

On the utilization of industrial/municipal sludges
as a source of desulfurization adsorbents

T. Bandoz

*Department of Chemistry, The City College of CUNY,
138th Street and Convent Ave.*

New York, NY 10031; Tel: (212) 650-6017; Fax (212) 650-6107;

E-mail: tbandosz@ccny.cuny.edu

Adsorbents for desulfurization of moist air were prepared from mixtures of sewage sludge, industrial sludges, and other carbonaceous wastes by their pyrolysis at 650 °C and 950 °C. The resulting inorganic/organic composite materials were characterized using sorption of nitrogen, thermal analysis, pH measurements, ICP, and X-ray diffraction. Their catalytic performance for hydrogen sulfide oxidation from air was evaluated in a dynamic test. The sludge-derived adsorbents have very high capacity for hydrogen sulfide removal and high selectivity of its conversion to elemental sulfur. While surface chemistry enhances oxidation, the developed volume of mesopores provides space for storage of elemental sulfur. Within that sulfur deposit in large pores secondary pore space is formed. The excellent performance in desulfurization process is governed by synergetic effects between the components of the sludges, which leads to the unique surface chemistry. This surface chemistry is a result of solid-state reactions in the reduced atmosphere during pyrolysis at high temperature.

1. INTRODUCTION

Utilization of various wastes [1-5], including sewage sludges [6-19] has been the topic of scientific interests for decades. As environmental regulations become stricter and the Earth more densely populated more and more scientists and environmental engineers focus their attention on minimization of wastes, their detoxification [20, 21] or recycling in other technological processes. Sewage sludge and industrial sludges are the wastes, which are produced by contemporary society in abundant quantity [6-7]. The latter category, can even

be considered as hazardous materials. So far sewage sludge has been mainly converted to fertilizer, burned with coal in energy production technology, converted into biofuel, or added to cements or other ceramic-based materials as for instance tiles [22-23]. Industrial sludges, on the other hand, are mainly disposed in lagoons or landfills. Recently, the thermal treatment prior to disposal was proposed to reduce their toxicity and leaching to soils [20, 21].

As described in the scientific literature, thermal treatment of sewage sludge leading to low cost unsophisticated adsorbents was proposed in the 70's of the last century [8-10]. The more advanced applications have been proposed recently when attention was focused on the catalytic properties of sludge-derived materials owing to their chemical composition [12, 24]. It was shown that sewage sludge based adsorbents are efficient media for removal of hydrogen sulfide from wet air stream as those in sewage treatment plants [11-18, 24]. The catalytic properties are even enhanced when other sludges such as waste oil sludge or metal sludge are added to the municipal sludge. This is the result of the basic pH of sludge-derived adsorbents, and the presence of iron. They are considered as the main factors governing their high catalytic activity [12, 24].

So far mainly activated carbons are used as hydrogen sulfide odor removal media [25, 26]. This is owing to their large surface area and high volume of micropores [27, 28]. To improve their odor removal capability the surface is treated either with oxidations, such as KI or potassium permanganate, or with bases such as KOH, NaOH or K_2CO_3 [28, 29]. While the first groups of compounds helps in direct oxidation of hydrogen sulfide, the second provides basic pH, which enhances dissociation of H_2S to HS^- . The latter is easily oxidized in the carbon pore system by dissociatively adsorbed oxygen. Based on this process the catalytic carbons such as Midas[®], Darco H_2S [®], or Centaur[®] were developed on which high removal capacities can be reached [30-33]. In the case of the latter material, since hydrogen sulfide is oxidized on its surface to sulfuric acid, the in situ regeneration is feasible [34]. All catalytic carbons, although very attractive from the point of view of the H_2S removal capacity, are much more expensive than the sludge derived adsorbents. Moreover, utilization of sludges, can lead to waste minimization and to a decrease in environmental pollution, which happens as a result of the heavy metal leaching to the soil when sludges are disposed in the landfills.

Taking into account the above, the objective of this paper is to present a summary of our recent work on the utilization of sludges as a source of desulfurization adsorbents. Since numerous experimental routes were explored, only the best adsorbents are presented in this paper with the emphasis on the surface features governing their performance as desulfurization media. Thus the effects of the pH, alkali metal content, iron content, chemical engagements of catalytically important elements, volume of pores and their sizes, dispersion of

inorganic/carbonaceous phases along with the preparation conditions such as temperature and time of pyrolysis are addressed.

2. EXPERIMENTAL

2.1. Materials

New York City dewatered sewage sludge, waste oil sludge and metal sludge (from Newport News shipyard) were dried to constant mass and then pyrolyzed, either as a single components or as a mixture in a horizontal furnace in nitrogen atmosphere with 10 deg/min heating rate and nitrogen flow 100 ml/min. Holding time was 0.5 or 1 hour and the final pyrolysis temperature was chosen as 650 °C, and 950 °C. The names of the samples discussed, their composition and the preparation conditions are presented in Table 1. After H₂S adsorption, E is added to the names of the samples, which refers to the exhausted material.

Besides samples obtained from only sludge containing precursors, the composite sample were prepared containing either polymer (polystyrene sulfonic acid co-maleic acid sodium salt) [16], waste paper [17], waste engine oil [35], or low cost activated carbon (S207-Waterlink Barnabey and Sutcliffe or WVB-Westvaco) [18] mixed with sewage sludge. In same case (waste paper) calcium hydroxide was added. Their description is included in Table 1. The details about the preparation of the adsorbents are described in references [16-18], [35]. In the case of sludges, the yields of the final products were between 30-50%.

According to the information supplied by the shipyard, the waste oil sludge was treated with CaCl₂, Na₃PO₄, NaOH and alum. Metal sludge treatment includes addition of sulfuric acid and sodium hydroxide for pH adjustments, Al₂SO₄ for coagulation, anionic and cationic polymers, sodium bisulfide for chromium reduction, lime and CaCl₂. Thus, besides alkaline or alkaline earth element-containing compounds and iron, the waste oil sludge also contains 0.4% Cu, 2 % Zn and between 200 and 1000 ppm of chromium, lead and nickel. In metal sludge there are less than 1% each of cadmium, chromium, copper, lead, manganese, selenium, vanadium and zinc. The content of volatile compounds in both waste oil sludge and metal sludge reaches 40% their dry mass, while the content of water in as-received materials is about 75%. The pH is neutral. The sewage sludge from NYC was characterized elsewhere [36]. It contains about 65% of fixed solids and about 35 % of volatile solids and has neutral pH.

Tab. 1. Sludge based adsorbents, their compositions and pyrolysis conditions.

