir and Freundlich models, since both exhibited satisfactory R^2 .

According to Gonçalves Jr. et al. (2012), usually there is more than one type of adsorption site interacting with the contaminant, and in this way, adsorption can occur in both mono and multilayer. This may be related to the morphological variation of the materials and the different characteristics of specific surface area pore volume and pore diameter.

CONCLUSION

The use of chemical activation with NaOH and $ZnCl_2$ caused significant changes in the tobacco *in natura*, producing transformations on the surface of the adsorbents (SEM), suggesting the formation of new groups in the activated carbon (FT-IR). Also, changing the zero charge point (pH_{PZC}) and the chemical composition. In addition, it causes a potential increase in the surface area of the activated carbons, increasing by 283 times for CT NaOH and 1775 times for CT $ZnCl_2$ in comparison to the precursor material.

All the adsorbents produced have applicability over a wide range of pH (3.00 to 7.00), because according to the obtained results, in this range there is no significant influence of the pH of the medium, which gives to the adsorbents a important advantage. However, the doses used influenced the removal process of Pb^{2+} , requiring four grams of the adsorbent to decontaminate one liter of solution (4 g L^{-1}).

The adsorption process is deeply influenced by the modifications applied to biomass: chemical activation using $ZnCl_2$ is superior to T *in natura*, being 1.5 X higher with occurrence of mono and multilayer adsorption.

The activated carbon of tobacco from smuggled cigarettes can be a useful adsorbent to lead removal from water.

REFERENCES

- Aoac (Association of Official Analytical Chemist). Official methods of analysis. Maryland (2005)
- Barrett, E.P., Joyner, L.G., Halenda, P.P.: The determination of pore volume and area distributions in porous substances. I. Computation from nitrogen isotherms, J. Am. Chem. Soc. (1951) <http://dx.doi.org/10.1021/ja01145a126>.
- Barros, N.B., Bruns, R.E., Scarminio, I.S.: How do experiments— applications in science and industry (2010)
- Bhatnagar, A., Hogland, W., Marques, M., Sillanpää, M.: An overview of the modification methods of activated carbon for its water treatment applications. Chemical Engineering Journal (2013) <https://doi.org/10.1016/j.cej.2012.12.038>
- Bohli, T., Ouederni, A., Fiol, N., Villaescusa, I.: Evaluation of an activated carbon from olive stones used as an adsorbent for heavy metal removal from aqueous phases. Comptes Rendus Chimie (2015) <https://doi.org/10.1016/j.crci.2014.05.009>

- Bouchelta, C., Medjram, M. S., Bertrand, O., Bellat, J. P. Preparation and characterization of activated carbon from date stones by physical activation with steam (2008) doi:10.1016/j.jaap.2007.12.009
- Brunauer, S., Emmett, P.H., Teller, E.: Adsorption of gases in multimolecular layers, J. Am. Chem. Soc. 60, 309–319 (1938)
- Dovbeshko, G. I., Chegel, V. I., Gridina, N. Y., Repnytska, O. P., Shirshov, Y. M., Tryndiak, V., Solyanik, G. I.: Surface enhanced IR absorption of nucleic acids from tumor cells: FTIR reflectance study. Biopolymers: Original Research on Biomolecules (2002) <https://doi.org/10.1002/bip.10165>
- Dubinin, M.M., Radushkevich, L.V.: The equation of the characteristic curve of the activated charcoal. Proc Natl Acad Sci USSR Phys Chem Sect. 55, 327-329 (1947)
- Eldridge A., Betson, T. R., Gama, M. V., McAdam, K.: Variation in tobacco and mainstream smoke toxicant yields from selected commercial cigarette products. Regul. Toxicol. Pharmacol. (2015) [10.1016/j.yrtph.2015.01.006](https://doi.org/10.1016/j.yrtph.2015.01.006)
- El-sadaawy, M., Abdelwahab, O.: Adsorptive removal of nickel from aqueous solutions by activated carbons from doum seed (*Hyphaenethebaica*) coat. Alexandria Engineering Journal (2014) <http://dx.doi.org/10.1016/j.aej.2014.03.014>
- Feng, N., Guo, X., Liang, S., Zhu, Y., Liu, J.: Biosorption of heavy metals from aqueous solutions by chemically modified orange peel. Journal of hazardous materials (2011) <https://doi.org/10.1016/j.jhazmat.2010.08.114>
- Feng, N., Guo, X., Liang, S., Zhu, Y., Liu, J.: Biosorption of heavy metals from aqueous solutions by chemically modified orange peel. Journal of hazardous materials (2011) <https://doi.org/10.1016/j.jhazmat.2010.08.114>
- Foo, K. Y., Hameed, B. H.: Preparation, characterization and evaluation of adsorptive properties of orange peel based activated carbon via microwave induced K₂CO₃ activation. Bioresource technology (2012) <https://doi.org/10.1016/j.biortech.2011.10.005>
- Freundlich, H.M.F.: Over the adsorption in solution. J Phys Chem. 57 (1906)
- Gao, Y.; Yuen, Q.; Xu, S.; Gao, B.: Activated carbons with well-developed mesoporosity prepared by activation with different alkali salts. Materials Letters (2015) <https://doi.org/10.1016/j.matlet.2015.01.161>
- Gonçalves Jr., A. C., Coelho, G. F., Schwantes, D., Rech, A. L., Campagnolo, M. A., Miola JR. A.: Biosorption of Cu (II) and Zn (II) with acai endocarp *Euterpe oleracea* M. in contaminated aqueous solution. Acta Scientiarum Technology (2016) <https://doi.org/10.4025/actascitechnol.v38i3.28294>
- Gonçalves Junior, A. C., Strey, L., Lindino, C. A., Nacke, H., Schwantes, D., Pereira Seidel, E.: Applicability of the Pinus bark (*Pinus elliottii*) for the adsorption of toxic heavy metals from aqueous solutions. Acta Scientiarum Technology (2012) <https://doi.org/10.4025/actascitechnol.v34i1.9585>
- Goulart, D., ENGROFF, P., ELY, L. S., SGNAOLIN, V., SANTOS, E. F., TERRA, N. L., DE CARLI, G. A.: Smoking in the elderly. Revista Brasileira de Geriatria e Gerontologia (2010) <http://www.scielo.br/pdf/rbgg/v13n2/a15v13n2.pdf>
- Ibrahim, W. M., Hassan, A. F., Azab, Y. A.: Biosorption of toxic heavy metals from aqueous solution by *Ulva lactuca* activated carbon. Egyptian Journal Of Basic And Applied Sciences (2016) <https://doi.org/10.1016/j.ejbas.2016.07.005>
- Iupac.: Pure Appl. Chem (1985) <http://dx.doi.org/10.1351/pac198557040603>

