

SUBTASK 1.5 – ACTIVATED CARBON FROM LIGNITE FOR WATER TREATMENT

Final Report

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U.S. Department of Energy
National Energy Technology Laboratory
PO Box 10940, MS 922-342C
Pittsburgh, PA 15236-0940

Cooperative Agreement No. DE-FC26-98FT40320
Performance Monitor: Ms. Paula Flenory

Prepared by:

Edwin S. Olson
Daniel J. Stepan

Energy & Environmental Research Center
University of North Dakota
PO Box 9018
Grand Forks, ND 58202-9018

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EXECUTIVE SUMMARY

High concentrations of humate in surface water result in the formation of excess amounts of chlorinated byproducts during disinfection treatment. These precursors can be removed in water treatment prior to disinfection using powdered activated carbon. In the interest of developing a more cost-effective method for removal of humates in surface water, a comparison of the activities of carbons prepared from North Dakota lignites with those of commercial carbons was conducted. Previous studies indicated that a commercial carbon prepared from Texas lignite (Darco HDB) was superior to those prepared from bituminous coals for water treatment. That the high alkali content of North Dakota lignites would result in favorable adsorptive properties for the very large humate molecules was hypothesized, owing to the formation of larger pores during activation.

Since no standard humate test has been previously developed, initial adsorption testing was performed using smaller dye molecules with various types of ionic character. With the cationic dye, methylene blue, a carbon prepared from a high-sodium lignite (HSKRC) adsorbed more dye than the Darco HDB. The carbon from the low-sodium lignite was much inferior. With another cationic dye, malachite green, the Darco HDB was slightly better. With anionic dyes, methyl red and azocarmine-B, the results for the HSKRC and Darco HDB were comparable.

A humate test was developed using Aldrich humic acid. The HSKRC and the Darco HDB gave equally high adsorption capacities for the humate (138 mg/g), consistent with the similarities observed in earlier tests. A carbon prepared from a high-sodium lignite from a different mine showed an outstanding improvement (201 mg/g). The carbons prepared from the low-sodium lignites from both mines showed poor adsorption capacities for humate. Adsorption isotherms were performed for the set of activated carbons in the humate system. These exhibited a complex behavior interpreted as resulting from two types of sorption sites. The effect of pH on adsorption was investigated using buffered solutions. The sorption capacity decreased with increasing pH.

A study of the effect of activation conditions on the adsorption capacity of the resulting carbon showed that steam activation at 750°C provides the optimum activity with the high-sodium char. An attempt to scale up the carbon production to the 2-kg scale failed to produce the same high activity that was obtained in the 100-g batch unit. Although this research demonstrated that a highly active carbon for water treatment can be produced from high-sodium lignites, much further work is needed to understand what methods and equipment will be needed for large-scale production of this carbon.

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INTRODUCTION

New federal regulations continue to be promulgated to limit the concentration of disinfection by-products (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs) formed during the treatment of public water supplies. These federal mandates require additional treatment operations or a change in existing treatment operations. Many options have been evaluated, including membrane processes, granular activated carbon, powdered activated carbon (PAC), enhanced coagulation, and alternative disinfectants (e.g., chlorine dioxide, ozone, and chloramines). Of all the processes being considered, PAC appears to offer an attractive benefit-to-cost advantage for many water treatment plants, particularly small systems (those serving less than 10,000 customers).

PAC has traditionally been used in water treatment for the removal of compounds contributing to taste and odor problems. PAC also has the potential to remove naturally occurring organic matter (NOM) from raw waters prior to disinfection, thus controlling the formation of THMs and HAAs. The major advantage of using PAC for the removal of NOM is that it requires a relatively small expenditure to set up a PAC system compared to the other process alternatives. Many small water systems are currently using PAC for taste and odor control and have the potential to use PAC for controlling DBPs.

During disinfection of surface waters by chlorination, the natural organic material is chlorinated and oxidized to form chloroform, trichloroacetic acid, and other chlorinated DBPs that are carcinogens or toxic to humans. Since it is difficult to remove these compounds from treated water, the precursor humates are removed during drinking water treatment in a municipal plant. Powdered activated carbon is used to adsorb some of the soluble organic compounds in treatment basins.

