ELSEVIER

Effect of activated carbons modification on porosity, surface structure and phenol adsorption

G.G. Stavropoulos [a,*], P. Samaras [b], G.P. Sakellaropoulos [a,c]

[a] *Chemical Engineering Department, Aristotle University of Thessaloniki, TEI campus, P.O. Box 1520, 54006 Thessaloniki, Greece*
[b] *Department of Pollution Control Technologies, Technological Educational Institute of West Macedonia, 50100 Kozani, Greece*
[c] *Chemical Process Engineering Research Institute, 6th km Harilaou Thermi Road, 57001 Thessaloniki, Greece*

Abstract

The primary objective of this work was the examination of modified activated carbons with tailored adsorption capacity properties. Production of activated carbons with desired properties was accomplished by modification of surface functional groups and introduction of acidic/basic properties. Modification of an activated carbon was performed using partial oxygen gasification, nitric acid treatment, urea impregnation followed by pyrolysis and pyrolysis in a urea saturated stream. The surface properties of the produced samples were estimated by the multibasic titration method of Boehm and by the CO/CO_2 gas evolution profiles, while pore structure development was measured by the N_2 and CO_2 gas adsorption isotherms. Oxygen gasification resulted in samples with surface area slightly lower that the raw activated carbon; the introduction of surface functional groups depended upon the severity of the treatment: carbonylic and phenolic type groups were introduced in all partially gasified samples, while low temperatures and short reaction times enhanced the basic character of the carbon. However, nitric acid treatment resulted in the introduction of high nitrogen amounts in the samples, the reduction of surface area and the development of a surface containing carboxylic, lactonic, phenolic and carbonylic groups with negligible HCl neutralization capacity. Treatment of activated carbon by urea supported the formation of basic groups and carbonyls. The presence of surface functional groups affected the adsorption capacity of the produced samples for the removal of specific pollutants such as phenols. Urea treated samples with a basic character and high nitrogen content presented the highest phenol uptake capacity; nitric acid treated carbons and oxygen gasified samples presented an acidic surface functionality and a low phenol adsorption capacity. The beneficial role of nitrogen on phenol adsorption was attributed to adsorbate–adsorbent interactions.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Activated carbon modification; Oxidation; Urea treatment; Porosity; Surface structure; Functional groups; Phenol adsorption

1. Introduction

Activated carbons are efficiently used in several pollution control processes due to their high adsorption capacity. A large number of contaminants may be removed from a liquid or gas stream during their passage through an activated carbon bed. The activated carbon adsorption properties are attributed to its physical and chemical structure. High surface area and pore volumes as well as large percentage of micropores are typical characteristics of activated carbons; activated carbons with tailored properties for the adsorption of particular compounds may be manufactured by controlling the activation process conditions

[1]. Surface chemical composition is mainly designated by the oxygen functional groups, assigning a Brönsted acidic than a basic property. Surface functional groups responsible for the carbon character include carboxyl, carbonyl, phenol, quinone, lactone and other groups bound to the edges of the graphite-like layers [2]. The nature and concentration of these groups may be modified by various post-activation treatment methods [3], the most important been oxidation. Oxygen or air streams are used for gas phase oxidation while nitric acid, hydrogen peroxide [4], and other oxidants [5], are applied in liquid phase oxidation. In addition to functional groups, oxidation may affect the pore structure development. Alternative modification processes have been reported, such as ammonia, urea and other nitrogen containing substances [6].

The effect of surface functional groups modification on the adsorption behavior of activated carbons has been of great

* Corresponding author. Tel.: +30 2310 995918; fax: +30 2310 996168.
E-mail address: gstaurop@cheng.auth.gr (G.G. Stavropoulos).

interest over the past years. Due to the increasingly stricter air and water legislation, the interest for the preparation of activated carbons with certain surface functional groups has been arisen, for the removal of particular substances with a variety of chemical properties. Adsorption of phenol in activated carbons has been intensively investigated [7], but relatively less work is reported related to modified carbons [8–10].

The objectives of this work were the examination of the modification of activated carbon by using various methods, the investigation of the modification effects on the pore structure and surface properties of the products, and the determination of the optimum experimental conditions for the preparation of materials with desired surface properties and adsorption capacities. Special emphasis was given to the surface nitrogen compounds and the corresponding adsorption mechanisms, as the examination of these groups for the adsorption of specific compounds is limited.

2. Experimental

2.1. Sample preparation

Activated carbon CarboTech D45/2 supplied by DMT Modern Fuels Unit, Essen, Germany, was used as raw material. Raw carbon was milled and sieved to size less than 180 μm. The alternative treatment steps that were applied for the modification of activated carbon surface functional groups consisted in:

(a) liquid phase oxidation by nitric acid solution;
(b) thermal partial oxidation by oxygen;
(c) thermal treatment of urea pre-impregnated samples;
(d) thermal treatment under a urea saturated helium flow.

Thermal partial oxidation of commercial activated carbons was carried out in a fixed bed reactor made of 1.5-in. diameter 316 SS tube, with a porous disc of Hastelloy plate (pore diameter 50 μm). The flow diagram of the reactor system has been given elsewhere [11]. A mixture consisting of 5% (v/v) oxygen in helium (200 mL/min) was used for the gas phase oxidation and the reaction operating temperatures were 400 and 450 °C. Different reaction times were tested, 4 and 6 h, respectively, in order to investigate the effect of residence time on product properties.