Name	Compositions*	Pyrolysis temp. [°C]	Holding time [min]
Sludges only:	SS-sewage sludge	WO-waste oil sludge	MS-metal sludge
SS-1	SS:100%	950	30
SS-2	SS:100%	950	60
WO-1	WO:100%	650	30
WO-2	WO:100%	950	30
WOSS-1	WO:50%; SS:50%	650	30
WOSS-2	WO:50%; SS:50%	950	30
WOMS-1	WO:50%; MS:50%	650	30
WOSSMS-2	WO:40%; SS:40%; MS:20%	950	30
Sewage sludge +	OL: waste car oil or	AC: S-207 or	WVB:AC
SS-2OL	SS:	950	60
SC-S207	SS:50%; S207:50%	950	60
SC-WVB	SS:50%; WVB:50%	950	60
Sewage sludge +	WP: Waste paper or/	and Ca: Ca(OH) ₂	
SSWP	SS:25%; WP:75%	950	60
SSWP-1 (3)	SS:42.5%; WP:42.5%; Ca:5%	950	60
SSWP-2 (4)	SS:38%; WP:58%; Ca:4%	950	60
Sewage sludge +	PS: Polymer		
CPS50/50	SS:50%; PS:50%	950	60
CPS70/30	SS:30%; PS70%	950	60

* sludges are used in wet form (about 25% solids) and other components are dry.

2.2. Methods

Evaluation of H₂S sorption capacity. A custom-designed dynamic test was used to evaluate the performance of adsorbents for H₂S adsorption from gas streams as described elsewhere [12]. Adsorbent samples were ground (1-2 mm particle size) and packed into a glass column (length 370 mm, internal diameter 9 mm, bed volume 6 cm³), and pre-humidified with moist air (relative humidity 80 % at 25 °C) for one hour. The amount of water adsorbed was estimated from the increase in the sample weight. Moist air (relative humidity 80 % at 25 °C) containing 0.3 % (3,000 ppm) of H₂S was passed through the column of adsorbent at 0.5 L/min. The flow rate was controlled using Cole Palmer flow meters. The breakthrough of H₂S was monitored using electrochemical sensors. The test was stopped at the breakthrough concentration of 350 ppm. The adsorption capacities of each adsorbent in terms of mg of hydrogen sulfide per g of adsorbent were calculated by integration of the area above the breakthrough curves, and from the H₂S concentration in the inlet gas, flow rate, breakthrough time, and mass of sorbent. For each sample the test was repeated at least twice.

The amount of water preadsorbed was evaluated from a difference in the weight of samples before and after the prehumidification. The check if SO_2 was a byproduct of surface reaction its concentration was monitored using an electrochemical sensor.

Adsorption of nitrogen. On the materials obtained sorption of nitrogen at its boiling point was carried out using ASAP 2010 (Micromeritics). Before the experiments, the samples were outgassed at $120\text{ }^\circ\text{C}$ to constant vacuum (10^{-4} torr). From the isotherms, the surface areas (BET method), total pore volumes, V_t , (from the last point of isotherm at relative pressure equal to 0.99), volumes of micropores, V_{mic} , mesopore volume V_{mes} along with pore size distributions were calculated. The last quantity was calculated using density functional theory, DFT [37, 38].

pH. The pH of a carbon sample suspension provides information about the acidity and basicity of the surface. A sample of 0.4 g of dry carbon powder was added to 20 mL of distilled water and the suspension was stirred overnight to reach equilibrium. Then the pH of suspension was measured.

Thermal analysis. Thermal analysis was carried out using TA Instrument Thermal Analyzer. The instrument settings were: heating rate $10\text{ }^\circ\text{C}/\text{min}$ and a nitrogen atmosphere with $100\text{ mL}/\text{min}$ flow rate. For each measurement about 25 mg of a ground adsorbent sample were used.

X-Ray Diffraction. X-ray diffraction measurements were conducted using standard powder diffraction procedure. Adsorbents were ground with methanol in a small agate mortar. Grinding of the adsorbents by hand ensures particle sizes between $5\text{-}10\text{ }\mu\text{m}$, which prevents line broadening in diffraction peaks. The mixture was smear-mounted onto the zero-background quartz window of a Phillips specimen holder and allow to air dry. Samples were analyzed by Cu K_α radiation generated in a Phillips XRG 300 X-ray diffractometer. A quartz standard slide was run to check for instrument wander and to obtain accurate location of 2θ peaks.

Elemental analysis. The content of metals was determined using ICP.

SEM. SEM analysis was one on Ziess DSM 942 scanning electron microscope.

3. RESULTS AND DISCUSSION

The results of H₂S breakthrough capacity measurements are summarized in Table 1. When the performance per unit mass is considered all composite materials behave much better than sewage sludge based adsorbents. In the case of some mixtures, as those with waste paper, about 3 times improvement in the capacity is recorded. The performance significantly increases when sewage sludge is mixed with waste oil sludge or metals sludge. On the other hand, when capacity is expressed per unit volume of the adsorbent bed the improvement in the performance reaches only about 50 mg/cm³, which is about twice more than the capacity obtained on coconut shell based activated carbon [28]. WO-1 and SSWP series of materials are exceptions. Their capacity is comparable to that obtained on caustic impregnated activated carbon and that of Centaur catalytic carbon [25, 30]. In all cases but WO-2 only small amount of SO₂ were emitted (less than 2 ppm). Although for WO-2 7 ppm of SO₂ were recorded, the emission occurred at the same time when H₂S was detected in the outlet gas. Thus the secondary pollution problem seems to be not important in the case of these materials.

Tab. 2. H₂S breakthrough capacity, water adsorption, and surface pH.

Name	H ₂ S Brth. Cap. [mg/g]	H ₂ S Brth. Cap. [mg/cm ³]	Water ads. [mg/g]	pH	pHE
SS-1	45	21	26	10.9	10
SS-2	82	46	62	10.8	9.9
WO-1	315	82	48	9.3	9.3
WO-2	109	52	0	9.9	9.4
WOSS-1	146	53	21	9.2	9.1
WOSS-2	108	50	11	10.8	9.1
WOMS-1	130	49	14	9.8	9.4
WOSSMS-2	121	56	4	10.5	9.4
SS-2OL	115	54	65	11.3	9.5
SC-S207	84	41	ND	10.1	4.3
SC-WVB	92	24	ND	8.1	3.9
SSWP (5)	237	57	74	12.3	9.8
SSWP-1 (3)	211	105	61	12.0	11.5
SSWP-2 (4)	351	120	64	12.0	11.2
CPS50/50	160	21	245	8.7	6.6
CPS70/30	111	31	134	9.0	9.9

The differences are also observed in the behavior of sludge-derived materials as water adsorbents. While the samples obtained entirely from sludges adsorb relatively small amounts of water and some of them can be considered as hydrophobic (WO-2 or WOSSMS-2), the addition of a carbon phase

significantly increases the surface hydrophilicity. One can see these results as contradictory to the general knowledge about composition of our samples. It is well known that activated carbons are considered as hydrophobic materials [39, 40], whereas inorganic compounds are more hydrophilic. In fact the latter ones are the predominate species in the sludge based materials which consists of only up to 25% of carbon [12, 41-44]. This apparent discrepancy can be explained by changes occurring within the solid matrices during the pyrolysis in the reduced atmosphere in the presence of char. As indicated based on the study of hydrogen sulfide removal on activated carbons, the presence of water is crucial for the oxidation process [26, 28, 45, 46]. Provided that the pH is basic enough to enable dissociation of hydrogen sulfide [26, 28, 47], water facilitates oxidation via enhancing formation of HS^- ions, which react with dissociatively adsorbed oxygen. More HS^- ions are produced, more efficient the desulfurization process is [28]. While a high capacity of hydrophobic surfaces of WO-1 can be explained by changes in surface chemistry when the sample is exposed for long time to moisture (during the breakthrough experiment), which results in formation of surface hydroxides, the low capacity of very hydrophilic samples can be linked to their relatively low pH [28]. These pH values are the results of reactivity of the polymer-derived carbons with oxygen, which causes formation of surface acidic groups [39, 40, 48]. Their presence in the local pore environment limits the extent of hydrogen sulfide dissociation. It has to be pointed out here that the surface pH represents the average acidity and in the specific pore of the carbon the environment can be much more acidic. The strongly basic surfaces of the samples obtained from the mixtures of sewage sludge with waste paper are the results of the addition of significant amounts of calcium or the addition of calcium carbonate to paper during its production process (SSWP).