In the interest of developing a more cost-effective method for removal of humates and other NOM from surface water, a comparison of the activities of carbons prepared from North Dakota lignites with those of commercial carbons was desired. Initial studies at the Grand Forks Water Treatment Plant (GFWTP) indicated that carbon from Texas lignite gave better removal than carbon from bituminous coals. The reason for the better performance is not understood, and whether the performance is better for all lignite-derived carbons is unknown.

Two aspects of activated carbons determine their effectiveness for removal of organic or inorganic contaminants in water: 1) the physical features (pore structure and surface area) and 2) the chemical features (reactivity factors, such as complexing abilities, reduction potential, or, in some cases, catalytic factors such as unpaired electrons or electron vacancies that are required for stabilizing intermediates of transition states). The effectiveness of the physical features in promoting adsorption is related to the ease of diffusion and access to surfaces. The effectiveness

of the chemical features is dependent on the energies required for bond formation as well as the concentration of accessible active sites for the reactions.

BACKGROUND

Current literature describes the pore volume distribution in lignite-based activated carbons as low in micropore volume (17% of the distribution) and high in concentration of macropores (35%–50%)(Bansal, Wilson). Although the pore structure of the original lignite shows considerable micropores, these are "burned out" in the charring and activation process, owing to the high volatility and reactivity of the lignite. Mass transfer within the carbon is slow for sorption in aqueous systems; thus a higher proportion of larger pores is desired for distribution of solute to the sorbent surfaces. Therefore, the lignite-derived carbons with the larger meso- and macropore distributions are more appropriate for adsorption from the liquid phase. If the goal is to remove humate matter from water, the very large humate molecules will not fit into the micropores anyway, so sorption will be facilitated in a carbon with larger meso- and macropore distribution. For gas treatment applications, the lignite-based carbons are at a severe disadvantage because of their low concentration of micropores.

Rist and Harrison reported that the pore size distribution of Darco (Texas lignite-based) carbon was bimodal, but with substantial pore sizes of 22 and 75 Å. Samples of Louisiana lignite-based carbons had mostly the 20-Å pores, but in this set of carbons, the total surface area and the total pore volumes were low (20%–40% of the Darco carbon). Since the Louisiana lignites are highly aliphatic, they give a much different pore distribution when activated. No similar pore characterization exists for the highly aromatic North Dakota lignites, but they should give carbons similar to the Texas lignite carbons.

Removal of mineral matter from the precursor lignite has recently been shown to improve the micropore volume of the activated carbon (Samaras). The reason for this is that the mineral matter catalyzes the pyrolysis and carbonization reactions that gasify the char and enlarge the pores. Thus lowering the activity of the char slows down the loss and allows the microporosity to develop. Earlier, Mochida demineralized Metla coal and improved the carbonization (decreased isotropic area). Our recent studies with acid-extracted leonardite demonstrated that higher adsorptive capacity was achieved with an acid-treated leonardite.

Not only does the mineral content of the coal significantly affect the pore structure of the subsequent carbon, but it can also significantly affect the chemical factors that are important in sorption. Large concentrations of divalent cations in the carbon sorbent could promote binding to the negatively charged humate macromolecules in the water.

It is therefore very important to adequately characterize the structures and inorganic contents of the lignites that are carbonized in this study and to correlate these properties with the pore distributions, surface areas, and sorption activities of the carbons prepared from the various lignites.

OBJECTIVE

The objective in this project was to determine the effects of the high alkali metal content of the North Dakota lignites on the properties of the resulting activated carbons when utilized for adsorption of humates in municipal water supplies.

