

Process for Enhanced Chloramine Removal from Water with Activated Carbon

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ABSTRACT

As regulations regarding disinfection by products tighten, more municipalities are switching from free chlorine addition to chloramines as a method of maintaining residual disinfectant in distribution systems. Chloramines react with beverages in the same manner as other oxidants, making removal essential. Although activated carbon is very efficient at removal of free chlorine, the reactions between chloramines and activated carbon are more complex and have slower kinetics, making removal less efficient.

This paper presents results of pilot experimentation with a simple in line process designed to improve efficiency of chloramine removal by carbon. The process uses carbon dioxide (CO₂) gas to adjust the pH of the water before entering the carbon contactor. Results from varying pH levels and standard types of beverage carbons including bituminous, anthracite, lignite and coconut shell are presented which indicate that lowering the pH speeds reaction kinetics and allows for more complete removal using shorter contact times.

INTRODUCTION

Chloramine is a generic term describing the products from the reaction of ammonia and chlorine. While chlorine is an effective disinfectant for municipal water supplies, the use of chloramine compounds has increased recently. The main reason for this is the relative stability of chloramines over free chlorine.¹ Free chlorine tends to react with organic compounds in water systems creating tri-halo-methanes (THM's) and other disinfection byproducts (DBP's). Chloramines are less reactive in water systems and therefore less likely to form these EPA regulated substances. In addition, chloramines tend to maintain a residual concentration throughout large distribution systems. They are also much more difficult to remove from water than free chlorine. This can become a problem in many applications.

Historically, chloramines have not been of undue concern to beverage plants using coagulation systems that incorporated high dosage levels of chlorine. Chlorination targeting a residual above 6 mg/L free chlorine was, for the most part, easily capable of breaking down the chloramines through the breakpoint reactions.² The exception would be for cases with high chlorine demand, such as heavy organic loading.

With more and more plants installing membrane technology, chloramine removal has become a critical water treatment concern. Chloramines, just like any other oxidant, can react with certain compounds in the beverage to effect the taste and shelf life of the final product. Most public water utilities maintain a residual of 2.5 to 3.5 mg/L.³ Reverse osmosis (RO) and nanofiltration (NF) membranes that are made of cellulose acetate can easily handle these levels, but then the chloramine in the permeate must be removed before the water can be used for beverage and syrup making purposes. Membranes that are polyamide (PA) or thin film composite (TFC) will be damaged by strong oxidants, such as free chlorine, even in low concentrations. While chloramines are not as aggressive as chlorine, they are still capable of damaging the membranes and should be removed.

Other membranes such as those used in ultrafiltration (UF), microfiltration (MF), electrodialysis (ED) and electrodeionization (EDI) may also be damaged by the oxidizing potential of chloramines, but they must be evaluated on a membrane by membrane basis. In all cases however, whether removed before or after membrane treatment, chloramine must be removed from product water before usage in beverage manufacturing.

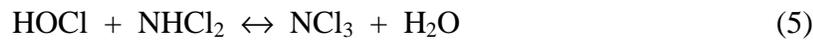
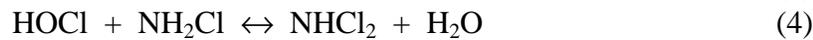
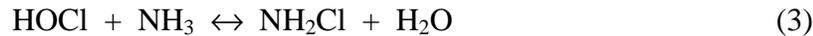
Chloramines can cause problems in other applications as well. In hemodialysis, chloramines must be removed from the dialysis water to a level below 0.1 mg/L.⁴ When present in the makeup water, they can oxidize hemoglobin to methemoglobin, resulting in Heinz body anemia, inhibition of erythrocyte hexose monophosphate shunt activity, and sensitivty to the oxidant effects of various drugs⁵, making removal a must. In ultra high purity applications, such as pharmaceutical and microelectronics where even trace contaminants must be removed, chloramines may pass through certain treatment steps leaving the product water out of specification.