Fig. 1. Sulfur (light particles) removed from pore system of the sludge-derived adsorbent (black particles) via heating at 100 °C in vacuum.

After H₂S adsorption the pH only slightly decreases for the samples, which are based on sludges as their main components. This indicates deposition of elemental sulfur. Figure 1 shows sulfur phase separated from the sludge-derived adsorbent (black particles) just by heating at 100 °C in vacuum. In the case of the samples containing the porous carbon phase, either that coming from an addition of activated carbons or formation of carbon from the polymer during carbonization, the pH decreases up to 4 pH units and becomes very acidic. This indicates formation of sulfuric acid in the small pores of carbons [28].

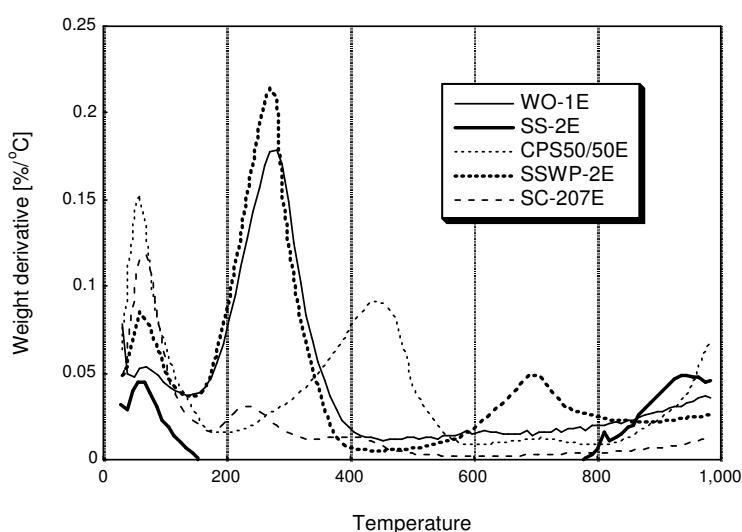


Fig. 2. Examples of DTG curves for exhausted samples. The initials samples (not shown) do not have well pronounced peaks between 150 and 600 °C.

The difference in the speciation of sulfur compounds formed on the surface of our adsorbents and their location on the surface can be seen on the examples of DTG (differential thermal gravimetry) curves (Figure 2). In all cases the position and intensity of the DTG peaks located between 150 and 600 °C are important for the analysis. These peaks represent the weight loss due to the removal of hydrogen sulfide surface oxidation products, elemental sulfur and/or sulfuric acid. The first peak at about 120 °C represents removal of physically adsorbed water and weakly adsorbed SO₂. For the samples containing activated carbons the peak located at 200 °C represents the mixture of SO₂ from decomposition of sulfuric acid and sulfur adsorbed in the large pores of the sludge-derived phase [26]. The second peak at over 400 °C represents the removal of elemental sulfur from small pores of the adsorbents. In the samples containing only sludges or nonporous carbon phase originated from waste paper

(cellulose) only one intense peak is present between 150 and 200 °C [17, 41-43]. This peaks represents removal of elemental sulfur deposited in large pores of the adsorbents. The shift of the peak toward higher temperature is related to the presence of smaller pores. The effect of that sulfur deposition on porosity of the samples is discussed further in this paper.

The high initial pH of our materials is the result of the presence of calcium, magnesium and sodium compounds added to sludges during their processing at the generator plants [41, 42]. The content of catalytically important metals for hydrogen sulfide oxidation via its reactive adsorption [26, 28] is presented in Table 2 for selected samples. In this table the content of carbon is also listed. The content of magnesium and calcium in all samples is very high. These alkaline earth elements are critical for feasible desulfurization. On catalytically active carbon, Midas®, manufactured by USFilters about 60 wt % hydrogen sulfide is oxidized to sulfur owing to MgO and CaO in its composition [30, 32]. The homogeneous mixture of these oxides with porous carbon is crucial for good desulfurization performance [32]. Contrary to alkali metal compounds, these oxides are not water-soluble. In spite of this, in the presence of water they are able to provide basic pH, which facilitates dissociation of hydrogen sulfide. The presence of carbon particles in the vicinity of the oxide particles enables migration of HS⁻ to the carbon pore system and its oxidation by dissociatively adsorbed oxygen. Thus the basic catalytic centers are “refreshed” to facilitate the dissociation of other H₂S molecules. The capacity is exhausted not due to the catalyst deactivation but due to the filling of the carbon pores with elemental sulfur [30].

Tab. 3. Content of catalytically important metals and carbon in selected samples [%].

Name	C	Fe	Ca	Mg	Cu	Zn
SS-1	20	6.1	5.1	1.1	0.17	0.09
SS-2	19	6.6	4.7	ND	0.17	<0.05
WO-1	11	3.2	4.0	11.0	0.20	0.54
WO-2	9	3.7	5.1	8.4	0.25	0.51
WOSS-1	ND	4.0	4.4	6.15	0.16	0.36
WOSS-2	ND	4.9	5.1	4.7	0.21	0.30
WOMS-1	ND	8.3	6.9	3.9	0.32	0.27
WOSSMS-2	ND	4.5	7.0	3.9	0.34	0.30
SS-2OL	23	6.7	4.9	ND	0.17	ND
SSWP (5)	50	ND	10	ND	ND	ND
SSWP-1 (3)	64	ND	8	ND	ND	ND
SSWP-2 (4)	60	ND	7	ND	ND	ND

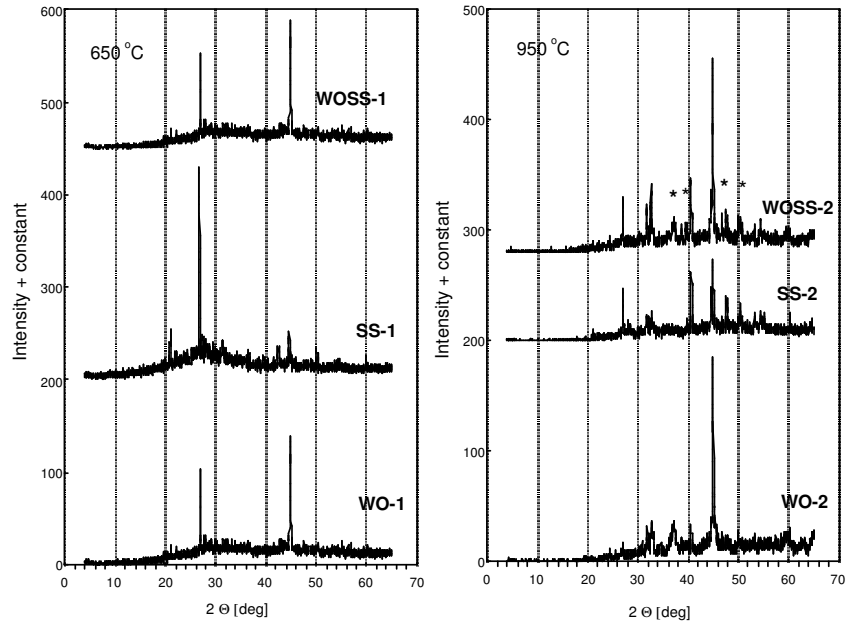


Fig. 3. X-ray diffraction pattern for the samples pyrolyzed at different temperatures. Stars indicate the new phases formed as a result of solid-state reactions.

