

SEWAGE SLUDGE ENRICHED CARBONACEOUS MATERIALS AS MEDIA FOR GAS PHASE DESULFURIZATION

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Introduction

Adsorbents obtained by pyrolysis of sewage sludge can be considered as complex pseudocomposite materials. However, the process of carbonization of biosolids has been studied in detail previously and it is described in the literature [1-9, 11] so far the most promising results were obtained in our laboratory [10, 12-15]. It has been recently shown that by simple pyrolysis of sewage sludge derived fertilizer, Terrene®, exceptionally good adsorbents for removal of sulfur containing gases can be obtained. Their removal capacity is twice that of coconut shell based activated carbon. The data also showed that the oxidation of hydrogen sulfide occurs until all micropores (mainly about 6 Å in size), likely within carbonaceous deposit or on the carbon/oxide interface, are filled with the reaction products. The form of that carbonaceous deposit is not known but based on the previous results that deposit is important from the point of view of adsorption capacity. The products of oxidation immobilized on the surface are stored there. For a toxic gas containing reduced sulfur the capacity is much greater than that of activated carbons. It happens in spite of the fact that the carbon content is small (about 20 %) and pore volume much smaller than that of activated carbons [13-15].

Since pore volume seems to be a limiting factor for the capacity of sewage sludge derived materials, an increase in the content of carbonaceous deposit and pore volume with maintaining the desired content of a catalytically active phase (sewage sludge) seems to be the desired direction of future research. In such a case the products of oxidation will be stored in a sufficient quantity in the pore system making the removal capacity for sulfur containing gases exceptionally high.

Experimental

Materials

The adsorbents were prepared from dewatered sewage sludge, polystyrene sulfonic acid-co maleic acid sodium salt, and mixture of dewatered sewage sludge and polymer (50:50 weight %). In all cases the pyrolysis was done at horizontal furnace at nitrogen atmosphere with heating rate 30 deg/min. The final pyrolysis temperature was 950 °C with holding time 1 hour. Since polymer (polystyrene sulfonic acid-co maleic acid sodium salt) contains a lot of sodium, after preparation the materials were washed in a Soxhlet apparatus to constant pH of water leachate. That process resulted in opening of

the pore structure of the adsorbents as a result of the removal of sodium salts. The names of adsorbents, and their yields are collected in Table 1. For the names of exhausted samples after H₂S adsorption a letter "E" is added.

Table 1.
Names of samples, yields on various stages, bulk density and ash content.

Sample	Yield [%]	Yield Washed [%]	Amount of dry sludge [%]	Density [g/cm ³]	Ash Content [%]
Carbonized Dried Sludge (CS)	40	40.1	100	0.55	75
Carbonized Polymer (CP)	35	7.7	0	0.10	0.9
CPS 50/50	39	17	20	0.12	32

Methods

A custom-designed dynamic test was used to evaluate the performance of adsorbents for H₂S adsorption from gas streams as described in the technical literature. 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 100 ppm. The adsorption capacities of each sorbent in terms of mg of H₂S 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 average surface pH was estimated by placing 0.4 g of carbon powder in 20 mL of water and equilibrated during night. Then the pH of the suspension was measured.

Nitrogen isotherms were measured using an ASAP 2010 (Micromeritics) at 77 K. The isotherms were used to calculate the specific surface areas (S), micropore volumes (V_{mic}), total pore volumes (V_t), average micropore sizes (L_{mic}), and pore size distributions by DFT method.

Thermal analysis was carried out using TA Instruments Thermal Analyzer. The instrument settings were: heating rate 10 °C/min in nitrogen atmosphere with 100 mL / min flow rate.

The chemistry was evaluated first using potentiometric titration experiments described [16]. Here, it is assumed that the population of sites can be described by a continuous

pK_a distribution, $f(pK_a)$. The experimental data can be transformed into a proton binding isotherm, Q , representing the total amount of protonated sites, which is related to the pK_a distribution by the following integral equation

$$Q(pH) = \int_{-\infty}^{\infty} q(pH, pK_a) f(pK_a) dpK_a \quad (1)$$

The solution of this equation is obtained using the numerical procedure [17], which applies regularization combined with non-negativity constraints. Based on the spectrum of acidity constants and the history of the samples, the detailed surface chemistry shall be evaluated.

Results and Discussion

The data presented in Table 1 shows the yield of the materials obtained. It is clearly seen that yields of the polymer based material and its mixture with sewage sludge is very low. This is the result of the high water content in dewatered sludge (about 75 %) and the presence of sodium in the polymer. Washing with water decreases yields even more as a result of removal of that sodium salts and hydroxides. However, washing is expected to open the pore structure, it may also have a negative effect on the capacity due to the removal of some water soluble basic compounds from carbonized sewage sludge based component.

