VIRGIN VERSUS CAUSTIC-IMPREGNATED CARBONS FOR CONTROL OF HYDROGEN SULFIDE EMISSIONS FROM SEWAGE PLANTS

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Introduction

Caustic carbons are widely used for removal of acidic gases such as hydrogen sulfide in municipal water treatment facilities [1, 2]. The risk of self-ignition due to the exothermic reaction direct our attention to study virgin activated carbons as H_2S adsorbents. The long term tests have been carried out for almost two years at North River Water Pollution Control Plants operated by New York City Department of Environmental Protection.

Experimental

Materials:

Caustic carbon (NRC) and virgin (NRVA) coconut based carbon supplied by Waterlink Barnabey and Sutcliffe were used in this test. Three testing periods referred to as 1, 2, and 3 (every six months) are reported in this study.

Methods

H_2S breakthrough capacity was measured using humidified air containing 1% (10,000ppm) of H_2S which was passed through a column of carbon. The test was stopped at breakthrough concentrations of 50 ppm. The pH of carbon surface was evaluated according to ASTM D 3838 standard procedure. Potentiometric titration measurements were performed with a DMS Titrino 716 automatic titrator (Metrohm). Thermal analysis was carried out using TA Instruments Thermal Analyzer. The content of sulfur in initial and exhausted carbons was measured by Huffman Laboratories, Golden, CO. Nitrogen isotherms were measured using a ASAP 2010 (Micromeritics) at 77K.

Results and Discussion

However, the pH values collected in Table 1 for NRVA-1 and NRC-1 are almost the same their breakthrough capacities measured using accelerated test significantly differ. Figure 1 shows that during two years the capacity decreased 98% for the caustic carbon and only about 21 % for the virgin material.

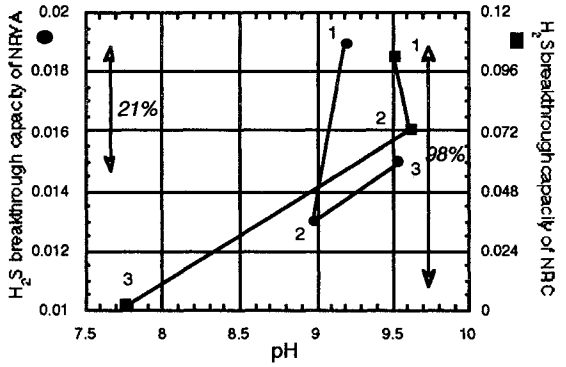

Figure 1. Dependence of H_2S breakthrough capacity upon pH for virgin and caustic carbons.

The differences in the behavior between virgin and caustic carbons as H_2S adsorbents are the result of the distinguishably different features of their surfaces. From the nitrogen sorption isotherms the structural parameters such as surface area (S_{BET}) and micropore volume (S_{mic}) were calculated (Table 1). After duration of the test (adsorption and oxidation of hydrogen sulfide), the surface areas and V_{mic} consequently decrease for virgin carbons due to the deposition of sulfur and its conversion to sulfur species adsorbed in small pores [1, 3]. In the case of caustic carbons, NRC, surface area and micropore volumes does not change significantly which suggests replacement of caustic in pores by sulfur and sulfur salts

Information about surface chemistry of carbons studied in the pK_a range between 3 and 10 is obtained from potentiometric titration experiments. The detailed description of the method is given elsewhere [4]. The results showed that after the second test, the number of groups representing carboxylic groups decreased. This decrease in the population of oxygen groups can be due to their contribution to oxidation of H_2S to elemental sulfur. After the third test, the numbers of carboxylic groups (pK_a<7) remains almost unchanged whereas the population of species at pK_a about 7 almost doubled. This pK_a is

equal to the first pK_a of hydrogen sulfide and it is likely the result of the presence of physically adsorbed H_2S or SO_2 on the surface of activated carbon. In the case of caustic carbon the influence of atmospheric CO_2 is seen as a peak at pK_a 6.93.

Thermal behavior of virgin and caustic carbons is presented in Table 2. Comparison of NRVA and NRC does not show significant differences in their ignition temperature taken as a maximum of the biggest exotherm on DTA curves measured in air. The curves obtained for NRVA carbons, besides the exotherms due to the ignition of carbon material, are almost featureless, whereas in the case of the NRC samples a small exotherm at about 350 °C is noticed [1]. This is likely due to the oxidation of elemental sulfur to sulfur oxides [5]. The intensity of this exotherm increases with an increasing content of sulfur.

In the case of the NRVA carbons, TG curves measured in nitrogen, besides the removal of physically adsorbed water and weakly adsorbed H_2S and SO_2 at temperature smaller than 120 °C, are almost featureless; only on NRVA-3 curve some change in a slope due to decomposition of sulfur species can be noticed [1, 5]. On the other hand, curves for caustic materials show significant changes after each testing period. The weight loss in the temperature range between 200 °C and 400 °C becomes more pronounced (Table 2) and the amount of weakly adsorbed species decreases with the duration of the test.

Conclusions

The results presented in this paper show the feasibility of using virgin carbon instead of caustic one to control odor in water treatment plants. However, its initial capacity shown by accelerated laboratory test is lower than caustic, it lasts longer as odor adsorbent. In the case of virgin carbon, especially when concentration of H_2S is low (real plant conditions) the developed pore system along with the catalytic impact of the carbon matrix promotes dissociative adsorption of H_2S and its oxidation.

Acknowledgment

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Table 1. pHs of carbon surfaces, H_2S breakthrough capacities, sulfur content and structural parameters.

Sample	pH	H_2S Breakthrough Capacity [g H_2S/g of carbon]	S content [%]	S_{BET} [m^2/g]	V_{mic} [cm^3/g]
NRVA-1	9.20	0.019	0.10	1010	0.460
NRVA-2	8.98	0.013	0.12	940	0.446
NRVA-3	9.54	0.015	0.34	720	0.308
NRC-1	9.51	0.103	0.26	560	0.240
NRC-2	9.62	0.073	0.60	580	0.215
NRC-3	7.76	0.002	2.01	590	0.192

Table 2. Ignition temperature, ash content and weight loss.

Sample	Ignition temperature [°C]	weight loss (30 °C -120°C) [%]	weight loss (300 °C -400 °C) [%]	Ash content [%]
NRVA-1	490	16.8	1.1	1.9
NRVA-2	480	27.1	1.4	2.4
NRVA-3	520	21.9	2.0	3.4
NRC-1	480	16.3	6.5	13.0
NRC-2	650	12.8	6.5	19.7
NRC-3	440	5.0	8.8	15.0