CARBONACEOUS MATERIALS FOR GAS PHASE DESULFURIZATION: ROLE OF SURFACE HETEROGENEITY

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Introduction

Removal of sulfur containing species becomes nowadays a strategic issue [1, 2]. It is due to strict environmental regulations combined with searching for new clean sources of energy such as fuel cell. For fuel cell application gaseous fuel has to be almost free of sulfides or mercaptans. Those species poison the reforming catalysts thus causing shortening of the life-time of a cell and an increase in the costs of energy. Since sulfur containing gases are toxic and they have very low odor threshold all efforts are made to filter air form facilities where anaerobic digestion can occur such as, for instance form municipal waste water treatment plants [3-6].

Among various methods used to remove hydrogen sulfide, adsorption on activated carbons is considered as a very efficient and cost effective approach. This is the result of unique surface properties of carbonaceous adsorbents [7-10] such as high surface area, and pore volume, along with surface chemistry, which promotes catalytic oxidation of H_2S in the presence of even small amounts of air and moisture [11-23]. As a result of surface reaction, hydrogen sulfide is oxidized either to sulfur or sulfur dioxide. The latter process, in order to retain a significant amount of sulfur species on the surface, has to proceed further and SO_2 is oxidized to sulfuric acid. Due to the reactions mentioned occur at room temperature and under atmospheric pressure the physical adsorption of hydrogen sulfide is negligible at these conditions [15].

To enhance the catalytic properties of activated carbon various methods have been used [2] from which the most common is impregnation of activated carbon with sodium or potassium hydroxide or salts containing potassium such as potassium carbonate [3, 5, 23-27]. Doing this only slightly increases the cost of materials leading to the much better performance [6]. But since an ideal solution never exists the application of caustic impregnated carbons carries certain drawbacks. The most significant is a low ignition temperature. In the presence of caustic a strong exothermic reaction occurs and a carbon bed can easily self-ignite resulting in enormous cost of extinguishing and a widely spread environmental damage. Another issue is related to safety of working with hazardous materials, as is a caustic solution present on the surface of carbons.

All of these resulted in a search for better adsorbents that, with sustained efficiency, would be much safer to work with. The window of opportunity opened in surface chemistry of carbons. This is an important factor governing their catalytic properties [10, 28, 29]. One method of modification, usually applied during production of adsorbent, is introduction of nitrogen containing groups [30-32]. Like in the case of caustic materials, such carbons are basic and the high dispersion of catalytic sites in the pore system provides efficient oxidation. The catalytic action is so pronounced that a surface of such carbons not only converts hydrogen sulfide to sulfur as in the case of caustic impregnated materials, but oxidation proceeds even further to sulfuric acid. The presence of sulfuric acid was seen as another “plus” in application of nitrogen enriched adsorbents. They can be washed out with water and thus they regeneration is inexpensive. The Calgon patent describing the performance of Centaur® claims that after loosing 20% the initial capacity as a result of the first run, the carbons maintain their performance on 80% level practically forever [31]. Taking into account that the capacity of such carbon is about half of the capacity of the caustic impregnated materials the situation looked almost ideal. But, as mentioned above an ideal solution does not exit. Additional step in the preparation of carbon (impregnation with urea of low temperature chars) increases the cost of materials. Although the smaller capacity than that of caustic impregnated carbon can be compensated by many steps of inexpensive regeneration, once again the practical and safety reasons limit the applications of such carbons. Concentrated sulfuric acid present on the surface can lead to health hazard (skin burning) and many facilities do not feel comfortable with regeneration system where strong acid is generated.

The mentioned above factors directed the attention of scientists and engineers to virgin materials. During the last few years the performance and suitability for hydrogen sulfide removal of many types of unmodified carbon have been described in the literature [6, 13-16, 33]. When the concentration of hydrogen sulfide in air is less then 100 ppb virgin carbons can provide the sufficient protection for few years [6]. It was shown that the capacity and the degree of hydrogen sulfide oxidation depend on the porosity and the surface chemistry [13-16]. Moreover, the content of inorganic matter in ash has proven to be important [34]. This concept led to the development of new, sewage sludge adsorbents [35-38]. Although their content of carbon is only about 20 %, their capacity is much better than that of virgin, coconut shell based activated carbon. An important advantage of those materials is conversion of hydrogen sulfide to sulfur and low costs of production.