Chemistry

Municipalities accomplish chlorination of water using chlorine gas or hypochlorite salts such as sodium or calcium hypochlorite, via the following reactions:



Chloramines are then formed by the reaction of hypochlorous acid (HOCl) and ammonia (NH₃) according to the following three reactions:



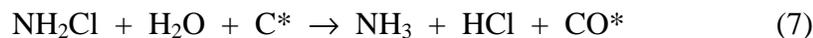
The term chloramine describes three species: mono-, di-, and tri-chloramine, the formations of which are shown in reactions (3), (4), and (5) respectively. Exactly which species or what combination of species is present depends on pH and the available free chlorine. At pH 7.5 and above and a molar concentration ratio of less than 1:1 chlorine: ammonia, all of the free chlorine is converted to monochloramine. At slightly lower pH values, dichloramine is formed and in the range of pH 4-4.5, nitrogen trichloride predominates.²

Removal of free chlorine and combined chlorine (i.e., chloramines) can be accomplished in several ways. Activated carbon treatment is one very effective method. Free and combined chlorine react on the surface of the carbon to create surface oxides and reduced chloride and nitrogen compounds. Chloramine compounds tend to react much more slowly with activated carbon than free chlorine. However, dichloramine has been shown to be more readily destroyed than monochloramine.⁶ The reactions with activated carbon are shown below:

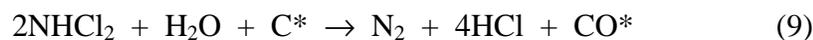
Free chlorine:



Monochloramine:



Dichloramine:



In reactions (6), (7), (8) and (9), C* is the activated carbon surface site and CO* is a surface oxide. According to equations (7) and (8), the removal of monochloramine occurs through a catalytic mechanism. That is, the carbon site that is oxidized in reaction (7) will react with two

more monochloramine molecules in reaction (8) to become reactivated. This is in contrast to the removal of free chlorine or dichloramine where an active carbon surface site will only react once to form a surface oxide. Therefore, the carbon used in the removal of free chlorine and dichloramine will have a finite lifetime, which may be extremely long, whereas the carbon used to remove monochloramine will theoretically have an indefinite life as a catalytic reactant.

The focus of this report will be to determine the effect of pH on chloramine removal using several types of activated carbon typical of the beverage industry. The pH is reduced using carbon dioxide (CO₂) gas injection. CO₂ acts to reduce the pH by dissolving in water to form carbonic acid according to the following equation:



CO₂ is the preferred chemical for pH adjustment in beverage manufacturing plants because it is already used to add carbonation to various soft drinks. Adding it in the water treatment part of the process will lower the pH and also reduce the amount of carbonation that has to be added later in the manufacturing process. Besides increasing the rate of removal on activated carbon, there are other potential benefits of lowering the pH of the water. Dichloramine has been reported to be a more efficient germicidal agent than monochloramine², possibly lowering microbial counts in the system. The reaction product of dichloramine and activated carbon, inert nitrogen gas, may be preferable to the reaction products of monochloramine and activated carbon, which are nitrogen and NH₃, a bionutrient. If reverse osmosis is used downstream, a lower pH may prevent scale buildup on the membranes typically caused by high hardness and alkalinity.

