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Efficient removal of lipophilic compounds from eucalyptus wood by sewage sludge-based adsorbents

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ABSTRACT: Sewage sludge is a byproduct of wastewater treatment. When processed, this residue can also be used as adsorbent. The aim of this study was to produce adsorbents from the sewage sludge, characterize its structure and evaluate the efficiency in adsorption of lipophilic wood compounds. The sewage sludge was calcinated at seven temperatures (400-1000°C) for five hours. The morphology and texture properties of the materials were evaluated by scanning electron microscopy and nitrogen isotherms. The presence of chemical functional groups at their surface was analyzed by Fourier transformed infrared spectroscopy. Lipophilic compound adsorption rate was evaluated by gas chromatography-mass spectrometry. The results were compared with talc, an adsorbent traditionally used by the industry. The increase in temperature directly contributed to a decrease in the specific surface area. The adsorbents obtained between 600 and 700°C removed more than 60% of the lipophilic wood compounds, corresponding to 94.1% of the total amount of lipophilic compounds. These values are much higher than those presented by talc, being 2 and 11.8%, respectively. Therefore, the produced adsorbents can be studied as a new material in the removal of lipophilic wood compounds.

Key words: adsorption; deposit; extractives; pitch; pulp and paper

Remoção eficiente de compostos lipofílicos da madeira de eucalipto por adsorventes à base de lodo de esgoto

RESUMO: O lodo de esgoto é um subproduto do tratamento de efluentes. Quando processado, este resíduo também pode ser usado como adsorvente. O objetivo deste trabalho foi produzir adsorventes a partir do lodo de esgoto, caracterizar sua estrutura e avaliar a eficiência na adsorção de compostos lipofílicos de madeira. O lodo de esgoto foi calcinado a sete temperaturas (400-1000°C) por cinco horas. As propriedades de morfologia e textura dos materiais foram avaliadas por microscopia eletrônica de varredura e isotermas de nitrogênio. A presença de grupos funcionais químicos em sua superfície foi analisada por espectroscopia de infravermelho por transformada de Fourier. A taxa de adsorção do composto lipofílico foi avaliada por cromatografia gasosa -espectrometria de massa. Os resultados foram comparados com o talco, adsorvente tradicionalmente utilizado pela indústria. O aumento da temperatura contribuiu diretamente para a diminuição da área superficial específica. Os adsorventes obtidos entre 600 e 700°C removeram mais de 60% dos compostos lipofílicos da madeira, correspondendo a 94,1% da quantidade total de compostos. Esses valores são muito superiores aos apresentados pelo talco, sendo 2 e 11,8%, respectivamente. Portanto, os adsorventes produzidos podem ser estudados como um novo material na remoção de compostos de madeira lipofílicos.

Palavras-chave: adsorção; depósito; extrativos; pitch; papel e celulose

Introduction

One of the current problems with pollution in urban areas is sewage disposal, which is mostly dumped directly into rivers and streams. In an attempt to minimize the contamination of water resources, sewage from several Brazilian cities has been treated in sewage treatment plants. The by-product of these stations is sewage sludge and the nature of this residue is complex and depends on the type of treatment applied and the original source (Andreoli, 2001; Smith et al., 2009; Fonts et al., 2012).

Due to strict legislation regarding the disposal and use of sewage sludge, it would be beneficial to find alternative applications for managing this industrial residue. One option is to convert the sludge into adsorbents (Singh & Agrawal, 2008; Velghe et al., 2012).

Sewage sludge has been used to produce adsorbents utilizing chemical activation followed by pyrolysis (Rozada et al., 2005; Smith et al., 2009; Zaini et al., 2013). The results have shown that these adsorbents can be used in different applications with high efficiency, such as in metal adsorption (Kurniawan et al., 2006; Fang et al., 2010; Abdel-Aziz et al., 2017; Aliakbari et al., 2018; Li et al., 2018; Nguyen et al., 2018), textile dyes (Rafatullah et al., 2010; Zaini et al., 2013; Fan et al., 2017; Xiao et al., 2018;), pharmaceuticals (Rivera-Utrilla et al., 2013; Ocampo-Pérez et al., 2012; He et al., 2017; Tang et al., 2018) and as water treatment material (Rozada et al., 2005; Yu & Zhong, 2006; Khandaker et al., 2018; Zhang et al., 2018).

