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Tailoring Activated Carbon by Surface Chemical Modification with O, S, and N Containing Molecules

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In this work the surface of activated carbon was chemically modified in order to introduce O, S and N containing groups. The activated carbon surface was selectively oxidized with concentrated HNO_3 under controlled conditions. Characterization by thermogravimetric analyses, infrared spectroscopy and NaOH titration suggested the formation of mainly –COOH and small amounts of –OH groups, with concentration of approximately 4.10^{21} groups/g of carbon. These -COOH functionalized carbons showed high adsorption capacity for metal cations in aqueous solution in the following order: $Pb^{+2}>Cu^{+2}>Ni^{+2}>Cd^{+2}\sim Co^{+2}>Ca^{+2}$, suggesting a cation exchange mechanism via a surface complex $[–COO^{-}M^{+2}]$. These $–COOH_{surf}$ groups can be reacted with $SOCl_2$ to produce a surface acylchloride group, -COCl. This surface -COCl group proved to be a very reactive and versatile intermediate for the grafting of different S and N containing molecules onto the carbon surface, such as 1,2-ethaneditiol (EDT-, $HSCH_2CH_2SH$) 1,7-dimercapto-4-thioheptane (DMTH-$HSCH_2CH_2CH_2SCH_2CH_2CH_2SH$) or 1,2-ethylenediamine (EDA- $NH_2CH_2CH_2NH_2$) and triethyltetraamine, TEA ($H_2NCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$). The characterization of these materials was carried out by TG, IR and TPDMS (Temperature Programmed Decomposition Mass Spectrometry) experiments suggesting the formation of thioesther and amide surface groups, i.e. –COSR and –CONHR, with yields of approximately 50 and 75% for the reaction with DME and EDA, respectively. Preliminary adsorption experiments showed that these materials can efficiently remove metals such as Pb^{+2}, Cu^{+2} and Ni^{+2} from aqueous medium.

Keywords: *activated carbon, surface modification, functionalization, cation exchange, heavy metals*

1. Introduction

Surface modification[1] has a fundamental role on the application of organic and inorganic supports in industrial and environmental processes, such as selective purification processes, gas separation, solvent recovery, drinking water purification, adsorption of taste, odor and other micro-pollutants[2], ion exchange properties for metal adsorption[3], catalyst preparation[4], adhesion phenomenon[4,6], electrode modification[7] and polymer technologies[8].

Activated carbon is one of the most important industrial adsorbent/support and can be prepared by carbonization and activation of a large number of raw materials such as coconut shells, wood, peat and coal. These carbons show high-developed porous structure and a large internal specific surface area, which is generally greater than 400 m^2/g but often exceeds this value, reaching 1000 m^2/g [3-5]. Due to this high surface area and porous structure[9] it can adsorb gases and compounds dispersed or dissolved in liquids[10,11]. The type of contaminant to be adsorbed and the adsorption/remotion efficiency of these carbons is strongly dependent on their surface chemical features. Therefore, the surface chemical modification of carbon is of great interest in order to produce materials for specific applications. This modification has been mainly carried out by oxidative methods, producing a more hydrophilic structure with a large number of oxygen-containing groups. Various reagents have been used as oxidants: concentrated nitric or sulfuric acid, sodium hypochlorite, permanganate, bichromate, hydrogen peroxide, transition metals and ozone-based gas mixtures[12]. It was found that the type of surface structures and the extent of their formation depends on the oxidizing agent, the concentration and the pH of the oxidizing solution[13-15]. Although the creation of oxygen groups on the carbon surface

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is relatively well known, the functionalization with S and N containing molecules has been much less investigated.

In this work the activated carbon surface was chemically modified in order to introduce oxygen, nitrogen and sulfur containing groups.

2. Experimental

2.1 HNO_3 Treatment (C/HNO_3)

The activated carbon (20 g, Aldrich Norit, 930 m^2/g) was treated with 100 ml of concentrated HNO_3 under reflux for 2, 4, 8, 16 or 38 h. After reflux, the resulting material was filtered and extensively washed with hot distilled water until the cleansing water pH was approximately 7. The carbons were dried in vacuum at 60 °C for 24 h.

