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Mercury removal from aqueous solution by adsorption on activated carbons prepared from olive stones

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Abstract The textural characterization of a series of activated carbons prepared from olive stones, by carbonization at different temperatures (400, 550, 700 and 850 °C) and thermal activation with CO_2, has been investigated using N_2 adsorption at −196 °C and CO_2 adsorption at 0 °C. The effect of pre-oxidation of the carbonized precursor has also been studied, using temperature-programmed decomposition (TPD), to evaluate the effect of oxygen content of the chars in the performance of the obtained activated carbons for mercury removal. The adsorption of Hg(II) cations from aqueous solutions at room temperature by the prepared activated carbons was studied. Experimental results show that all samples exhibit a large microporosity (pore diameter below 0.56 nm). The amount of surface oxygen groups increased after pre-oxidation treatment, this enhancing the Hg(II) uptake (up to 72%). It can be concluded that these groups make the support more hydrophilic, thus providing a more efficient adsorption of Hg(II). The formation of a great amount of surface oxide groups such as carboxyl, phenol and lactone alters the surface charge properties of the carbon, this enhancing the surface-Hg(II) interaction.

Keywords Mercury removal · Adsorption · Activated carbon · Surface oxygen groups

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1 Introduction

Heavy metals are considered among the most problematic polluting agents, due to their harmful effect on human physiology as well as on other biological systems. Mercury is generally considered as the most toxic metal in natural ecosystems (Clarkson 1993), and important emissions regulations are implemented (Griffiths et al. 2007). It can alternate among different possible forms, mainly elemental mercury, inorganic mercury compounds and organic mercury compounds, depending on temperature, pH and the presence of combination agents such as chlorine, sulphur, etc. (Lee et al. 2006). In particular, methyl mercury has been shown to be very detrimental for childhood development at very low doses (Dobes et al. 2006). In general, all the mercury species are highly toxic, although the toxicity degree varies according to the species in particular. The mercury absorption way into the human body depends on its chemical form and on the ingest mode, as inhaled or ingested. The metal is accumulated in the living tissue, particularly in the brain (Baran 1994). Concretely, mercury is one of the priority pollutants listed by USEPA, as it can easily pass the blood-brain barrier and affect the fetal brain (Zabihi et al. 2009). High concentration of Hg(II) causes impairment of pulmonary function and kidney, chest pain and dyspnea (Berglund and Bertin 1969; Krishnamoorthi and Vishwanathan 1991). According to the standards, the tolerance limit of Hg(II) for discharge into inland surface waters is 10 μg/L and for drinking water it is 1 μ/L (Zabihi et al. 2009). The principal sources of mercury pollution in aquatic environment are the chlor-alkali plants, paper and pulp industries, oil refining, electrical, rubber processing and fertilizer industries (Baeyens et al. 1996). In general, the currently available technologies for the reduction of heavy metals contamination include

precipitation (Mauchauffée and Meux 2007), reverse osmosis (Mohsem-Nia et al. 2007), ion exchange (Verma et al. 2008), coagulation (El Samrani et al. 2008) and adsorption (Gupta et al. 1999, 2003, 2004, 2005). Adsorption is considered an appropriate technology for the treatment of liquid effluents with high pollutant load (Gupta and Ali 2006; Manchester et al. 2008; Legrouri et al. 2005). However, its application on great scale, as in industrial plants for example, may be relatively expensive. Activated carbon is one of the most popular adsorbents for the removal of mercury containing wastewaters (Huang 1978; Koshima and Onishi 1980). Several studies have evaluated the use of low-cost available materials as precursors for the preparation of activated carbon (Ali and Gupta 2007; Gupta et al. 2009; Gupta and Rastogi 2008a, 2008b, 2008c), such as waste rubber tires (Rowley et al. 1984; Netzer and Wilkinson 1974; Knocke and Hemphill 1981; Meng et al. 1998), fly ashes (Kapoor and Vieraraghavan 1993; Sen and De 1987), carbon fibres (Kaneko 1988), activated charcoal cloths (Jayson et al. 1984), wood (Morita et al. 1987) and peat (Viraraghavan and Kapoor 1995).

Generally, there are two basic methods for the preparation of activated carbons: physical and chemical activation. The physical or thermal activation method involves carbonization of raw material followed by activation at high temperature in a carbon dioxide or steam atmosphere. Chemical activation, which is a well-known method for the preparation of activated carbons, involves one step heat treatment at lower temperature than physical activation in the presence of some chemical dehydrating agents (Zabihi et al. 2009). The objective of this work has been to prepare activated carbons from olive stones, by using physical activation and a pre-oxidation treatment, for the removal of the mercury cations, Hg(II), from aqueous solutions. The choice of adsorption as mercury removal technique has been based on its low energy consumption during the effective treatment. This technique is considered clean and, practically, the addition of any chemical reagents, which can represent another source of contamination, is not required. In that way, this technique can constitute a good solution to remove mercury from wastewater. However, this technique turns out relatively expensive for industrial scale applications. On this basis, the aim of this work was the search of efficient and low cost alternatives to commercial adsorbents.