However, none of these adsorbents have been used in removing lipophilic compounds present during the treatment of eucalyptus wood for paper manufacturing. The accumulation of these extracts produced during paper pulping can generate a sticky deposit called pitch. This deposit sticks on paper, generating spots which reduce the paper quality and consequently its commercial value. Furthermore, pitch can also deposit on machinery and equipment, thereby demanding more maintenance and resulting in production losses. The main method for mitigating pitch formation consists in using talc (magnesium silicate) as an adsorbent (Hubbe et al., 2006; Stack et al., 2014).

In this context, finding a new material obtained from industrial waste can offer a sustainable alternative for the wood industry. Thus, the aims of this study were to produce adsorbents from sewage sludge, characterize their structure (specific surface area and porosity), and evaluate their efficiency in the adsorption of lipophilic compounds contained in eucalyptus wood and to compare their performance with talc.

Material and Methods

Materials

The standards (tetracosane and hexanedioic acid) were obtained from Sigma-Aldrich (St. Louis, USA). Chloroform, dichloromethane, HPLC-UV grade hydrochloric acid, anhydrous sodium sulfate (≥ 99%) and sodium hydroxide were obtained from Vetec (Rio de Janeiro, Brazil). Industrial talc was obtained from Xilosorb (Sao Paulo, Brazil). The wood shavings were obtained from *Eucalyptus grandis* x *E. urophylla* plantations in Guanhães (MG), and harvested at six years of age. The adsorbents were synthesized using sewage sludge samples from the sewage treatment plant (STP) in Montes Claros (Minas Gerais, Brazil).

Adsorbents from sewage sludge

Seven samples of 10 g of sewage sludge were calcinated in a muffle furnace. After reaching the final temperature, the sample remained in the furnace for five hours. Adsorbents were treated at the following temperatures: 400, 500, 600, 700, 800, 900 and 1000°C. Each calcination residue was washed with a NaOH solution 0.4% (25 mL per gram of adsorbent), and dried in an oven for 20 h at 60°C. Post-treatment with alkaline washings was used to reduce the ash content and to improve the surface area and porosity of the adsorbents (Xu et al., 2015). Thereafter, the adsorbents were crushed and sieved with a 32 mesh sieve to obtain particles smaller than 0.500 mm. The prepared adsorbents were identified as Ad400, Ad500, Ad600, Ad700, Ad800, Ad900 and Ad1000; indicating the temperatures at which they were produced.

Characterization of the Adsorbents

The samples were sputter-coated with gold and observed under a scanning electron microscope to investigate the surface morphology of the adsorbents prepared from sewage sludge (SEM, HITACHI TM 3000).

Nitrogen adsorption/desorption isotherms were measured at 77 K by using a Micrometrics TriStar® II 3020 analyzer. Samples were outgassed for 16 h at 573 K before the measurements. The Brunauer Emmett Teller (BET) equation was used to calculate the specific surface area (SSA) from the adsorption data obtained at p/p_o between 0.05 and 0.3. The average pore diameter (Dp) was calculated by the Barrett Joyner Halenda (BJH) method using the adsorption branch. The t-plot method was applied to characterize the microporosity of the samples.

The functional surface groups of the adsorbents were studied by Fourier transformed infrared spectroscopy (FTIR) with a spectroscope (Varian 640) at the range of 400-4000 cm^{-1}, using attenuated total reflectance (Gladi ATR, Pike technologies).

Adsorption experiment of lipophilic compounds

The manufacturing conditions of the pulp and paper industries were simulated in the laboratory. The lipophilic extractives of wood were extracted using chloroform in a Soxtec device. The extractives were then mixed in a 0.4% NaOH solution in order to obtain an extractive concentration of 2 g L^{-1}. This colloidal system (adsorbate) was homogenized using a magnetic stirring plate for one hour at 40°C.

Twenty milliliters of the adsorbate were added to 400 mg of the adsorbent obtained from the sludge under constant

agitation (100 RPM) at 25°C for two hours. The procedure was performed in triplicate in a water bath with stirring (Dubnoff New Ethics - Marcon). Then, the system was centrifuged at 3000 RPM for ten minutes. The liquid phase was collected and acidified with an HCl solution of 2 mol L^{-1} until reaching pH~1 and then subjected to a liquid-liquid extraction with chloroform (3 x 10 mL). The combined organic layer was dried with anhydrous sodium sulfate, filtered, and recovered on a rotary evaporator under reduced pressure. The mass of the obtained residue was measured. The same procedure was replicated with the adsorbate using talc as adsorbent for comparison.

