KIWA

KEURINGSINSTITUUT VOOR WATERLEIDINGARTIKELEN

AWWA RESEARCH FOUNDATION

ACTIVATED CARBON IN DRINKING WATER TECHNOLOGY

COOPERATIVE RESEARCH REPORT

KEURINGSINSTITUUT VOOR WATERLEIDINGARTIKELEN

AWWA RESEARCH FOUNDATION

ACTIVATED CARBON IN DRINKING WATER TECHNOLOGY

COOPERATIVE RESEARCH REPORT

KEURINGSINSTITUUT VOOR WATERLEIDINGARTIKELEN
Sir Winston Churchill-Laan 273
Postbus 70, 2280 Ab Rijswijk
The Netherlands

AWWA RESEARCH FOUNDATION
6666 West Quincy Avenue
Denver, Colorado 80235
U.S.A.

ISBN 0-915295-00-8

ACKNOWLEDGEMENTS

This project was conceived by the AWWA Research Foundation and The Netherlands Waterworks Testing and Research Institute (KIWA) as a means of demonstrating the productive results of a joint effort by the two water supply research organizations. The development of the following technical report as a part of this effort was directed by KIWA through a committee approach.

KIWA wishes to thank all (co)authors of this report and all members of the committee for their collective and valuable effort:

Ir. J.G. den Blanken
Ir. R.H.M. Bos
Dr.ir. A. Graveland
Ir. P. Hiemstra
Ir. J. Hrubec
Ir. J.G. Janssens
Ir. D. van der Kooij
Dr. J.C. Kruithof
Ing. R.Chr. van der Leer
Drs. W.C. van Lier
Dr.ir. G. Lettinga
Dr.ir. A.P. Meijers
Ir. P.A.N.M. Nuhn
Ir. J. van Puffelen
Ing. J. Roelands
Dr. J.J. Rook
Drs. L.J. Schultink
Ir. J.G.M.M. Smeenk
Ing. E.A.M. van Soest
Ir. A.J. van der Veer
Ing. A.D. Visser

Dr. J.C. Kruithof and Ing. R.Chr. van der Leer produced the final report with valuable help of Drs. W.C. van Lier, Dr.ir. A.P. Meijers, Ir. J. van Puffelen and Drs. L.J. Schultink.

As a last step the AWWA Research Foundation undertook to edit the report and to change it into common American terminology. We at KIWA express our gratitude to the Foundation for the excellent way in which this difficult and time consuming job was completed.

Ir. Th.G. Martijn
KIWA
Managing Director

INTRODUCTION

The AWWA Research Foundation and The Netherlands Waterworks Testing and Research Institute (KIWA) joined forces in a cooperative effort to develop a comprehensive resource on the problem of organic chemical contamination of drinking water supplies. Within this framework two technical reports were produced. One, dealing with occurrence and removal of volatile organic chemicals (VOCs) was produced by the AWWARF, while KIWA directed the production of a report concerning granular activated carbon (GAC) technology.

After each organization had independently produced their reports, a conference was held among the authors to critically assess and correct the contents of each report. The resulting reports are presented now in two volumes.

This volume on GAC technology is a comprehensive summary of the research efforts and the operational experience with activated carbon in the water supply industry of The Netherlands. As such, it covers such topics as selection criteria and testing, design and operation of full-scale plants, biological processes, and toxicological assessment.

The report, in short, is designed as a comprehensive practical resource of technical information for water utility managers, engineers and others involved in the design and operation of water treatment plants.

KIWA and AWWARF share the hope that it will provide useful and practical information to water supply professionals on both sides of the Atlantic.

EXECUTIVE SUMMARY

Since 1971, The Netherlands Waterworks Testing and Research Institute (KIWA) and The Netherlands Waterworks have been carrying out investigations in the field of activated carbon filtration and adsorption for the treatment of drinking water. These investigations have been carried out within the framework of the research program of The Netherlands Waterworks Association.

The present report, drafted by the KIWA study group on "Activated Carbon," reviews the current state-of-the-art in the use of activated carbon for the removal of organic contaminants from drinking water in The Netherlands. The manual summarizes all knowledge acquired by KIWA and The Netherlands Waterworks over the period 1971-1981, together with the evaluation of the more important results and the recommendations for further investigation.