2 Materials and methods

2.1 Preparation of the adsorbents

The precursor used for the preparation of the activated carbons was olive stones from the north of Morocco. The raw material was crushed and sieved to obtain particles of about 1 mm diameter. It was washed with decalcified water and treated with a 10 wt.% sulphuric acid aqueous solution for 4 h. Then, it was washed with decalcified and distilled water, to remove the residual acid, and dried at 80 °C and stored. Before carrying out the pyrolysis process, the washed raw material was dried again in a stove at 120 °C for 24 h (Zhang et al. 2005). Then, it was carbonized under flowing N_2 (100 $cm^3 \cdot min^{-1}$) at 400, 550, 700 and 850 °C for 2 h. The carbonized samples were separated in two series: carbonized material destined to pre-oxidation before activation, designated as CPA_{400}, CPA_{550}, CPA_{700} and CPA_{850}, and carbonized material destined to conventional activation, labelled as CA_{400}, CA_{550}, CA_{700} and CA_{850}. The pre-oxidation process was carried out by heating the carbonized material to 250 °C at a rate of 2 $°C \cdot min^{-1}$ under a constant synthetic air (O_2 20% (±1% Abs.)/N_2) flow of 100 $cm^3 \cdot min^{-1}$, and maintaining the temperature for a soaking time of 5 h. The activation was performed by heating the sample for 8 h at 900 °C in a flow of CO_2 of 120 $cm^3 \cdot min^{-1}$.

In order to determine the optimal pre-oxidation temperature, the stability of the char in air was determined by thermogravimetric analysis with a thermobalance (2960 SDT Simultaneous DSC-TGA. TA instruments).

Temperature-programmed decomposition (TPD) experiments were carried out in a U-shaped quartz reactor connected on-line with a quadruple mass spectrometer (Omnistar TM PFEIFFER VACUUM). The samples (100 mg) were first flushed with a He flow of 50 $cm^3 \cdot min^{-1}$ at room temperature. Subsequently, the temperature was increased up to 1000 °C with a heating rate of 10 $°C \cdot min^{-1}$.

The textural characteristics of the samples were determined by N_2 adsorption at −196 °C and CO_2 adsorption at 0 °C. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) equation (Bunauer et al. 1938). The Dubinin-Radushkevich (DR) equation was used to calculate the micropore volumes, V_{N2} and V_{CO2} (Dubinin and Walker 1966).

2.2 Adsorption studies

Before the adsorption tests, the adsorbents were dried in an oven at 70 °C for 24 h (Jayson et al. 1984). To study the adsorption capacity of the carbons towards Hg(II) ions, an aqueous solution of Hg(II), with concentration of 20 $mg \cdot l^{-1}$, was prepared from $HgCl_2$ in hydrochloride acid with a pH value of 2 (Yardim et al. 2003). The adsorption kinetics measurements were carried out by contacting 0.5 g of activated carbon with 100 ml of the solution, for a period of 5 to 24 h at room temperature, with a constant agitation rate of 200 rpm, in a shaker bath. The contact time was selected on the basis of previous studies that demonstrated that the equilibrium was established in 6–8 h, and that between 10–24 h the uptake was practically unmodified (Mohan et al. 2001).

The suspensions were filtered through a microporous filter before the determination of the amount of Hg(II) in solution, which was accomplished spectrophotometrically with an ATI Unicam UV/Vis Spectrometer, at 230 nm (Nabais et al. 2006).

3 Results and discussion

3.1 Optimal temperature for the oxidation pre-treatment

During the pyrolysis stage, the obtained yield decreased with increasing the temperature. This decrease was about 10% in the low temperature range, from 400 to 600 °C, whereas for higher carbonization temperatures the yield remained nearly unmodified, centred at about 36% (Fig. 1). This indicates that the carbonization process was completed at this temperature, given that the condensation-aromatization reactions take place from 400 °C, such as other authors reported before (Tang and Bacon 1964). Thus, practically all the volatile compounds have been removed at this temperature.

The estimation of the optimal temperature for the oxidation pre-treatment of the char was determined by thermogravimetric analysis. Figure 2 shows the weight loss during the heat treatment in synthetic air. As it can be observed in this figure, there are two stages of weight loss, with different rate. The first one starts at about 125 °C, with a constant loss rate up to about 460 °C. At this temperature, the total combustion of the char starts, and it is nearly complete at about 500 °C. Taking into account these results, the preoxidation temperature was fixed at 250 °C.