Qualitative and quantitative analyses of the lipophilic compounds before and after adsorption was performed by gas chromatography coupled with mass spectrometry (GC-MS). The residue obtained after adsorption was derivatized with 100 μL of BSTFA (N,O-bis (trimethylsilyl) trifluroacetamide) in 60 μL of pyridine. The system was heated to 70°C for 30 minutes. 1 μL of the obtained solution was injected. Hexanedioic acid and tetracosane were used as internal standards.

The analysis of the solutions was performed on a gas chromatograph from Agilent Technologies (7890A GC) coupled with mass spectrometry (MS5975C) using a capillary column DB-5MS (Agilent Technologies), stationary phase of fused silica composed of 5% phenyl and 95% dimethylsiloxane with a length of 30 m, 0.25 mm internal diameter, and a 0.25 μm film. Helium (99.9999% purity) was used as carrier gas at a flow rate of 1 mL min^{-1}, the injector division rate (*split*) 1:10, injected volume was 1 μL. The chromatographic conditions used were: injector temperature 290ºC, oven temperature starting at 80ºC for 5 minutes, increasing from 80 to 285ºC at a rate of 4ºC min^{-1}, and the final temperature remained at 285ºC for 40 minutes. The temperature of the detector and the GC/MS system was 290°C. The mass detector was operated in the electron impact mode (70 eV) and the quadrupole mass analyzer operated at a scanning range from 65 to 650 Da. Identification of the extract components was performed by comparison with the mass spectra database (NIST 2.0), as well as by injecting samples of standard substances.

The percentage of extractives adsorbed was calculated according to the Eq. 1, and the adsorption capacity (q_e) were measured using Eq 2., where C_i and C_e represent the initial and equilibrium concentration (mg L^{-1}) of extractives solution, respectively, M is the sludge adsorbent mass (g) and Vt is the extractives solution volume (L). The variables were tested by univariate analysis of variance (ANOVA) with a completely randomized design (CRD), and the Tukey test at 5% significance level was applied when significant differences were found.

$$\%Ads = \frac{(C_i - C_e)\times 100}{C_i} \quad (1)$$

$$q_e = \frac{(C_i - C_e)\times V_t}{M} \quad (2)$$

Results and Discussion

Characterization of the adsorbents

Scanning electron microscopy (SEM) showed the surface morphology of the adsorbents prepared from sewage sludge. All the synthesized adsorbents have similar surface structure corresponding to irregularly-shaped solids presenting cracks and crevices distributed in a heterogeneous pattern. In contrast, the talc has a homogeneous surface, with a standard laminate distribution (Figure 1).

Adsorbents obtained from the sewage sludge have irregular surface, with large pore diameter and inorganic matter (Velghe et al., 2012). The pyrolysis has a catalytic effect on forming porous structures in these adsorbents (Xie et al., 2013), because it modifies the surface morphology going from dense, relatively smooth and without perceptible pores, to becoming a porous surface (Pan et al., 2011; Zaini et al., 2013). Washes with hydrochloric acid and distilled water also modify the surface of adsorbents from a structure in