The report begins by discussing the objectives in the use of activated carbon for the treatment of drinking water. Originally its only goal was the removal of taste and odor, but now the main objective is the removal of toxic substances. The control of taste and odor-producing compounds and the removal of organic substances that cause aftergrowth still remain important secondary goals.

This modification of the primary objective for the application of carbon by Dutch waterworks has caused a shift from the use of powdered activated carbon (PAC) to use of granular activated carbon (GAC) in filter installations. This, of course, affects the application point of activated carbon in the treatment process inasmuch as PAC is commonly applied before coagulation and/or filtration, while GAC contactors are generally placed at the end of the treatment process.

Chapters 2 and 3 of the manual deal with testing methods for GAC and the selection of a carbon based on its adsorptive properties. Testing methods are critical to establish and control the delivery specifications of carbon. Draft instructions have been prepared for sampling, sample handling, determining moisture content, ash content, bulk density and particle size distribution of delivered carbon. These draft instructions will be further tested and validated by interlaboratory comparative investigation. Instructions are currently being prepared for determining the adsorption of organic substances, head loss, extractable substances and metal loading of carbon as additional evaluative tools.

Presently there are no specifications governing correct selection of a carbon brand and KIWA's investigations have not yet led to development of a simple laboratory type test. Consequently, selection is carried out by the waterworks itself on the basis of pilot plant tests with the water to be treated. Also, there is an urgent need for surrogate parameters to measure the removal efficiency of carbon for toxic substances.

In the absence of suitable parameters, selection is based on organic parameters such as UV-extinction and TOC; the experimentation carried out by various waterworks has resulted in the development of some general trends with respect to these parameters and carbon usage. Should these preliminary results prove to be valid, the need for selection tests based on these parameters will be greatly reduced in the future.

Chapter 4 discusses the location of carbon adsorption in the treatment process and the part played by design parameters such as the bed depth, linear velocity and empty-bed-contact-time as investigated on a pilot plant scale. Carbon filtration should be, in all cases, preceded by sand filtration and, also by coagulation for a surface water source. Preozonation can also have a favorable effect upon the effluent from carbon filters with regard to organic parameters.

For the removal of organic substances the length of filter run depends very little on the filtration rate; oxygen consumption hardly increases at low velocities but increases sharply with longer empty-bed-contact-times. In some cases the increase in the filter run is proportionally greater than the increase in the empty-bed-contact-time, which may signify that biological activity is contributing to the removal of organic matter. In other cases this relation is linear and thus the biological removal contribution is slight.

Finally, this chapter discusses the removal of some specific compounds by GAC adsorption, finding that trichloroethylene (TCE) can be removed very efficiently but that trihalomethanes are reduced with only moderate efficiency.

Based on the results from selection tests at the waterworks and pilot plant experiments, seven carbon filter installations have been built in The Netherlands; between 1982-1984 two more waterworks will start to utilize carbon filtration. Though all have the same objective of removing toxic compounds from the raw water, the process conditions chosen by the various waterworks differ considerably. The empty-bed-contact-time ranges from 9 to 54.5 minutes, velocity from 1.1 to 30 m/h and bed volumes per regeneration cycle from 14,000 to 55,000. This range of application demonstrates dramatically the need for design criteria for GAC facilities. In all instances carbon filtration is preceded by rapid sand filtration but opinions differ on the problems encountered when backwashing carbon filters is deleted. In all cases selection of the type of carbon was based partly on its capability for removing organic substances measured as TOC.

With respect to operational regeneration of GAC the waterworks have experienced regeneration losses amounting to 5-12% and one waterworks reports a decline of carbon life after regeneration. It is a conclusion of the study group that the use of regenerated carbon accentuates the need for the development of testing methods.

Chapter 6 describes the biological processes which occur in carbon filters. An attempt is made to summarize the data available in the literature in order to give a better understanding of the significance of biological processes in carbon filters. Discussion centers first upon the effect of GAC and the method of determination on the total plate count in the effluent; also, there is some discussion on the sharp rise of zooplankton content when surface water is treated by GAC.

In addition to using plate counts, the biological activity in carbon filters was also estimated from oxygen consumption measurements. A semi-quantitative picture was developed regarding the contribution made by biological processes to the removal of organic substances. In some instances, the removal attributed to biological activity may reach some 75% of the total removal, depending on type of water and running time.