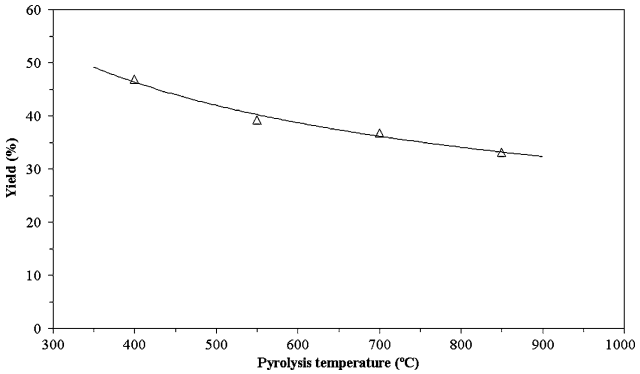

Fig. 1 Variation of pyrolysis yield for different carbonization temperatures

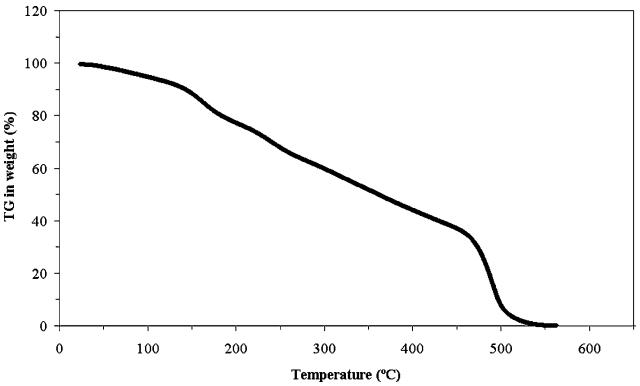

Fig. 2 Thermogravimetric curve of char under synthetic air flow

3.2 Temperature-programmed decomposition

Temperature-programmed decomposition (TPD) experiments under an inert gas such as He, Ar and N_2 are effective for the determination of the amount and type of the oxygen groups present on the surface of carbon materials (Hydar et al. 2000; Zielke et al. 1996; Jia and Thomas 2000). In this work, the TPD analysis has been carried out in order to determine the effect of the pre-oxidation treatment on the surface properties of the activated carbons.

Figure 3 reports the amounts of CO (Fig. 3a) and CO_2 (Fig. 3b) evolved from the different adsorbents in the TPD experiments, obtained from the integration of the TPD peaks. The increase of the amount of oxygen surface groups after pre-oxidation was evidenced by the increase of the amounts of CO and CO_2 evolved (Table 1).

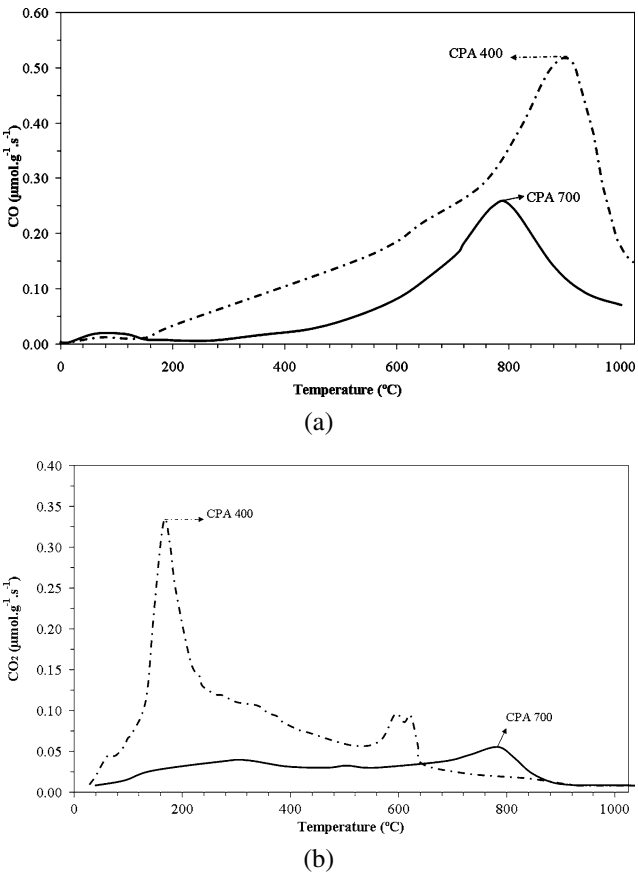

Fig. 3 TPD spectra for CPA_{400} and CPA_{700} samples: (**a**) CO evolution; (**b**) CO_2 evolution as well as amounts of CO and CO_2 evolved