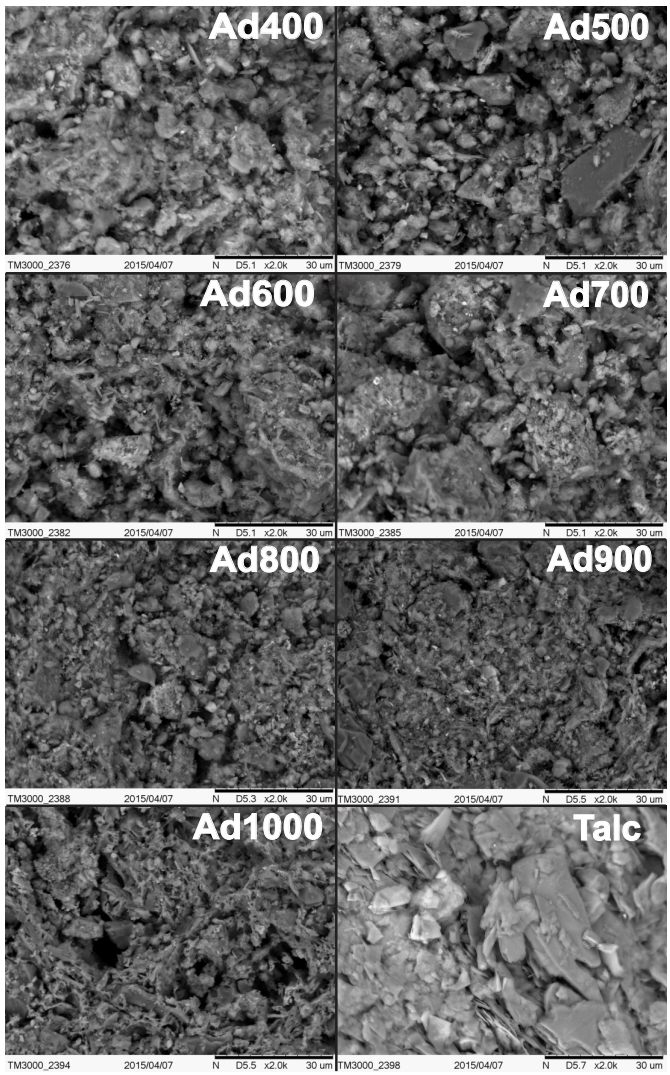


Figure 1. Electron micrographs obtained by scanning electron microscopy of the adsorbents prepared from the sewage sludge (Ad400 to Ad1000) and talc.

which it is difficult to identify pores into a porous and rough structure (Fang et al., 2010).

On the other hand, a uniform surface was observed for the talc, with standard distribution in laminate, being common due to the homogeneous composition of the mineral (Gao et al., 2011).

All adsorbents, including talc, presented type II Isotherms and type H3 hysteresis (Figure 2) according to the IUPAC classification (Sing, 1985), indicating that the adsorbents' surface is mainly composed of mesopores and exhibits adsorption characteristics in multilayers. The average pore diameter of the adsorbents varied between 15-24 nm (Table 1), remaining within the range established by the IUPAC for mesopores (2-50 nm).

Researchers have obtained isotherms with the same profile and classification for the adsorption of cadmium ions by chitin magnetic granules (Tang et al., 2014) and for adsorption studies with chemical oxygen demand by sludge adsorbents (He et al., 2014).

The pyrolysis temperature influenced the morphology and surface structure. The increase of the thermal treatment temperature directly contributed to the SSA decrease of the solids (Figure 3). The specific surface area and pore volume values generally increase with temperature increase,

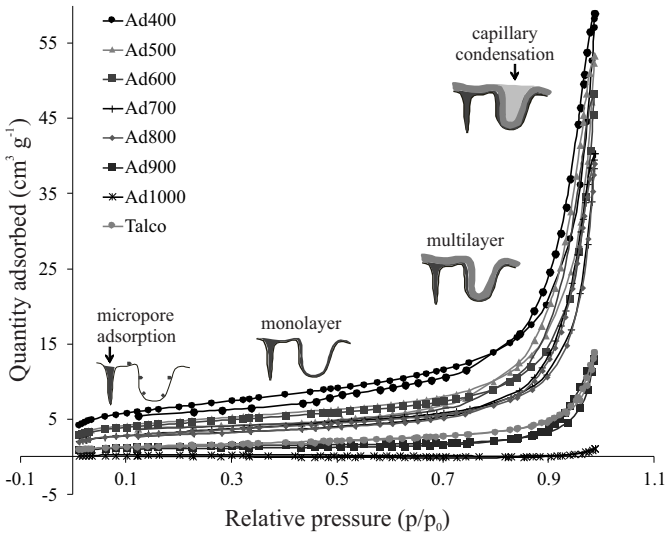


Figure 2. Nitrogen adsorption and desorption isotherms of adsorbents Ad400 toAd100 and talc.

Table 1. Specific Surface Area (SSA) and average Pore Diameter (D_p) of the adsorbents produced from sewage sludge and talc.