Liquid phase oxidation took place by treatment of the raw activated carbon with nitric acid solution. About 100 mL of nitric acid solution were added to 2 g of coal in a glass beaker and the mixture was stirred for a certain reaction time at solution boiling point. The effect of acid solution concentration on the treatment efficiency was examined by using two different concentrations, 2 and 5 M, respectively. Subsequently, the carbon was filtered off, washed with distilled water and dried at 100 °C in an inert atmosphere.

The urea impregnation procedure included the addition of about 5 g of activated carbon samples in a glass beaker containing 150 mL of saturated urea solution. The mixture was stirred for 1 h at 60 ± 2 °C. The treated coal was then filtered off, washed by water to remove any excess of urea, and dried overnight

under a nitrogen flow at 100 °C. Nitrogen enriched carbons were then produced by carbonization of impregnated samples under a helium flow. The heat treatment was carried out in the fixed bed reactor used for the oxygen gasification runs. The reactor was heated at the desired temperature and purged under a flow of helium (100 mL/min). About 2.5 g of impregnated samples were flashed into the reactor and carbonized for 1 h. After a certain time, the reactor was cooled to room temperature and the sample was withdrawn.

Nitrogen enrichment of raw samples by thermal treatment included reactor heating to the desired temperature and introduction of about 2.5 g of raw activated carbon. Carbonization took place for 1 h under a helium flow (100 mL/min), passed through a gas phase trap containing about 200 mL of a saturated urea solution. At the end of the reaction period, samples were removed and further analyzed. The reaction operation temperatures in both treatment methods were 450 and 800 °C.

The experimental conditions used in the production of modified activated carbon samples and the corresponding symbols that were used in this work are presented in Table 1.

2.2. Pore structure characterization

The elemental analysis of all samples (C, H, N, S) was performed by a CHNS ThermoFinnigan FlashEA™ 1112 analyzer, while oxygen content was estimated by difference. Characterization of the pore structure development of the treated activated carbon samples was made by measurement of the N_2 and CO_2 adsorption isotherms. Nitrogen adsorption isotherms were utilized for the calculation of BET surface area and total pore volume, while micropore volumes were calculated by the α_s method. CO_2 adsorption isotherms were used for micropore volume determination by the Dubinin–Radushkevic equation. Prior to the measurement of N_2 adsorption, samples were out gassed

Table 1
Experimental conditions used for the production of modified activated carbon samples

Sample	Temperature (°C)	Time (h)
Samples oxidized in a 5% O_2 in He stream		
O1	450	6
O2	450	4
O3	400	4
O4	400	6

Sample	Acid concentration	Time (h)
Samples oxidized in HNO_3 solutions		
N1	5 M	6
N2	5 M	3
N3	2 M	3
N4	2 M	6

Sample	Urea deposition	Temperature (°C)	Time (h)
Samples treated with urea			
U1	From gas stream	450	1
U2	From gas stream	800	1
U3	Impregnation	450	1
U4	Impregnation	800	1

at 110 °C overnight under a helium flow, while prior to making a CO_2 adsorption measurement, samples were out gassed at 110 °C for 12 h at low pressure (about 10 Pa).

2.3. Surface chemistry

The acid/basic properties of the treated samples were studied by measuring the surface functional groups of treated activated carbon samples using the multibasic titration method of Boehm and Diehl [12]. According to this method, about 0.1 g of activated carbon sample was placed into a 200 mL conical flask containing 100 mL of each of the following 0.05N aqueous solution: sodium hydroxide, sodium carbonate, sodium bicarbonate, sodium ethoxide and hydrochloric acid. The flask was then sealed and the mixture was shaken for 24 h at 25 °C. The carbon sample was removed by filtration, and about 15 mL of accurately withdrawn aliquot of filtrate was titrated by 0.01N hydrochloric acid in order to estimate the excess base or 0.01N sodium hydroxide for the excess acid. The amount of acidic/basic functional groups was then calculated using the titration data.

Additional measurements were conducted for the assessment of the acidic properties of the samples, by the estimation of CO_2/CO evolved during their thermal treatment. About 0.2 g of activated carbon sample were placed in a laboratory manufactured fixed bed reactor, and the system was heated up to 1000 °C, with a heating rate of 5 °C/min, under a helium flow of 20 mL/min. An IR analyzer (Bernt Messtechnic) adapted to the reactor exit was used for continuously monitoring the concentration of evolved CO_2 and CO in the flue gases.

2.4. Liquid phase adsorption

The study of phenol adsorption took place in a constant temperature bath (20 °C) under continuous shaking. Ultra pure phenol was obtained from Merck. A stock phenol solution was prepared initially at concentration of 500 mg/L, using distilled and deionised water. Sodium hydrogen phosphate (analytical grade, obtained from Merck), was also added at concentration of 10^{-3} M in order to provide sufficient buffer capacity. Equilibrium experiments were carried out by the placement of various amounts of activated carbons in 250 mL Erlenmeyer flasks and addition of the phenol solution. The mixtures were then shaken for 8 days; this time was considered adequate for phenol adsorption to reach equilibrium. At the end of the reaction time, the content of each flask was filtered and the filtrate was analyzed by a UV-spectrophotometer (Shimadzu A-1201) at 270 nm for the determination of phenol.