Table 1 Oxygen content for all samples obtained from the integration of TPD signals

Sample	CO_2 (μmol/g)	CO (μmol/g)
CA_{400}	0.07	0.45
CA_{550}	0.05	0.11
CA_{700}	0.06	0.10
CA_{850}	0.06	0.18
CPA_{400}	0.37	0.99
CPA_{550}	0.06	0.20
CPA_{700}	0.12	0.42
CPA_{850}	0.15	0.85

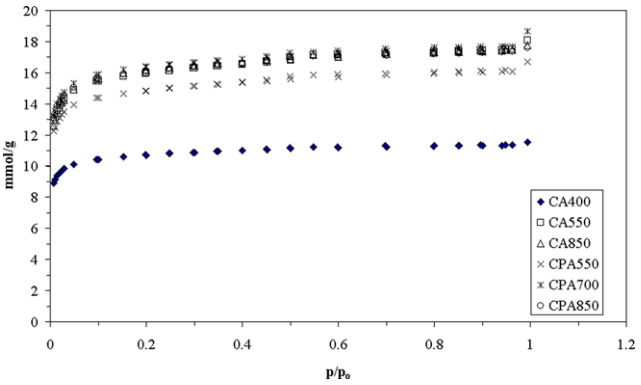

Fig. 4 N_2 adsorption isotherms at −196 °C and textural properties of CA and CPA samples

On the other hand, it can be seen that the highest values were obtained for CA_{400} and CPA_{400}. This can be explained by chain scissions, or de-polymerization, and breaking of C–O and C–C bonds within ring units evolving water, CO and CO_2, between 240 and 400 °C. Above 400 °C, the aromatization starts to lead to graphitic layers (Byrne 1997). Similar profiles were obtained for all samples with exception of CPA_{400}. There is overpowering evidence observed from thermal decomposition studies that there were two types of surface chemical structures: one evolved CO_2 during decomposition, and the other one evolved CO. CO was more abundant than CO_2, and an appreciable amount of CO was evolved at higher temperature ranging from 800 to 1000 °C. As it can be clearly observed, CPA_{400} exhibited a higher amount of oxygen surface groups than CPA_{700}. The TPD profile of sample CPA_{400} showed two CO_2 desorption peaks at 175 °C and 600 °C. The first desorption peak at low temperature must correspond to the decomposition of less stable carboxylic acid groups, while the other peak must be attributed to structures which are thermally more stable like are lactones and carboxylic anhydrides. Whereas, CPA_{700} showed only one peak at 750 °C due to lactones and carboxylic anhydrides (Rodríguez-Reinoso and Molina-Sabio 1998; Figueiredo et al. 1999). Regarding to CO evolution, CPA_{700} showed a single peak at about 800 °C which was shifted to higher temperature, 900 °C, in the case of CPA_{400}. This peak may be originated from phenol, ether and/or carbonyl/quinone groups (Ríos et al. 2007).

3.3 Porous texture

The N_2 adsorption-desorption isotherms at −196 °C for the prepared carbons are shown in Fig. 4. Additionally, it reports the specific surface area, the mesopore volume as well as the micropore volume deduced from the corresponding N_2 adsorption isotherms at −195 °C for the activated carbons. All isotherms correspond to microporous carbons. It can be seen that as the carbonization temperature was increased, the BET surface area increased and reached its maximum at 700 °C (Table 2). This tendency was similar for both CA and CPA samples. On the other hand, BET surface areas of non pre-oxidized samples were larger than those of samples without pre-oxidation, and this was likely due to micropore blockage by oxygen-containing functional groups. However, in the case of samples carbonized at 400 °C, the highest surface area was found for the pre-oxidized sample CPA_{400}. This behaviour can be explained by the incomplete carbonization at 400 °C which may inhibit the development of porosity.

Table 2 Surface area, micropore volume and mesopore volume of activated carbons

Sample	S_{BET} ($m^2 \cdot g^{-1}$)	V_{N2} ($cm^3 \cdot g^{-1}$)	V_{mes} ($cm^3 \cdot g^{-1}$)
CA_{400}	953	0.38	0.02
CA_{550}	1371	0.57	0.04
CA_{700}	1591	0.62	0.13
CA_{850}	1402	0.56	0.04
CPA_{400}	1212	0.49	0.03
CPA_{550}	1274	0.52	0.04
CPA_{700}	1410	0.57	0.04
CPA_{850}	1383	0.56	0.04

3.4 Mercury removal

Figure 5 shows the Hg(II) cation removal capacity in aqueous solution of the prepared activated carbons. The mercury removal for pre-oxidized carbons was higher than for the non pre-oxidized samples. Thus, it can be concluded that the presence of oxygen surface groups on the activated carbons was beneficial for mercury adsorption. CPA_{850} exhibited the maximum mercury removal, 72%.