EXPERIMENTAL

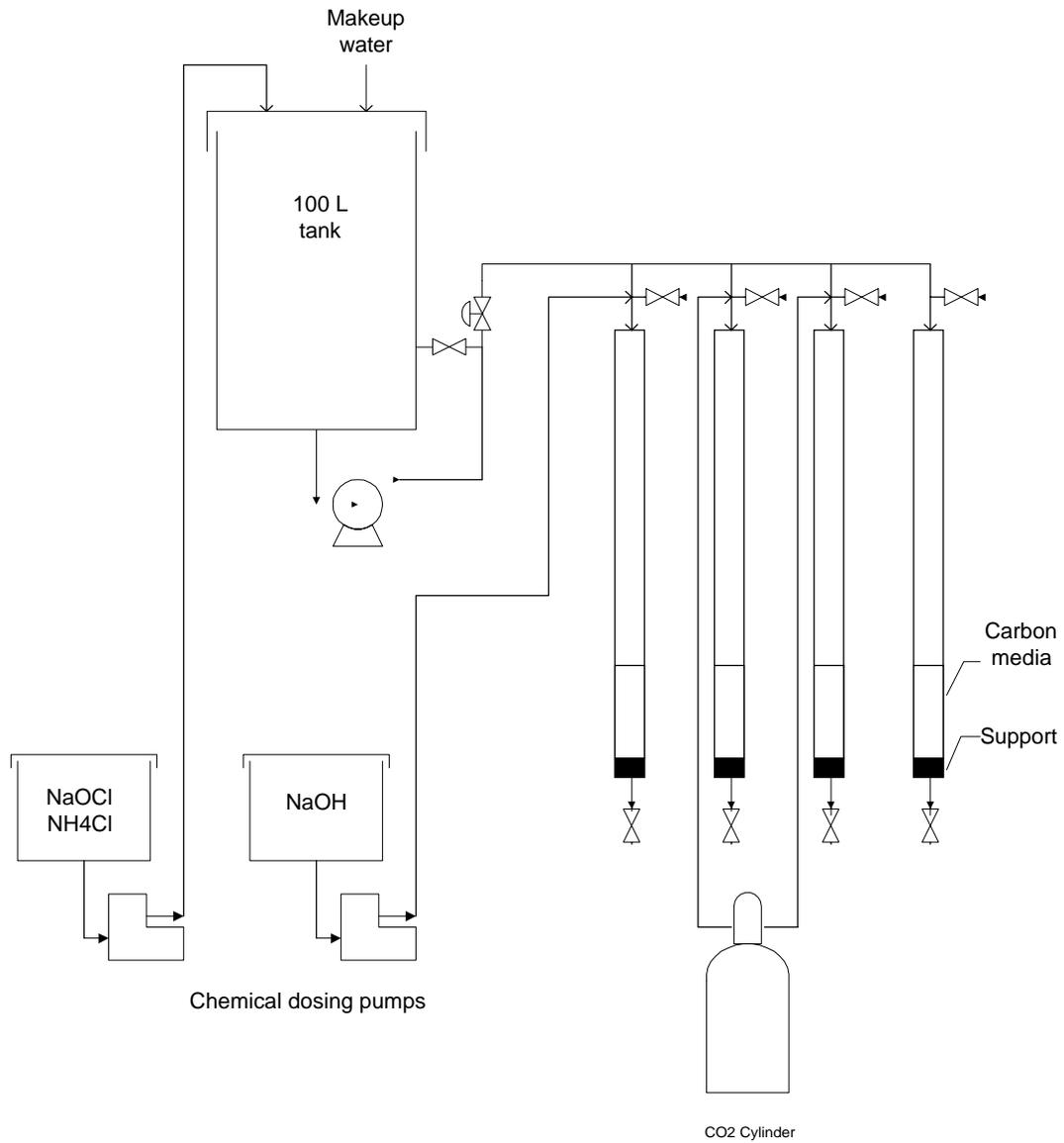
Breakthrough Tests

A test apparatus was assembled to allow for testing of up to four 1-inch inside diameter (ID) columns simultaneously. A schematic of the apparatus is shown in Figure 1a. The makeup water was municipal tap water treated by a multimedia filter and a 5-micron cartridge filter. This water contained approximately 1 ppm of total organic carbon (TOC) at a pH of 7.5 with a residual of 0.1 mg/L of free chlorine. Sodium hypochlorite (NaOCl) and ammonium chloride (NH₄Cl) were mixed in a 35-liter chemical feed tank and injected into the makeup tank to maintain 1-2 mg/L of total chlorine with a slight excess of ammonia. Because of the excess ammonia and the neutral pH, the majority of the combined chlorine in the makeup tank solution was monochloramine.