Table 2.
H₂S breakthrough capacity results (at 100 ppm)

Sample	H ₂ S brth. Cap.[mg/cm ³]	H ₂ S brth. Cap.[mg/g]	Water Adsorption[mg/g]	pH _{in}	pH _E
CPS50/50	20.8	160	245	8.70	6.60
CP	0	0	150	6.02	----
CS	10.4	19	93	7.38	7.15

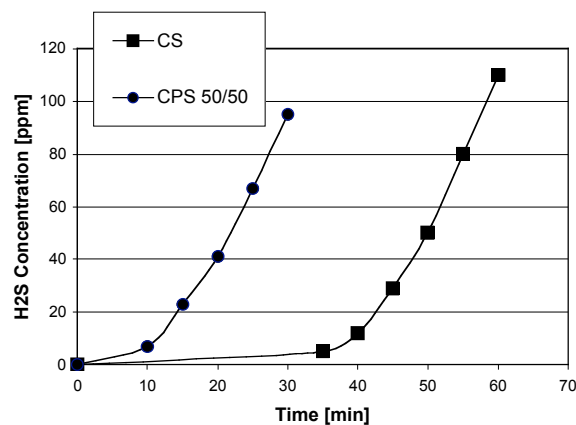


Figure 1. H₂S breakthrough capacity curves.

The results presented in Table 2 and Figure 1 show the differences in the performance of materials. The highest breakthrough capacity is obtained for a sewage sludge-polymer mixture. Its capacity is twice higher than that obtained from pure sludge. The differences are greater when the capacity per unit mass is considered. The CPS50/50 sample is very light so its capacity is substantial. Differences in the bulk density have an effect on the feasibility of the application of adsorbents in industry. Usually adsorbents have a limited size so the capacity per unit volume is important.

It is very interesting that the polymer based sample has no capacity for hydrogen sulfide removal. Another important finding is a smaller capacity of the sewage sludge based sample than that one reported previously [13] this is attributed to the removal of basic species from the surface during water washing. Those species enhance the adsorbent capacity maintaining basic pH of the surface. Washing with water was done in order to open the pores in the polymer based-phase, in spite of its negative effect on the capacity of the sludge-based phase. Such treatment enables us to fully compare and understand the processes/reactions taking place on the surfaces of adsorbents.

Table 3.
Structural parameters of adsorbents studied.

Sample	S_{N2} [m ² /g]	V_{mic} [cm ³ /g]	V_{mes} [cm ³ /g]	V_t [cm ³ /g]
CS	94	0.017	0.086	0.113
CSE	32	0.004	0.103	0.133
CP	1240	0.518	0.242	0.860
CPE	1240	0.518	0.242	0.860
CPS 50/50	581	0.212	0.088	0.366
CPS 50/50E	166	0.053	0.082	0.164

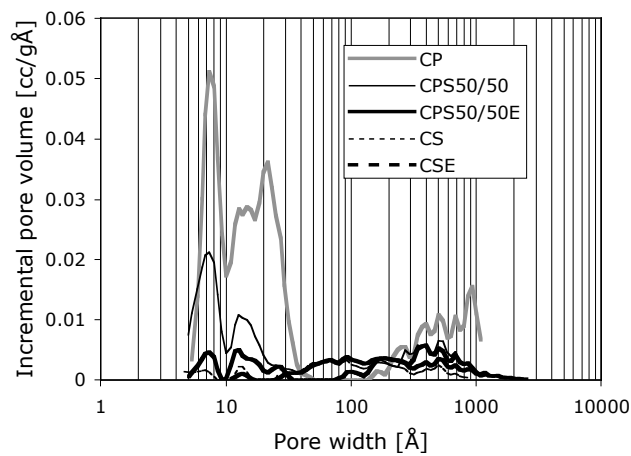


Figure 2. Pore size distributions.

The differences in the performance of our materials as H₂S adsorbents have to be linked to the differences in their pore structure (Table 3) and surface chemistry. The pore size distributions are collected in Figure 2.