KIWA and the Dutch waterworks attach a great deal of importance to the toxicological assessment of effluents from GAC facilities since toxicity or mutagenicity tests provide a direct assessment of the number one objective of GAC installation, the removal of toxic compounds. Preliminary toxicity investigations were carried out with tadpoles and trout eggs. Some qualitative conclusions could be drawn from these tests but the latter were time-consuming and insufficiently sensitive for assessing process performance.

Therefore, a great deal of attention has been devoted to the Ames mutagenicity test. Initial results show that carbon filters appear to remove mutagenic substances during long running times. The study group feels that further development of this test is an urgent requirement.

Finally, the manual describes the use of PAC in conventional fashion and in two new applications, namely the Haberer process and a new process based on flocculated PAC. The Haberer process, in which a special brand of powdered carbon is used in a filter on a carrier material, appears to have some interesting possibilities.

The report concludes with an evaluation and recapitulation of all relevant information, together with recommendations for further research. The most important recommendations relate to the development of mutagenicity and toxicity tests with a view to deriving criteria for carbon filtration. The establishment of test methods also merits great attention in connection with the assessment of regenerated carbon.

The appendices deal with the kinetics of carbon filtration and the regeneration of activated carbon, whereas the last appendix gives information on the set-up of the AWWARF-KIWA conference and on the discussion of the GAC technology part of it.

TABLE OF CONTENTS

TABLE OF CONTENTS (continued)

CHAPTER 1

THE IMPORTANCE OF ACTIVATED CARBON

by

Ir. Jan van Puffelen
Technologist
The Hague Waterworks
Buitenom 18, P.O. Box 710
2501 CS 'S - Gravenhage
The Netherlands

The importance of activated carbon as a means of treating surface water and ground water to be used for drinking water is evidenced by the many symposia and conferences held on the subject in recent years. In this report the importance of activated carbon in The Netherlands will be discussed. The advantages and disadvantages will be summarized, and to some extent weighed, from the standpoint of the principal use of activated carbon in the treatment of drinking water. At the same time, the place of activated carbon in the overall water treatment system will be examined. Many of these aspects will be discussed further in the following chapters so that a certain amount of overlap cannot be avoided. The purpose of this chapter is to discuss the various uses of activated carbon and to draw some cautious conclusions on the present and future importance of activated carbon.

OBJECTIVE OF USE

In order to understand the reasons for using activated carbon, the objective of water treatment as a whole must first be considered. The primary goal of water treatment is to turn hygienically unreliable water into reliable drinking water. Until about twenty years ago sanitary quality was seen primarily as a bacteriological problem and the cornerstone of water treatment was disinfection. Recently, however, the sanitary quality of drinking water has been questioned from another aspect. In part this is due to the publication of several scientific articles in America on the epidemiological consequences of traces of organic substances in drinking water in cities such as New Orleans, on the inadequate treatment of Mississippi River water, and on the formation of trihalomethanes as a result of chlorination. These articles and others have raised concerns about the presence of toxic and mutagenic substances in drinking water supplies throughout the world. While considering the serious public health implications, wide differences of opinion have arisen over the most effective treatment technique for the removal of these substances. However, it is generally considered that activated carbon is the best means for removing the organic contaminants which cause this toxicity and mutagenicity in drinking water. Proving the effectiveness of activated carbon however, meets with serious difficulties since there is no reasonably quick method for measuring the toxicity of the substances being treated. For determining mutagenicity, on the other hand, the Ames test seems to offer good possibilities. Investigations into the determination of toxicity and mutagenicity are currently underway as described in Chapter 7.