Adsorbent	SSA ($m^2 g^{-1}$)	Diameter Pore D_p (nm)
Ad400	23.4	16.7
Ad500	16.7	22.1
Ad600	15.6	21.0
Ad700	11.8	20.6
Ad800	11.5	21.3
Ad900	4.7	24.1
Ad1000	0.7	23.0
Talc	5.3	15.7

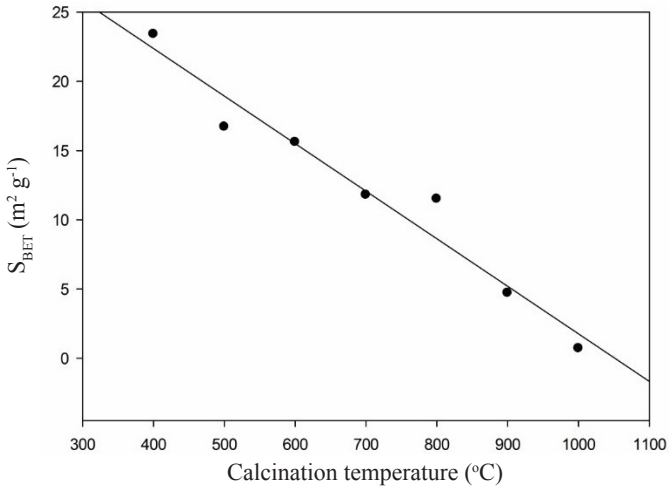


Figure 3. Influence of the calcination temperature on the S_{BET} values (specific surface area).

however when the temperature is too high, there is a decrease in surface area, probably due to the destruction of porous structure (Mahapatra et al., 2012; Xu et al., 2015).

The Ad400 presented the greatest SSA value, 23.4 $m^2 g^{-1}$, and talc adsorbent used by the companies showed an SSA value of 5.25 $m^2 g^{-1}$, corresponding to an SSA value only greater than that of Ad1000 (0.7 $m^2 g^{-1}$) and Ad900 (4.7 $m^2 g^{-1}$). The SSA values obtained for sewage sludge-based adsorbents in this study was less than some literature works (Yu & Zhong, 2006; He et al., 2014). However, in these cases chemical reagents were used to activate the adsorbents, which resulted in higher SSA values (Rozada et al., 2005; Velghe et al., 2012; Kong et al., 2013).

The FTIR spectra of the talc and the seven sludge-based adsorbents are presented in Figure 4. The adsorption band and peaks revealed the existence of surface functional groups on the produced adsorbents and talc. Similar adsorption

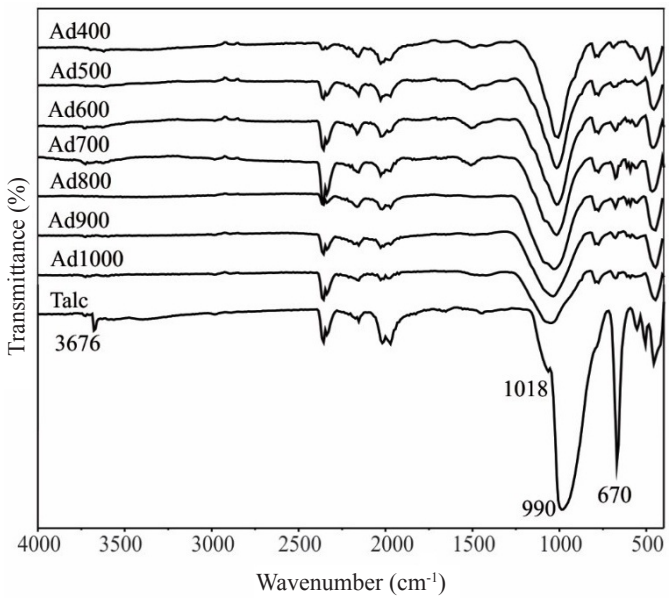


Figure 4. Fourier transformed infrared spectroscopy (FTIR) spectra of the adsorbents and talc.

bands were found for the seven adsorbents, evidencing the same functional groups on the surfaces of both types of adsorbents. The strong bands observed in 1100-900 cm^{-1} are assigned to groups containing Si-O-X (considering X=Al, Fe, Ca and Zn) (Fan et al., 2017). The infrared spectrum of the talc has an absorption band at 3676 cm^{-1} corresponding to the stretching of free OH bond, which is not involved in hydrogen bonding. The band in 670 cm^{-1} is related to the stretching of the Si-O-Si bond.

The presence of silicon-containing functional groups indicates adsorbents with less polar characteristics and thus higher affinity for non-polar organic matter (Chen et al., 2002). The main functional groups on the sludge-based adsorbents such as -OH, -C=C- and Si-O-C or Si-O-Si indicated that the adsorbents could uptake organic matter through surface complexation mechanisms (Pan et al., 2011).