3. Results

3.1. Pore structure development

The surface area values deduced from the N_2 isotherms by the BET equation and the CO_2 pore volume estimated by the D–R equation are given in Table 2. As shown, the type of the treatment greatly affected the textural properties of the materials. Oxygen gasification resulted in smaller changes in pore structure than nitric acid and urea treatment. Thus, nitrogen surface area decreased to about 900 m²/g by oxygen treatment while samples deduced by liquid phase oxidation had lower areas, reaching to values as low as 260 m²/g. In addition, samples with a high reduction in pore volumes were produced during oxygen treatment for prolonged reaction times.

The effect of oxidation on BET surface areas varies according to the treatment used and the raw material properties [13–16]. Pore volume and pore size development are in general affected by oxygen chemisorption on pore walls (volume reduction) and oxidation of the carbon material (widening and/or formation of new pores) [17]. According to the results of this work, oxygen chemisorption prevailed over carbon oxidation resulting to a decrease in surface area and pore volumes. Nevertheless, at low temperatures and extended reaction times chemisorption was favored producing modified activated carbons with a high percentage of oxygen functionalities and a slightly modified pore structure.

Table 2
Pore structure characteristics of modified carbon samples

Sample	Surface area (m²/g)	Total pore volume (cm³/g)	Micropore volume, α_s method (cm³/g)	Micropore volume, CO_2 adsorption (cm³/g)
D45/2	1003	0.374	0.338	0.252
O_1	917	0.374	0.313	0.147
O_2	1092	0.526	0.328	0.212
O_3	1021	0.369	0.323	0.204
O_4	983	0.404	0.334	0.245
N_1	260	0.116	0.104	0.132
N_2	725	0.323	0.283	0.257
N_3	630	0.263	0.212	0.338
N_4	597	0.258	0.217	0.193
U1	653	0.298	0.222	0.325
U2	712	0.334	0.263	0.492
U3	563	0.227	0.182	0.330
U4	468	0.207	0.152	0.090

Table 3
Modified carbon samples elemental analysis, wt%, dry basis

Sample	N_2	C	H_2	S	O_2
D45/2	0.37	87.6	0.53	0.68	5.46
O_1	1.01	82.39	0.44	0.55	10.25
O_2	0.87	81.29	0.45	0.56	11.47
O_3	0.74	85.93	0.49	0.66	6.82
O_4	0.63	85.87	0.46	0.69	6.99
N_1	1.23	70.69	1.28	0.41	21.03
N_2	1.08	75.87	0.91	0.49	16.29
N_3	0.94	78.53	0.80	0.53	13.84
N_4	0.97	76.17	0.90	0.47	16.13
U1	8.55	76.73	1.08	0.53	7.75
U2	6.52	79.72	0.89	0.52	6.99
U3	8.57	76.67	1.06	0.49	7.85
U4	6.58	79.78	0.92	0.63	6.73

Table 4
Multibasic titration results of modified carbon samples, meq/g carbon

Sample	NaOH	$NaHCO_3$	Na_2CO_3	$NaOC_2H_5$	HCl
D45/2	0.05	0.0	0.0	0.41	0.06
O1	0.35	0.1	0.2	0.50	0.00
O2	0.05	0.0	0.0	0.69	0.07
O3	0.06	0.0	0.0	0.19	0.13
O4	0.06	0.0	0.0	0.32	0.04
U1	0.0	0.0	0.0	0.07	0.12
U2	0.0	0.0	0.0	0.23	0.13
U3	0.0	0.1	0.0	0.10	0.11
U4	0.0	0.1	0.0	0.07	0.11
N1	0.78	0.29	0.44	1.15	0
N2	0.68	0.23	0.36	0.9	0
N3	0.36	0.06	0.21	0.64	0
N4	0.38	0.12	0.17	0.45	0

A significant reduction in the pore structure development was observed during nitric acid treatment. Micropore volume presented the highest values for samples treated at short reaction time, 3 h, while additional treatment resulted in the reduction of pore volume attributed to the incorporation of oxygen functionalities in pore walls and the erosive effect of nitric acid on the carbon structure [18–21].

The nitrogen enrichment of raw activated carbon enhanced the development of a microporous structure. Especially, thermal treatment of activated carbons in a urea saturated gas flow resulted in exclusively microporous samples with a high pore volume; similar results have been reported in the literature [6].

3.2. Elemental analysis

The results of the elemental analysis of the modified carbons are shown in Table 3. Oxygen gasification resulted in the reduction of carbon content to about 81%, while nitric acid treatment was more effective resulting in products with carbon content lower than 80%. The decrease in carbon content was accompanied by an increase in oxygen content. In addition, the increase in nitrogen content was significant for all samples treated by nitric acid solution, attributed to additional nitrogen groups adapted to the samples. Similar to acid treatment, urea treatment resulted in the reduction of carbon content and the increase of nitrogen content. It has been proposed that during urea treatment of coal substances, nitrogen is likely to exist in the form of amides, free and bonded NH and NH_2, or NH_4^+ species [22]. These species are decomposing at higher temperatures resulting in lower nitrogen content in the parent material. In nitrogen enriched samples prepared after thermal treatment at high temperatures, most of the nitrogen is incorporated into the carbon matrix as a component of an aromatic ring in a pyridine like configuration [23]. Furthermore, the effect of the method of urea addition on the introduction of nitrogen containing groups was not significant, as the differences in nitrogen content were negligible between the samples prepared by prior urea impregnation and the thermal treated samples in an urea saturated gas flow.