Until ten years ago the only use of activated carbon in The Netherlands was for the removal of taste and odor. While powdered carbon is still considered a suitable method for removing taste and odor by the Amsterdam Municipal Waterworks, Rotterdam Waterworks, the Hague Dune Waterworks, and the Provincial Waterworks of North Holland, the removal of these substances is no longer the primary use of activated carbon. The reasons are two-fold. First, since about 1970, with the clean-up of Holland's primary surface water supplies, the Rhine and the Meuse Rivers, there are fewer taste and odor-causing substances requiring treatment. Second is the discovery of many organic compounds in river and drinking water through use of advanced analytical mehtods and the possible use of activated carbon as an effective treatment for the removal of these organic contaminants. Thus, the removal of organic contaminants which cause chronic toxicity and mutagenicity is now the primary objective of activated carbon in The Netherlands. Furthermore, given the legal requirement in The Netherlands to provide drinking water of reliable quality, this aspect of drinking water treatment takes on an added significance. Additionally, the removal of substances causing aftergrowth is an important secondary use of activated carbon in The Netherlands. There are strong indications, however, that for the removal of chronic toxicity and mutagenicity, powdered carbon, as currently used, is insufficiently effective. Activated carbon in granular form or as powdered carbon on a carrier in a filter installation has proven to be more effective (see Chapters 7,9).

Table 1.1 lists the objectives which can be achieved by the use of activated carbon, the substances which are expected to be effectively removed, the preferred method of analysis as well as the standard to be achieved. This table was taken from Meijers[1], albeit with several changes. Not discussed in the table, however, is the use of activated carbon for countering "peak pollution" by a toxic substance. For example, extremely high concentrations of a given substance might be acutely toxic and/or can put a treatment system completely out of order. Activated carbon can be used as a means for countering or neutralizing the consequences of such a calamity. In Holland, "peaks" are mostly evened out with the storage of the water, or whenever necessary, the intake of water is stopped when "peak pollution" is discovered in the source.

It is with these objectives in view that the new carbon filter installations at Andijk, Zeist, Hilversum, Zevenbergen, and Kralingen have been built (see Chapter 5). Other waterworks have also, or still are, looking into the use of carbon filters to meet their own needs as described in the sections which follow. It is fair to say without exaggeration that nearly all waterworks in The Netherlands which have to produce drinking water from surface water either have considered or are considering the adoption of granular carbon filters even where there is already a facility for the addition of powdered carbon. Similarly, waterworks using ground water are also looking into the use of activated carbon filters to eliminate problem-causing substances.

Table 1.1

Objective of Activated Carbon Usage

Objective			Analytical Method	Recommended Drinking Water Standard	Standard Authority
I.	Removal of mutagenic and toxic substances				
	A.	Integral toxicity and mutagenicity	Ames tests and other tests	Unknown	-
	B.	Groups of organic micro-impurities			
		1. Chlorine-containing pesticides	Gas chromatography	0.5 ug/L	EG
		2. Polycyclic aromatic hydrocarbons	Thin layer chromatography; High-pressure liquid chromatography	0.2 ug/L	EG
		3. Phenols as phenol index	Colorimetry	0.5 ug/L	EG
		4. Extractable chlorinated substances	EOCl *	1 ug/L	EG
		5. Adsorbable chlorinated substances	AOCl *	-	-
		6. Trihalomethanes (THM)	Gas chromatography	100 ug/L 70 ug/L	EPA VEWIN
		7. Chlorinated volatiles	VOCl *	-	-
	C.	Individual potentially toxic substances	-	1 ug/L	VEWIN
II.	Removal of taste and odor		Testing panel[x]	None	VEWIN
III.	Removal of substances causing aftergrowth		AOC+ Bacteriology	Unknown	-
IV.	Removal of THM precursors		THM-Formation Gas Chromatography	Unknown	-
V.	Lowering total content of organic substances		TOC UV-extinction $KMnO_4$-consumption Color	5 mg/L - 8 mg/L 10 mg PT/L	VEWIN - VEWIN VEWIN
VI.	Removal of other substances such as residual chlorine and ozone		-	-	-

EG: Guideline for drinking water of December 8, 1978 in force since July 1, 1980.

EPA: U.S. Environmental Protection Agency.

VEWIN: The Netherlands Waterworks Association. Draft recommendations 1979; THM 0.55 umol, expressed in chloroform.

* EOCl, AOCl and VOCl meaning respectively extractable, adsorbable and volatile organo-chlorine content determined by microcoulometric titration. (Ref. 2.10-2.12)

\+ AOC assimilable organic carbon according to a bacteriological measuring method. (Ref. 2.13)

In principle it is difficult to overestimate the importance of using activated carbon filters for the objectives and problems described above. It is agreed that any potential chronic toxicity and mutagenicity must be removed. In practice, however, the importance may well be overestimated inasmuch as it is far from certain to what extent the risk may arise and/or whether the use of activated carbon will indeed provide the necessary protection against it. A lot of research is therefore needed in the fields of analysis, chemistry and toxicology.