- JOOSEENS, L., MERRIMAN, D., ROSS, H., RAW, M.: The impact of eliminating the global illicit cigarette trade on health and revenue. *Addiction* (2010) doi:10.1111/j.1360-0443.2010.03018.x
- Langmuir, I.: The constitution and fundamental properties of solids and liquids. *JACS* (1916) <https://doi.org/10.1021/ja02268a002>
- Libânio, M.: Fundamentos de qualidade e tratamento de água. Campinas, São Paulo (2010).
- Lin, S. H.; Juang R. S.: Heavy metal removal from water by sorption using surfactant-modified montmorillonite. *Journal of Hazardous Materials* (2002). [https://doi.org/10.1016/S0304-3894\(02\)00026-2](https://doi.org/10.1016/S0304-3894(02)00026-2)
- Lo, S. F., Wang, S. Y., Tsai, M. J., Lin, L. D.: Adsorption capacity and removal efficiency of heavy metal ions by Moso and Ma bamboo activated carbons. *Chemical Engineering Research and Design* (2012) <https://doi.org/10.1016/j.cherd.2011.11.020>
- Mimura, A. M. S., Vieira, T. V. A., Martelli, P. B., Gorgulho, H. F.: Utilization of rice husk to remove Cu²⁺, Al³⁺, Ni²⁺ and Zn²⁺ from wastewater. *Química Nova* (2010) <http://dx.doi.org/10.1590/S0100-40422010000600012>
- Nacke, H.; Gonçalves, A. C.; Coelho, G. F.; Schwantes, D.; Campagnolo, M. A.; Leismann, E. A. V.; Conradi, E. J.; Miola, A. J.: Removal of Cd (II) from water using the waste of jatropha fruit (*Jatropha curcas* L.). *App. Wat. Sci.*(2017) <https://doi.org/10.1007/s13201-016-0468-2>
- Novotny, T.E., Slaughter, E.: Tobacco product waste: an environmental approach to reduce tobacco consumption. *Environ. Heal. Reports Curr.* (2014) [10.1007/s40572-014-0016-x](https://doi.org/10.1007/s40572-014-0016-x)
- Penha, R. S., Santos, C. C., Cardoso, J. J., Silva, H. A., Santana, S. A., Bezerra, C. W. B.: Chemically Treated Rice Husk as Low-Cost Adsorbent for Metal Ions Uptake (Co²⁺ and Ni²⁺). *Revista Virtual de Química* (2016) <http://dx.doi.org/10.5935/1984-6835.20160045>
- Pintor, A. M., Silvestre-albero, A. M., Ferreira, C. I., Pereira, J. P., Vilar, V. J., Botelho, C. M., Reinoso, F. R., Boaventura, R. A.: Textural and surface characterization of corkbased sorbents for the removal of oil from water. *Indu. & Engi. Chem. Res.* (2013) <https://doi.org/10.1021/ie402038n>
- Ramos, P. H., Guerreiro, M. C., Resende, E. D., Gonçalves, M.: Produção e caracterização de carvão ativado produzido a partir do defeito preto, verde, ardido (PVA) do café. *Quim. Nova.* 32, 1139-1143 (2009)
- Rocha, W. D. D.; Luz, J. A. M. D.; Lena, J. C. D.; Bruña-romero, O.: Adsorção de cobre por carvões ativados de endocarpo de noz macadâmia e de semente de goiaba. *Rem: Revista Escola de Minas* (2006) <http://dx.doi.org/10.1590/S0370-44672006000400010>
- Rodriguez, M. H., Yperman, J., Carleer, R., Maggen, J., Dadi, D., Gryglewicz, G., Calvis, A. O.: Adsorption of Ni (II) on spent coffee and coffee husk based activated carbon. *Journal of environmental chemical engineering* (2018) <https://doi.org/10.1016/j.jece.2017.12.045>
- Schewe, J., Heinke, J., Gerten, D., Haddeland, I., Arnell, N. W., Clark, D. B., ...& Gosling, S. N.: Multimodel assessment of water scarcity under climate change. *Proceeding of the National Academy of Sciences* (2014) <https://doi.org/10.1073/pnas.1222460110>
- Schulz, H., Baranska, M.: Identification and quantification of valuable plant substances by IR and Raman spectroscopy. *Vibrational Spectroscopy* (2007) <https://doi.org/10.1016/j.vibspec.2006.06.001>