Adsorption experiments of lipophilic compounds

The wood extractives containing lipophilic compounds have been analyzed by gas chromatography before and after the adsorption process. Table 2 presents the percent of the chromatographic area corresponding to the analysis of the starting extractive and of the extractive after the adsorption process. Among these compounds, *β*-sitosterol (59) represented 41% of the total chromatographic area, while hexadecanoic acid (32) had 7.6% and (*Z*)-octadec-9-enoic acid (39) 5.2%.

The compound classes predominant in the analyzed extractives were steroids and fatty acids, representing 46% and 31.9% of the total chromatographic area, respectively. Fatty alcohols and aromatic compounds were also found.

Other fatty acids detected were (9Z,12Z)-octadeca-9,12-dienoic (38), (Z)-octadec-9-enoic (39), docosanoic (50), tetracosanoic (53) and hexacosanoic (55). These compounds have been previously identified in the extractives of eucalyptus wood by Brazilian researchers (Barbosa et al., 2005; Silvério et al., 2007) and Spanish (Rio et al., 2000; Fernandez et al., 2001; Rencoret et al., 2007).

The chromatogram of the lipophilic wood extractives revealed the presence of 64 compounds (Figure 5a). The analysis of the chromatograms obtained from the extractives after adsorption enabled monitoring which compounds were removed, *i.e.* signal disappearance, and enabled determining the total amount of removed compounds, *i.e.* measuring the areas of the signals (Figure 5 b-h).

Talc removed 2.0% of the compounds, while Ad700 removed 67% when it was used, followed by Ad600 (61%), Ad900 and Ad800 (50%). Among the sewage sludge-based adsorbents, those obtained at 400 and 500°C showed the lowest removal rates of 25% and 33%, respectively, despite these samples having a higher value of specific surface area.

Specifically, regarding the three compounds already mentioned which are in a major proportion in the starting extractive (*β*-sitosterol, hexadecanoic acid and (*Z*)-octadec-9-enoic acid), all the synthesized adsorbents (except AD1000) are more efficient than talc. This partial result evidences the potential of such materials for removing lipophilic wood. It is important to highlight that *β*-sitosterol and hexadecanoic and (*Z*)-octadec-9-enoic acids are ever present compounds in the pitch deposits. Their removal will directly impact the paper quality and maintenance problems of the paper industry.

Previous works have reported that in the case of materials containing meso and macropores, those showing low surface area values were more selective regarding the size of the molecules to be adsorbed (Pan et al., 2011; He et al., 2014). However, adsorbents studied obtained through calcination between 600 and 800°C showed intermediate values of SSA (16 to 12 $m^2 g^{-1}$), and showed the highest affinity with the studied molecules. It is noteworthy to mention that the compounds that had the greatest retention to the adsorbents were *β*-sitosterol and fatty acids, which have the highest molecule size among the lipophilic compounds.