PLACE IN WATER TREATMENT

The place where activated carbon should be located in the treatment process depends upon the purpose of its use and a number of practical factors.

On one hand, doses of powdered carbon for removing taste and odor must be made in places within the treatment process where good separation of the powder from the water is possible, e.g. before rapid filters or before a coagulation process. Most likely this will be somewhere near the beginning of the whole process. Use of powdered carbon near the beginning of the treatment process to remove taste and odor has created no practical difficulties even though competitive adsorption of many other substances is greatest early in the process. Whether this will also apply to the removal of chronically toxic and mutagenic substances is very questionable.

On the other hand, unlike powdered carbon, activated carbon adsorbers should be placed after sand filtration since the filters should be loaded with as low a suspended solids concentration as possible. Filtering water high in suspended solids requires that the carbon filters be backwashed much more frequently. Furthermore, during regeneration, the deposition of products containing, e.g. iron can adversely affect the adsorptive quality of the carbon (see Chapter 5 and Appendix B). (Obviously when unregenerable granular carbon is used the latter problem is not an issue).

However, placement of activated carbon filters near the end of the treatment process poses two potential problems. First, the filtrate from carbon filters may be contaminated by bacteria and zooplankton due to the presence (growth?) of these organisms in the filters themselves. To counter the problem of bacteriological contamination, the Andijk, Kralingen and Zevenbergen Waterworks, which employ carbon filters near the end of their treatment processes, have included a final disinfection stage. However, it is unknown whether a final disinfection stage is necessary since the bacteria may be innocuous. To control the problem of zooplankton, the Andijk Waterworks has added a microscreening stage as a final treatment. The second potential problem associated with the placement of the carbon filter near the end of treatment deals with the temptation to use it as a substitute for rapid filtration. In some cases, filter sand has been replaced with granular carbon in rapid sand filters but this is a temporary or emergency measure and can hardly be recommended as a permanent practice. Sand filters are not designed for use as carbon filters and thus do not allow for the maximum adsorptive efficiency for granular carbon. However, granular carbon has been used <u>in association with</u> the filtration process. For example, the Hague Dune Waterworks enhanced the efficiency of their slow sand filters by applying a layer of granular carbon on them. However, there are a number of drawbacks. First, the spreading and removal of a thin layer of carbon over a large surface area (22,000 m^2 in the case of the Dune Waterworks), is difficult and labor-intensive and after removal, the carbon contains a lot of sand. Second, the carbon is inefficiently used since adsorption does not proceed under optimum conditions of empty-bed-contact-time and filtration rate. In the case of the Dune Waterworks, the carbon consumption was about 40 mg/L.

With regard to the treatment stages coming before granular carbon filtration, Chapter 4 discusses the results of pilot plant studies carried out by the Overijssel Waterworks at Zwolle, the Amsterdam Municipal Waterworks at Leiduin, and the Provincial Waterworks of North Holland at Andijk. In these studies, various systems were investigated with different treatment processes before the carbon filtration stage.

Partially as a result of favorable reports from studies conducted in Germany, the combination of ozone plus carbon adsorption has attracted particular attention, but conclusions based upon further studies are not unanimous. Partly owing to a lack of good analytical methods, it cannot be positively concluded that use of ozone preceding carbon adsorption enhances the removal of chronically toxic substances. However, a good effect on lowering of UV-extinction and $KMnO_4$-number and on the running time between regenerations of granular carbon can sometimes, but not always, be shown. On the other hand, it has been shown that ozone addition can enhance the biological activity of carbon filters, especially in summertime. Additional studies are necessary to investigate whether prolonging the filter run on grounds of UV-extinction or $KMnO_4$-consumption might result in the breakthrough of toxic substances.

All in all it is fair to say that, in spite of the drawbacks noted above, granular carbon filtration should preferably be placed at the end of the treatment process. This is not an absolute requirement but it does promote good and efficient use of the activated carbon from the standpoint of present-day objectives. The water to be treated should have as low a content as possible of suspended matter and interfering organic components (fulvic acids, lignin-sulphonic acids). Specifically, coagulation directed at removal of interfering organic compounds, and rapid filtration should, in the case of surface water, precede granular carbon adsorption.