RESULTS

Carbonization/activation experiments were performed on selected low-rank coals (LRCs) from North Dakota and the results compared with those obtained in similar tests with commercial activated carbons prepared from other coals. Two coals (high-sodium and low-sodium) from Knife River Coal Company, two coals (high-sodium and low-sodium) from Dakota Gasification Company, and one high-calcium coal from the closed Velva mine were tested. Sample designations are listed in Table 1. Bench-scale carbonization/activation was conducted with 100–150-g samples that were dried in an oven at 100°C under nitrogen. The coal was heated to 400°C in a tube furnace until evolution of tars ceased. The char was then heated in the tube to 750°C or other temperature, and steam (in nitrogen) was passed through the char for activation. Yields of activated carbon were generally about 35%–40%.

Previous testing at the GFWTP indicated that activities for NOM removal did not correlate with BET surface areas. The micropore areas measured by the BET methods with nitrogen or CO₂ are appropriate for predicting gas adsorption, but have little relevance for adsorption of the very large molecules, such as humates that comprise the NOM. For sorption in liquids, we expect to find correlations of NOM removal efficiencies with probes of larger size and with charges.

TABLE 1

Activated Carbons		
Precursor Coal for Activated Carbon	Source	Acronym
High-Sodium Lignite (Knife River)	EERC	HSKRC
Low-Sodium Lignite (Knife River)	EERC	LSKRC
High-Sodium Lignite (Dakota Gasification)	EERC	HSDGC
Low-Sodium Lignite (Dakota Gasification)	EERC	LSDGC
Velva Lignite	EERC	VC
Texas Lignite (Darco, HDB)	(American Norit Co.)	Darco-HDB

Thus standard adsorption tests were performed with polar organic probes as listed in Table 2. These include a variety of charged dye substrates of different sizes. A standard humate solution for the tests was prepared using Aldrich humic acid.

TABLE 2

Substrates for Adsorption Tests

Substrate	Charge	Type of Functionalities
Methylene Blue	Cation	Heterocyclic ammonium
Methyl Red	Anion	Diazo carboxylate
Azocarmine-B	Anion (Zwitterion)	Heterocyclic trisulfonate
Malachite Green	Cation	Ammonium
Humic Acid (Aldrich)	Anion	Polycarboxylate

Adsorption Kinetics

Preliminary testing was conducted to determine the amount of time required for adsorption to occur. The carbon prepared from high-sodium Knife River lignite was stirred with methylene blue solution and the decrease in absorbance monitored. These results are given in Table 3. After 2 hours, the absorbance values reach the minimum, indicating completeness of the adsorption onto the carbon. This sets the minimum time interval for testing these carbons with the various probes.

TABLE 3

Kinetic Studies of Methylene Blue Adsorption on Activated Carbons

Carbon, g	Time, min	Absorbance, at 400 nm	Conc., mg/mL	Amount of MB, mg	MB Removed, mg	MB Removed, mg/g
None	0	0.92	0.0204	1.01	—	—
0.0100	10	0.39	0.0047	0.235	0.755	76
0.0103	20	0.28	0.0028	0.14	0.85	83
0.0102	30	0.16	0.0013	0.065	0.925	91
0.0104	60	0.05	0.0003	0.015	0.975	94
0.0104	120	0.04	0.0002	0.010	1.000	94
0	120	0.90	0.0198	0.99	—	—

Note: Activated carbon used = 1268S-162-3 (carbon from high-Na lignite). Volume of methylene blue (MB) solution added to each carbon = 50 mL. MB solution concentration = 0.0204 mg/mL.

Methylene Blue Adsorption by Activated Carbons

A comparison test for sorption of the cationic dye, methylene blue, by the series of carbons was performed. Results from the single-point tests are given in Table 4. At the concentration tested, the removal efficiency exhibited by the HSKRC carbon exceeded somewhat that of the commercial Texas lignite-derived Darco carbon. The high adsorption capacity for methylene blue by these carbons is a good indicator of their potential for use in aqueous sorption systems. The adsorption of methylene blue by the LSKRC carbon was significantly lower. The poor performance of this carbon could be attributed to the higher calcium content in this carbon that might result in pore blockage. Another possible explanation is that the activation process was incomplete, owing to the reduced extent of sodium-catalyzed reactions during the preparation of this material from the low-sodium coal. But the calcium can also catalyze the gasification during activation. The Velva coal also had a higher amount of calcium, which could result in deactivation of the carbon. The medium activity of the VC carbon is consistent with this concept.