3.3. Surface functional groups

Results of multibasic titration as suggested by Boehm are given in Table 4 and indicated that D45/2 activated carbon presented a mixed acidic–basic character. Carbonyl ($NaOC_2H_5$ adsorption) and phenol (NaOH adsorption) groups were the main constituents, while negligible amounts of other functional groups were found by $NaHCO_3$ and Na_2CO_3 titration. Partial oxygen gasification resulted in activated carbon samples with varying surface properties depending upon preparation conditions. Oxidation at the lowest temperature enhanced the formation of basic functional groups; higher temperature resulted in the production of samples with acidic behavior while samples gasified at mild conditions such as low temperature and short reaction time gave a mixed acid–basic character similar to the initial activated carbon. It can be concluded that preparation of carbons with desired basic or acidic surface properties may take place by selection of the most appropriate oxygen gasification conditions.

Nitric acid treatment resulted in samples with negligible basic properties and in the introduction of various acidic groups (carbonylic, phenolic, carboxylic and lactonic) as revealed by the adsorption of different strength alkaline solutions, depending upon the experimental conditions, i.e. acid concentration and treatment time. Urea treatment resulted in samples with weak acidic properties due to the presence of carbonyl groups, as measured by the $NaOC_2H_5$ titration results. However, the distinguish between Boehm's acid classes should not be used in these samples because nitrogen containing groups may behave as acids in water solution and do not fit under Boehm's categories [22].

Surface functional groups of samples were further characterized by measuring the corresponding CO/CO_2 gas profiles given in Figs. 1–6. CO_2 evolution at low temperatures (200–500 °C) has been attributed to carboxylic acid functional groups with different acid strengths or located on energetically different carbon sites [23–25]. CO_2 releases at higher temperatures might indicate the existence of different oxygen surface groups, such as carboxylic anhydrides and lactones. In addition, CO peaks have
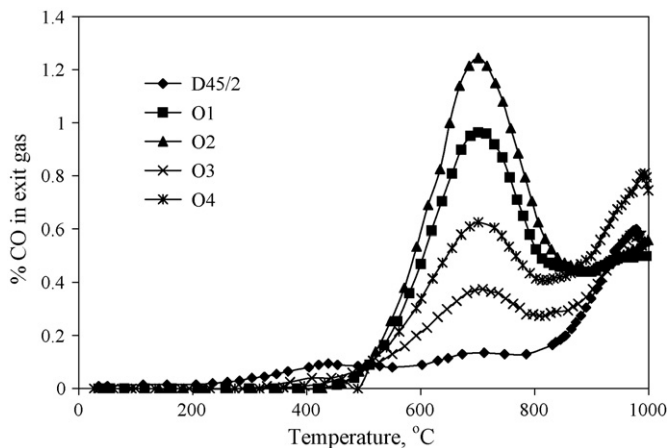
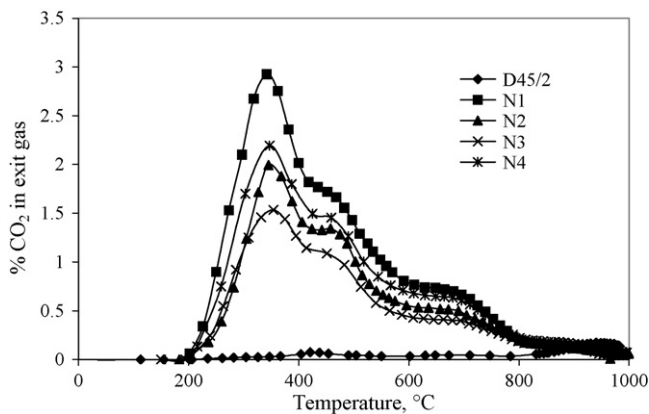Fig. 1. CO evolution profiles for the oxygen gasified activated carbon samples.

Fig. 4. CO_2 evolution profiles for the activated carbon samples treated by nitric acid.
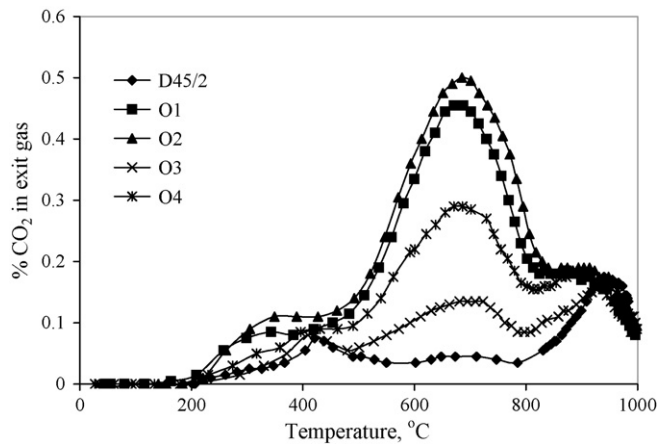