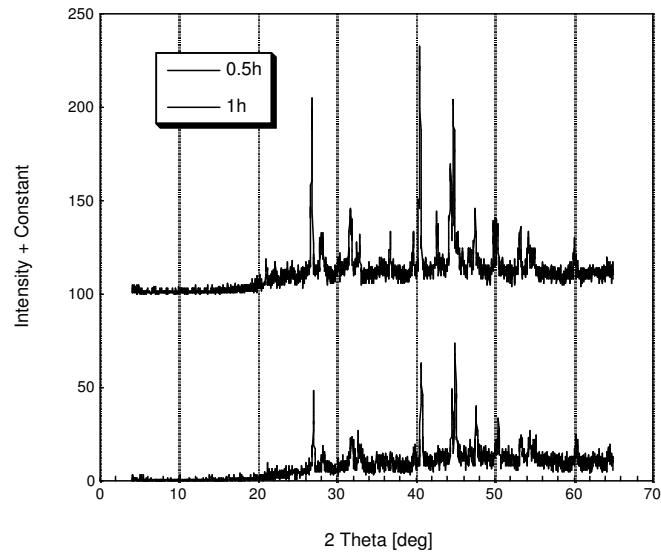


Fig. 4. X-ray diffraction patterns for the sewage sludge (SS) samples pyrolyzed at different times.

In spite of similarities in contents of magnesium and calcium in many of our samples and their very basic pH the capacity for hydrogen sulfide removal differs. The reason for this is in differences in porosity or/and in surface chemistry. The latter factor is critical for the performance of materials as catalysts. In fact, in some sludge-derived adsorbents such as SS-1 or SS-2, the content of catalytically active metals is almost identical but 100% difference in the performance as hydrogen sulfide adsorbents is found. The main difference between SS-1 and SS- is their pyrolysis time. Similar situation exists for other composite samples where with the same composition the pyrolysis temperature was either 650 °C or 950 °C (Table 1). These pyrolysis conditions appear to be crucial for the properties of adsorbents [42].

Figure 3 and 4 show the examples of the differences between X-ray diffraction patterns for samples of the same initial compositions obtained at various pyrolysis times (half an hour and an hour) and various temperatures (650 °C and 950 °C). As seen, the patterns significantly differ. Longer pyrolysis times or higher temperatures result in more diffraction peaks, which is related to the higher degree of mineralization. High temperature treatment of the sludge-derived materials causes solid-state reactions and formation of new crystallographic phases which are not present in the samples obtained at lower temperatures [41-44]. Moreover, new phases arise when the sludges are mixed owing to the broader spectrum of elements.

The detailed X-ray diffraction analysis indicated that at low temperature the main crystallographic phases are aluminosilicates with calcium and magnesium as exchangeable cations. Examples found for sludges addressed in this paper include magnesium calcite, sapphirine ((Mg₄Al₄)Al₄Si₂)O₂₀), CaAl₂(Si₂Al₂)O₁₀(OH)₂), almandine (Fe₃Al₂(SiO₄)₃), anorthite (CaAl₂Si₂O₈), and huntite (Mg₃Ca(CO₃)₄) [42-44, 50]. Detecting magnesium and calcium as exchangeable cations does not exclude the presence of amorphous oxides or carbonates of these metals, especially for samples containing waste oil sludge and having the exceptionally high hydrogen sulfide removal capacity. Besides alkaline earth metal arrangement, the state of iron is also important [24]. When pyrolyzed at low temperature it exists as metallic iron or in the form of goethite - FeO(OH) [42].

Taking into account the above, the following reactions enhancing oxidation of hydrogen sulfide are possible for materials pyrolyzed at low temperature, in our case 650 °C:





Pyrolyzing samples at 950 °C results in formation of reactive redox catalysts such as ferroxihite (FeO(OH)) and maghemite (Fe₂O₃) [42]. The presence of the latter promotes the following oxidation reactions



Ferrous oxide can be further oxidized to ferric oxide by oxygen from air.

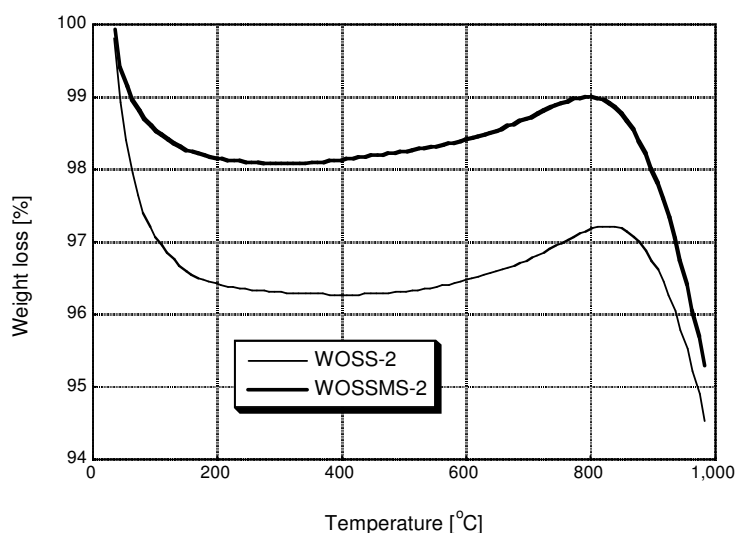


Fig. 5. TG curves in nitrogen curves for sludge derived samples.

High temperature pyrolysis also leads to a decrease in the content of aluminosilicates and to a formation of rare compounds in the reduced forms such as wurtzite (ZnS), chalcocite (Cu_{1.96}S), spinel (MgAl₂O₄), bornite (Cu₅FeS₄), zincite (ZnO), cohenite (Fe₃C), and smithsonite (ZnCO₃) [40]. They may also affect the oxidation of hydrogen sulfide [49].

Another interesting feature of some sludge-derived materials from the point of view of surface chemistry is an observed increase in weight when the samples are exposed to nitrogen (Fig. 5) [41, 42, 49]. This increase happens at a relatively low temperature (start as low as 400 °C) and at this stage of our study the only plausible explanation of this behavior is formation of nitrides. Although

it sounds thermodynamically unlikely at such low temperatures, the formation of nitrides at relatively low temperature [50] and in the presence of char [51] has been recently reported in the literature.