TABLE 4

Methylene Blue Adsorption on Activated Carbons					
Carbon, g	Absorbance, at 400 nm	Conc., mg/mL	Amount of MB, mg	MB Removed, mg	MB Removed, mg/g
None	0.95	0.0204	1.02	—	—
VC (0.0102)	0.29	0.0030	0.15	0.87	85.3
HSKRC (0.0104)	0.04	0.0005	0.025	0.995	98.0
LSKRC (0.0104)	0.62	0.0081	0.405	0.615	59.1
Darco-HDB (0.0104)	0.10	0.0013	0.065	0.955	91.8

Note: Volume of MB solution added to each carbon = 50 mL. MB solution concentration = 0.0204 mg/mL.

Malachite Green Adsorption by Activated Carbons

Malachite green is another cationic dye used in aqueous adsorption tests. Single-point tests were performed with the series of activated carbons, and the results are given in Table 5. The HSKRC and the Darco performed similarly, with capacities similar to those observed for methylene blue. The VC carbon also exhibited a high capacity for malachite green, which is not

consistent with the results for methylene blue, but remains unexplained. Again, the LSKRC capacity was poor.

TABLE 5

Malachite Green Adsorption on Activated Carbons					
Carbon, g	Absorbance, at 400 nm	Conc., mg/mL	Amount of MG, mg	MG Removed, mg	MG Removed, mg/g
None	0.86	0.0078 (0.0195)*	0.975	—	—
VC (0.0100)	0.035	0.00030	0.015	—	96
HSKRC (0.0105)	0.055	0.0005	0.025	0.950	91
LSKRC (0.0106)	0.037	0.0081	0.405	0.570	54
Darco-HDB (0.0101)	0.066	0.0013	0.065	0.974	96

Note: Volume of malachite green (MG) solution added to each carbon = 50 mL. MG solution concentration = 0.0200 mg/mL.

* Conc. was converted into original solution concentration by multiplying by 2.5.

Methyl Red Adsorption by Activated Carbons

Methyl red is an anionic (carboxylate-type) dye and might be expected to more closely resemble the humate NOM, which is also anionic in nature. A comparison test for adsorption of the methyl red dye by the series of carbons was performed. Results from the single-point tests are given in Table 6. As observed in the methylene tests, the removal efficiency exhibited by the HSKRC carbon matched closely that of the commercial Texas lignite-derived Darco carbon at the concentration tested. The capacity was not as high for the anionic dye on these carbons compared with the cationic methylene blue. The relatively high adsorption capacity for the methyl red carboxylate dye by these carbons is a good indicator of their potential for use in aqueous sorption systems containing NOM. The LSKRC and the Velva gave inferior adsorption results, as they did with methylene blue.

A separate test utilized the HSDGC carbon with methyl red dye at a somewhat different concentration. The results for this test are given in Table 7. The HSDGC appears to be comparable to the Velva and inferior to the Darco in this test.

Azocarmine-B Adsorption by Activated Carbons

Azocarmine-B is another anionic dye, which has three sulfonate groups. Because of the high concentration of negative charge, the dye should interact strongly with a carbon unless the carbon has picked up significant amounts of negative charge. Tests with the set of activated carbons using azocarmine-B gave results reported in Table 8. In these results, the capacities of all the carbons are depressed, so there is little difference between the carbons in the set. The capacity of the HSKRC is still the best of the set, however.