2.2 Reaction of the Activated Carbon with Thionyl Chloride (C/HNO_3/$SOCl_2$)

The HNO_3 treated carbon (0.80 g) was dried under vacuum at 80 °C to remove water and other substance which could interfere on the reaction. The reaction was carried out with 5 ml benzene and 5 ml of $SOCl_2$ under reflux for 24 h. The mixture was dried in a rotatory-evaporator and extensively washed with benzene to eliminate residual $SOCl_2$.

2.3 Reaction with Ethaneditiol (EDT, $HSCH_2CH_2SH$) or 1,7-dimercapto-4-thioheptane (DMTH, $HSCH_2CH_2CH_2SCH_2CH_2CH_2SH$)

After treatment with $SOCl_2$ the material C/HNO_3/$SOCl_2$ (0.80 g) was reacted with 9 mmol of 1,2-ethaneditiol or 1,7-dimercapto-4-thioheptane in 5 ml of chloroform under reflux for 48 h. The product was washed extensively with $CHCl_3$ and separated by centrifugation.

2.4 Reaction with Etilenodiamina (EDA$H_2NCH_2CH_2NH_2$) or Triethyltetraamine ($H_2NCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$)

After treatment with $SOCl_2$ the material (0.80 g) was reacted with of the amine (2.6 ml) in 6 ml of chloroform under reflux for 48 h. The product was extensively washed with $CHCl_3$ and separated by centrifugation.

Thermogravimetric analyses were carried out in a Mettler TA 4000 System under N_2 or air flow with a heating rate of 10 °C/min. Infrared spectroscopic analyses were obtained in a FTIR Mattson Instrument using KBr. BET surface areas were obtained in a Quantachrome Nova 1200 equipment with the carbon samples treated at 200 °C under vacuum for 3 h.

2.5 Temperature Programmed Decomposition Coupled with a Mass Spectrometer (TPDMS)

The TPDMS experiments were carried out in a HP 5989 II mass spectrometer using 5 mg sample in a direct probe equipped with a heating system which was inserted in the MS chamber ($P = 6.10^{-6}$ Torr). The probe was heated at 5 °C/min up to 275 °C and all the volatile decomposition products were analyzed by the mass spectrometer.

2.6 Potentiometric Titration of the Carbon C/HNO_3 with NaOH

The carbon (0.1 g) suspended in 25 ml of distilled water was titrated with a 0.02 M NaOH solution with continuous stirring. The titration was carried out under nitrogen atmosphere to avoid interference of CO_2 from the air. NaOH solution was added stepwise in 0.5 ml in intervals of 5-10 min to allow the reaction to take place and the pH to stabilize.

3. Results and Discussion

3.1 Treatment with HNO_3

The controlled oxidation of the activated carbon was carried out with concentrated HNO_3 under reflux for different periods. After this treatment the obtained material was extensively washed with hot water and carefully dried in vacuum at 60 °C. For comparison, the untreated original activated carbon was also washed with water and dried under vacuum. The mass balance with the weight losses observed after different reflux times is shown in Fig. 1.

It can be observed that the weight loss increases with the reflux time, probably due to the oxidation of the activated carbon to gaseous products, e.g. CO_2, and water soluble derivatives such as mellitic acid[16].

Infrared spectroscopic analyses of the HNO_3 treated carbons (Fig. 2) showed strong absorption at approximately 1720 cm^{-1} (-C=O), 1550 cm^{-1} (-COO^-), 1250 cm^{-1} (-C-O) and