The concentrations of free and total chlorine were measured using an EPA approved DPD method.⁷ Total chlorine measures all combined and free chlorine including chloramines - NH₂Cl, NHCl₂, and NCl₃, and free chlorine compounds - HOCl and OCl⁻. Free chlorine measures only the chlorine that is not combined, i.e. HOCl or OCl⁻.

Carbon dioxide (CO₂) gas was connected to the inlet of two columns so that it could be injected to lower the pH. A second chemical feed tank and pump containing sodium hydroxide (NaOH) was connected to the inlet of one other column so that it could be injected to raise the pH.

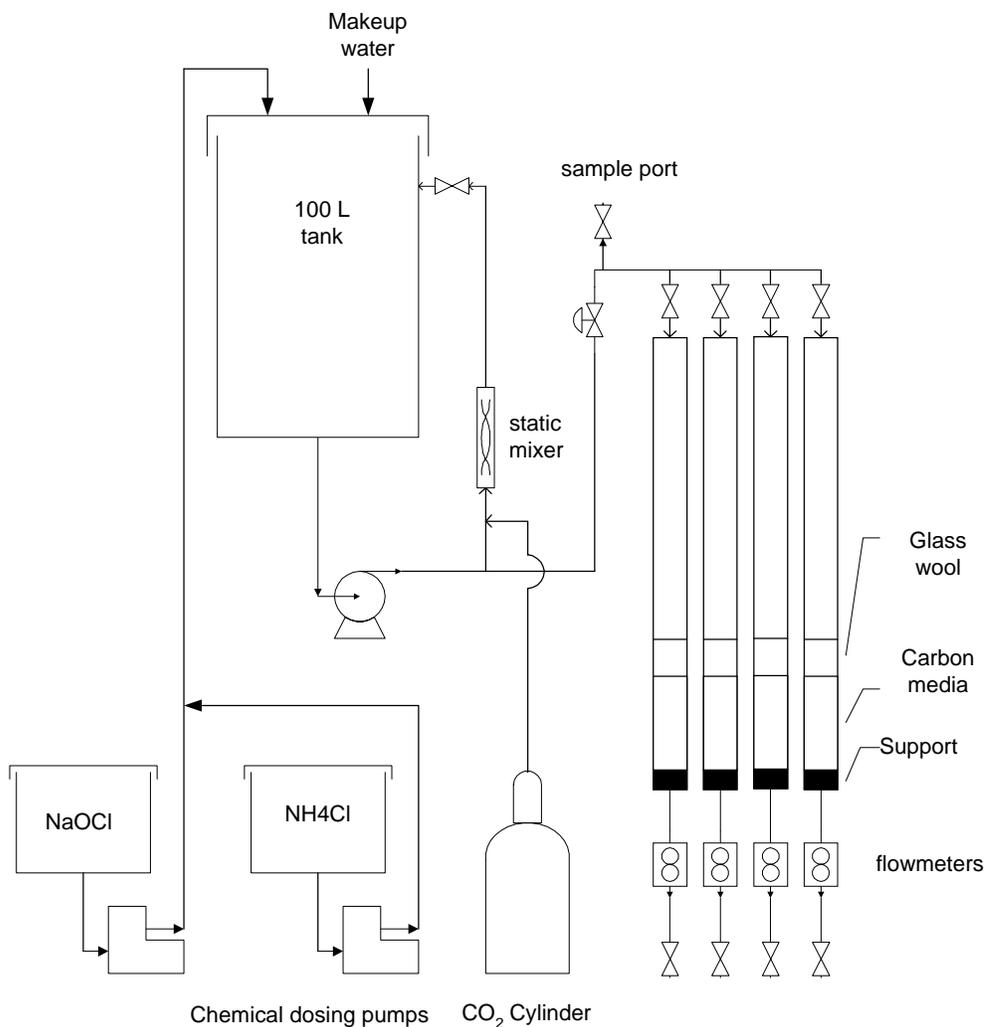
Figure 1a. Column Test Apparatus
Breakthrough Tests



