

FUNCTIONALIZATION OF ACTIVATED CARBON BRIQUETTES

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Introduction

The surface chemistry of activated carbons has been extensively studied due to its importance for many applications [1]. Carbon functionalization with oxygen, nitrogen and sulfur groups has been widely investigated [2, 3]. Surface oxygen containing groups such as carboxylic, phenolic, lactone, ether, pyrone, chromene, are by far the most important being responsible for several properties of carbons such as hydrophilicity, acidic, redox and catalytic.

In this work, it was studied the functionalization of briquettes by two simple reactions, *i.e.* the oxidation with HNO₃ and the sulfonation with H₂SO₄/SO₃. Functionalized activated carbon briquettes may present several technological applications, for example in the adsorption of especial molecules or metallic ions. Hereon it is investigated whether these classical reagents HNO₃ and H₂SO₄/SO₃ are capable of functionalizing the carbon located in the most internal part of the briquettes.

Experimental

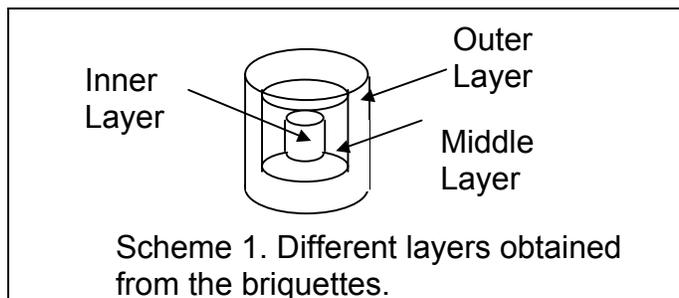
The briquettes (1 g, 10 mm diameter x 13 mm length) have been prepared from chars obtained from two different precursors, eucalyptus and poplar trees, using concentrate grape must as binder (binder:char ratio of 1:4) in a mold held in a hydraulic press at 1400 kg cm⁻². The briquettes were thermally treated at 15 K/min up to 1153 K under N₂ flow, and activated with steam (1.7 g_{H₂O} g_{carbon}⁻¹ h⁻¹) for 105 min in a stainless steel reactor. Detailed characterization of these briquettes have been published elsewhere [4].

The oxidation with concentrated HNO₃ was carried out under reflux for 15 and 60 min. After reaction the carbons were extensively washed with water until the pH rinsing water was neutral. The sulfonation reaction used fuming sulfuric acid for 1 h at 298 and 353 K. The obtained materials were dried in oven at 333 K for 24 h. The number of acid sites was determined by acid-base titration according to the literature [5]. The obtained briquettes were separated using a blade into three layers: outer, middle and inner layer, all with same weight.

The obtained materials were analyzed by TG (Metler, 10 K/min, N₂), BET (Quantachrome Autosorb 1, 77K, N₂), IR (Perkin Elmer).

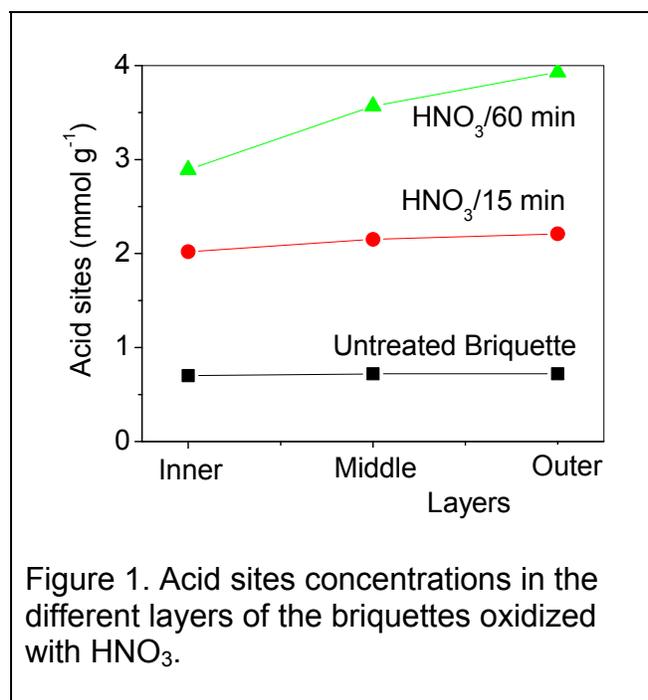
Results and Discussion

The activated carbon briquettes were functionalized by oxidation with HNO_3 and sulfonation with $\text{H}_2\text{SO}_4/\text{SO}_3$. To investigate whether the more internal layers of carbon were functionalized, the briquettes were divided into three layers according to Scheme 1.