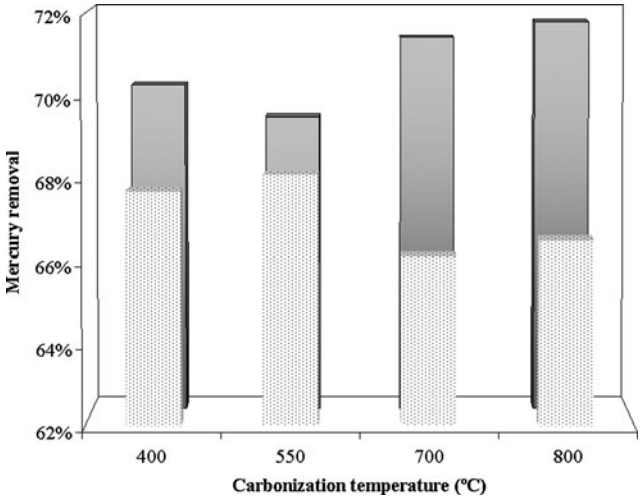

Fig. 5 Mercury removal with pre-oxidized carbons (*full bars*) and non pre-oxidized carbons (*hatched bars*) at 25 °C, with initial concentration of mercury of 20 mg·l^{-1} and pH = 2

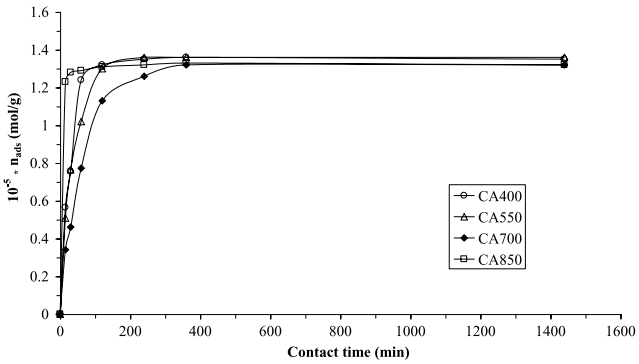

Fig. 6 Kinetics of Hg(II) removal with several non pre-oxidized carbons at 25 °C

3.5 Adsorption kinetics

Figure 6 shows the kinetic curves for the adsorption of Hg(II) on non pre-oxidized carbons, from a solution with an initial Hg(II) concentration of 20 mg·l^{-1}. The removal efficiency increased sharply at short contact times, and slowed down towards the equilibrium. This behaviour can be attributed to the saturation of the active sites by the metal cation.

The kinetics of Hg(II) adsorption on the pre-oxidized carbons were quite similar following the first order rate expression given by Lagergren (Namasivayam and Kadirvelu 1997).

$$\log_{10}(q_e - q) = \log_{10} q_e - \frac{k_{ad}t}{2.303} \quad (1)$$

where q is the amount of Hg(II) adsorbed (mg·g^{-1}) at time t, q_e is the amount adsorbed (mg·g^{-1}) at equilibrium time, and K_{ad} is the constant adsorption rate of 1 min^{-1}. The linear plots of $\log_{10}(q_e - q)$ versus t obtained with the pre-oxidized carbons showed the applicability of (1). The corresponding values of K_{ad} were calculated from the slopes of the plots (Fig. 7), and they were presented, together with the correlation coefficients, in Table 3.

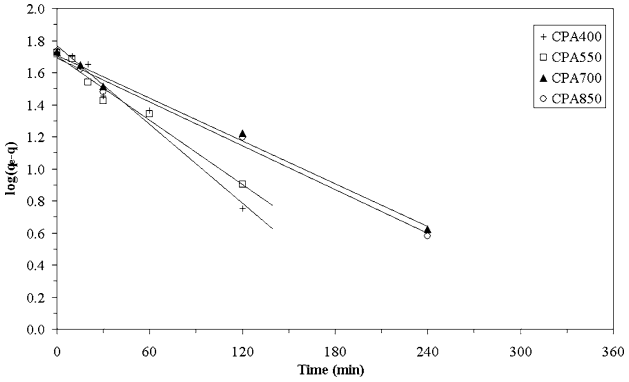

Fig. 7 Lagergren plots for Hg(II) adsorption onto different pre-oxidized carbons

Table 3 Adsorption rate constants and correction coefficients

Sample	Lagergren rate constant K_{ad} (1 min^{-1})	R^2
CPA_{400}	9×10^{-3}	0.9742
CPA_{550}	8×10^{-3}	0.9741
CPA_{700}	5×10^{-3}	0.9918
CPA_{850}	6×10^{-3}	0.9966