Fig. 2. CO_2 evolution profiles for the oxygen gasified activated carbon samples.
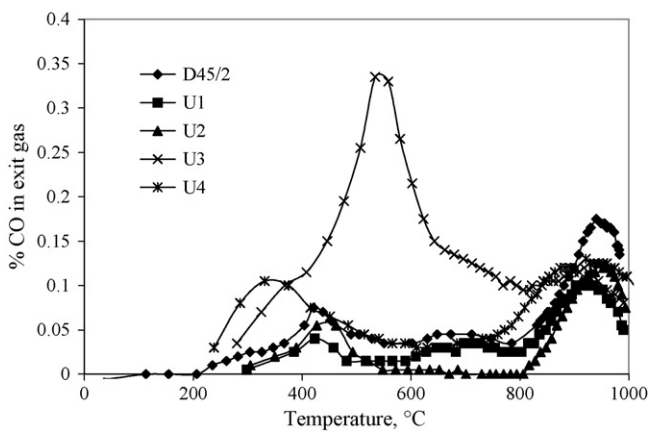

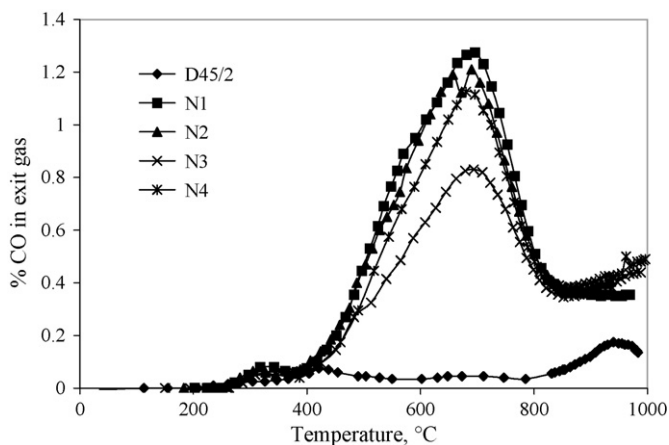Fig. 5. CO evolution profiles for the activated carbon samples treated by urea.

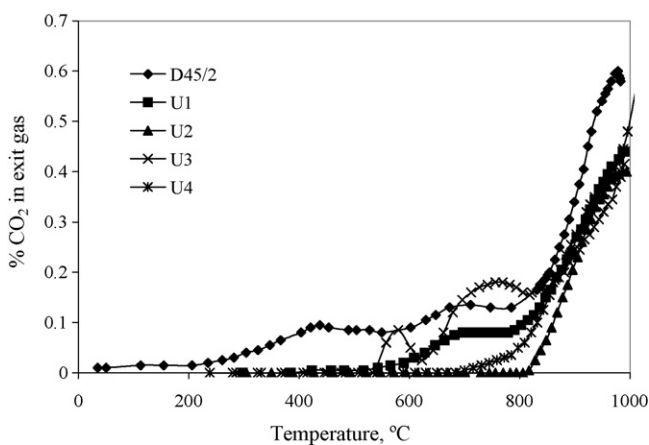Fig. 3. CO evolution profiles for the activated carbon samples treated by nitric acid.

Fig. 6. CO_2 evolution profiles for the activated carbon samples treated by urea.

been attributed to phenolic, anhydrite, ether (at 350–450 °C) and carbonyl, quinone complexes (at 450–700 °C).

CO/CO_2 profiles in the raw activated carbon presented peaks at three distinct temperature ranges (300–550, 650–750 and around 1000 °C), indicating the presence of various functional groups; however, functional groups prevailing were of carbonyl and quinone type as observed by the CO peaks at high temperature, and lactone type as revealed by the CO_2 peak at 900 °C. Oxygen gasification of activated carbon resulted in increased CO/CO_2 peaks around 700 °C, depending upon the reaction temperature and residence time, attributed to carbonyl and quinone groups (from CO profiles) and lactone and anhydrite groups (from the high temperature CO_2 profiles).

Treatment of activated carbon by nitric acid resulted in the formation of carbonyl groups and the absence of lactone groups, in agreement to the multibasic titration results. Samples treated by urea presented similar CO/CO_2 profiles to the corresponding profile of the raw activated carbon, indicating that urea deposition did not impose significant changes in surface functional groups.

The incorporation of nitrogen groups on the surface of activated carbons by urea involves a number of complex reactions taking place between the coal substance, urea and its derivatives produced under heat treatment [6]. At certain reaction conditions, potential urea transformations include the formation of triazines and cyanuric acid as by-products, which may serve as nitrogen introducing reagents on the coal surface. In general, treatment of coal substances by nitrogen containing reagents may result in the enrichment of parent material by thermally stable nitrogen groups of pyridinic form, which accordingly may influence the selective adsorption behavior of the samples [23,26].