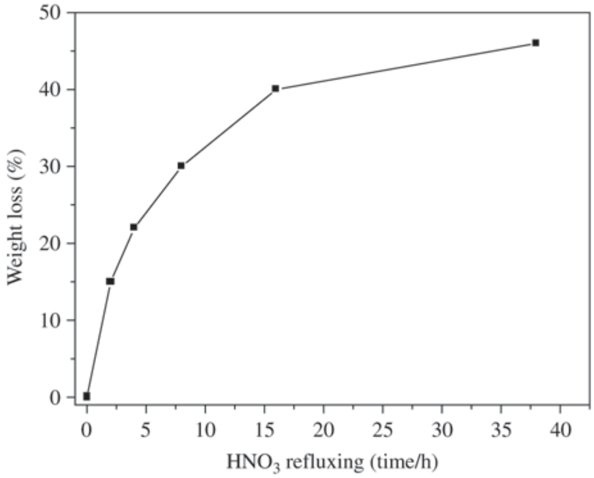


Figure 1. Weight losses after refluxing activated carbon with concentrated HNO_3 for different periods.

3450 cm^{-1} (-OH) which can be assigned to carboxylic acid groups[16].

The HNO_3 treated carbons were also analyzed by thermogravimetry. Figure 3 shows the TG profiles for the different HNO_3 treated carbons.

It can be observed that the untreated activated carbon showed very small weight decrease during TG analysis. On the other hand, the treated carbons showed significant weight loss after 200 °C. These weight losses observed for HNO_3 treated carbons have been assigned mainly to the decomposition of carboxylic surface groups and in a lesser extension to –OH groups according to the following processes[2,16]:

$$-COOH_{surf} \rightarrow CO_2$$

$$-OH_{surf} \rightarrow CO$$

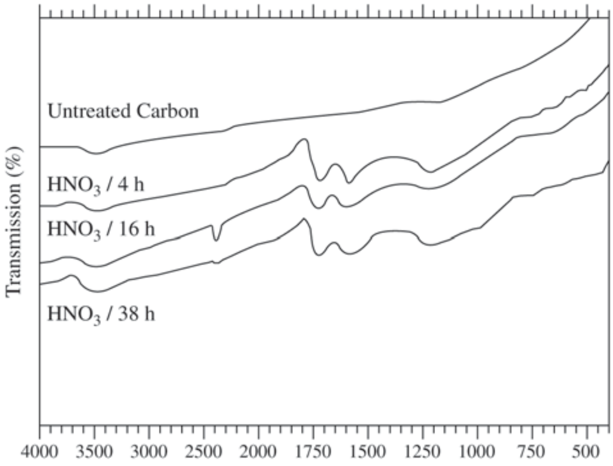


Figure 2. IR spectra of the HNO_3 treated carbons.

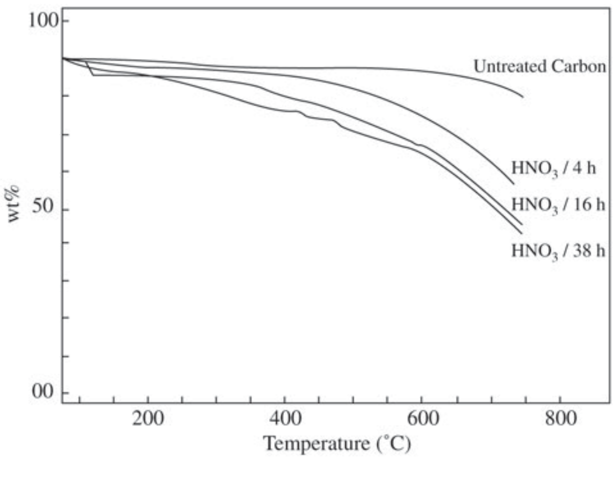


Figure 3. TG profiles for the different HNO_3 treated carbons.

To estimate the surface concentration of carboxylic groups, TG experiments were carried out keeping the temperature at 750 °C until no weight loss was observed. The total weight loss obtained from 200 °C was considered to be related to the amount of CO_2 formed. It was also carried out potentiometric titrations of the carbons with NaOH to obtain the number of acid sites.

The number of acid (COOH) sites for the different reflux time obtained by both TG and NaOH titration is displayed in Fig. 4.

