

# REMOVAL OF NO<sub>2</sub> ON ACTIVE CARBONS OBTAINED FROM WASTE TIRES

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## Introduction

The production of scrap tires only in the EU, USA and Japan is around 6 million tones per year. As the associated automotive industries grow the huge quantity of waste tires presently produced in the world will certainly increase in the future [1].

Thus the disposal of scrap tires becomes a serious environmental problem. The production of activated carbons from solid wastes is one of the most environment-friendly solutions by transforming negative-valued wastes to valuable materials.

Waste tires have a high content of volatile matter as well as fixed carbon that makes them an interesting solid as a fuel for energy production or hydrogenation processes and moreover in pyrolysis processes to obtain different fractions of solid, liquid, and gaseous products [2]. The product obtained by pyrolysis of material in which around 30-40% is the rubber from tire, could be a suitable precursor for activated carbon production.

The activated carbons produced from rubber tire could have commercial value in the water purification e.g. in dissolving organics and toxic compounds, dechlorination, dye removal, municipal drinking water treatment, as well as in the air purification e.g. volatile inorganic and organic removal, solvent recovery, gas desulfurization, etc. [2,3] Moreover they can be useful in special application such as batteries, fuel cells, and others such as cigarette filters and food industry.

The main aim of the study was to obtain active carbon adsorbents from waste tires by their treatment with CO<sub>2</sub> or KOH and test the adsorbents obtained in the process of nitrogen dioxide removal. Also the effects of the pyrolysis temperature on the sorption properties of the char adsorbents obtained were analysed. Pyrolysed and active carbon samples obtained were tested for NO<sub>2</sub> adsorption in dry conditions.

## Experimental

The starting scrap tires (O) were ground with a roller mill and sieved to a uniform size range of 1.5–2.5 mm. Next they were subjected to carbonization and/or activation processes. The pyrolysis (K) was carried out in a horizontal furnace under a stream of argon with a flow rate of 170 mL/min. The sample was heated (5 °C/min) from room temperature to the final pyrolysis temperature of 550 °C and 800 °C (K550 and K800), respectively maintained for 1 h. Chemical activation

(with potassium hydroxide – A800KOH) or physical activation (with carbon dioxide-A800CO<sub>2</sub>) were taken at 800 °C, respectively.

The elemental analysis of the starting sunflower husks and chars were performed on an elemental analyser CHNS Vario EL III (Elementar Analysensysteme GmbH, Germany).

Evaluation of NO<sub>2</sub> sorption capacity: Samples were packed into a glass column (length 300 mm, internal diameter 9 mm, bed volume 3 cm<sup>3</sup>). Dry air with 0.1% of NO<sub>2</sub> was passed through the column of adsorbent at 0.450 L/min. The breakthrough of NO<sub>2</sub> were monitored using Q-RAE PLUS PGM-2000/2020 with electrochemical sensors. The tests were stopped at the breakthrough concentration of 20 ppm. The interaction capacities of each sorbent in terms of mg of NO<sub>2</sub> per g of adsorbent were calculated by integration of the area above the breakthrough curves, and from the NO<sub>2</sub> concentration in the inlet gas, flow rate, breakthrough time, and mass of adsorbent [4].

## Results and Discussion

According to the results presented in Table 1, the elementary components of waste tires are carbon, oxygen, hydrogen and sulphur.

**Table 1. Elemental Analysis of Investigated Samples (wt%).**

Sample	Ash	C	H	N	S	O <sup>dif*</sup>
O	3.8	84.3	7.6	0.5	1.9	5.7
OK550	6.5	83.0	1.4	0.4	1.7	13.5
OK800	4.4	78.5	0.5	0.3	2.4	18.3
OA800CO <sub>2</sub>	9.8	87.3	0.5	0.3	2.1	9.8
OA800KOH	4.2	93.2	0.5	0.3	0.4	5.4