An objective of this paper is to demonstrate the importance of surface heterogeneity and its effect on the amount of hydrogen sulfide adsorbed on carbonaceous materials and on the products of surface reactions. Very often the choice of adsorbent is governed not only by its cost and removal capacity but also by the other factors such as, for instance, the possibility of regeneration or the level of toxicity of the spent materials. The results presented here summarize the effects of surfaced features on the capacity and chemistry of the processes occurring during adsorption of H_2S on carbonaceous materials.

Experimental

Materials. Five carbonaceous materials were investigated in this research. They are as follows: STIX (cautic impregnated bituminous cola based- Watrelink Barnabey and Sutcliffe) Midas OCM^{TM} (US Filters) [39], Centaur® (Calgon), S-208 (coconut shell based- Waterlink Barnabey and Sutcliffe), and laboratory made sewage sludge derived adsorbent, referred here as SC carbon. After exhaustion in H_2S breakthrough capacity test the letter E is added to the name of the samples.

Methods

H_2S breakthrough capacity. The standard dynamic test (ASTM D 6646-01) [40] was used to evaluate the performance of carbons for H_2S adsorption. Humidified air (relative humidity 80% at 293K) containing 1% (10,000ppm) of H_2S was passed through a column of carbon (diameter 1", bed height 9"). The test was stopped at breakthrough concentrations of 50 ppm. Then the breakthrough capacity for H_2S adsorption was calculated using concentration of adsorbat, flow rate, breakthrough time and volume of carbon.

pH of carbon surface. A pH of the carbon surface was evaluated according to ASTM D 3838 standard procedure. Briefly, 10 g of activated carbon was placed in 100 mL of hot water and boiled gently for 900 s. Then the flask content was filtered, filtrate was cooled, and pH was measured.

Sorption of nitrogen. Nitrogen isotherms were measured using a ASAP 2010 (Micromeritics) at –196 ^{o}C. Before the experiment the samples were heated at 120 ^{o}C and then outgassed at this temperature under a vacuum of 10^{-5} Torr to constant pressure. The isotherms were used to calculate the specific surface area, micropore volume (DR method), V_{mic}, mesopore volume, V_{mes}, total pore volume, V_t,, and pore size distributions [41-42].

Thermal analysis. Thermal analysis was carried out using TA Instruments Thermal Analyzer. The instrument settings were: heating rate 10 deg/min and either air or nitrogen atmosphere with 100 mL/min flow rate. The residues after heating in nitrogen and air (ash content) at 1000°C are reported. From the experiments run in air the ignition temperature was determined [6]. Experiment carried out in nitrogen provided information about the speciation of surface oxidation products.

Apparent density. Apparent density of carbons was evaluated using ASTM Method D 2854 [43]. It is determined on a granular sample be measuring the volume packed by a free fall from a vibrating feeder into an approximately sized graduated cylinder and determining the mass of the known volume.

Moisture. Content of moisture was evaluated using ASTM Method D 2867 [43]. A sample of carbon is put into a dry, closed weighting dish and weighted accurately. Then the dish is opened and placed with the lid in a preheated oven. The sample is dried to constant weight and cooled in dessicator. The weight loss is expressed as a percentage of the weight of the original sample.

Results and Discussion

From the measurement of the hydrogen sulfide breakthrough curves, taking into account the density of materials, the breakthrough capacity was calculated. The results are summarized in Table 1 along with the pH values of the carbon surfaces. Analyzing the data it is seen that Midas® outperforms other materials. Its capacity per unit volume bed is twice higher than that of Centaur® whereas the capacity the sewage sludge derived material is twice higher than that of STIX. The carbons also behave differently when water adsorption is considered. As shown previously [34], presence of water is a crucial factor enhancing hydrogen sulfide adsorption. It enables dissociation of to HS^- ions [13], when the pH allows it. It is well known that activated carbon surface is considered as hydrophobic. Adsorption of water usually occurs as a result of the presence of oxygen or nitrogen containing functional groups and inorganic matter [44]. High adsorption of water on Midas® and Centaur® is the result of long exposure to humidified air (longest breakthrough time) and also affinity of surfaces to retain water. In the case of Centaur® this is linked to the nitrogen containing groups whereas in the case of Midas® hydration of inorganic matter likely plays a role.