It can be observed that up to 8 h reflux with HNO_3 the –COOH concentration increases to *ca.* 2-4 . 10^{21} sites/g, but it remains approximately constant even if the carbon is

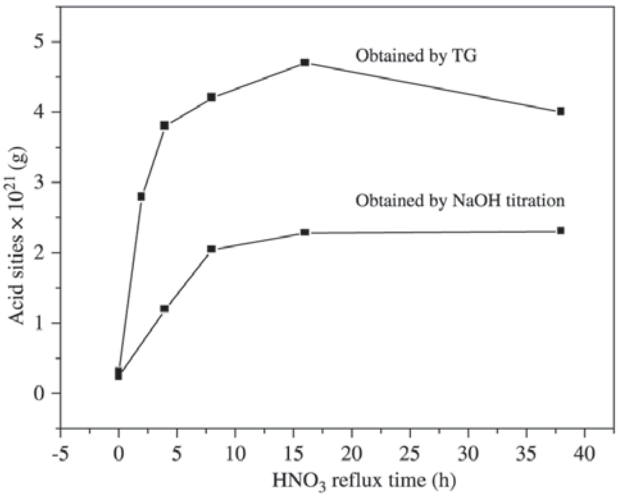


Figure 4. Acid sites concentration (as –COOH) on carbon surface for the different reflux time.

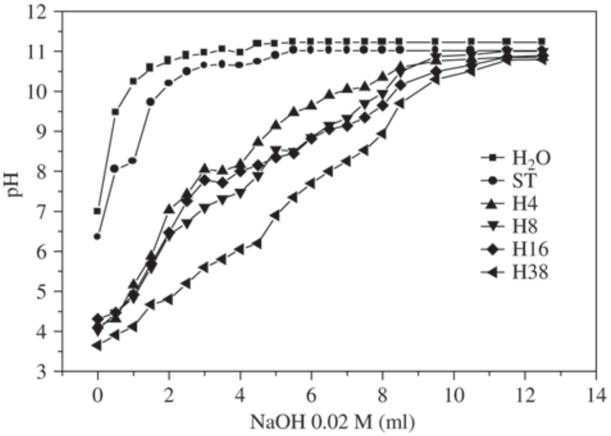


Figure 5. Potentiometric titration of the carbons C/HNO_3 with NaOH (0.02 M).

further refluxed with HNO_3.

Figure 5 shows the NaOH titration curves. The obtained titration curves suggested that the number and the strength of surface acid sites tends to increase as the reflux time in HNO_3 increased. For example, the carbon treated for 38 h with concentrated HNO_3 showed the strongest acid sites whereas the treatment for 2-16 h did show much difference. Moreover, it can be observed the presence of two or more inflection points in the titration curve, which suggests the presence of sites with different acid strength.

It was also investigated the effect of the HNO_3 treatment on the carbon surface area (Table 1).

The oxidation with concentrated HNO_3 has a strong effect on the carbon surface area, decreasing from 912 for the untreated carbon to 605 m^2/g after 38 h reflux. This decrease in surface area is related to the destruction of the porous structure caused by the severe oxidation with concentrated nitric acid.

These results suggest that a treatment with reflux time of 2 up to 8 h, will not strongly affect the activated carbon properties, since it produces a high concentration of surface acid sites, causes low weight losses and a relatively low decrease on surface area.

3.2 Adsorption Properties of –COOH Functionalized Carbons

The adsorption of chlorobenzene from water onto the carbons treated with HNO_3 for different reflux time is shown in Fig. 6.

The treatment with HNO_3 almost inhibit the adsorption of chlorobenzene. This is likely related mainly to presence of –COOH groups, which gives to the hydrophobic carbon surface a strong hydrophilic character.

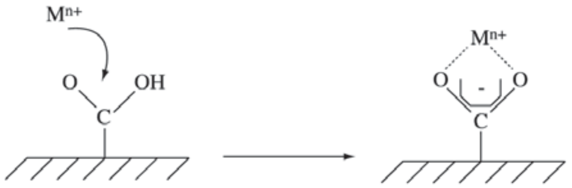
On the other hand, the presence of these –COOH surface groups strongly increases the adsorption capacity for metal cations in water (Fig. 7).