\*by difference

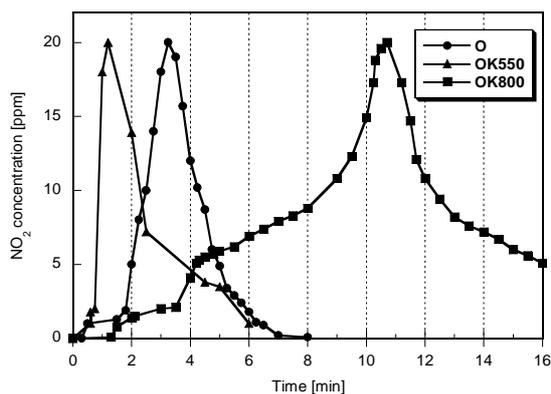
In non modified sample (O) carbon, oxygen and hydrogen make over 90 wt.% of the sample, while the rest is mainly sulphur and some nitrogen. The content of ashes is very small. In the case of modified samples it is well seen that the method of preparation markedly influences the elementary composition. The pyrolysis of above samples (OK550 and OK800, respectively) leads to small changes in carbon content joined with decrease in hydrogen content. Furthermore, amount of sulphur and nitrogen is in the same level, whereas the amount of oxygen dramatically increases, what can be caused by degasification process. In case of activated samples a differences in chemical and physical kind of the process can be clearly seen. It is worth to notice that chemical treatment cause changes in the proportions of elements. Physical activation (OA800CO<sub>2</sub>) leads to a small changes in oxygen content and the amount of hydrogen decreases, as compared with non modified sample (O). Accordingly, chemical process (OA800KOH) cause increase in carbon content and the amount of sulphur decreases.

**Table 2. NO<sub>2</sub> Breakthrough Capacities and Surface pH Values for the Initial and Exhausted Samples in Dry Conditions.**

Sample	NO <sub>2</sub> breakthrough capacity		pH	
	mg/g of ads	mg/cm <sup>3</sup> of ads	Initial	Exhausted
O	1.7	0.5	7.65	4.21
OK550	0.7	0.2	6.78	5.32
OK800	5.7	1.5	6.28	3.31
OA800CO <sub>2</sub>	2.3	0.7	8.42	8.05
OA800KOH	11.4	1.8	7.96	3.18

All the char samples produced were tested for the NO<sub>2</sub> adsorption in dry conditions. Table 2 presents the calculated NO<sub>2</sub> breakthrough capacities of investigated samples and surface pH values for the initial and exhausted samples. According to above data, the chars modified in higher temperatures, pyrolysis as well as chemical activation, are characterized with high values of capacity comparing to the all the rest samples. However, the non modified material shows the middle value of breakthrough capacity what may be caused by the presence of different surface functional groups which may bond with the NO<sub>2</sub>. Moreover, in case of all investigated samples even small values of NO<sub>2</sub> adsorbed lead to a decrease in pH of the exhausted samples relative to that of the initial ones. It is clearly seen, that the sample with the highest NO<sub>2</sub> breakthrough capacity is characterized with the lowest pH value. The similar observation were taken in previous reports with the samples obtained on the base of sawdust pellets [5].

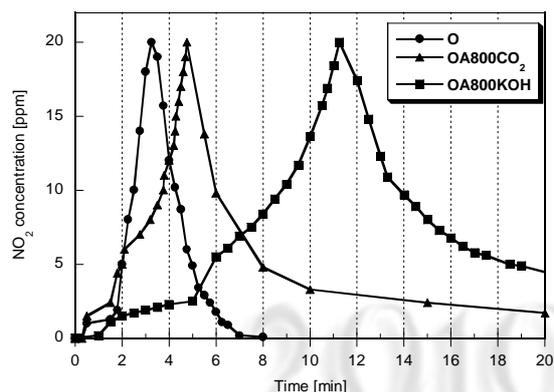
Fig. 1 and 2 present the NO<sub>2</sub> breakthrough curves recorded in dry conditions.



**Fig. 1** NO<sub>2</sub> breakthrough curves for raw and pyrolysed samples.

The shapes of all NO<sub>2</sub> breakthrough curves samples exhausted in dry condition are very similar and indicate that the samples carbonized at 800 °C show better performance as

NO<sub>2</sub> adsorbents. Moreover, the sample obtained as a result of chemical activation (OA800KOH) show the highest performance as NO<sub>2</sub> adsorbent. For NO<sub>2</sub> removal the pyrolysis temperature effect the performance but this influence is not significant. Surprisingly, the samples obtained as a result of physical activation at 800 °C (OA800CO<sub>2</sub>) shows the lowest value of NO<sub>2</sub> removal capacity. The highest values of NO<sub>2</sub> breakthrough capacities are obtained for the samples labeled as OK800 and OA800KOH, respectively. In case of above samples similarities in the specific shapes of the breakthrough curves can be noticed.



**Fig. 2** NO<sub>2</sub> breakthrough curves for raw and activated samples

Relatively early in experimental run, they show an increase in concentration of NO<sub>2</sub>, followed by a slow down in its release demonstrated as a plateau. The above phenomena must be related to the surface chemistry, specially the activation of the surface active sites.

## Conclusions

The obtained results indicate that sorption capacity depends on both way of activation as well as conditions of the adsorption process.

## References

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