Activated carbons from oil-fired fly ashes

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Introduction.

The aim of this investigation is to prepare activated carbons with good sorbent characteristics from oil-fired fly ash, looking for suitable activation processes to produce surface sites with high reactivity on the carbonaceous matrices [1-4]. In particular, the nitrogen surface sites, formed by gaseous ammonia reaction at 800°C, could greatly increase the adsorption of gaseous species with acidic characteristics, enhancing the overall efficiency of the treatment process of the flue gases [2].

Experimental.

An oil-fired fly ash (after an extraction with xylene) was treated with acidic solutions ([1]) and submitted to a CO_2 activation step at 900°C. The carbon obtained was then treated at 900°C with a gaseous mixture obtained by vaporisation of aqueous solutions containing between 2% and 8% ammonia ([2]). Several activated carbon samples were obtained that were characterised by detecting surface areas (S_{N2} and S_{CO2}), content of surface sites with acidic or basic characteristics (by adsorption of diphenylguanidine and of benzoic acid, [22-24]) and nitrogen and oxygen percentage. The adsorption of SO_2 (SO_2=2000 ppm, NO_X=350 ppm, O_2=3%, water vapour=10% and N_2) on the carbon samples was checked a 100°C using a fixed bed reactor. The SO_2 adsorbed was detected by desorption with N_2 flow at 360°C bubbling in quartz traps containing H_2O_2. By a method already reported [1, 12, 13], the sum of the amounts of SO_2 and NOx adsorbed is detected. In order to know the variations of the sorbent characteristics of the activated carbons, ten cycles of adsorption - desorption of SO_2 were carried out, as reported elsewhere [1, 2] on the activated carbon obtained by treatment at 900°C, vaporising a solution containing 5% NH_3.

Results and discussion.

The **Table** shows that the preliminary acidic treatment of the oil-fired fly ash with causes a marked decrease in its inorganic material (ash) content and a considerable increase in the BET surface area.
Surface areas S_{CO2} and S_{N2} of the activated carbons obtained as a function of the temperature of the thermal treatment and of the NH_3 amount are reported in Figure 1. Also if S_{N2} values do not show a high variation percentage, they reach a maximum when the treatment temperature is 900°C and the activation gaseous mixture is obtained by vaporisation of an aqueous solution containing 5% ammonia.
The percentage of oxygen and nitrogen in the carbonaceous matrices as a function of the treatment temperatures and of the percentage of ammonia in the vaporised solutions is reported in Figure 2. When the temperature is increased, the percentage of oxygen shows a slight decrease, while the ammonia has a negligible effect. The percentage of nitrogen shows variations both with temperature and with quantity of NH_3, reaching a maximum when the temperature is 900°C and the quantity of NH_3 in its aqueous solution is 5%.
The quantity of benzoic acid and diphenylguanidine adsorbed is reported in Figure 3 as a function of the thermal treatment temperature and the quantity of ammonia. The adsorption of diphenylguanidine is small and remains practically constant, while quantity of benzoic acid increases with the temperature and reaches a maximum when the temperature is 900°C and the amount of ammonia in the solution is 5%.
Figure 4 shows an increasing relationship between the sulphur dioxide adsorbed at 100°C by all of the activated carbons and their nitrogen content. Thus the presence of nitrogen surface groups (having basic characteristics more enhanced than the surface oxygenated groups, [2]) appears to be a predominant parameter in the SO_2 adsorption process on activated carbon.
Submitting the activated carbon obtained by treatment at 900°C with 5% NH_3 solution to some SO_2 adsorption-desorption cycles we observe (figures are not reported) that the treatment with ammonia

causes the formation of a carbon type that not only adsorbs more SO_2, but its sorbent characteristics have a lower decrease during its utilisation in cyclic processes of SO_2 adsorption and desorption.

Conclusions.

The activated carbons prepared by treatment of an oil-fired fly ash treated with CO_2 a 900°C and then at 850°C - 950°C with gaseous flows obtained by vaporising aqueous solutions containing NH_3 (from 2% to 8%) show to have nitrogen groups bonded on the surface. The use of a solution containing 5% NH_3 and a treatment temperature of 900°C seem to favour the formation of a type of activated carbon containing a larger amount of nitrogen surface groups with basic characteristics that increase its SO_2 adsorption properties. By submitting this carbon to some SO_2 adsorption-desorption cycles we observe that the ammonia treatment produces a carbon type that not only adsorbs more SO_2, but its sorbent characteristics have a lower decrease during its utilisation in cyclic processes of SO_2 adsorption and desorption. Then, the methodology just reported permits to prepare valuable activated carbons from oil fired fly ash, normally considered a waste product.