In order to discuss the performance of materials as removal media in the process where catalytic action is expected to enhance their performance, the structural and chemical features of surfaces have to be described. The simplest estimation of carbon surface chemistry is the measurement of the pH of its water suspension [13]. As listed in Table 1 all materials are basic and the pH of Midas and SC is over 10. That pH is the result of the presence of inorganic matter (basic oxides). In the case of Centaur® the closest to neutral pH value is caused by protonation of the nitrogen containing groups [45]. High pH of STIX is caused by the presence of potassium hydroxide.

Table 1. H_2S Breakthough Capacity, Amount of Water Adsorbed and pH Values of the Carbon Surfaces.

Sample	H_2S breakthrough capacity [g/g of carbon]	H_2S breakthrough capacity [g/cm^3 of carbon]	Water adsorbed [mg/g]	pH initial	pH exhausted
S208	0.036	0.02	0.04	9.8	8.82
Centaur®	0.130	0.060	0.41	8.30	1.47
Midas®	0.608	0.251	0.12	10.85	10.38
STIX	0.230	0.140	0.06	10.2	7.2
SC	0.079	0.052	0.03	10.58	9.63

The amount of ash in each material may indicate the importance of the presence of catalytic inorganic phase (Table 2). In the case of SC and Midas® the ash content is the highest. In SC it comes as a natural component of the sewage sludge precursor [35-38] whereas, in the case of Midas it was added as a part of the material preparation procedure [39]. It is important to mention that the ash content of Midas® twice exceeds the content of basic metals oxides described in the patent [39]. Relatively high amount of ash in Centaur® is linked to its bituminous coal origin. In the case of STIX about 13% of ash has its main origin in potassium hydroxide used for impregnation along with ash coming from a bituminous coal precursor.

Table 2. Density, Ash Content, Ignition Temperature and the Initial Moisture Content.

Sample	Bulk density [g/cm^3]	Ash content [%]	Moisture [%]	T_{ign} [^{o}C]
S208	0.55	1.9	5.2	425
Centaur®	0.48	5.5	6.6	510
Midas®	0.41	26.8	12.2	524
STIX	0.60	12.9	8	320
SC	0.66	76.9	2.5	426

From the nitrogen adsorption isotherms the structural parameters were calculated. They are collected in Table 3. The data clearly shows that Midas® has the highest surface area and pore volume whereas SC- the lowest. Also, either for the latter carbon or Midas® a significant contribution of mesoporosity is found. On the other had, S-208, Centaur®, and STIX, are very homogenously microporous. The highest nitrogen uptake noticed for Midas®, the lowest for SC, which is related to the differences in the chemical composition of materials. Midas® contains 70% of carbonaceous phase, SC- only 20.

Not only porosity but also the density of materials is liked to their content of inorganic matter. The densest is SC, then Midas, Centaur and S-208. This has an effect on the capacity calculated per gram (Table 1) and thus affects the cost of materials in real life operations.

The evaluation of the materials' performance is more valid when the products of surface reaction are discussed. The pH values of exhausted carbons listed in Table 1 clearly indicate the differences in the surface reaction products. Highly acidic pH of Centaur® and a noticeable decrease in the pH for S-208 and STIX suggest a significant degree of sulfuric acid formation. For SC and Midas® the pH, however slightly decreases, is still on a very high level. Such a

decrease can be caused by formation of sulfides and sulfates from oxides. Those species and sulfur, should not cause dramatic decrease in the pH value.

Table 3. Structural Parameters Calculated from Sorption of Nitrogen.