The adsorption kinetics of the non pre-oxidized carbons was slower than the adsorption kinetics of the pre-oxidized carbons. The periods of time needed to attain equilibrium were different according to pyrolysis temperature for pre-oxidized carbons. Equilibrium was indeed attained at 120 min for CPA_{400} and CPA_{550}, with values of the Lagergren constant of 0.009 and 0.008 min^{-1} respectively, and at 240 min for CPA_{700} and CPA_{850}, with values of Lagergren constant of 0.005 and 0.006 min^{-1} respectively. CPA_{850} and CPA_{700} showed the maximum adsorption capacity for Hg(II), with relatively slower rates than the CPA_{400} and CPA_{550} samples. This behaviour can be attributed to the textural properties of the samples (surface area, porosity, pore size distribution, etc.); that is, the porous texture determinates the kinetics of mercury adsorption, by imposing restrictions to the diffusion of mercury species through the inner porosity. Thus, in addition to a developed surface chemistry, an ideal adsorbent should also exhibit a well-developed porous texture.

In summary, these results can be attributed to the presence of a synergy between surface and textural proprieties of the carbons. The carbon surface-mercuric ion interaction was favoured by the presence of oxygen surface

groups on the adsorbent, which make the carbon more hydrophilic (Savova et al. 2003). It has been shown that the pre-oxidation treatment introduced carboxylic groups which evolved as CO_2 under thermal decomposition, and phenolic groups which decomposed at higher temperatures as CO. These oxygen surface groups play an important role in the adsorption process. They make the support more hydrophilic, allowing a better accessibility of the Hg(II) cations in the aqueous solution to the carbon surface and leading to a more efficient adsorption. On the other hand, they could also alter the surface-ion interaction by the modification of the surface charge properties (Coloma et al. 1994). Thus, formation of a great number of surface oxygen groups such as carboxyl, phenol and lactone favours the interaction between the carbon surface and the mercury cation, this enhancing the adsorption process, what can be represented by the following reaction (Namasivayam and Kadirvelu 1999):

$$2C_xOH^+ + Hg^{2+} \rightarrow (C_xO)_2\ Hg^{2+} + 2H^+$$

It is worth noting that the mechanism could also be a direct electrostatic interaction between the positively charged surface and mercury anionic species:

$$C_xOH^+ + HgCl_3^- \rightarrow C_xOH(HgCl_3)$$

4 Conclusions

In this study, two series of activated carbons were prepared from olive stones. An increase of the amount of surface oxygen groups after pre-oxidation was evidenced by TPD. The removal of Hg(II) ions from aqueous solution by these carbons was effectively demonstrated. The mercury removal was higher than 65% for both series of prepared carbons. Pre-oxidized carbons had the highest adsorption capacity, what can be explained by the formation of oxygen surface groups during pre-oxidation. These groups make the support more hydrophilic, allowing a more efficient adsorption of Hg(II). On the other hand, the formation of a great amount of surface oxide groups such as carboxyl, phenol and lactone altered the surface charge properties of the carbon, this enhancing the surface-Hg(II) interaction.

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References

Ali, I., Gupta, V.K.: Advances in water treatment by adsorption technology. Nat. Protocols **1**, 2661–2667 (2007)

Baeyens, R., Ebinghous, R., Vasilev, O.: Global and Regional Mercury Cycles: Sources Fluxes and Mass Balances. Kluwer Academic, Dordrecht (1996)

Baran, E.J.: Química Bioinorgánica. McGraw-Hill, New York (1994)

Berglund, F., Bertin, M.: Chemical Fallout. Thomas Publishers, Springfield (1969)

Bunauer, S., Emmett, P.H., Teller, F.: Adsorption of gases in multimolecular layers. J. Am. Chem. Soc. **60**, 309–319 (1938)

Byrne, C.E.: Carbonization of wood for advanced materials applications. Carbon **35**, 259–266 (1997)

Clarkson, T.W.: Mercury major issues in environmental health. Environ. Health Perspect. **100**, 31–38 (1993)

Coloma, F., Sepúlveda-Escribano, A., Fierro, J.L.G., Rodríguez-Reinoso, F.: Preparation of platinum supported on pregraphitized carbon blacks. Langmuir **10**, 750–755 (1994)

Dobes, F., Budtz-Jorgensen, E., Weihe, P., White, R.F., Grandjean, P.: Impact of prenatal methylmercury exposure on neurobehavioral function at age 14 years. Neurotoxicol. Teratol. **28**, 536–547 (2006)

Dubinin, M.M., Walker, P.L.: Porous structure and adsorption properties on active carbon. Chem. Phys. Carbon **2**, 51–120 (1966)