TABLE 6

Methyl Red Adsorption on Activated Carbons

Carbon, g	Absorbance, at 400 nm	Conc., mg/mL	Amount of MR, mg	MR Removed, mg	MR Removed, mg/g
Blank	0.69	0.0072 (0.018)*	0.90	—	—
VC (0.0108)	0.30	0.0032 (0.008)*	0.40	0.50	46.3
HSKRC (0.0111)	0.25	0.0021 (0.0053)*	0.26	0.64	57.7
LSKRC (0.0112)	0.43	0.0044 (0.011)*	0.55	0.35	31.3
Darco-HDB (0.0116)	0.18	0.0018 (0.0045)*	0.22	0.68	58.6

Note: Volume of methyl red (MR) solution added to each carbon = 50 mL. MR solution concentration = 0.0208 mg/mL.

* Conc. was converted into original solution concentration by multiplying by 2.5.

TABLE 7

Methyl Red Adsorption on HSDGC Activated Carbons

Carbon, g	Absorbance, at 400 nm	Conc., mg/mL	Amount of MR, mg	MR Removed, mg	MR Removed, mg/g
None	0.79*	0.0204	1.02	—	—
HSDGC (0.0106)	0.34*	0.0102	0.51	0.51	48.11

Note: Volume of MR = 50 mL. MR solution concentration = 0.0204 mg/mL.

*Conc. was converted into original solution concentration by multiplying by 2.5.

TABLE 8

Azocarmine-B Adsorption on Activated Carbons

Carbon, g	Absorbance, at 400 nm	Conc., mg/mL	Amount of AC, mg	AC Removed, mg	AC Removed, mg/g
None	0.88	0.0200	1.00	—	—
VC (0.0104)	0.70	0.0170	0.85	0.15	14
HSKRC (0.0101)	0.54	0.0145	0.725	0.0.275	27
LSKRC (0.0105)	0.63	0.016	0.800	0.200	19
Darco-HDB (0.0103)	0.56	0.0150	0.750	0.25	24

Note: Volume of azocarmine-B (AC) solution added to each carbon = 50 mL. AC solution concentration = 0.0200 mg/mL.

Humate Adsorption Tests by Activated Carbons

Since the major portion of NOM in the surface water in this region is humate derived from peat, a more specific test for carbon effectiveness would be to determine the amount of humate adsorbed from an aqueous solution. Aldrich humic acid was chosen as the standard substrate for this test, and a 100-mg/L solution was prepared for the tests. This is actually a larger concentration compared with the water humates (about 10–30 mg/L); thus the tests represent a high-loading condition. A calibration curve was determined using dilutions of this standard at pH = 6, with absorbance measured at a wavelength of 400 nm. The absorbance was linearly related to the concentration of humate.

A series of single-point tests was performed with the set of carbons. Approximately 0.01 g of dried activated carbon was placed in a 250-mL Erlenmeyer flask. Humic acid solution (50 mL) was added to the flask and stirred at room temperature for 2 hours. The resulting solution was centrifuged to remove carbon, and the absorbance of the supernatant liquid was measured. From these data, concentrations were used to calculate the sorption capacity of the activated carbons. The test results are shown in Table 9.

The HSKRC and the Darco gave equally high adsorption capacities for the humate (138 mg/g), consistent with the similarities observed in earlier tests. The HSDGC gave outstanding improvement in adsorption capacity (201 mg/g). A second test with slightly more

HSDGC carbon gave 134 mg/g. As expected from other conventional carbon isotherm data, larger amounts of carbon result in significantly lower loadings. The one-point test is in fact very sensitive to carbon in this range, so one must be careful to compare one-point data from the same carbon amount.

The capacities of the LSKRC and the VC were only one-quarter and one-half as large, respectively, as that of the HSKRC using the same carbon amount (10 mg). Finally, the capacity of the LSDGC was extremely poor. These carbons are all higher in calcium than the high-sodium carbons discussed above.

TABLE 9

Humate Adsorption on Activated Carbons

Carbon, g	Absorbance, at 400 nm	Conc., mg/mL	Amount of HA, mg	HA Removed, mg	HA Removed, mg/g
None	0.80	0.101	5.001	—	—
VC (0.0100)	0.71	0.088	4.4	0.601	60
HSKRC (0.0104)	0.60	0.0725	3.625	1.375	138
LSKRC (0.0104)	0.74	0.0930	4.65	0.35	35
HSDGC (0.0106)	0.47	0.0576	2.88	2.125	201
HSDGC (0.0127)	0.51	0.0660	3.30	1.70	134
LSDGC (0.0253)	0.79	0.0968	5.808*	0.25	10
Darco-HDB (0.0104)	0.60	0.0725	3.625	1.375	138

Note: 50-mL humate (HA) solution (0.1001 mg/mL) added to each carbon.