3.4. Phenol adsorption capacity

The adsorption capacity of raw activated carbon and treated samples was evaluated by the performance of phenol adsorption experiments and the measurement of the corresponding adsorption isotherms, shown in Figs. 7–9, respectively. The adsorption of this particular substance was tested, as it represents a standard
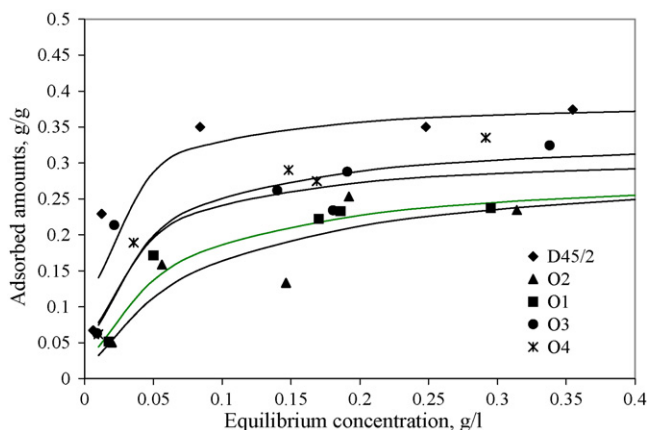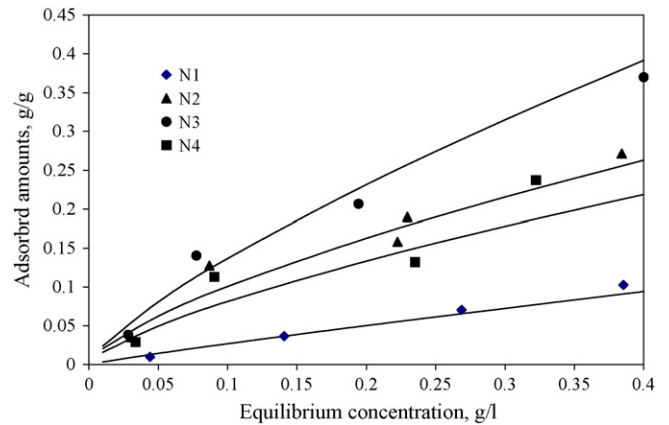

Fig. 8. Phenol adsorption isotherms for activated carbon samples treated by nitric acid and the corresponding Freundlich isotherm.

compound used in a large number of adsorption capacity studies. The Langmuir and Freundlich adsorption equations were applied to the experimental isotherms and the corresponding coefficients are given in Table 5, together with the maximum adsorption capacity, i.e. the adsorbent loading at an equilibrium concentration $C_e = 0.4$ g/L. Oxygen and nitric acid samples isotherms were of L type [27], although the latter showed a lower affinity between adsorbent–adsorbate as deduced by the lower adsorbed amounts at low adsorbate concentrations. However, adsorption isotherms on urea samples represented H type isotherms corresponding to a high adsorbent–adsorbate affinity.

Phenol is considered as a weak acid; thus phenol adsorption should be enhanced in activated carbons with basic surface functional groups. Several studies have shown that phenol adsorption is dependent on both the porosity and the presence of surface groups [28,29]. Oxidation may affect the phenol adsorption since it affects the surface functional groups. Introduction of acidic functional groups may cause the π-electrons to be removed from the carbon matrix, leading to a decrease in the strength of the interactions between the aromatic ring of the phenol molecule and the carbon basal planes [8]. An overall effect is a decrease in the average energy of phenol adsorption sites [30]. Samples prepared by oxygen gasification presented lower

Fig. 7. Phenol adsorption isotherms for oxygen gasified activated carbon samples and the corresponding Langmuir isotherm.
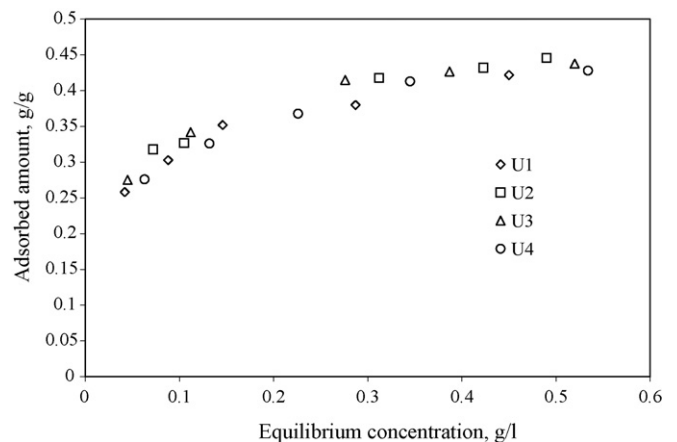

Fig. 9. Phenol adsorption isotherms for activated carbon samples treated by urea.

Table 5
Parameters of the Freundlich and Langmuir models for phenols adsorption on the modified carbon samples

Sample	Freundlich coefficients			Langmuir coefficients			Loading at $C_e = 0.4$ g/L (g/g AC)
	K_F	n	R^2	q_m	K_L	R^2	
D45/2	0.6260	2.9	0.7172	0.338	56.7	0.9966	0.350
O1	0.5394	1.9	0.8442	0.291	17.7	0.975	0.250
O2	0.5230	1.8	0.9344	0.301	11.9	0.7371	0.250
O3	0.4768	2.9	0.7091	0.313	33.0	0.9778	0.280
O4	0.6339	2.2	0.8915	0.340	28.0	0.0045	0.300
N1	0.2153	1.1	0.9911	0.371	0.8	0.7911	0.090
N2	0.7858	1.3	0.9487	0.457	4.6	0.6403	0.250
N3	0.4964	1.4	0.9837	0.461	3.1	0.9334	0.250
N4	0.4213	1.4	0.8882	0.311	4.1	0.8202	0.200
U1	0.4990	4.9	0.9839	0.540	24.8	0.9968	0.400
U2	0.5104	5.3	0.9878	0.480	22.8	0.999	0.420
U3	0.5143	5.1	0.9792	0.467	27.9	0.9997	0.410
U4	0.5032	4.7	0.9862	0.469	18.9	0.9984	0.410