El Samrani, A.G., Lartiges, B.S., Villiéras, F.: Chemical coagulation of combined sewer overflow: Heavy metal removal and treatment optimization. Water Res. **42**, 951–960 (2008)

Figueiredo, J.L., Pereira, M.F.R., Freitas, M.M.A., Órfão, J.J.M.: Modification of the surface chemistry of activated carbons. Carbon **37**, 1379–1389 (1999)

Griffiths, C., McGartland, A., Miller, M.: A comparison of the monetized impact of IQ decrements from mercury emissions. Environ. Health Perspect. **115**, 817–841 (2007)

Gupta, V.K., Ali, I.: Adsorbents for water treatment: development of low-cost alternatives to carbon. In: Encyclopedia of Surface and Colloid Science, 2nd edn., pp. 149–184. Taylor & Francis, New York (2006)

Gupta, V.K., Rastogi, A.: Biosorption of lead from aqueous solutions by green algae Spirogyra species: Equilibrium and adsorption kinetics. J. Hazard. Mater. **152**(1), 407–414 (2008a)

Gupta, V.K., Rastogi, A.: Biosorption of lead from aqueous solutions by non-living algal biomass Oedogonium sp. and Nostoc sp.—a comparative study. Colloids Surf. B **64**(2), 170–178 (2008b)

Gupta, V.K., Rastogi, A.: Sorption and desorption studies of chromium (VI) from nonviable cyanobacterium Nostoc muscorum biomass. J. Hazard. Mater. **154**(1–3), 347–354 (2008c)

Gupta, V.K., Mohan, D., Sharma, S., Park, K.T.: Removal of chromium (VI) from electroplating industry wastewater using Bagasse fly ash—a sugar industry waste material. Environmentalist **19**, 129–136 (1999)

Gupta, V.K., Jain, C.K., Ali, I., Sharma, M., Saini, V.K.: Removal of cadmium and nickel from wastewater using Bagasse fly ash—a sugar industry waste. Water Res. **37**, 4038–4044 (2003)

Gupta, V.K., Singh, P., Rahman, N.: Adsorption behavior of Hg(II), Pb(II) and Cd(II) from aqueous solution on duolite C-433: a synthetic resin. J. Colloid Interface Sci. **275**, 398–402 (2004)

Gupta, V.K., Saini, V.K., Jain, N.: Adsorption of As(III) from aqueous solutions by iron-oxide coated sand. J. Colloid Interface Sci. **288**, 55–60 (2005)

Gupta, V.K., Carrott, P.J.M., Carrott, Ribeiro, Suhas, M.M.L.: Low cost adsorbents: Growing approach to wastewater treatment—a review. Crit. Rev. Environ. Sci. Technol. **39**, 783–842 (2009)

Huang, C.P.: Chemical interactions between inorganic and activated carbon. In: Carbon Adsorption Handbook, pp. 281–329. Ann Arbor Science, Ann Arbor (1978)

Hydar, S., Moreno-Castilla, C., Ferro-Garcia, M.A., Carrasco-Marin, F., Rivera-Utrilla, J., Perrard, A., Joly, J.P.: Regularities in the temperature-programmed desorption spectra of CO_2 and CO from activated carbons. Carbon **38**, 1297–1308 (2000)

Jayson, G.G., Sangster, J.A., Thompson, G., Wilkinson, M.C.: Adsorption and electron sorption of Hg(II) acetate onto activated charcoal cloth from aqueous solution. Carbon **25**, 523–531 (1984)

Jia, Y.F., Thomas, K.M.: Adsorption of cadmium ions on oxygen surface sites in activated carbon. Langmuir **16**, 1114–1122 (2000)

Kaneko, K.: Dynamic Hg(II) adsorption characterization of iron oxide-dispersed activated carbon fibers. Carbon **26**, 903–905 (1988)

Kapoor, A., Vieraraghavan, T.: Adsorption of mercury from wastewater by fly ash. Adsorp. Sci. Technol. **9**, 130–147 (1993)

Knocke, W.R., Hemphill, L.H.: Mercury sorption by water rubber. Water Res. **15**, 275–282 (1981)

Koshima, H., Onishi, H.: Collection of mercury from artificial sea- water with activated carbon. Talanta **27**, 795–799 (1980)

Krishnamoorthi, C.R., Vishwanathan, P.: Toxic Metal in Indian Environment. Tata McGraw Hill, New Delhi (1991)

Lee, S.H., Rhym, Y.J., Cho, S.P., Baek, J.I.: Carbon-based novel sorbent for removing gas-phase mercury. Fuel **85**, 219–226 (2006)

Legrouri, K., Khouya, E., Ezzine, M.: Production of activated carbon from a new precursor molasses by activation with sulphuric acid. J. Hazard. Mater. B **118**, 259–263 (2005)

