AN EXPERIMENTAL STUDY OF ACTIVATED CARBON IN INDUSTRIAL WASTE TREATMENT

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An Experimental Study of Activated Carbon in Industrial Waste Treatment

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STATEMENT OF THE PROBLEM

The object of this problem is to study the uses of activated carbon in the removal of odor and taste producing compounds from certain industrial wastes, particularly, those containing phenol-like compounds. The study is to include a determination of the quantity of carbon necessary, the extent to which the taste and odor are removed, and the practical application of the process to industrial waste treatment.

Mantel gives a list of nineteen vapors and gases that, Hunter, in several articles published 1863 to 1872, showed were adsorbed by charcoal to a marked extent. Hunter's experiments covered more ground than those of anyone else at the time. The use of poison gas during the World War brought back into use the vegetable chars, largely because they had a greater adsorptive capacity than bone char. It also started a vast amount of research work on the adsorptive powers of the active carbons and methods for producing the most active materials. The work of Chaney, Fay and St. John on the preparation of active carbons, and Miller and his coworkers on the characteristics of the active carbons, has done much to extend their use into various fields of gas adsorption and adsorption from solution.

The activation of carbon requires careful heat control and is usually done in closed retorts. The activation must be done in the absence of hydrocarbons or other strongly absorbed compounds. The hydrocarbons are recovered by careful adjustment of the temperature and the concentration of the oxidizing material. Air, steam and CO_2 and chlorine have been used for the oxidizing material. Steam activa-

A HISTORY OF ACTIVATED CARBON

The extensive use of bone char and active carbon in the sugar industry for removing color, and their use as an absorbing material in gas masks, give us an abundance of information on the characteristics of such materials. The active carbons, however, have been used so little in water purification that not much is known regarding them from actual experience. Bone char, and perhaps some of the vegetable chars have been used to a limited extent in household and other small filters for a number of years.

Charcoal has remarkable adsorptive powers. Strachan says it seems to have been known that it could be used for removing coloring matter from solutions in the fifteenth century. He also states that according to Lippman wood char was utilized about 1794 in an English refinery for purifying sugar solutions. Peter and John Martineau patented in England the use of bone char in 1815, and this kept the use of vegetable carbons in the background for several years. In fact it was not until gas masks were required in the World War that vegetable carbons came into extensive use.

tion seems to be regarded as being better than air. Most authors give a temperature of 900 to 950 degrees centigrade as that which produces the most active carbon. This, however, depends somewhat on the ease with which the hydrocarbons are driven off. The hydrocarbons are slightly less resistant to oxidation than the active carbon.

Baylis explains the activity of carbon in the following way: "Carbon as we know has a valency of four and every atom of carbon on the surface has at least one free valency. With the irregular shape of the amorphous particles some of the surface atoms may have two and occassionally three free valencies. These free valencies have the power of uniting with or at least attracting to their surface certain compounds that come in contact with or near them."

Work on use of activated carbon so far has been confined to removal of phenolic compounds and the di-chlorination of water. That they will remove all such taste producing compounds is not likely but it is evident that they will remove other taste producing compounds which appear in water.

Adsorption of phenols by the active charcoals probably has been known for some time but it was

not until the publication of adsorption curves by Freundlich in 1926 that it became widely known. In December 1927 Chicago experienced in its water supply the greatest phenolic occurence of any large city in the country. With the hope of developing a treatment that would be less subject to failure, experiments on the use of activated carbon for removing or preventing taste and odor were started in June 1928.

The first laboratory filter was made of 27 inches of equal parts of Carco and bone char. Water was polluted with waste liquor from a by-product coke oven plant. The phenol content of the liquor was determined and the proportional amounts added to the Lake Michigan waters to give desired phenol concentration. In addition to the phenols there were other compounds in the waste liquor that were removed by the carbon.

The filter was not run continually but when water was passed through at the rate of two gallons per square foot per minute about fifty liters would be passed through in six and a half hours. Increasing amounts of phenol were added and none or only a trace passed through the bed until the amount was

increased to 100 p. p. m. It was also noted that it was not until 10 p. p. m. of phenol was being added that a faint taste was produced after the addition of chlorine, and even then the taste was so slight that it could not be definitely stated that it was a chlorophenol taste.

If the theory of adsorption is correct, complete removal of phenol is not accomplished. There is considerable adsorption before enough phenol will remain in solution to cause a chlorophenol taste. It is not believed that .001 p. p. m. of phenol can be made to produce a taste, and so long as that amount is not exceeded there should never be a taste produced by the phenol alone.