phenol uptake than the raw activated carbon, ranging from 0.250 to 0.300 g/g AC. The sample O1 prepared at the higher reaction temperature, 450 °C, presented the lowest phenol adsorption, due to its increased acidic properties. However, samples prepared at the lower temperature, presented a higher amount of basic functional groups and these samples had a higher phenol uptake capacity. Furthermore, oxygen gasification resulted in the reduction of pore volume, contributing thus to the reduced phenol uptake.

Treatment of activated carbon by nitric acid resulted in samples of higher acidity than the oxygen gasified ones, while surface area and micropore volumes were further decreased; thus, a substantial decrease in phenol removal capacity was observed for samples N1–N4, reaching up to 0.250 g/g AC. However, samples treated in urea atmosphere presented a strong basic characteristic, as revealed by the titration method and the CO/CO_2 gas evolution profiles, resulting in an increased phenol uptake. Depending upon the treatment conditions, phenol adsorption capacity varied between 0.400 and 0.420 g/g AC and was higher than the corresponding value of the raw activated carbon. Furthermore, the decreased surface area of these samples did not affect the phenol adsorption. Similar results related to phenol adsorption capacity have been reported on activated carbons treated by nitric acid and air [8].

At a pH value of about 7, basic carbons present a positive surface charge, while the un-dissociated form of phenol molecules are prevailing over the ionic forms ($pK_a = 9.95$). Urea treated samples presented the highest nitrogen content than the other samples; nitrogen moieties are possibly located at the edges of graphitic layers, resulting in a lower porosity and in an increased basic character [31]. Several forms of nitrogen groups have been reported including pyridinic, pyrrolic, etc. [6,26,32]. The enhancement of phenol adsorption under these conditions, has been attributed to the nitrogen functional groups in treated samples [33]; the π–π dispersion forces were increased in samples impregnated with nitrogen containing substances, due to the corresponding increase in electronic density of basal planes resulting, thus, to the enhancement of the adsorption process

[32]. In conclusion, nitrogen functionalities improved the phenol adsorption capacity of raw activated carbon, while the samples prepared by nitric acid and oxygen treatment showed reduced phenol removal uptake.

4. Conclusions

Activated carbons with various surface functional groups and tailored adsorption capacity were produced by the application of different oxidation techniques. Samples treated by urea presented basic characteristics, which enhanced the removal capacity of phenols; the enhancement of the phenol adsorption was associated to the increased nitrogen content of these samples. Activated carbons treated by oxygen and nitric acid presented significant acidic character and a lower phenol adsorption capacity. Furthermore, the oxidation treatment affected the pore structure development in different modes: oxygen gasification slightly affected the surface area and pore volumes of the produced samples, while the highest reduction in pore structure was observed for the samples treated by nitric acid solutions. As a result, urea and possibly other nitrogenous compounds may be used as effective mediums for the enhancement of phenol adsorption potential in activated carbons.

References

[1] M.V. Navarro, N.A. Seaton, A.M. Mastral, R. Murillo, Analysis of the evolution of the pore size distribution and the pore network connectivity of a porous carbon during activation, Carbon 44 (2006) 2281–2288.

[2] J.S. Mattson, H.B. Mark Jr., Activated Carbon, Marcel Dekker, New York, 1971.

[3] C.Y. Yin, M.K. Aroua, W.M.A.W. Daud, Review of modifications of activated carbon for enhancing contaminant uptakes from aqueous solutions, Sep. Purif. Technol. 53 (2007) 403–415.

[4] T. García, R. Murillo, D. Cazorla-Amorós, A.M. Mastral, A. Linares-Solano, Role of the activated carbon surface chemistry in the adsorption of phenanthrene, Carbon (2004) 1683–1689.

[5] M. Santiago, F. Stüber, A. Fortuny, A. Fabregat, J. Font, Modified activated carbons for catalytic wet air oxidation of phenol, Carbon 43 (2005) 2134–2145.

[6] J. Bimer, P.D. Salbut, S. Berlozecki, J.-P. Boudou, E. Broniek, T. Siemieniewska, Modified active carbons from precursors enriched with nitrogen functions: sulfur removal capabilities, Fuel 77 (1998) 519–525.

[7] A. Dąbrowski, P. Podkościelny, Z. Hudicki, M. Barczak, Adsorption of phenolic compounds by activated carbon—a critical review, Chemosphere (2005) 1049–1070.

[8] F. Villacañas, M. Fernando, R. Pereira, J.J.M. Órfão, J.L. Figueiredo, Adsorption of simple aromatic compounds on activated carbons, J. Colloid Interface Sci. 293 (2006) 128–136.

[9] K. Lázló, Adsorption from aqueous phenol and aniline solutions on activated carbons with different surface chemistry, Colloids Surf. A: Physicochem. Eng. Aspects 265 (2005) 32–39.