Mentioned above changes in surface chemistry have their influence on the differences in water adsorption during the prehumidification. In samples pyrolyzed at 650 °C, calcium and magnesium oxides are present which react with water to form hydroxides. After heating at 950 °C much less oxides is present and more complex hydrophobic structures appear. In spite of this, water can still interact with spinel, $\text{FeO}(\text{OH})$, $\text{Al}(\text{OH})_3$ or carbonates [41, 44]. Besides, the location of those species is also important and when hydrophilic species is located in small pores, the amount of water adsorbed will be enhanced.

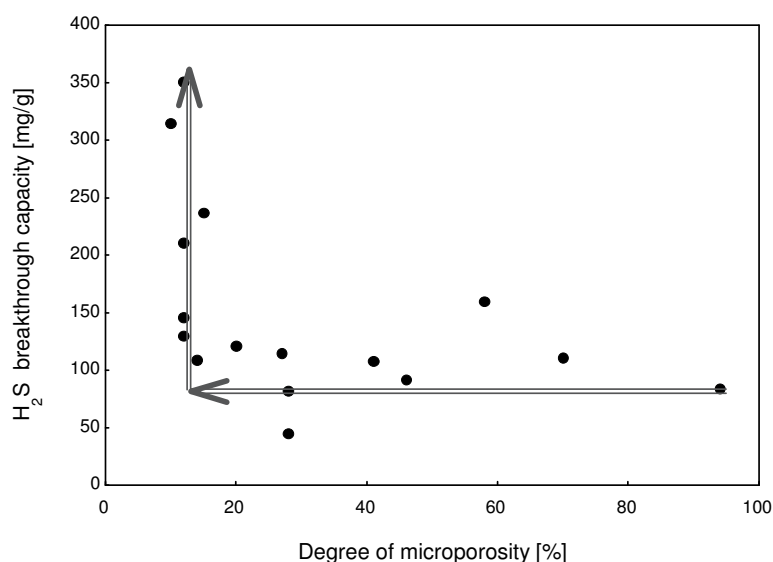


Fig. 6. Dependence of the H₂S removal capacity on the degree of microporosity.

Besides surface chemistry, porosity is also important for the performance of materials as adsorbents [27, 39, 40]. The pores are expected to provide the space for storage of oxidation products and they are also considered as microreactors where oxidation of hydrogen sulfide occurs. From the point of view of selectivity of oxidation reaction, very small pores as those in microporous activated carbons leads to formation of sulfuric acid [28, 37]. In such pores HS- is oxidized to sulfur radicals, which, owing to the location in confined space, are not able to get in contact with other radicals to form oxidation resistant elemental sulfur polymer. In such a situation the radicals are oxidized to sulfur dioxide and than sulfuric acid is formed. In larger pores, supermicropores or

mesopores, bulky sulfur polymers can exist. This suggests that the adsorbents for hydrogen sulfide reactive oxidation should be rather meso- not microporous in their texture [49].

The structural parameters of the samples addressed in this paper calculated from nitrogen adsorption isotherms are collected in Table 4. The majority of the sludge-derived samples has the surface area about $100 \text{ m}^2/\text{g}$ with a small volume of micropores. Only the composite – sewage sludge-activated carbon samples have surface area over $500 \text{ m}^2/\text{g}$ owing to the contribution of carbon. These samples have also the highest degree of microporosity. On the other hand, the sludge-derived materials can be considered as mesoporous with the degree of mesoporosity reaching maximum 40%. In fact the best performing samples in hydrogen sulfide removal are those whose degree of mesoporosity is about 10%. Figure 6 shows that 10% degree of microporosity is the threshold value to reach a high capacity. Since on some samples (WO-1 or SSWP-1 or SSWP-2) about 30 wt % hydrogen sulfide can be adsorbed, it seems that not a high degree of mesoporosity but the absolute volume of mesopores should be a factor determining the capacity, providing that the similar catalytic chemistry is available in whole pore space. This is an important statement since the reactive adsorption, not physisorption is the mechanism of desulfurization in this case.

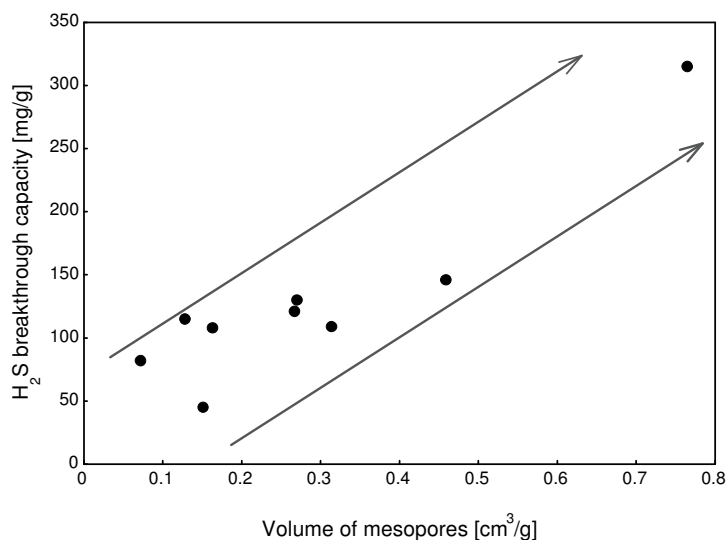


Fig. 7. Dependence of H_2S breakthrough capacity on the volume of mesopores.

Figure 7 shows the dependence of the H_2S breakthrough capacity on the volume of mesopores. If the samples containing activated carbons (either added

to sludge or obtained from polymer) and calcium added as a separate phase are excluded from the correlation due to differences in the mechanism of hydrogen sulfide oxidation, the trend is clearly seen, which supports our hypothesis about the specific catalytic effect of the sludges surfaces.

Tab. 4. Structural parameters calculated from nitrogen adsorption at $-196\text{ }^{\circ}\text{C}$.

Name	S_{BET} [m^2/g]	V_{mic} [cm^3/g]	V_{mes} [cm^3/g]	V_{t} [cm^3/g]	$V_{\text{mic}}/V_{\text{t}}$ [%]
SS-1	141	0.058	0.151	0.209	28
SS-1E	121	0.032	0.190	0.222	17
SS-2	122	0.028	0.072	0.100	28
SS-2E	21	0.002	0.063	0.065	3
WO-1	202	0.074	0.765	0.839	10
WO-1E	83	0.032	0.434	0.517	6
WO-2	132	0.050	0.314	0.364	14
WO-2E	96	0.034	0.355	0.389	8
WOSS-1	154	0.058	0.459	0.517	12
WOSS-1E	72	0.027	0.281	0.308	10
WOSS-2	150	0.061	0.163	0.224	41
WOSS-2E	89	0.030	0.258	0.288	31
WOMS-1	92	0.036	0.270	0.306	12
WOMS-1E	65	0.026	0.265	0.291	9
WOSSMS-2	144	0.053	0.267	0.320	20
WOSSMS-2E	59	0.022	0.183	0.205	11
SS-2OL	117	0.048	0.128	0.176	27
SS-2OLE	30	0.011	0.104	0.115	10
SC-S207	832	0.363	0.023	0.386	94
SC-S207E	616	0.257	0.116	0.373	69
SC-WVB	1023	0.393	0.456	0.849	46
SC-WVBE	726	0.262	0.401	0.663	39
SSWP (5)	73	0.018	0.101	0.119	15
SSWPE	16	0	0.057	0.064	0
SSWP-1 (3)	72	0.012	0.084	0.097	12
SSWP-1E	20	0	0.068	0.077	0
SSWP-2 (4)	67	0.012	0.089	0.102	12
SSWP-2E	14	0	0.047	0.052	0
CPS50/50	581	0.212	0.154	0.366	58
CPS50/50E	166	0.053	0.111	0.164	32
CPS70/30	948	0.377	0.162	0.539	70
CPS70/30E	334	0.134	0.128	0.262	51