*Test used LSDGC = 60 mL.

To characterize the adsorption behavior of the carbons at a variety of carbon amounts, several isotherms were obtained. For the HSDGC, an isotherm was obtained using 10- to 100-mg carbon amounts with 50 mL of the 100-mg/L humate solution. The Freundlich log-log plot of these data is shown in Figure 1. For the two high-carbon loadings (81 and 102 mg of carbon), most of the humate is adsorbed and the absorbances of the solution at equilibrium were very low

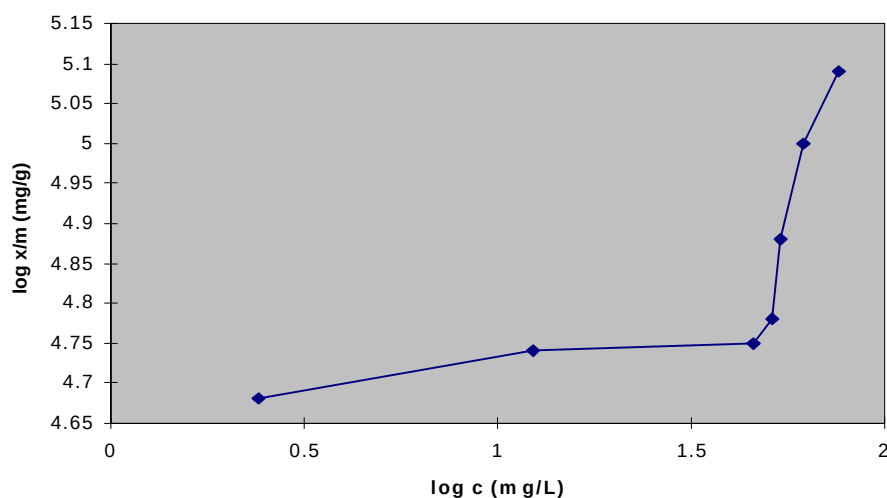


Figure 1. Adsorption isotherm for HSDGC carbon with leonardite humate.

is operating in the steep slope region, adding a lot of carbon makes little difference in the equilibrium concentration. Isotherms such as this with two or more slopes are usually interpreted as showing two types of sorption sites. Since humate is not a homogeneous substrate, the interactions in this testing may be complex, and to understand these is beyond the scope of this work. The plots are useful in comparing sorbents for use in water treatment in the northern states with substantial humate in the water supply.

The adsorption isotherm study was repeated with a similar concentration of humate and with amounts of the HSDGC ranging from 12.5 to 64 mg per 50 mL of humate solution. The log-log plot showed a similar high adsorption occurring at the low end of the curve at 64 mg of carbon.

It should be pointed out that the pHs of the solutions in this initial work were not identical for each carbon, owing to dissolution of mineral oxides on the carbons. There was not enough buffering capacity on the humate at high pH to compensate. Since pH can significantly affect the adsorption, the method was improved by using buffers and washing steps as described below.

Effects of Washing on Adsorption Properties

Further testing of the carbons was performed after washing the carbons extensively with water or with acid to remove sodium and calcium salts. Humate adsorption tests were performed that were similar to that described above, except that 25-mg amounts of carbon were used. The results are presented in Table 10. The pH of carbon-aqueous humate system after stirring was close to neutral in all the tests.

results are presented in Table 10. The pH of carbon–aqueous humate system after stirring was close to neutral in all the tests.

Note that the capacity of the HSDGC at the 0.025 g of carbon amount, which is twice that used previously, is considerably lower, as expected. Comparison of the results at this amount of washed and unwashed HSDGC carbon shows that the capacity of the HSDGC is substantially increased by the water washing, and this can be attributed to cleaning out the pores and active surfaces by washing away more of the sodium oxides or other sodium salts.