Sample	S_{N2} [m^2/g]	V_{mic} [cm^3/g]	V_t [cm^3/g]	V_{mic}/V_t
S208	877	0.43	0.46	0.96
S208E	800	0.40	0.42	0.95
Centaur®	987	0.44	0.56	0.79
Centaur®E	443	0.18	0.26	0.69
Midas®	1110	0.43	0.81	0.53
Midas®E	95	0.03	0.14	0.21
STIX	620	0.30	0.35	0.85
STIXE	340	0.18	0.26	0.69
SC	98	0.04	0.16	0.25
SCE	28	0.01	0.10	0.10

Comparison of the DTG results obtained on exhausted samples (the low temperature peak, < 250 ^oC for pure carbon materials represents removal of SO_2 from reduction of sulfuric acid [13-16] and the peaks between 300- 500 ^oC are linked to removal of sulfur from various pore sizes (from larger to smaller) [13-16]) revealed that indeed in the case of Centaur® almost only SO_2 is released, for -S208 and STIX there is a mixture of SO_2 and elemental sulfur . In the case of Midas® a huge peak representing removal of sulfur from pores of various sizes was found. For sewage sludge derived adsorbent a broad peak present between 200-400 ^oC represents sulfur [36-38]. Although its position is close to that for sulfuric acid ion S208 that shift is caused by removal of sulfur from large pores, which are present in this material. This process requires much less energy (lower temperature) than evaporation of sulfur polymers from the microporous structure as that in S-208.

Those significant amounts of sulfur adsorbed on the materials studied are stored in their pore system. As shown from Table 1 for all carbons the volumes of pores, micropores in particular, significantly decreases. This is of course linked to the decrease in the surface areas. An exact location of oxidation products is seen from the analysis of pore size distributions for carbons after exhaustion. Whereas for S-208 and Centaur® mainly volumes in pores smaller than 20 Å are affected for SC and Midas® sulfur is deposited in all pore sizes and smaller micropores are completely filled. It looks like the capacity lasts until that volume is exhausted and more pore volume would provide more capacity as expected when the catalytic actions is involved.

Another important factor which should be evaluated here is the ignition temperature of adsorbents (Table 3). The evaluation of temperature of self-ignition based shows high ignition temperature of catalytic carbons. The ignition temperatures of S-208 and SC are almost identical and about 100 ^oC lower that that for Centaur® and Midas®. Since manufacturing of those carbons requires additional steps some additive may work as fire retardants. Low ignition of caustic impregnated carbon is the result of the presence of highly reactive potassium hydroxide.

Based on the comparison presented above, and the results published elsewhere where the mechanisms of adsorption/oxidation are discussed [13, 26, 33, 36-38], the materials containing a catalytically active inorganic phase mixed with the activated carbon seem to be the best performing adsorbents. On their surface, thanks to the presence of catalytic oxides, hydrogen sulfide is oxidized to sulfur. The catalytic action is complex and consists of two different mechanisms: one on pure activated carbon surface and one on the catalytic phase. It is likley that the reaction of H_2S oxidation occurs on the carbon and oxides surfaces simultaneously with formation of elemental sulfur, metal sulfides and sulfuric acid which later reacts with carbonates.

As indicated above, the presence of water on activated carbons contributes to the dissociation of hydrogen sulfide and facilitates to its oxidation to sulfur and sulfur dioxide [33] The proposed mechanism involves 1) H_2S adsorption on the carbon surface, 2) its dissolution in a water film, 3) dissociation of H_2S in an adsorbed state in the water film , 4) surface reaction with adsorbed oxygen with formation of elemental sulfur 4a) or sulfur dioxide 4b), and 5) further oxidation of SO_2 to H_2SO_4 in the presence of water :