It can be observed that as the –COOH surface concentration increases the adsorption capacity also increases, suggesting that the adsorption is probably taking place at the carboxylic groups via a cation exchange mechanism.

The following cation adsorption order was observed $Pb^{+2} > Cu^{+2} > Ni^{+2} > Cd^{+2} \sim Co^{+2} > Ca^{+2}$, suggesting that the stability of the surface complex formed is important for the adsorption of the cation. In fact, the adsorption capacity is very well correlated with the stability constant of cation

Table 1. BET N_2 surface area for the HNO_3 treated carbons.

HNO_3 treatment time (h)	BET surface area (m^2/g)
0	912
2	831
4	821
8	792
16	722
38	605



Scheme 1. Cation exchange mechanism with the carbon surface carboxylic groups.

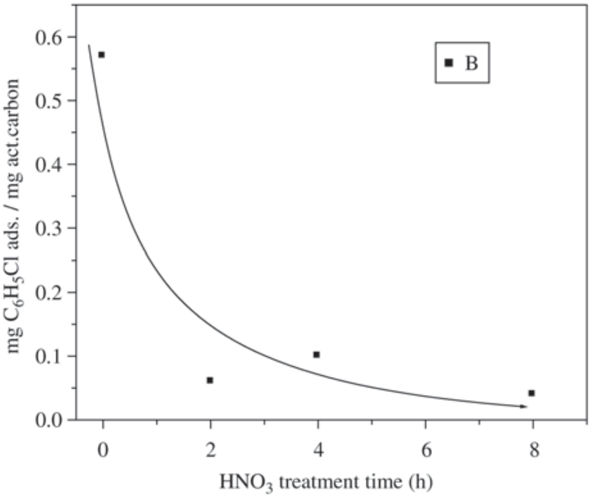


Figure 6. Chlorobenzene adsorption capacity on carbon treated with HNO_3 for different reflux time.

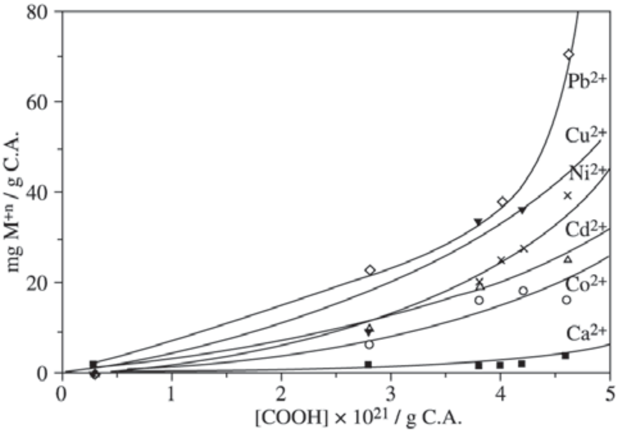


Figure 7. Metal cations adsorption on functionalized activated carbons.

complex formation with acetate (a model for the surface –COO$^-$ groups) in solution:

$$M^{+2} + CH_3COO^- \leftrightarrow [M(CH_3COO)]^+ \quad \boldsymbol{K} = \frac{[M(CH_3COO)]^+}{[M^{+2}].[CH_3COO^-]}$$

Figure 8 shows the correlation of the stability constants with the adsorption capacities.

It can be observed that as the stability (log K) increases the adsorption capacity of the carbons increases linearly.

This excellent cation exchange properties shown by these carbon containing –COOH surface groups makes them promising adsorbents to remove metal contaminants in aqueous effluents.