Table. Composition of the starting carbonaceous materials

Sample	C %,wt	H %,wt	N %,wt	S %,wt	Ash %,wt	O^a %,wt	$S_{CO_2}{}^b$ m^2/g	$S_{N_2}{}^c$ m^2/g	Particle size μm
A^d	74.95	0.45	0.85	2.36	11.34	10.05	40	15	53-74
B^e	86.58	0.30	0.90	1.32	0.75	10.15	41	24	53-74

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a) By difference.
b) Surface area detected by CO_2 adsorption at 273 K following the Dubinin–Radushkevich (DR) equation
c) Surface area detected by N_2 adsorption at 77 K following the classical Brunauer–Emmett–Teller (BET) equation.
d) Original particulate matter dried at 120°C for 24 h in N_2 flow.
e) Obtained from A by extraction with xylene and by subsequent treatment with aqueous solutions of HCl and HF (see Experimental Section).

References

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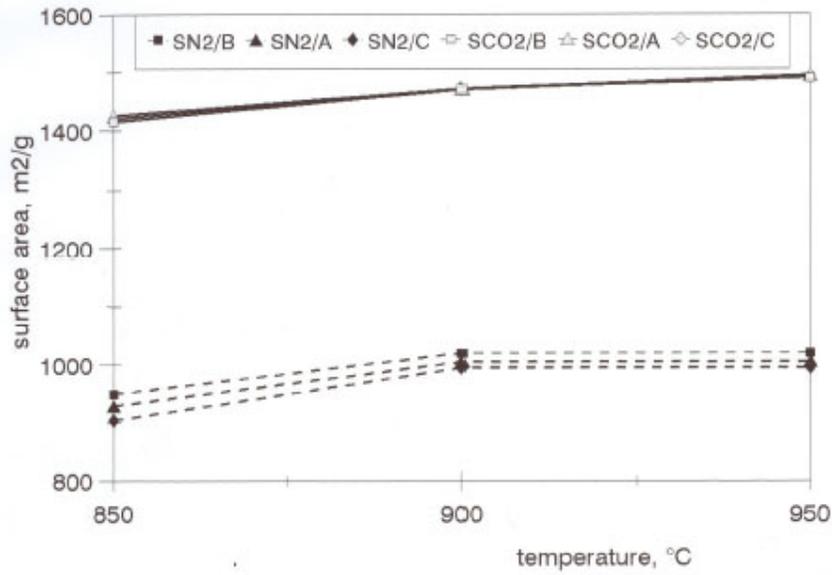12] Davini P. Carbon 1999;37(9):1363–71.
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Fig. 1

Figure 1. Surface areas of activated carbons versus the temperature and the percentage of vaporised solution of NH_3 (NH_3 content in the vaporised solution: A=2%, B=5%; C=8%).
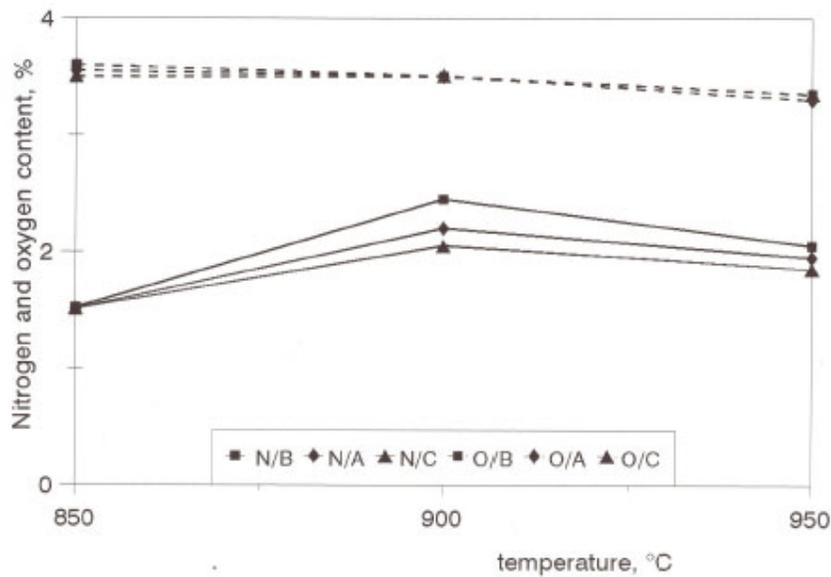