More phenol is actually adsorbed in a filter bed when higher concentrations of phenol are used. This is probably due to the carbon in the upper part of the bed adsorbing considerably more phenol than the lower part; that is, the phenol concentration diminishes as the water passes through the bed and the equilibrium where the water contains considerable phenol is much higher. This makes such materials particularly adapted for handling occasional high phenol occurrences which is the way phenol generally occurs.

A very good advantage of an activated carbon filter bed is that a chemist is not needed to be on duty to find out when pollution starts and ends. As soon as pollution starts the bed is taking out phenols.

The usual method of applying activated carbon is by means of a suitable dry feed machine equipped with a water eductor which sucks in the carbon and delivers the suspension to the point of application. The volume of water is of no importance; it is merely the means of insuring effective distribution of carbon through the water to be treated, as the powdered carbon mixes readily with the water to produce and effective suspension. As soon as it becomes wet and the pores of the carbon thoroughly filled with the water in which it is held in suspension it can be transported any distance desired without harming it's absorptive properties.

Another means is to add it to the slum either dry or in solution. If added to the solution tank, agitation must be provided during the periods of use in order to make a thorough distribution.

The usual point of application of the powdered carbon suspension is to the water leaving the distribution chambers and flowing to the coagulation basins, where the carbon has a good contact period and settles out in the basin to some extent. The sludge carbon mixture does not show the tendency to putrifaction exhibited by ordinary sludge and consequently periods between basin cleanings can be materially increased.

Some plants use split treatment applying part of the carbon to raw water to stabilize the sludge that settles out. The remainder to the water in the settling basins and is filtered out on the filters, thereby increasing their efficiency.

APPLICATION OF ACTIVATED CARBON IN WATER SUPPLIES

During 1930-1931 experiments were conducted at the waterway purification plant at Rahway, New Jersey by Mortimor Gibbons on the effectiveness of activated carbon in removing objectionable odors.

It has been effective on vegetable odors but is difficult to wash out of the filters. Both granular and pulverized carbon have been used. The results generally indicate that the material is selective in its action, being most effective against medicinal odors.

The effect of powdered activated carbon on sand filters is worthy of consideration. Filter runs have not been appreciably shortened except when large doses of carbon, more than 5 p. p. m., have been used. At such times filter runs have been reduced as much as 50%. The carbon is not completely washed out of the sand with the wash water velocity of 24 inches per minute.

E. F. Dugger wrote of the use of activated carbon at Newport News, Virginia. On account of low water the water supply was taken by low intakes from the reservoirs. The water was devoid

of oxygen. Carbon was applied from a Coca Cola barrel that had an electric hand drill with paddles as an agitator. Carbon is insoluable and is taken out at the filters which makes it a very desireable factor in treatment.

F. H. Waring, Chief Engineer of the Ohio Department of Health writes of activated carbon. It has been known that carbon in a simple form like char coal possessed peculiar affinity for absorbing certain gaseous and liquid foreign substances present in a fluid. Activated carbon is the term applied to carbon that has been processed to render it more than usually active in its adsorptive power. No special equipment is needed, only a dry feed machine and water eductor. Points of application very, raw water, mixing chambers with chemicals, coagulation basins, or influent water just prior to filtration.

At New Castle, Pennsylvania in 1930 the removal of taste and odor from the water supply became an unusual problem. A faint musty to woody taste appeared in the far end of the dis-

tribution system, not detected in the plant. Increasing the chlorine dose stopped complaints for a while but as the temperature lowered, the excessive chlorine dose aggravated rather than helped conditions. A ratio of one part of NH_3 to four of five parts of chlorine gave good results but the NH_3 treatment just concealed tastes at the plant and failed to control after tastes in the distribution system.

By December 1931 it was apparent that some other type of treatment was necessary. A sample of activated carbon known as Nuchar was obtained for laboratory tests. Jar tests containing 0.5 grains per gallon of activated carbon showed complete removal of all taste and odor. After trying different points of application good results were obtained.

To control chlorophenol tastes Louis H. Harrison at Bay City converted two sand filters into carbon units, Hydro-Darco is used with the flow downward. The results are considered quite satisfactory. Dr. Harrison does not approve of the dry feed method, although he uses it when the taste in the water supply is bad. He says that

if carbon is used in large doses it gives a sulfur taste to the water and to get the best results a carbon filter should be used.

Probably the most difficult raw water in the United States for treatment is at Saginaw, Michigan, because of a very bad trade waste, as well as algae and sewage pollution. At this plant a split treatment of powdered activated carbon has been used, part of it going to the mixing basin where it acts to stabilize the sludge, the other part being applied at the sedimentation basins, just before the water goes to the filters, whereby the cumulative effect of the carbon collecting on the filters is made use of. This treatment has reduced the bad taste and odor but has not done away with it altogether.