Manchester, S., Wang, X., Kulaots, I., Gao, Y., Hurt, R.H.: High capacity mercury adsorption on freshly ozone-treated carbon surfaces. Carbon **46**, 518–524 (2008)

Mauchauffée, S., Meux, E.: Use of sodium decanoate for selective precipitation of metals contained in industrial wastewater. Chemosphere **69**, 763–768 (2007)

Meng, X., Hua, Z., Dermatas, D., Wang, W., Kuo, H.Y.: Immobilization of mercury(II) in contaminated soil with use tire rubber. J. Hazard. Mater. **57**, 231–241 (1998)

Mohan, D., Gupta, V.K., Srivastava, S.K., Chander, S.: Kinetics of mercury adsorption from wastewater using activated carbon from fertilizer waste. Colloids Surf. A, Physicochem. Eng. Asp. **177**, 169–181 (2001)

Mohsem-Nia, M., Montazeri, P., Modarress, H.: Removal of Cu^{2+} and Ni^{2+} from wastewater with a chelating agent and reverse osmosis processes. Desalination **217**, 276–281 (2007)

Morita, M., Higuchi, M., Sakata, I.: Binding of heavy metal ions by chemically modified wood. J. Appl. Polym. Sci. **34**, 1013–1023 (1987)

Nabais, J.V., Carrott, P.J.M., Ribiero-Carrott, M.M.L.: Mercury removal from aqueous solution and flue gas by adsorption on activated carbon fibres. Appl. Surf. Sci. **252**, 6046–6052 (2006)

Namasivayam, C., Kadirvelu, K.: Uptake of mercury(II) from wastewater by activated carbon from an unwanted agricultural solid by-product: coirpith. Carbon **37**, 79–84 (1999)

Namasivayam, C., Kadirvelu, K.: Agricultural solid wastes fro the removal of heavy metals: Adsorption of Cu(II) by coirpith carbon. Chemosphere **34**, 377–399 (1997)

Netzer, A., Wilkinson, P.: Removal of heavy metals from wastewater utilizing discarded automotive tyres. Water Pollut. Res. J. Can. **9**, 62–66 (1974)

Ríos, R.V.R.A., Silvestre-Albero, J., Sepúlveda-Escribano, A., Rodríguez-Reinoso, F.: Liquid phase removal of propanethiol by activated carbon: Effect of porosity and functionality. Colloids Surf. A, Physicochem. Eng. Asp. **300**, 180–190 (2007)

Rodríguez-Reinoso, F., Molina-Sabio, M.: Textural and chemical characterization of microporous carbons. Advance. Colloid. Interface. Science **76–77**, 271–294 (1998)

Rowley, A.G., Husband, F.M., Cuningham, A.B.: Mechanisms of metal adsorption from aqueous solutions by waste tyre rubber. Water Res. **18**, 981–984 (1984)

Savova, D., Petrov, N., Yardim, M.F., Ekinci, E., Budinova, T., Razvigorova, M., Minkova, V.: The influence of the texture and surface properties of carbon adsorbents obtained from biomass products on the adsorption of manganese ions from aqueous solution. Carbon **41**, 1897–1903 (2003)

Sen, A.K., De, A.K.: Adsorption of mercury(II) by cool fly ash. Water Res. **21**, 885–888 (1987)

Tang, M.M., Bacon, B.: Carbonization of cellulose fibers-I. Low temperature pyrolysis. Carbon **2**, 211–220 (1964)

Verma, V.K., Tewari, S., Rai, J.P.N.: Ion exchange during heavy metal bio-sorption from aqueous solution by dried biomass of macropyhtes. Bioresour. Technol. **99**, 1932–1938 (2008)

Viraraghavan, T., Kapoor, A.: Adsorption of mercury from wastewater by peat. J. Environ. Sci. Health A **30**, 553–566 (1995)

Yardim, M.F., Budinova, T., Ekinci, E., Petrov, N., Razvigorova, M., Minkova, V.: Removal of mercury(II) from aqueous solution by activated carbon obtained from furfural. Chemosphere **52**, 835–841 (2003)

Zabihi, M., Ahmadpour, A., Haghighi Asl, A.: Removal of mercury from water by carbonaceous sorbents derived from walnut shell. J. Hazard. Mater. **167**, 230–236 (2009)

Zhang, F.S., Nriagu, J.O., Hideaki, I.: Mercury removal from water using activated carbons derived from organic sewage sludge. Water Res. **39**, 389–395 (2005)

Zielke, U., Hüttinger, K.J., Hoffman, W.P.: Surface-oxidized carbon fibers: I. Surface structure and chemistry. Carbon **34**, 983–998 (1996)