POSSIBLE DISADVANTAGES OF ACTIVATED CARBON FILTERS

Many references are made in the literature to possible disadvantages of activated carbon filtration. Some of these are biological and others are chemical in nature.

One result of the strong biological activity in carbon filters can be the reproduction of harmful substances. A known example is the formation of nitrosamines(2) which are carcinogenic.(3) Whether, or to what extent, nitrosamines are present in carbon filtrates is at present unknown and ought to be a subject for research. Another example is the rise in content of endotoxins after carbon filtration.(4) However, investigations in the United States (EPA) have failed to confirm this phenomenon.(5)

The elution of impurities from fresh carbon is an example of an adverse chemical effect. Investigations have shown that the elution of heavy metals(6) and poly-cyclic aromatic hydrocarbons(7) from fresh carbon is negligible. In addition, in some cases it has been shown, such as by the RID in tests carried out at Leiduin on the pretreatment of WRK water for infiltration in tanks filled with Veluwe sand, that granular carbon continues to give off fine black dust. When carbon filters are placed at the end of the treatment process these effects will not always be noticeable unless the carbon filtrate is continuously monitored. This again is a matter that calls for further research.

Finally, the possible appearance of undesirable substances formed via chemical reactions on the large surface area of activated carbon should be mentioned. The catalytic action of activated carbon is recognized in this connection but the importance of these reactions is uncertain. One such example is the formation of butyl disulphide from butyl mercaptan by active oxides on the surface of the carbon.(8)

In conclusion it can be said that the number of possible disadvantages in using activated carbon does not seem very great. However, as discussed above, there are a number of points that need to be clarified by further research.

DISCUSSION

The American National Academy of Science (NAS) has recently published its own review of the state-of-the-art in the use of activated carbon.(9) This review is directed more at the scientific side than that of direct practical application. There is a lot of information on individual components of activated carbon filtration and one of the final conclusions is a major endorsement for activated carbon. This conclusion reads as follows: "Well operated granular carbon filters can remove or greatly reduce the concentration of organic substances which occur in sources of drinking water supply and which are demonstrably carcinogenic or toxic in animal experiments or toxic in epidemiological studies. Observing the nature of the adsorption technique, this may be expected to apply also for other substances of unknown type and nature."

The advantage of activated carbon is that its treatment capabilities are obtained without use of chemicals, which are nearly always liable to produce unwanted byproducts and/or to be contaminated. The weak point of activated carbon filtration is found in the words "well operated." Although research over the last few years has greatly increased our knowledge and understanding of how carbon filters should be operated, it must nonetheless be admitted that there are still questions which must be addressed. These include the following:

a. The extent to which chronic toxicity and mutagenicity of drinking water occur.

b. Whether activated carbon filters remove chronically toxic and mutagenic substances.

c. Which analytical methods must be used to determine a. and b. above.

d. Once an analytical method has been chosen, what criteria must be applied in order to establish the time for regeneration or replacement.

e. The extent to which displacement, breakthrough and desorption of harmful substances may occur as a result of variations in type and quantity of organic substances in the water before carbon filtration.

The latest improvements relate, among other things, to greater knowledge of the effects of empty bed contact time, filtration rate, and bed depth on the removal of organic substances measured as TOC, UV-extinction and $KMnO_4$-number. Thanks to this new knowledge, more accurate bed depths can be chosen and filter units can be placed in series and brought into operation successively. Experience in The Netherlands has also shown that the time between regenerations should not be too long. This view is in contradiction to the outlook envisaged by Sontheimer in Germany where, thanks to the concept of "biological regeneration," it was hoped to obtain very long filter runs with particular respect to UV-extinction of the water. But it is shown in Chapter 6, that despite the intensified biological activity on the carbon surface, biological regeneration is really very doubtful. If our primary objective was the removal of substances causing aftergrowth, the intensified biological degradation would certainly be an advantage. Otherwise, the potential disadvantages outweigh any advantage.

In conclusion then, the advantages and disadvantages of using activated carbon are not clear cut but instead depend closely on water quality, the objective of GAC filtration, and upon the available knowledge on proper use of the installation.