After H_2S adsorption a decrease in the surface area is noticed for all samples. This is mainly due to the blocking of the small pores either by sulfur/sulfuric acid deposited inside or at their entrances. In all cases the volume of micropores decreases significantly or disappears. An interesting phenomenon is an increase in the volume of mesopores found for some sludge derived samples such as

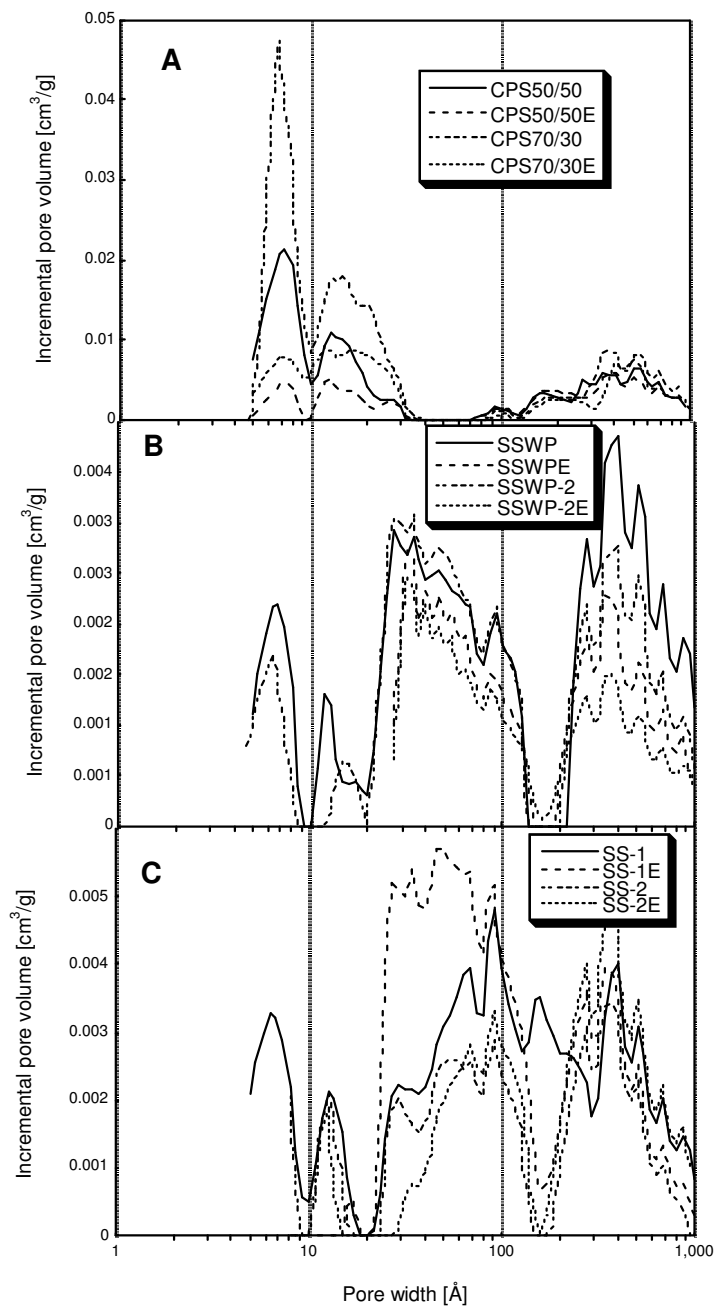


Fig. 8. Examples of pore size distributions for samples before and after H_2S adsorption.

SS-1, WO-2, and WOSS-2. Taking into account the excellent performance of these samples in desulfurization and a significant quantity of sulfur deposited on the surface of large pores, that increase must be the result of formation of the secondary pore network in those large pores. Elemental sulfur is deposited there in a significant quantity in the amorphous state and thus new pore volume arises within that deposit.

The examples of the changes in the pore volume are presented in Figure 8. For the samples containing the significant amount of a porous carbon phase active in the adsorption, and for which a decrease in the pH occurred, a marked decrease in the volume of micropores is found. Since this decrease generally does not correspond to the amount of sulfur adsorbed, this indicates that the pore volumes are blocked by sulfur for penetration by nitrogen molecules [28]. For the samples with a nonporous carbon phase present such as SSWP, (Fig. 8B) a marked decrease in the volume of pores between 100 and 1000 Å is found. These pores exist between the granules of sludge-derived phase and nonporous carbon aggregates and they are responsible for a low density of these materials (Figure 9). They are the main depository of sulfur formed on the surface. On the other hand, in the case of sewage sludge based materials (Figure 8 C) an increase in the volume of pores between 30 to 100 Å occurs as a result of the mentioned above secondary pore network formation with the sulfur deposit in large pores.

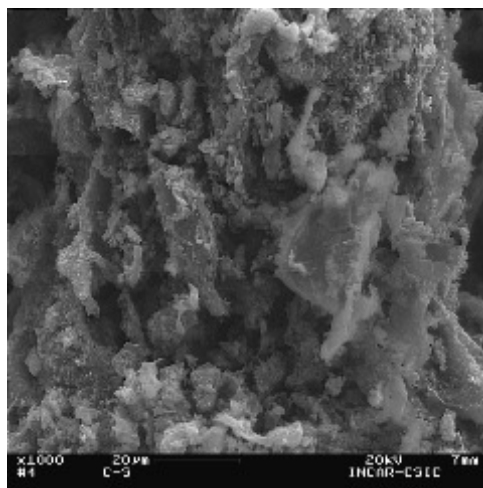


Fig. 9. SEM image of the SSWP sample.

An interesting phenomenon is an increase in the hydrogen sulfide removal capacity for the sample saturated with the spent car oil (SS-2OL). Since no changes in the content of catalytic metals were found and the porosity was not

affected significantly that increase was attributed to the rearrangement in the organic carbonaceous phase [35]. It has been found recently that on the sludge derived materials carbon nanotubes are formed in the process addressed as self imposed chemical vapor deposition (SICVD) as a result of the presence of catalytic metals [49]. It is likely that an addition of more carbonaceous phase can contribute to the development of more nanotubes and thus cause an increase the volume of large pores formed between those randomly arranged tubes (Fig. 10).