The functionalization of eucalyptus carbon briquettes with concentrated HNO_3 was carried out by reactions under reflux for 15 and 60 min. The different layers (outer, middle and inner) for the original and the functionalized briquettes, were analyzed by IR, TG, BET and acid titration. The IR spectroscopic analyses of the different layers clearly shows the presence of strong bands at ca. 3440 and 1720 cm^{-1} characteristic of COOH groups formed by the oxidation with HNO_3 . It was also observed bands located at ca. 1595 cm^{-1} likely related to NO_2 groups produced by the nitration of the carbon. TG analysis of the original briquette does not show any significant weight loss up to 400°C . On the other hand, the oxidized carbons, especially the outer layer of $\text{HNO}_3/60\text{ min}$ shows a ca. 20% weight loss in the temperature range $393\text{--}673\text{ K}$ due to the decomposition of the COOH and $-\text{NO}_2$ groups to produce CO_2 and NO_2 . The acid site concentrations in the different layers of the briquettes oxidized with concentrated HNO_3 are shown in Figure 1.

It can be observed that the original briquette shows approximately 0.7 mmol acid sites per gram of carbon, homogeneously distributed in the different layers. As the briquette was treated with HNO_3 for 15 min the number of acid sites increased to ca. 2 mmol g^{-1} , also homogeneously distributed in the layers. On the other hand, for the oxidation for 60 min the increase in the concentration of acid sites is much more pronounced in the outer layer (ca. 4 mmol g^{-1}) whereas the inner layer showed only 3 mmol g^{-1} . These results suggest that for longer reaction times the functionalization of the carbon occurs preferentially on the briquettes surface.



The treatment with HNO_3 for 60 min also caused a significant decrease on the surface area from ca. $780\text{ m}^2\text{ g}^{-1}$ for the different layers of the original briquette to 484 , 466 and $421\text{ m}^2\text{ g}^{-1}$ for the outer, middle and inner layers, respectively.

The carbon briquettes were also submitted to sulfonation with fuming sulfuric acid ($\text{H}_2\text{SO}_4/\text{SO}_3$). In this study it was used briquettes made with char from poplar wood. It is interesting to observe that the poplar briquettes were not homogeneous in the different layers.

Acid titration showed that the more external layer had a higher concentration of acid sites of 2.2 mmol g^{-1} compared to the inner layer, 1 mmol g^{-1} . Moreover, the surface area also decreases from $621 \text{ m}^2 \text{ g}^{-1}$ for the outer layer to $578 \text{ m}^2 \text{ g}^{-1}$ for the inner layer. These results suggested that during the activation process of the outer layer of the briquette was more efficient due the better contact between solid and gas phase.

Figure 2 shows that no significant sulfonation was observed throughout the briquette even after 4 h reaction. On the other hand, when powder activated carbon was sulfonated a high concentration of acid sites, 5 mmol g^{-1} , was produced.

These results suggest that the compacted activated carbon in the briquette form hindered the sulfonation reaction. This is likely related to the high viscosity of fuming sulfuric acid (6 mPa s^{-1}) which cannot penetrate the body of the briquette.

Conclusions

The surface oxidation of activated carbon briquettes with HNO_3 can be carried out homogeneously throughout the briquette body whereas sulfonation does not take place. Apparently the high viscosity of the fuming sulfuric acid hinders its penetration into the internal surface of the briquette.

References

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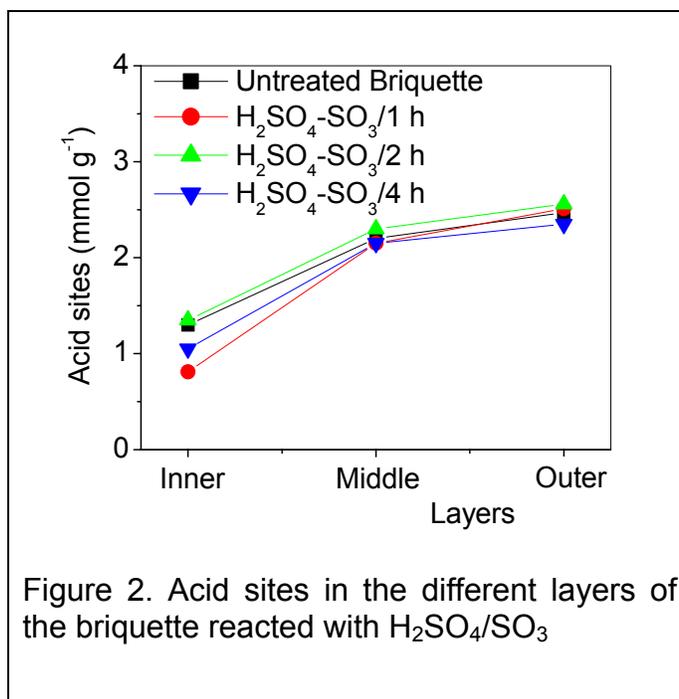


Figure 2. Acid sites in the different layers of the briquette reacted with $\text{H}_2\text{SO}_4/\text{SO}_3$