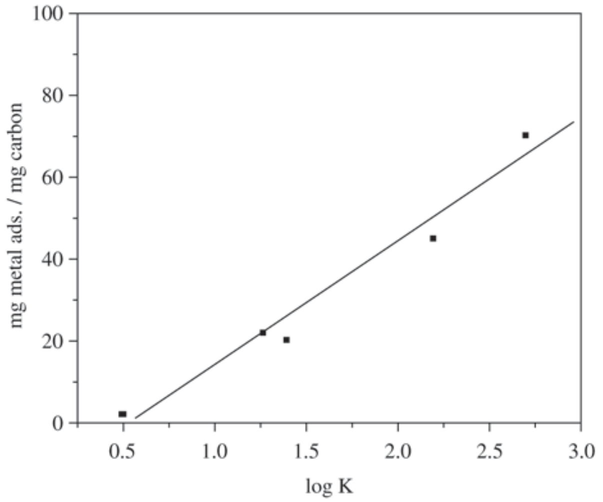


Figure 8. Stability constants versus adsorption capacity for the different metal cations onto 16 h reflux treated carbon.

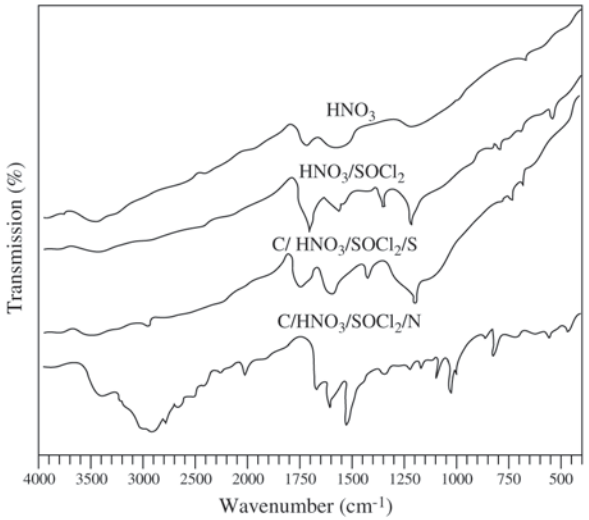


Figure 9. IR spectra for the (a) carbon treated with HNO_3 (8 h); (b) after reaction with $SOCl_2$, followed by reaction with; (c) $HSCH_2CH_2SH$ (EDT) or (d) $H_2NCH_2CH_2NH_2$ (EDA).

3.3 Carbon Surface Functionalization.

Functionalization of carbon surfaces with S and N containing groups have been carried out by different methods such as: treatment with sulfur[17] and CS_2 [18] at high temperatures, direct reaction of surface COOH groups with H_2NR compounds[19] and direct surface deposition of pyrazolone derivatives[20]. However, these proposed methods show in general complex procedures with low efficiency. Hereon, it is described a simple and versatile method for the introduction of heteroatoms such as S and N containing molecules onto carbon surface.

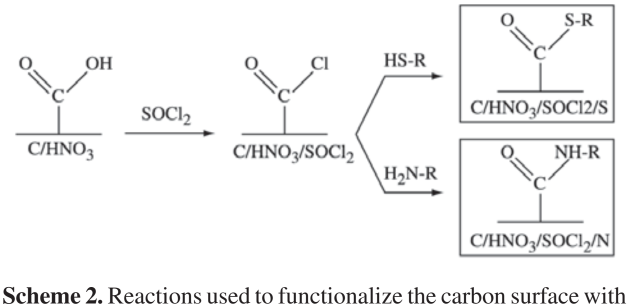
The following reaction scheme was used to introduce S and N groups on the carbon surface starting from the –COOH groups.

The S and N molecules used in this work are described in Table 2.

The IR spectra obtained for the –COOH, -COCl intermediates and the materials obtained by the reaction with EDT and EDA are shown in Fig. 9.

After the reaction with $SOCl_2$, the IR spectrum (Fig. 9b) showed new and well defined bands at approximately 1700, 1350, 1210 and 790 cm^{-1} which are clearly related to the formation of the group –COCl. The IR spectrum for C_6H_5COCl shows exactly the same bands. On the other hand, it can also be noticed the presence of the original bands, which might be indicating that not all the –COOH groups present on the carbon surface reacted with $SOCl_2$ [21].