The results demonstrate significant differences in the porosity of samples. The polymer derived sample, CP, is very porous, with the majority of pores having sizes smaller than 20 Å. Besides those pores, also noticeable volume of mesopores is found. The surface area and micropore volume reach 1240 m²/g and 0.5 cm³/g, respectively. Such high surface area could be developed owing to the decomposition of a precursor and chemical changes in the organic matrix. During carbonization organic polymer decomposes to CO₂, SO₂, H₂S, and hydrocarbons. Those gases act as pore formers in the carbon matrix after completion of polycondensation of benzene-like rings. Moreover, migration of sodium and its reaction with the released gases contributes also to the development of porosity [18]. In fact, the surface area of the sample without water washing was almost negligible as a result of the pore blocking by sodium species. It is interesting that with such characteristics that sample shows no capacity for hydrogen sulfide adsorption. As described elsewhere [19], hydrogen sulfide to be oxidized on the surface of carbon has to dissociate in the film of water. That dissociation occurs only when the local pH in the pore system enables it. It was established that when an average pH of carbon is higher than 4.6, the capacity for H₂S removal is noticeable. Of course, that average pH does not necessary represents the actual pH in the pore environment. Taking into account that CP has high volume of pores, which should be accessible for water and hydrogen sulfide, the only plausible explanation is that the pH of its surface is apparently acidic and it may suppress dissociation of hydrogen sulfide. In fact, when the sample was exposed to air a strong exothermic effect was noticed. This was likely the result of the combined reactions of sodium with moisture and oxygen with carbon at the edges of thin graphene layers. Indeed, the average surface pH reported in Table 2 for this samples is in the acidic range.

The surface area of the CPS50/50 sample is the combination of the low surface area of the sludge derived sample and the high surface of the polymer derived material. In fact, for this sample the volume of pores smaller than 10 Å is very high. Comparison of the pore size distributions presented in Figure 2 suggests that polymer based carbon mainly contributes to this porosity. Besides the features of the CP and CS samples, the unique pores, only characteristic for this sample, are formed with the sizes between 30 Å and 100 Å.

Exposure to H₂S significantly decreases the pore volume and surface area of CPS50/50 and CS samples. That decrease is much more pronounced for the former sample since its capacity was the highest. This clearly demonstrates that the products of oxidation, either sulfur or SO₂/sulfuric acid are deposited in the micropore system of this material.

That sulfur species can be detected from TA analysis. As seen from Table 4 a significant increase in the amount of desorbed species occurred for CPS50/50E sample in the temperature range 380-500 °C, which represents desorption of elemental sulfur. Besides elemental sulfur, some sulfuric acid can be also present as suggested from the decrease in the pH and an increase in the weight loss between 200-380 °C for the sample exposed to H₂S. For activated carbon, at this temperature range SO₂ desorbs from decomposition of sulfuric acid. On the other hand, on the sludge based sample a low temperature peak at 200-350 °C is linked to the removal of elemental sulfur. For this sample only a slight decrease in the pH was noticed.

Table 4.
Weight losses [%] in nitrogen at various temperature ranges.

Sample	100-200 °C	200-380 °C	380-500 °C	500-650 °C	650-850 °C	850-980 °C	Total Weight loss (30- 980°C)
CS	0.9	0.22	0.27	0.90	3.05	6.30	13.34
CSE	1.5	4.47	0.91	0	0.33	3.42	14.15
CP	0.50	2.0	1.0	1.95	5.26	4.17	17.06
CPE	---	---	---	---	---	---	---
CPS50/50	1.84	3.94	1.16	1.29	3.14	5.14	19.74
CPS50/50E	1.98	5.26	10.75	1.44	2.09	3.78	34.33

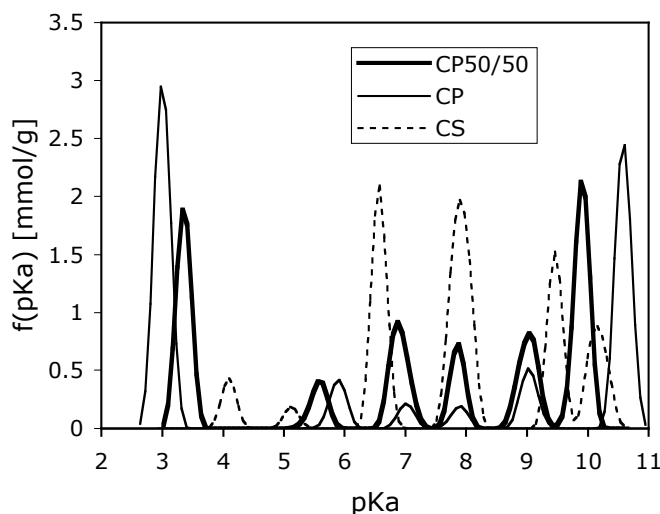


Figure 3. Distributions of acidity constants.

As mentioned above, developed porosity is not enough to guarantee the high capacity of carbonaceous adsorbents for H₂S removal. While presence of pores of certain sizes is important for formation of sulfur radicals and polymers, and storage of oxidation products, surface chemistry has to favor high concentration HS⁻ ions, which are further

oxidized to sulfur and/or sulfur dioxide. The differences in the average pH (Table 1) showed that the most basic is CS and the least - CP. More details about acidity can be derived from the potentiometric titration data (Figure 3). The peaks on the distribution curves represent the amounts of acidic groups. Those having $pK_a < 8$ are considered as carboxylic groups, and those with $pK_a > 8$ can be classified as phenols. Of course this assumption can work only for carbon where inorganic phase is absent. That inorganic phase can also contribute to acidity/basicity of the sample. Analysis of the pK_a distributions collected in Figure 3 indicates strong acidic character of the carbon derived from the polymer. This supports our hypothesis about the effect of surface oxidation on diminishing the H_2S capacity of the material. The least acidic, as expected based on the pH values is the CS sample. The acidity CSP 50/50 is between the acidities of the other two samples derived from the pure precursors.