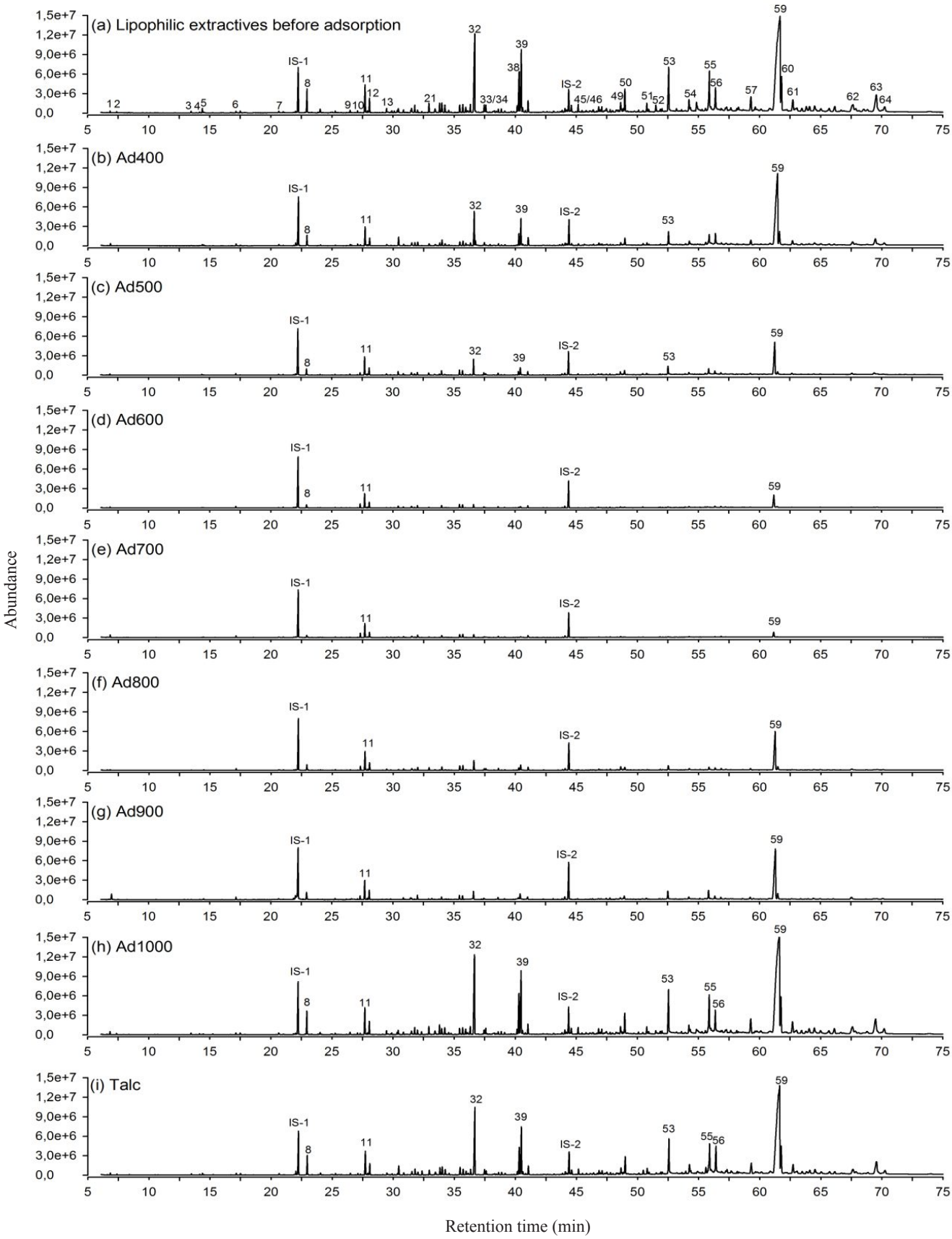
The compounds β-sitosterol and stigmastanol were present in the wood of all the studied species, and steroids are the main compounds found in pitch deposit during the paper production process (Rencoret et al., 2007). Thus, high levels of β-sitosterol (96% adsorption), β-sitostanol (97% adsorption), campesterol (100% adsorption) and fatty acids (90% adsorption) by Ad700 evidence the efficiency of this adsorbent in removing pitch forming compounds.

The results obtained for percentages of adsorption and adsorption capacity (q_e) for the seven adsorbents compared with the value obtained for talc are shown in Figure 6.

Table 2. Relative areas of chemical classes from detected compounds in the lipophilic wood extractive and the percentage of compounds not removed after treatment with the sewage sludge-based adsorbent.

Chemical class		Rela ve area (%)								
		Ext[1]	Talc	Ad400	Ad500	Ad600	Ad700	Ad800	Ad900	Ad1000
Ni[2]		15.0	14.9	4.7	2.4	1.0	1.1	1.4	1.7	13.2
Alcohol		1.0	1.2	0.3	0.1	0.1	0.2	0.2	0.2	0.9
Fa y acid		31.9	24.1	9.5	4.7	1.1	0.8	2.6	3.4	28.3
Aroma c compounds		6.0	6.1	3.2	2.3	1.8	2.1	2.5	2.7	5.5
Sterol	Campesterol	1.6	2.2	0.5	0.1	0.0	0.0	0.1	0.1	1.6
	β-sitosterol	41.0	36.6	16.8	5.3	1.8	1.5	5.9	5.2	40.9
	β-sitostanol	3.4	3.1	1.3	0.3	0.1	0.1	0.4	0.3	3.5
		100.0	88.2	36.3	15.3	5.9	5.9	13.0	13.7	94.0

[1]Ext: extract before adsorption.
[2]Ni: Not identified.



IS-1 and IS-2: Internal standards: hexanedioic acid and tetracosane, respectively.