The IR spectrum of the carbon after reaction with EDT (Fig. 9c) suggests the occurrence of the reaction of –COCl with the HSR compound to form –COSR. Typical bands of –COCl disappeared and well defined absorptions at 1400, 1200, 750 and 700 cm^{-1} related to the EDT molecule are observed. The IR spectrum for the material obtained by the reaction with EDA (Fig. 9d) also suggested the reaction of HNHR with the surface group –COCl, with the presence of



Scheme 2. Reactions used to functionalize the carbon surface with S and N groups.

Table 2. S and N molecules grafted on carbon surface.

Molecule	Formulae
1,2-ethaneditiol (EDT)	$HSCH_2CH_2SH$
1,6-dimercapto-4-thioheptane (DMTH)	$HSCH_2CH_2CH_2SCH_2CH_2CH_2SH$
1,2-diaminoethane (EDA)	$NH_2CH_2CH_2NH_2$
Triethyltetraamine (TEA)	$H_2NCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$

the following bands: ~1720 cm^{-1} (-C=O), 1675 and 1600 cm^{-1} (-N-H), 1520 cm^{-1} (-RCONHR), 950-1000 cm^{-1} (DTE characteristic bands) and 1200 cm^{-1} (-C-N) and 3000-3500 cm^{-1} (N-H). Similar results have been observed for the functionalization with DMTH and TEA, with the presence of bands typical of –COSR and –CONHR groups and also characteristic absorption presented by the R groups.

3.4 Thermogravimetric Analyses of the Functionalysed Carbons

TG analyses of the DMTH and TEA functionalysed carbons are shown in Fig. 10

It can be observed for the EDT functionalyzed material in Fig. 9b a weight loss of *ca.* 46% centered at 250 °C. From this weight loss it is possible to estimate the concentration of the EDT groups grafted on the carbon surface of approximately 2 mmol/g of carbon. Therefore, considering the –COOH concentration of *ca.* 4.10^{21} sites/g this weight loss suggests that approximately 50% of these sites have been actually converted to the thio surface group $-COSCH_2CH_2SH$. From the EDA analysis (Fig. 9c), the weight loss of 62% at the temperature 300 °C, it can be estimated a concentration of surface groups of 3.4 mmol/g of carbon corresponding to a yield of approximately 75%. For both analyses the weigh losses observed at temperatures higher than 500 °C are related to the oxidation of the carbon by air.

3.5 Temperature Programmed Decomposition/Mass Spectrometry Experiments (TPDMS)

In these TPDMS experiments the functionalized carbons were heated in a He flow at 10 °C/min and upon the thermal decomposition the volatile products were analyzed by a mass spectrometer. The results are displayed in Fig. 11.

The TPDMS profile show two peaks in the total ion signal (TIC) centered at 150 and 225 °C. It was observed that the peak at 150 °C is composed by several m/z fragments such as 182 ($HSCH_2CH_2CH_2SCH_2CH_2CH_2SH^+$) (Fig. 11) and 74 ($CH_2CH_2CH_2SH^+$) suggesting that these fragments originate from the thermal decomposition of the surface DMTH group, which is released to the gas phase and detected by the mass spectrometer. The TPDMS peak at 225 °C is composed by a m/z signal 44, CO_2, formed by the thermal decomposition of –COOH surface groups. Similar TPD profile was obtained for the HNO_3 treated carbon.

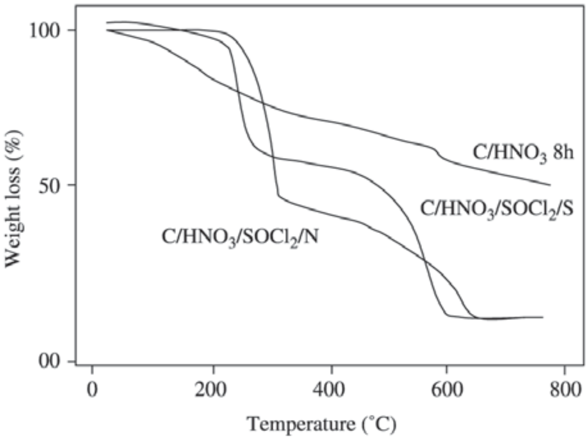


Figure 10. TG analyses of the (a) HNO_3; (b) EDT; (c) EDA functionalyzed carbons in air.