- Schwantes, D., Gonçalves JR, A. C., Campagnolo, M. A., Tarley, C. R. T., Dragunski, D. C., De Varennes, A., Silva, A. K. D. S., Junior, E. C.: Chemical modifications on pinus bark for adsorption of toxic metals. *Journal of Environmental Chemical Engineering* (2018)
<https://doi.org/10.1016/j.jece.2018.01.044>
- Schwantes, D., Gonçalves, A. C., Campagnolo, M. A., Tarley, C. R. T., Dragunski, D. C., Manfrin, J., Schiller, A. D. P.: Use of Co-Products from the Processing of Cassava for the Development of Adsorbent Materials Aiming Metal Removal. In: *Cassava. InTech* (2018)
<http://dx.doi.org/10.5772/intechopen.71048>
- Shafeeyan, M. S., Daua, W. M. A. W.: A review on surface modification of activated carbon dioxide adsorption (2010)
<https://doi.org/10.1016/j.jaap.2010.07.006>
- Silva, C. P., Almeida, T. E., Zittel, R., Domingues, C. E., Stremel, T. R. O., Barbola, I. F., Campos, S. X. Determination of smuggled cigarette characteristics in Brazil and their potential risk to the human health. *Orbital* (2016)
<http://dx.doi.org/10.17807/orbital.v8i3.832>
- Smidt, E., Meissl, K.: The applicability of Fourier transform infrared (FT-IR) spectroscopy in waste management. *Waste management* (2007)
<https://doi.org/10.1016/j.wasman.2006.01.016>
- Souza, C. F., Bacicurinski, I., De França, Ê. F.: Water quality assessment of Paraíba do Sul River in Taubaté-SP. *Revista Biociências*. 16, 1-8 (2010)
- Tagliaferro, G. V., Pereira, P. H. F., Rodrigues, L. Á., Silva, M. L. C. P. D. Cadmium, lead and silver adsorption in hydrous niobium oxide prepared by homogeneous solution method. *Química Nova* (2011)
<http://dx.doi.org/10.1590/S0100-40422011000100020>
- Tural, B., Ertaş, E., Tural, S.: Removal of phenolic pollutants from aqueous solutions by a simple magnetic separation. *Desalination and Water Treatment* (2016) <https://doi.org/10.1080/19443994.2016.1162202>
- Wan ngah, W. S., Hanafiah, M. A. K. M. Biosorption of copper ions from dilute aqueous on base treated rubber (*Hevea brasiliensis*) leaves powder: Kinetics, isotherm, and biosorption mechanism. *Journal of Environmental Science*. 20, 1168-1176 (2008)
- Welz, B., Sperling, M.: Atomic absorption spectrometry. (2008).
- Yang, H., Rong, Y., Hanping, C., Lee, D. H., Zheng, C.: Characteristics of hemicellulose, cellulose and lignin pyrolysis. *Fuel* (2007)
<https://doi.org/10.1016/j.fuel.2006.12.013>