The numbers of the peaks referring to the compounds: (8) 4-Hydroxy-3-methoxybenzaldehyde, (11) 2-(4-Hydroxy-3-methoxyphenyl) ethanol, (12) Not identified, (32) Hexadecanoic acid, (38) (9Z,12Z)-octadec-9,12-dienoic acid, (39) (Z)-octadec-9-enoic acid, (50) Docosanoic acid, (53) Tetracosanoic acid, (55) Hexacosanoic acid, (56) Not identified, (57) Campesterol, (59) β-sitosterol, (60) β-sitostanol, (63) Not identified.

Figure 5. Total ions chromatogram of the lipophilic extractives of the wood (a) before adsorption; (b-h) after the adsorption using the synthesized adsorbents and Talc (i).

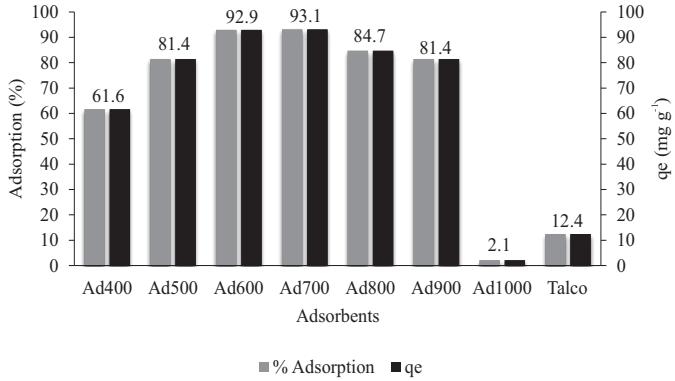


Figure 6. Percentage of adsorption of wood extractives and adsorption capacity (q_e) for the adsorbents.

The adsorption capacity of the adsorbents Ad500, Ad600, Ad700, Ad800 and Ad900 is not statistically different by the Tukey test at 5% significance level. Previous studies have also reported that the adsorbents obtained at 600°C and 700ºC are effective for removing organic and phenolic compounds (Martin et al., 2004; Smith et al., 2009; Pan et al., 2011; Gómez-Pacheco et al., 2012; Ocampo-Pérez et al., 2012; Xie et al., 2013).

Talc and Ad1000 have statistically similar means in the removal of the wood lipophilic constituents (12.4 and 2.1%, respectively). This result corroborates the results found in Figure 5, as the talc had a lower adsorption capacity in number of compounds when compared to the other six adsorbents.

Both Ad600 and Ad700 removed 92.9 and 93.1%, respectively, of the lipophilic compounds present in wood extractives, of which 39% was *β*-sitosterol, which was the most predominant compound found in the extractives. Previous studies utilizing waste water sludge-based adsorbents for the removal of organic compounds in water treatment reported adsorption of about 50% of the hydrophobic fraction (Pan et al., 2011) and approximately 95% removal of phenols in water treatment (Martin et al., 2004). However, these adsorbents were produced by chemical activation with sulfuric acid and a preparation time of 73 hours, which increases the cost of producing the adsorbents.

The adsorbents and talc presented adsorption capacities ranging from 2 to 94 mg g^{-1}, and the statistical means followed the results obtained with the percentage of adsorption (Figure 6). These values are higher than those found in the literature for adsorbents prepared from the non-activated sewage sludge used to remove phenol, which presented q_e of 9.8 mg g^{-1} (Rozada et al., 2005).

Ad1000 and talc presented q_e of 2.1 and 12.4 mg.g^{-1}, respectively, the lowest means among the adsorbents prepared in this work. Adsorptive capacity is influenced by the sludge composition, the preparation of the adsorbent and the compound to be adsorbed. Adsorbents from sludge and activated with NaOH that reach up to 672.0 mg of tetracycline per g (Ocampo-Pérez et al., 2012) and non-activated adsorbents showed adsorptive capacities of 2.3 mg.g^{-1} copper (Velghe et al., 2012).

Conclusions

The roughness of the produced adsorbents is superior to that of talc. Adsorbents prepared at temperatures of 500-900°C were found to be about eight times more effective than talc in the adsorption of lipophilic compounds. These materials can potentially aid talc in removing compounds from pitch in the pulp and paper industry. Therefore, preparing such adsorbents and their application in the pulp and paper industry is a viable proposal for sludge recovery.

Complementary studies that clarify issues such as the affinity of the adsorbent for the compounds and their maximum adsorptive capacity are still necessary, in addition to application methodologies of this adsorbent in the industrial process.

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