[10] P. Cañizares, M. Carmona, O. Baraza, A. Delgado, M.A. Rodrigo, Adsorption equilibrium of phenol onto chemically modified activated carbon F400, J. Hazard. Mater. B131 (2006) 243–248.

[11] A.A. Zabaniotou, G. Stavropoulos, Pyrolysis of used automobile tires and residual char utilization, J. Anal. Appl. Pyrolysis 70 (2003) 711–722.

[12] H.P. Boehm, E. Diehl, Angew. Chem. Int. Ed. 3 (1964) 669–677.

[13] A. Swiatkowski, M. Pakula, S. Biniak, M. Walczyk, Influence of the surface chemistry of modified activated carbon on its electrochemical behavior in the presence of lead (II) ions, Carbon 42 (2004) 3057–3069.

[14] J.L. Figueiredo, M.F.R. Pereira, M.M.A. Freitas, J.J.M. Orfao, Modification of the surface chemistry of activated carbons, Carbon 37 (1999) 1379–1389.

[15] X. Zheng, S. Zhang, J. Xu, K. Wei, Effect of thermal and oxidative treatments of activated carbon on its surface structure and suitability as a support for barium-promoted ruthenium in ammonia synthesis catalysts, Carbon 40 (2002) 2597–2603.

[16] F. López, F. Medina, M. Prodanov, C. Güell, Oxidation of activated carbon: application to vinegar decolorization, J. Colloid Interface Sci. 257 (2003) 173–178.

[17] Z.-M. Wang, N. Yamashita, Z.-X. Wang, K. Hoshinoo, H. Kanoh, Air oxidation effects on microporosity, surface property, and CH_4 adsorptivity of pitch-based activated carbon fibers, J. Colloid Interface Sci. 276 (2004) 143–150.

[18] P.C.C. Faria, J.J.M. Órfão, M.F.R. Pereira, Adsorption of anionic and cationic dyes on activated carbons with different surface chemistries, Water Res. 38 (2004) 2043–2052.

[19] C.O. Ania, J.B. Parra, J.J. Pis, Influence of oxygen-containing functional groups on active carbon adsorption of selected organic compounds, Fuel Process. Technol. 79 (2002) 265–271.

[20] A.N.A. El-Hendawy, Influence of HNO_3 oxidation on the structure and adsorptive properties of corncob-based activated carbon, Carbon 41 (2003) 713–722.

[21] C. Moreno-Castilla, F. Carrasco-Marin, F.J. Maldonado-Hodar, J. Rivera-Utrilla, Effects of non-oxidant and oxidant acid treatments on the surface properties of an activated carbon with very low ash content, Carbon 36 (1998) 145–151.

[22] F. Adib, A. Bagreev, T.J. Bandosz, Adsorption/oxidation of hydrogen sulfide on nitrogen-containing activated carbons, Langmuir 16 (2000) 1980–1986.

[23] S. Biniak, M. Pakula, G. Szymanski, A. Swiatkowski, Effect of activated carbon surface oxygen- and/or nitrogen-containing groups on adsorption of copper (II) ions from aqueous solution, Langmuir 15 (1999) 6117–6122.

[24] H.P. Boehm, Surface oxides on carbon and their analysis: a critical assessment, Carbon 40 (2002) 145–149.

[25] D.M. Nevskaia, A. Santianes, V. Munoz, A. Guerrero-Ruiz, Interaction of aqueous solutions of phenol with commercial activated carbons: an adsorption and kinetic study, Carbon 37 (1999) 1065–1074.

[26] P. Burg, P. Fydrych, D. Cagniant, G. Nanse, J. Bimer, A. Jankowska, The characterization of nitrogen-enriched activated carbons by IR, XPS and LSER methods, Carbon (2002) 1521–1531.

[27] C.H. Giles, D. Smith, A. Huiton, A general treatment and classification of the solute adsorption isotherm. I. Theoretical, J. Colloid Interface Sci. 47 (1974) 755–765.

[28] R.D. Vidic, C.H. Tessmer, L.J. Uranowski, Impact of surface properties of activated carbons on oxidative coupling of phenolic compounds, Carbon 35 (1997) 1349–1359.

[29] A.P. Terzyk, Molecular properties and intermolecular forces—Factors balancing the effect of carbon surface chemistry in adsorption of organics from dilute aqueous solutions, J. Colloid Interface Sci. 275 (2004) 9–29.

[30] I.I. Salame, T.J. Bandozs, Role of surface chemistry in adsorption of phenol on activated carbons, J. Colloid Interface Sci. 264 (2003) 307–312.

[31] A. Bagreev, J.A. Menendez, I. Dukhno, Y. Tarasenko, T.J. Bandosz, Bituminous coal-based activated carbons modified with nitrogen as adsorbents of hydrogen sulfide, Carbon 42 (2004) 469–476.

[32] J. Rivera-Utrilla, M. Sánchez-Polo, Ozonation of naphthalenesulphonic acid in the aqueous phase in the presence of basic activated carbons, Langmuir 20 (2004) 9217–9222.

[33] A. Arenillas, F. Rubiera, J.B. Parra, C.O. Ania, J.J. Pis, Surface modification of low cost carbons for their application in the environmental protection, Appl. Surf. Sci. 252 (2005) 619–624.