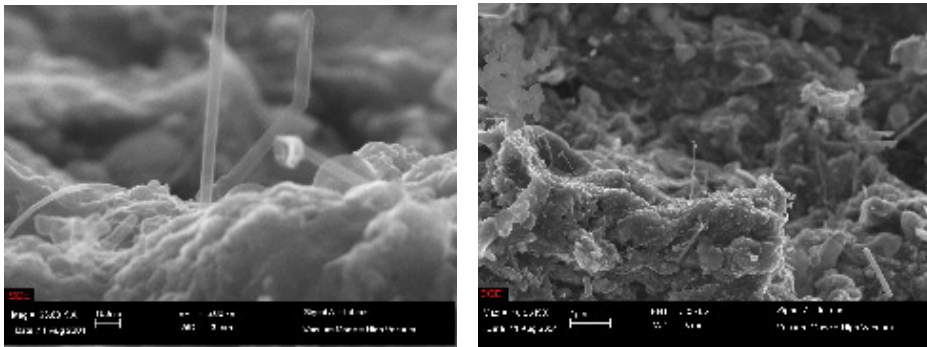


Fig. 10. Carbon nanotubes grown on the surface of sewage sludge derived adsorbents.

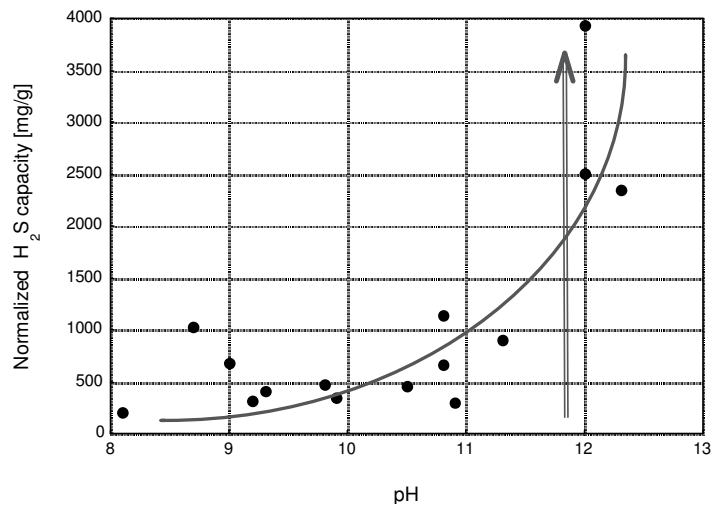


Fig. 11. Dependence of the normalized H₂S removal capacity (per unit volume of mesopores) on the surface pH.

Figure 11 shows the dependence of the normalized capacity in grams per unit volume of mesopores on the surface pH. All samples but those having extremely high pH have more or less similar quantity of sulfur adsorbed (about 0.5 g/cm^3), which indicates similarities in the chemistry and mechanism of the deposition process. This suggests that in the pH range between 4.5 (as indicated from our previous research [26]) and 12 the first stage of H_2S dissociation to HS^- occurs. The 4.5 average pH of the activated carbon surface was found as sufficient to enhance dissociation of H_2S although it was about 3 units less than pK_{a1} of hydrogen sulfide (7.02). Taking this into account, it is likely that at pH about 12 the mechanism changes and the formation of S^{2-} ions occurs even though it is about 2 pH unit less than pK_{a2} for hydrogen sulfide (13.89). Formation of these species can decrease the number of oxidation reaction paths and thus can increase the feasibility of H_2S oxidation by Fe_2O_3 .

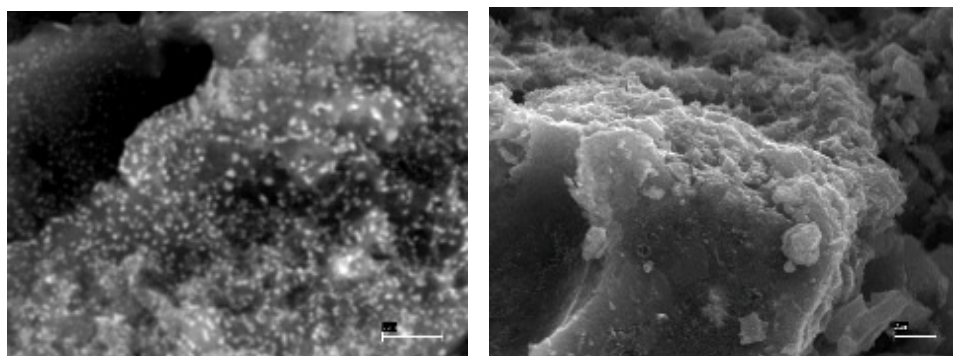


Fig. 12. SEM images for the sample containing a microporous carbon phase derived from a polymer and sewage sludge derived phase (magnification bars: $2 \mu\text{m}$)

Another important factor for the performance of adsorbents is the dispersion of the catalyst. It was shown as crucial for the best performing carbon, Midas[®] [30, 32]. Sludge in their nature are physically very homogeneous mud-looking materials. In this apparent homogeneity the high chemical heterogeneity is preserved. When well mixed with other carbonaceous materials the high dispersion of catalytic centers can be achieved. Figure 12 shows the SEM images of the SSWP surface where the bright spots represent the dispersion of metals in the carbonaceous phase.

4. CONCLUSIONS

The results presented in this paper demonstrate the possibility of obtaining the valuable desulfurization catalysts from industrial sludges either alone or in the mixtures with other low cost materials/waste materials. Up to 30 wt % hydrogen sulfide can be retained on the surface of these adsorbents as a result of the combined effects of their surface chemistry and porosity. Hydrogen sulfide is oxidized to elemental sulfur in the combined process of alkali-enhanced dissociation followed by oxidation on catalytic iron centers. These highly active centers are formed as a result of solid-state reaction/ synergy between the alkaline earth and transition metal components of the sludges during the pyrolysis process. The mesoporosity/macroporosity is crucial either for formation of elemental sulfur or its storage. Addition of new carbonaceous phase to sludges has to be done with precaution. Although it provides the pore space it results also in a decrease in the pH and thus in a decrease in the extent of hydrogen sulfide dissociation.

Acknowledgment. This work was a summary of our few years study and it would be not possible from the contributions of my students, colleagues and friends: Andrey Bagreev, Ph.D., David Frey, Ph.D., Svetlana Bashkova, Ph.D., Adil Ansari, Evi Sioukri, Karin Block, Neil Schultz, Anna Kleyman and Vyacheslav Starkov.