Conclusions

Based on the results described above, addition of polymer to the sludge significantly improves the capacity compared to the materials derived from pure precursors. The reason for this is likely in an increase in porosity (an increase in the amount of carbon phase) along with the “buffering” effect of sludge components towards maintaining the surface basicity. Adding sludge to the polymer likely suppresses oxidation of the carbon phase, which occur when the sample is derived from pure polymer.

References

- [1] Manahan SE. Environmental Chemistry, 6th ed.; CRC Press: Boca Raton, FL, 1994
- [2] [www.epa.gov Biosolids regeneration, Use, and Disposal in the United States: EPA530-R-99-009; U.S.EPA: Washington, D.C. Septemeber 1999.](http://www.epa.gov/Biosolids_regeneration,_Use,_and_Disposal_in_the_United_States:_EPA530-R-99-009;_U.S.EPA:_Washington,_D.C._Septemeber_1999)
- [3] Piskorz J, Scott DS, Westerberg IB. Flash pyrolysis of sewage sludge. IEC Process Des. Dev. 1996; 25: 265 .
- [4] Chiang PC, You JH. Use of sewage sludge for manufacturing adsorbents, Can. J. Chem. Eng. 1987; 65: 922 .
- [5] Lewis FM. Method of pyrolyzing sewage sludge to produce activated carbon US Patent 4,122,036 (1977).
- [6] Sutherland J. Preparation of activated carbonaceous material from sewage sludge and sulfuric acid US patent 3,998,757 (1976).
- [7] Nickerson RD, Messman HC. US patent 3,887,461 (1975).
- [8] Abe H, Kondoh T, Fukuda H, Takahashi M, Aoyama T, Miyake M. US Patent 5,338,462 (1994).
- [9] Lu GQ, Low JCF, Liu CY, Lau AC. Surface area development of sewage sludge during pyrolysis Fuel 1995; 74: 3444.
- [10] Bagreev A, Bandosz TJ. H_2S Adsorption/Oxidation on Adsorbents Obtained from Pyrolysis of Sewage Sludge-Derived Fertilizer Using Zinc Chloride Activation. Ind. Eng. Chem Res. 2001; 40: 3502.

- [11] Lu GQ, Lau DD. Characterization of sewage sludge-derived adsorbents for H₂S removal. Part 2: Surface and pore structural evolution in chemical activation Gas Sep. Purif. 1996; 10: 103.
- [12] Bagreev A, Bandosz TJ, Locke DC. Pore Structure and Surface Chemistry of Adsorbents Obtained by Pyrolysis of Sewage Sludge-Derived Fertilizer. Carbon 2001;39: 1971.
- [13] Bagreev A, Bashkova S, Locke DC, Bandosz TJ. Sewage Sludge Derived Materials as Efficient Adsorbents for Removal of Hydrogen Sulfide Environ. Sci. Technol, 2001; 35: 1537.
- [14] Bashkova S, Bagreev A, Locke DC, Bandosz TJ. Sewage Sludge Derived materials as Adsorbents for H₂S and SO₂. Fundamentals of Adsorption -7, K. Kaneko, H. Kanoh, Y. Hanzawa Eds., IK International, Chiba, Japan, p. 239-246, 2002
- [15] Bagreev A, Bashkova S, Reznik B, Zibat V, Bandosz TJ. Heterogeneity of Sewage Sludge Derived Materials as a Factor Governing their Performance as Adsorbents Of Acidic Gases. Proceeding of Conference on Characterization of Porous Solids-6, F. Rodriguez-Reinoso, Ed. Amsterdam 2003, p.217-224.
- [16] Jagiello J, Bandosz TJ, Putyera K, Schwarz JA. Determination of proton affinity distributions for chemical systems in aqueous environments using stable numerical solution of the adsorption integral. J. Colloid Interface Sci. 1995; 172: 341.
- [17] Jagiello J. Stable numerical solution of the adsorption integral equation using splines Langmuir 1994; 10: 2778.
- [18] Hines D., Bagreev, A., Bandosz, TJ. Surface properties of porous carbon obtained from polystyrene sulfonic acid-based organmc salts. Langmuir, 2004, in press.
- [19] Adib F, Bagreev A, Bandosz TJ. Analysis of the Relationship between H₂S Removal Capacity and Surface Properties of Unimpregnated Activated Carbons. Environ. Sci. Technol. 2000; 34: 686.