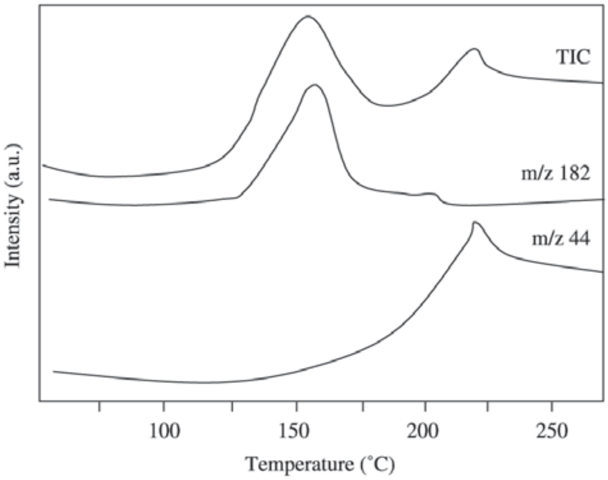


Figure 11. TPDMS experiment with the DMTH functionalised carbon.

4. Metal Adsorption

These sulfur and nitrogen functionalyzed carbons show great potential for the adsorption of heavy metals such as Hg^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} ions due to the presence of surface –SH and –NH groups[22]. The materials obtained in this work

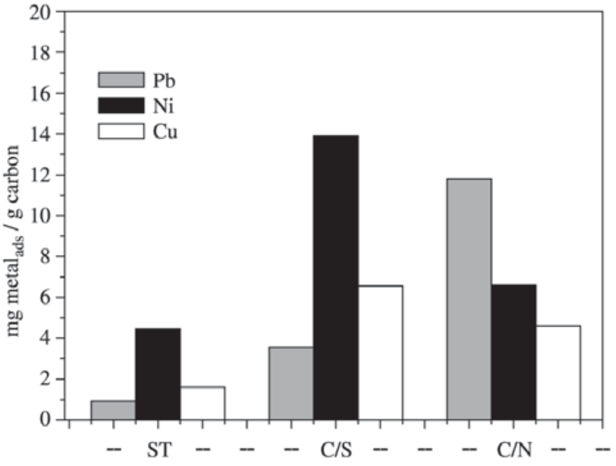


Figure 12. Adsorption of Pb^{+2}, Cu^{+2} and Ni^{+2} in aqueous solution on untreated carbon (ST) and on the EDT (C/S) and EDA (N/C) functionalyzed carbons.

were also tested for the adsorption of Pb^{+2}, Cu^{+2} and Ni^{+2} in aqueous solution. The comparison of the adsorptions on the untreated carbon, the EDT (C/S) and EDA (N/C) functionalyzed carbons are shown in Fig. 12.

It can be seen that the functionalization of the carbon strongly increases its adsorption for the different metals studied. The results suggested that the EDT funtionalyzed material can adsorb more efficiently Ni^{+2} whereas the EDA carbon showed a stronger interaction with Pb^{+2} cations.

5. Conclusion

Activated carbon can be tailored by surface chemical modification to produce materials with unique properties and for specific applications. These modifications can be carried out via the key surface intermediate: -COOH. The carbon containing –COOH groups shows excellent cation exchange properties and can be used as adsorbent for metal contaminants in water. These –COOH$_{surf}$ groups can be converted to -COCl $_{surf}$ which is a very reactive and versatile group for the grafting of other molecules onto the carbon surface. From this acylchloride intermediate several S and N molecules, for example HSR and HNR_2, can be easily bounded to the carbon surface. These S and N functionalized carbon show great potential as adsorbent of metals, specially heavy metals which represent a serious environmental problem nowadays.

Acknowledgements

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