In contrast, little effect is noticed for the LSDGC as a result of the water washing. The calcium salts are less soluble in water and presumably do not wash out. However, the activity of the LSDGC improved markedly after hydrochloric acid washing. This can be attributed to removal of calcium in the acid wash. This test provides support for the argument that calcium oxides present in the LSDGC may have blocked the pores, resulting in low activity for the low-sodium carbons.

TABLE 10

Humate Adsorption on Washed Activated Carbons

Carbon, g	Absorbance, at 400 nm	Conc., mg/mL	Amount of HA, mg	HA Removed, mg	HA Removed, mg/g
None	0.80	0.10	6.1	—	—
HSDGC Unwashed (0.254)	0.53	0.068	4.1	2.0	78
HSDGC H ₂ O-washed (0.0250)	0.49	0.060	3.6	2.46	98
LSDGC Unwashed (0.0253)	0.79	0.097	5.8	0.3	9
LSDGC H ₂ O-washed (0.0253)	0.78	0.096	5.7	0.33	13
LSDGC HCl-washed (0.0252)	0.56	0.069	4.1	2.0	77

Note: 60-mL HA solution (0.1001 mg/mL) was added to each carbon.

Effects of pH on Adsorption of Humate

To determine the effect of pH on the adsorption of humate, tests were performed in buffered solutions at several pHs from 5.5 to 9.0 using the HSDGC carbon. The results for single-point tests are shown in Table 11. A significant increase in adsorption activity is observed at lower pH. This conclusion is consistent with a postulated negative charge buildup at high pH that would repel the negatively charged humate molecules. The buildup of negative charge on the carbon is attributed to removal of hydrogen ions from hydroxyl groups on edge carbons. The pKa would be about 8–9 for these groups. Alternatively, hydroxide could add to lactone groups on edge carbons and generate additional negatively charged carboxylate groups.

These data suggest that the current practice of removing humate by carbon addition in an initial settling basin, where the pH is lower due to alum addition, is correct for obtaining higher efficiency. It is unlikely that municipal water treatment would be carried out at lower or higher pH than this pH 5–9 range.

TABLE 11

Humate Adsorption on HSDGC in Buffered Solutions					
pH	Absorbance, at 400 nm	Conc., mg/mL	Amount of HA, mg	HA Removed, mg	HA Removed, mg/g
No carbon	0.80	0.101	6.1		
5.5	0.49	0.060	3.6	2.5	96
8.0	0.59	0.072	4.3	1.8	71
9.0	0.62	0.076	4.6	1.5	59

Note: Carbon = HSDGC (0.026 g). Volume of HA solution added to each carbon = 60 mL. HA solution concentration = 0.1001 mg/mL.

Effects of Activation Temperatures on the Properties of High- and Low-sodium Lignite Chars

To investigate the effects of the mineral content on the activation process and the subsequent carbon adsorptive properties, activated carbons were prepared from a high-sodium and low-sodium (high-calcium) coal from Dakota Gasification. The typical drying (at 100°C) and char-forming (400°C) stages were performed as before, but the activation temperature parameter was changed. The char so produced was activated in steam. For steam activation, the char was heated to 600°–750°C in a gentle flow of steam and nitrogen and held at this temperature for 30 minutes. The activated carbon was removed from the tube, weighed, and stored under nitrogen for further use. The yields of carbons produced under different conditions are listed in Table 12. Analysis of the carbon prepared from steam activation of high-sodium coal (DGC) at 750°C indicated 2.32% sodium in the carbon.

The steam-activated carbons were ground to -325-mesh size prior to using for water testing. Tests were performed with water-washed carbons, and the results are given in Table 12.