EXPERIMENTAL WORK

Solutions of phenol-like compounds namely: di-chlorophenol, phenol, ortho di-chlorophenol, and cresol were prepared.

The odor value of each of the above solutions was found by the following procedure.

1. Boil a quantity of distilled water until free from odor and cool to room temperature.
2. Clean six or more 500 ml. Erlenmeyer flasks and remove the last traces of odor by boiling water in them for 5 minutes.
3. Discard the water and cool the flasks, covering them with watch glasses.
4. Determine the approximate odor as follows:
   a. Place 100 ml. of odor-free water in each of two flasks.
   b. Warm to 70 C. and add to one flask 5 ml. of the sample.
   c. Shake both flasks vigorously, uncover and determine whether or not the water in the flask receiving the sample has an odor when compared with that in the flask.

d. If the odor is present, repeat using a smaller sample.

e. If not present, add more of the sample to the water in the flask until the odor is present.

5. Knowing the approximate odor, a more accurate determination is made as follows:

a. Add 100 ml. of the odor-free water to each of the several flasks.

b. Cover with watch glasses and warm to 70 C.

c. To the first five flasks add increasing volumes of the sample, taking in the value determined by the approximate method. For example, if the odor was found with 5 ml. of the sample in the approximate method, add 3, 4, 5, 6, and 7 ml. respectively to the five flasks.

d. Shake vigorously and determine the flask in which the odor first appears.

Calculations

$$\frac{\text{ml. of odor free water} \quad \text{ml. of sample}}{\text{ml. of sample}} \quad \text{odor value}$$

The taste value of the solutions was found by diluting them and finding the value in p. p. m.

where the taste could very faintly be distinguished. These determinations were carried out with taste-free water prepared by boiling until free from taste.

Various amounts of activated carbon, known as Nuchar, were weighed out and kept in suspension for a detention period of 20 minutes in liter samples of each of the prepared solutions. The solutions were then filtered and tests made to see if all the taste and odor had been removed.

The odor tests were made by heating the filtrate to 70 C. and finding out whether any odor was still left.

The taste determination was made by tasting the filtrate and comparing it with taste-free water to see if any taste remained.

These procedures were repeated until the amount of carbon was found that would remove all of the taste and odor from water so polluted.

LAB. AND RESULTS

Compound	Odor Factor	Taste Factor p.p.m.	Concentration	Grams Act. Carbon
Di-chloro-phenol	34.3	.001	1 p.p.m.	.11
Phenol	5.0	.005	1 p.p.m.	.03
Ortho di-chloro-benzol	21.0	.001	1 p.p.m.	.124
Cresol	11.0	.002	1 p.p.m.	.1154

One liter samples were used in each of the above determinations.

Compound	Concentration	Carbon Water Ratio	lbs. Carbon p.m.g.
Di-chloro-phenol	1 p.p.m.	.00011	932.87
Phenol	1 p.p.m.	.00003	252.18
Ortho di-chloro-benzol	1 p.p.m.	.000124	1356.90
Cresol	1 p.p.m.	.0001154	1187.30

The cost of Nuchar is five cents a pound. From the preceding results it would seem to be very expensive to remove taste and odor due to phenolic compounds by the use of activated carbon. There is not, however, a concentration such as 1 p.p.m. of phenols in any water supply. There is no data available as to how much the average amount of phenol in polluted waters is. To prepare a cost table .05 p.p.m. has been selected and it is a high enough value to take for the average plant.

Compound	Concentration	Cost p.m.g.
Di-chloro-phenol	.05 p.p.m.	$2.33
Phenol	.05 p.p.m.	.63
Ortho-di-chloro-benzol	.05 p.p.m.	3.39
Cresol	.05 p.p.m.	2.97

ctivated carbon will remove the taste and odor of phenol-like compounds from water.

The dry feed method of using activated carbon is economical only when there is small amounts of phenols in the water supply because large amounts of carbon will clog the filters and make it necessary to wash them frequently.

The carbon filter bed seems to be the best arrangement for the removal of tastes and odors from water supplies. The Carbon water ratio is much higher and thus will cause much higher removal at times of heavy pollution. The carbon filter is easy to control. It is not necessary for a chemist to be on duty all the time as in the case of dry feed to change the dosage at times of starting and stopping of pollution because when pollution starts the filter is already adsorbing the phenols.

It is safe to say that active carbon in water treatment has come to stay, and that its use will increase rapidly.

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