REFERENCES

- [1] A. Bousher, X. Shen, R.G.J. Edyvean, *Water Res.* 31 2084 (1997)
- [2] S. Netpradit, P. Thiravetyan, S. Towprayoon. *Water Res.* 37 763 (2003)
- [3] A. Bhatnagar, A. K. Jain. *J. Coll. Interface Sci.* 281 49 (2005)
- [4] D.C. Sharma, C.F. Forster, *Water Res.* 27 1201 (1993)
- [5] C. Raji, T.S. Anirudhan. *Ind. J. Chem. Technol.* 3 345 (1996)
- [6] www.epa.gov Biosolids regeneration, Use, and Disposal in the United States: EPA530-R-99-009; U.S.EPA: Washington, D.C. Septemeber 1999
- [7] M. Lundin, M. Olofsson, G.J. Pettersson, H. Zetterlund, H. *Res. Conserv. Rec.* 41 255 (2004)
- [8] F.M. Lewis, US Patent 4,122,036 (1977)
- [9] J. Sutherland, US Patent 3,998,757 (1976)
- [10] R.D. Nickerson, H.C. Messman, US Patent 3,887,461 (1975)
- [11] G.Q.Lu, J.F.C Low, C.Y. Liu, A.C. Lau, *Fuel* 74 3444 (1995)
- [12] A. Bagreev, S. Bashkova, D.C. Locke, T.J. Bandosz, *Environ. Sci. Technol.* 35 1537 (2001)
- [13] S. Bashkova, A. Bagreev, D.C. Locke, T.J. Bandosz, T.J. In *Fundamentals of Adsorption -7*, K. Kaneko, H. Kanoh, Y. Hanzawa Eds. IK International, Chiba, Japan, p. 239-246, (2002)
- [14] M.J. Martin, E. Serra, A. Ros, M.D. Balaguer, M Rigola, M., *Carbon* 42 1389 (2004)
- [15] S. Rio, C. Faur-Brasquet, L. Le Coq, P. Courcoux, P. Le Cloirec, *Chemosphere* 58 423 (2005)
- [16] A. Ansari, A. Bagreev, T.J. Bandosz, *Carbon* 43359 (2005)

- [17] A. Ansari, T.J. Bandoz. *Environ. Sci. Technol.* 39 6217 (2005)
- [18] E. Sioukri, T.J. Bandoz. *Environ. Sci. Technol.* 39 6225 (2005)
- [19] S. Rio, C. Faur-Brasquet, L. Le Coq, P. Le Cloirec. *Environ. Sci. Technol.* 39 4249 (2005)
- [20] G.C.Harrison, US Patent 4,872,993 (1989)
- [21] B.H. Jones, US Patent 4.781,994 (1988)
- [22] K-S Wang, C-J. Tseng, I-J Chiou, M-H Shih. *Cem. Conc. Res.* 35 803 (2005)
- [23] K-S Wang, I-J Chiou, C-H Chen, D. Wang. *Constr. Bulg. Mat.* 12 627 (2005)
- [24] A. Ros; M.A. Montes-Moran, E. Fuente, D.M. Nevskaiia, M.J. Martin, M. J. 40, 302 (2006)
- [25] T.J. Bandoz, A. Bagreev, F. Adib, A. Turk. *Environ. Sci. Technol.* 34 1069 (2000)
- [26] T.J. Bandoz. *J Colloid Interface Sci.* 246, 1 (2002)
- [27] R.C. Bansal, J.B. Donnet, F. Stoeckli. *Active Carbon*; M. Dekker: New York, 1988
- [28] T.J. Bandoz. In *Activated Carbon Surface in Environmental Remediation*. T.J Bandoz Ed. Elsevier, Oxford, 231-292, (2006)
- [29] J. Przepiorski, A. Oya. *J. Mat. Sci. Lett.* 17679 (1998)
- [30] A. Bagreev, T.J. Bandoz, *Ind. Chem. Eng. Res.* 44 530 (2005)
- [31] M.Seredych, T.J. Bandoz, *Ind. Chem. Eng. Res.* In press
- [32] J.R Graham, C-J. Yuan. US Patent 6.858,192
- [33] T. M. Matviya, R.A. Hyden US Patent 5,356,849 (1994)
- [34] R. A. Hyden. International Patent WO95/26230 (1995)
- [35] A. Bagreev, T. J. Bandoz. *Environ. Sci. Technol.* 38 345. (2004)
- [36] Bagreev, A., Bandoz, T.J. Locke, D. *Carbon* 39 1971 (2001)
- [37] C.M. Lastoskie, K.E. Gubbins, N.J. Quirke, *J. Phys. Chem.* 97 4786 (1993)
- [38] J.P. Olivier, *J.Porous Materials* 2, 9 (1995)
- [39] C. Leon y Lean, L.R. Radovic. In *Chemistry and Physics of Carbon*; Thrower, P.A. Ed. M. Dekker: New York, 1992; Vol.24, pp.213-310
- [40] T. J. Bandoz and C. O.Ania. In *Activated Carbon Surfaces in Environmental Remediation*; T.J. Bandoz Ed. Elsevier: Oxford 2006; pp 159-230
- [41] T.J. Bandoz and K. Block, *Environ. Sci. Technol.* In press
- [42] T. J. Bandoz, K. Block, *Ind. Chem. Eng. Res.* In press
- [43] T.J. Bandoz, K. Block. *Appl. Catal: Environ.* In press
- [44] T.J. Bandoz, A. Bahryeyev, US Patent 6,962,616 (2005)
- [45] A. Primavera, A. Trovarelli, P. Andreussi, G. Dolcetti. *Appl. Catal. A: Gen.* 173, 185 (1998)
- [46] A. N. Kaliva, J.W. Smith. *Can. J. Chem. Eng.* 61 208 (1983)
- [47] K. Hedden, L. Humber, B.R. Rao, *VDI-Bericht* Nr 253 S. 37/42, VDI-Verlang, 1976
- [48] D. Hines, A. Bagreev, and T.J. Bandoz, *Langmuir* 20 3388 (2004)
- [49] M. Seredych, and T.J. Bandoz, *Chem. Eng. J.*, In press
- [50] O. Yamamoto, M. Ishida, Y. Saitoh, T. Sasamoto, S. Shimada, *Int. J. Inorg. Mat.* 3 715 (2001)
- [51] R. Koc, S. Kaza. *J. European Ceramic Soc.* 18 1471 (1998)

CURRICULUM VITAE

Teresa J. Bandoz graduated from AGH University of Science and Technology in Kraków, Poland with master in Chemical Engineering/Coal Processing Technology. In 1989 she received Ph.D. in Chemical Engineering from Technical University of Kraków (Polytechnic). Her D.Sc. Degree in Physical Chemistry/ Analytical Chemistry was awarded from Maria Curie-Skłodowska University in Lublin, Poland, in 1998. From 1991



till 1996 she was working as a research associate in Syracuse University, Department of Chemical Engineering and Materials Science in the group of Professor James Schwarz on the hydrogen storage program. In 1996 she was offered a faculty position at the Department of Chemistry, the City College of the City University of New York where she is still working as a full professor. Her research interests focus on application of adsorption to environmental problems which include development of new adsorbents based on activated carbons, clays and industrial wastes, desulfurization of air, fuel gases and liquid fuel, removal of odoriferous pollutants from air and removal of toxic industrial gases. She also works as a consultant for such companies as Dupont, Synagro, or Fuel Cell Energy. She is responsible for controlling odor removal from New York City Water Pollution Control Plants and her work on this subject was featured by New York Times (Feb. 21, 2005). Her scientific achievements include over 160 peer review publications, 2 book reviews, and 5 book chapters, 5 US patents. Recently she edited a book on “Activated Carbon Surface in Environmental Remediation” published by Elsevier. She also serves on Editorial Board of Adsorption Science and Technology and was an organizer of ACS Fuel Division Symposiums on carbon-based materials.