Yields for the initial carbonization are similar for the high-sodium coal, as expected, but are more variable for the low-sodium coal. The activated carbon yield results indicate that the higher-temperature steam activation proceeds with greater burnout (lower carbon yield) as expected. Only the 750°C conditions produce a good activity with the high-sodium char. All the temperatures produce a poor activity with the low-sodium char. As discussed above, this is due to the effect of calcium in blocking the pores in the carbon.

Large Batch Preparation (IBG Reactor)

The high-sodium Dakota Gasification coal was sized to -1/4 in. ±1/8 in. In a large batch run, 2277 g of the granular coal was placed in the integrated bench-scale gasifier (IBG) reactor and heated to 400°C in a gentle flow of nitrogen. The tube was held at this temperature until tarry material ceased to evolve. For steam activation, the char was added to the IBG reactor preheated to 750°C. The char was heated to 750°C in a gentle flow of steam and nitrogen and held at this temperature for 30 minutes. The activated carbon was removed from the reactor, weighed and stored under nitrogen for further use. The yield of the char intermediate was 1171 g (52%) and the carbon yield was 697 g (31%). Both of these are significantly lower than the yields obtained in the small-tube carbonizations described above. During heatup of the char at

TABLE 12

Effect of Steam Activation Temperature on Yields and
Activity for Humate Adsorption

Coal	Activation Temp., C°	Char, g wt%	Carbon, g wt%	HA Removed, mg/g
HSDGC (182)	750	128 70	70 38	98
HSDGC (60)	700	43 72	28 46	25
HSDGC (66)	650	48 73	29 44	13
LSDGC (62)	750	46 74	28 45	13
LSDGC (58)	700	37 64	24 43	13
LSDGC (61)	650	40 66	31 51	22

Note: Initial carbonization at 400°C°; steam activation for 30 min at stated temperature; adsorption determined on 0.025 g of water-washed activated

750°C, additional tar was evolved. In small-tube carbonizations, the carbon was already fixed at the 400°C stage. Thus the difference in heating rates produced a much different carbon in this experiment.

Testing of Carbon from Steam Activation of High-Sodium Coal at 750°C in the IBG

The steam-activated carbons were ground to -325-mesh size prior to testing. In order to understand the sorption behavior of EERC activated carbons for surface water treatment, the same leonardite humate solution was used, but at a set of various concentrations from 40 to 150-mg/L in a buffered pH = 8.0 solution. The results are reported in Table 13.

TABLE 13

Effect of Preparation Method on the Sorption Activity of Activated Carbons

Carbon,* g	HA Soln., mg/L	pH	Abs.**	Conc., mg/L	HA, mg	HA Removed, mg	HA Removed, mg/g
(0.0249)	(150)	8	2.506	116	2.32	0.68	27
(0.0252)	(100)	8	1.670	77.3	1.546	0.454	18
(0.0248)	(70)	8	1.224	56.7	1.134	0.266	11
(0.0250)	(40)	8	0.730	33.8	0.676	0.124	5
(0.0250)*	(150)	8	1.850	85.6	1.712	1.288	51
(0.0247)*	(100)	8	0.37	45	0.90	1.10	45

Note: 20 mL of HA (pH = 8) added.

* Carbon prepared in quartz tube.

** Absorbance at 280 nm.

The results of these tests demonstrate the inferior adsorptive properties of the activated carbon produced in the IBG reactor. Further samples of HSDGC for testing will employ multiple small batches that give the high-performance carbon. Further work is needed to define conditions for production in a large-scale process.

CONCLUSIONS

This work has demonstrated that activated carbons prepared from high-sodium lignites are highly effective for removal of humates. Comparison tests with Darco HDB showed comparable activity in several dye tests, as well as the humate tests. One carbon showed superior activity in the humate test. Carbons from low-sodium coals were ineffective. Thus, the hypothesis that the

high alkali content of the coals would result in effective pore size distributions and high activity for removal of polar molecules from water was not rejected.

Optimum carbonization and activation conditions for the high-sodium coals were defined in this project. Although this research demonstrated that a highly active carbon for water treatment can be produced from high-sodium lignites, much further work is needed to understand what methods and equipment will be needed for large-scale production of this carbon.

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