$$H_2S_{gas} \xrightarrow{K_H} H_2S_{ads} \quad (1)$$

$$H_2S_{ads} \xrightarrow{K_S} H_2S_{ads\text{-}liq} \quad (2)$$

$$H_2S_{ads\text{-}liq} \xrightarrow{K_a} HS^-_{ads} + H^+ \quad (3)$$

$$HS^-_{ads} + O^*_{ads} \xrightarrow{K_{R1}} S_{ads} + OH^- \quad (4a)$$

$$HS^-_{ads} + 3\,O^*_{ads} \xrightarrow{K_{R2}} SO_{2\,ads} + OH^- \quad (4b)$$

$$SO_{2ads} + O^*_{ads} + H_2O_{ads} \xrightarrow{K_{R3}} H_2SO_{4\,ads} \quad (5)$$

$$H^+ + OH^- \longrightarrow H_2O \quad (6)$$

where H_2S_{gas}, $H_2S_{ads\text{-}liq}$, and H_2S_{ads} correspond to H_2S in gas, liquid and adsorbed phases, respectively; K_H, K_S, K_a and K_{R1} , K_{R2} , K_{R3} are equilibrium constants for related processes (adsorption, gas solubility, dissociation, and surface reaction constants); O^*_{ads} is dissociatively adsorbed oxygen, S_{ads} , SO_{2ads} , $H_2SO_{4\,ads}$ represent sulfur, SO_2 and H_2SO_4 as the end products of the surface oxidation reactions.

It is known that oxides of iron, zinc and copper are used in industry as absorbents and /or catalysts of H_2S removal from different gaseous media at low (20-200^oC) and high (300-800^oC) temperatures [2]. The H_2S removal at low temperatures mainly occurs due to gas-solid reactions in a thin hydrated lattice of metal oxides. This process leads to sulfides formation:

$$ZnO + H_2S \longrightarrow ZnS + H_2O \quad (7)$$

$$CuO + H_2S \longrightarrow CuS + H_2O \quad (8)$$

$$Fe_2O_3 + 3H_2S \longrightarrow FeS + FeS_2 + 3H_2O \quad (9)$$

$$Fe_2O_3 + 3H_2S \longrightarrow Fe_2S_3 + 3H_2O \quad (10)$$

$$2Fe_2S_3 + 3O_2 \longrightarrow 2Fe_2O_3 + 6S \quad (11)$$

Carbonates of calcium and magnesium are also supposed to have high affinity for H_2S adsoption in wet condition due to neutralization reactions ([7]

$$CaCO_3 + H_2S \longrightarrow Ca(HCO_3)_2 + Ca(HS)_2 \quad (12)$$

Moreover, transition metal ions can catalyze the H_2S oxidation in aqueous solutions by molecular oxygen due to the redox process

[2]. For example, in the case of iron the following reactions may occure:

$2Fe^{3+} + HS^- \text{---->} 2Fe^{2+} + S + H^+$ (13)
$4Fe^{2+} + O_2 + 2H^+ \text{---->} 4Fe^{3+} + 2OH^-$ (14)

On the surface of caustic impregnated carbon the following reaction path have been proposed in addition to those occurring on the surface of pure carbon [21]s:

$NaOH + H_2S \text{---->} NaHS + H_2O$ (15)
$2NaOH + H_2S \text{---->} Na_2S + H_2O$ (16)
$NaHS + 0.5O_2 \text{---->} S + NaOH$ (17)
$Na_2S + 0.5O_2 + H_2O \text{---->} S + 2\ NaOH$ (18)
$2\ NaOH + H_2SO_4 \text{---->} Na_2SO_4 + 2H_2O$ (19)

And side reactions:
$NaOH + CO_2 \text{---->} NaHCO_3$ (20)
$2NaOH + CO_2 + H_2O \text{---->} Na_2CO_3 + 2\ H_2O$ (21)
$Na_2CO_3 + H_2S \text{---->} NaHCO_3 + NaHS$ (22)