Fig. 2

Figure 2. Oxygen and nitrogen percentage versus the temperature and the percentage of vaporised solution of NH_3 (NH_3 content in the vaporised solution: A=2%, B=5%; C=8%).

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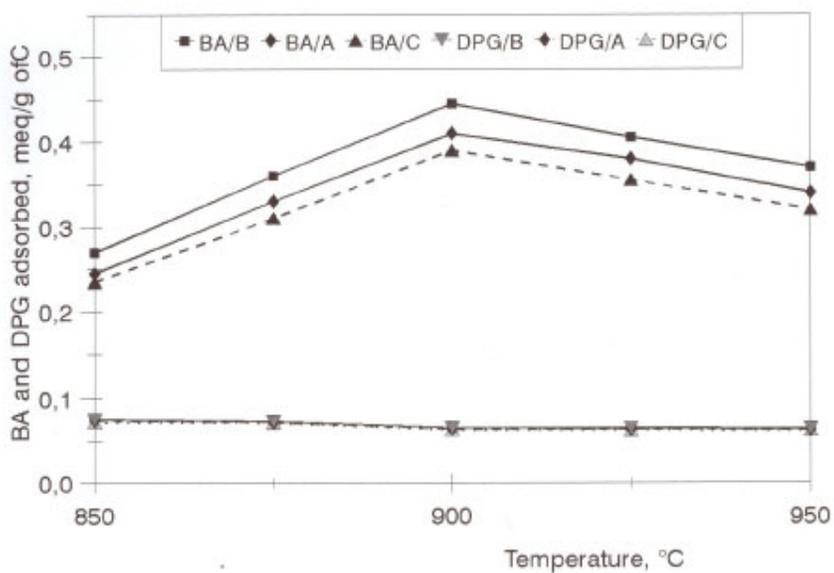Fig.3

Figure 3. Benzoic acid (BA) and diphenylguanidine (DPG) adsorbed versus the temperature and the percentage of vaporised solution of NH_3 (NH_3 content in the vaporised solution: A=2%, B=5%; C=8%).
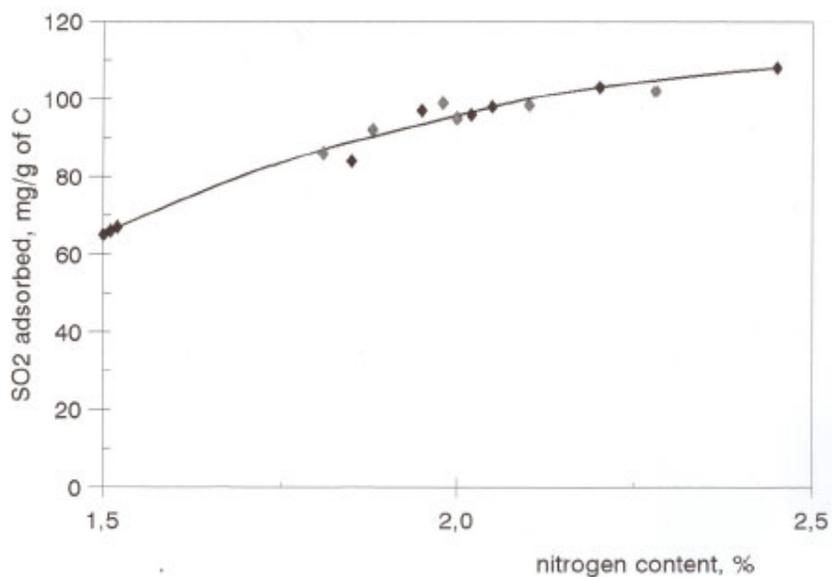

Fig.4

Figure 4. SO_2 adsorbed by the activated carbons versus their nitrogen percentage.