The presence of NaOH and strongly basic environment enhances the dissociation of hydrogen sulfide. Moreover, according to the reactions 17-18, NaOH and basic environment is regenerated in the system enabling more H_2S to be dissociated and, as a final product, oxidized to elemental sulfur following reaction 17. The results published elsewhere [28] showed that on one mole of NaOH 3 to 4 moles of H_2S are adsorbed which clearly indicates the catalytic effect of the carbon surface. A question raises what causes that the reaction stops and it stops when almost the same capacities are reached on all materials. The possible reason for this is "inactivation" of sodium hydroxide. This may happen as a result of reactions 19-20 where carbonates and sulfates are formed on the surface. Although the pH remains basic in most cases, this can be due to the presence of carbonates not hydroxide. It makes the formation of sodium sulfides, sodium hydrogen sulfides, sodium sulfates, and sulfuric acid the most important reactions in this system. When all NaOH is used sulfuric acid is formed which was observed as very low pH of exhausted samples used in sewage treatment plants [6]. On the other hand, following reactions 1-11, and 17, sulfur must be formed in the system and it does not affect the surface pH.

Slightly different pattern than that on the virgin carbon surface is proposed to occur on the surface of catalytic carbon , Centaur®. This is a very microporous carbon enriched with nitrogen [32]. That nitrogen is likely in the form of pyridinic-like groups. As in the case of sodium, their basicity enhances the dissociation of hydrogen sulfide to HS- ions. Owing to high microprosity of this carbon, that process occurs in the confined space where big sulfur polymers cannot be formed following reaction 4. Thus small sulfur radicals are readily oxidized to sulfur dioxide and further to sulfuric acid. Reaction likely proceeds from small pores to larger until low pH of sulfuric acid suppresses the dissociation of H_2S, which results in the observed breakthrough.

Conclusion

The results presented here show the differences in the performance of various materials as hydrogen sulfide adsorbents. For comparison, only the best commercial materials are used. As demonstrated, the variety of the oxidation products can be found on the surface and the speciation depends on textural and chemical heterogeneity of their surfaces. However, the desired speciation depends on the final application and options of disposal, a good carbonaceous material for H_2S removal should be basic in its nature and have available pore space to store oxidation products.

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References

(1) http://www.epa.gov/air/caaac/dieselreview.pdf
(2) Stirling, D. *The Sulfur Problem: Cl;eaning up Industrial Feedstocks*, RCS, Cambridge, 2000.
(3) Turk, A.,;Sakalis, S.; Lessuck, J.,; Karamitsos, H.; and Rago, O. *Environ. Sci. Technol.* 1989, **33**, 1242
(4) Stuetz, R. M.,;Fenner, R. M; Engin, G; *Wat. Res.* **1999**, *33*, 453.
(5) Turk, A.,; Sakalis, E.; Rago, O.; Karamitsos, H. *Annals New York. Academy of Sciences* **1992**, *661*, 221
(6) Bandosz, T. J.; Bagreev, A.; Adib, F.; Turk, A. *Environ. Sci. Technol*. **2000**, *34*, 1069.
(7) Bansal, R. C.; Donnet, J. B.; Stoeckli, F. *Active Carbon*: Marcel Dekker: New York, 1988.
(8) Avgul, N.N.; Kiselev, A. V. in *Chemistry and Physics of Carbon*; Walker, P. L., Jr., Ed.; Marcel Dekker: New York, 1970; Vol.6.
(9) Puri, B. R., In *Chemistry and Physics of Carbon*; P.J. Walker, Jr. Ed.; M. Dekker: New York, 1970; Vol. 6, p. 191.
(10) Leon y Leon, C. A., and Radovic, L. R. In *Chemistry and Physics of Carbon*; P.A. Thrower, Ed.; M. Dekker: New York, 1992; Vol. 24., pp. 213-310.
(11) Kaliva, A. N.; Smith, J. W. *Can. J. Chem. Eng.* **1983**, *61*, 208 .
(12) Bandosz, T. J., In *Fundamental of Adsorption 6,* Munier, F., Ed.: Elsevier: Paris 1998; p. 635.
(13) Adib, F.; Bagreev, A.; Bandosz, T. J. *Environ. Sci. Technol***. 2000,** *34*, 686.
(14) Adib, F.; Bagreev, A.; Bandosz, T. J. *J. Coll. Interface Sci*. **1999**, *214*, 407
(15) Adib, F.,; Bagreev, A.; Bandosz, T. J. *J. Coll. Interface Sci.* **1999,** *216*, 360.
(16) Adib, F.; Bagreev, A.; Bandosz, T. J. *Ind.Eng.Chem.Res*. **2000**, *39*, 2439.
(17) Klein, J.; Henning, K-D. *Fuel* **1984**, *63*, 1064.
(18) Hedden, K.,; Humber, L.; Rao, B. R. *VDI-Bericht* **1976**, *37/42*, 253.
(19) Meeyoo, V.; Lee, J. H.; Trimm, D. L.; Cant, N. W. *Catalysis Today* **1998**, *44*, 67.
(20) Meeyoo, V.; Trimm, D. L.; Cant, N. W. *J. Chem. Tech. Biotechnol*. **1997**, *68*, 411.
(21) Coskun, I; Tollefson, E. L..*Can. J. Chem. Eng.* **1986,** *58*, 72.
(22) Ghosh, T. K.; Tollefson, E. L. *Can. J. Chem. Eng.* **1986**, *64*, 960.
(23) Bagreev, A.,Adib, F.; Bandosz, T.J. Carbon, **2001**, 39, 21987.
(24) Choi, J. J.; Hirai, M.; Shoda, M., *App. Catal. A*, **1991**, *79*, 241.
(25) Li, C. T., U. S. *Patent No. 4,196,183*, (1980).
(26) Bagreev, A.; Bandosz, T.J. *Ind. Eng. Chem. Res*. **2002**, *41*, 672.
(27) Przepiorski J.; Oya A. *J Mat Sci Lett* **1998**, *17*, 679-82
(28) Radovic, L.R.; Rodriguez-Reinoso F. In *Chemistry and Physics of Carbon*; Thrower PA, Ed.: M. Dekker; New York, 1997; Vol.25, pp. 243-358.
(29) Salame, I.I.; Bandosz, T.J. *Langmuir* **2000**, *16*, 5435.
(30) Matviya, T. M., Hayden, R. A., *U.S. Patent 5,356,849* (1994).
(31) Hayden, R.A. *U.S. Patent 5,444,081* (1995).
(32) Adib, F.; Bagreev, A.; Bandosz, T. J. *Langmuir* **2000**, *16*, 1980.
(33) Bandosz, T.J. J. *Colloid Interface Sci.* **2002**, *246*, 1.
(34) Bagreev, A., Bandosz, T.J. Carbon, **2001**, *39*, 2303.
(35) Bagreev A.; Bandosz T.J.; Locke DC. *Carbon* **2001**, *39*, 1971.
(36) Bagreev, A.; Bashkova, S.; Locke, D.C.; Bandosz T.J. *Environ. Sci. Technol.* **2001**, *35*, 1537.

(37) Bashkova, S.; Bagreev, A.; Locke, D.C; Bandosz, T.J. Fundamentals of Adsorption -7, Kaneko K, Kanoh H, Hanzawa Y. Eds., IK International, Chiba, Japan, 239-246, 2002
(38) Bagreev, A.; Bandosz, T.J. *Environ. Sc.i Technol* **2004**, *38*, 345.
(39) Graham, J. US Patent No. 60.254,9000 (2004)
(40) ASTM D6646-01.
(41) Lastoskie, Ch. M.; Gubbins, K. E.; Quirke, N., *J. Phys. Chem.* **1993**, 97**,** 4786 ;
(42) Olivier ,J. P.; Conklin, W. B. *Presented at 7th International Conference on Surface and Colloid Science*, Compiegne, France, 1991
(43) ASTM Standards (1998). Vol.15.01. Refractories; Carbon and Graphite Products; Activated Carbon; Advanced Ceramics.
(44) Brennan, J.K.; Bandosz, T.J.; Thomson, K.T.; Gubbins, K.E. *Colloids and Surface A,* **2001**, *187-188*, 539.
(45) Kortum, G.; Vogel, W.; Andrussow, K. In *Dissociation Constants of Organic Acids in Aqueous Solutions*. Butterworth, London, 1961.