Kinetic Tests

For the second part of the testing, two separate chemical feed tanks and pumps were used to control the concentration of chloramine in the makeup tank (see Figure 1b). One tank contained NaOCl and the other contained NH₄Cl. Both chemicals were injected into a 1-inch ID, 12-inch long piece of pipe connected to the makeup tank acting as a reaction chamber. The pH of the makeup water was controlled by adding either NaOH to the NaOCl tank or by injecting CO₂ gas into the tank recirculation line. This method of pH adjustment allowed more time for the chloramine solution to reequilibrate before being fed to the columns, but did not allow the flexibility of changing the pH to individual columns.

Figure 1b. Column Test Apparatus
Kinetic Tests



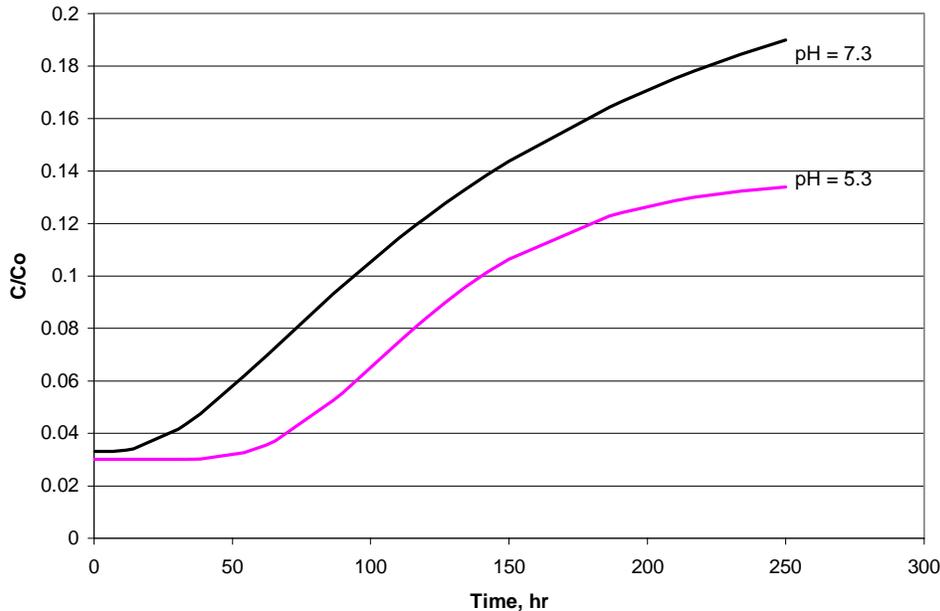
RESULTS

Breakthrough

Two columns were filled to an 8-inch bed depth with a 12X40 mesh anthracite based carbon and run with a product flow of 103 mL/min equating to a superficial velocity of 5 gpm/ft² and an empty bed contact time (EBCT) of 1 minute. EBCT is calculated as the bulk volume of carbon divided by the volumetric flow rate. Nothing was injected into the feed water to the first column, denoted as pH 7.3 in the figure, and CO₂ gas was injected into the feed water to the second column to lower the feed water pH to 5.3. The results are shown in Figure 2 plotted as C/C₀, which is the effluent concentration of total chlorine (C) divided by the feed concentration of total chlorine (C₀) vs. run time.

Taking breakthrough as C/C₀ = 0.05, these results indicate that for the column with a feed pH of 7.3, breakthrough occurred at about 40 hours, whereas with a feed pH of 5.3, breakthrough occurred at about 80 hours.

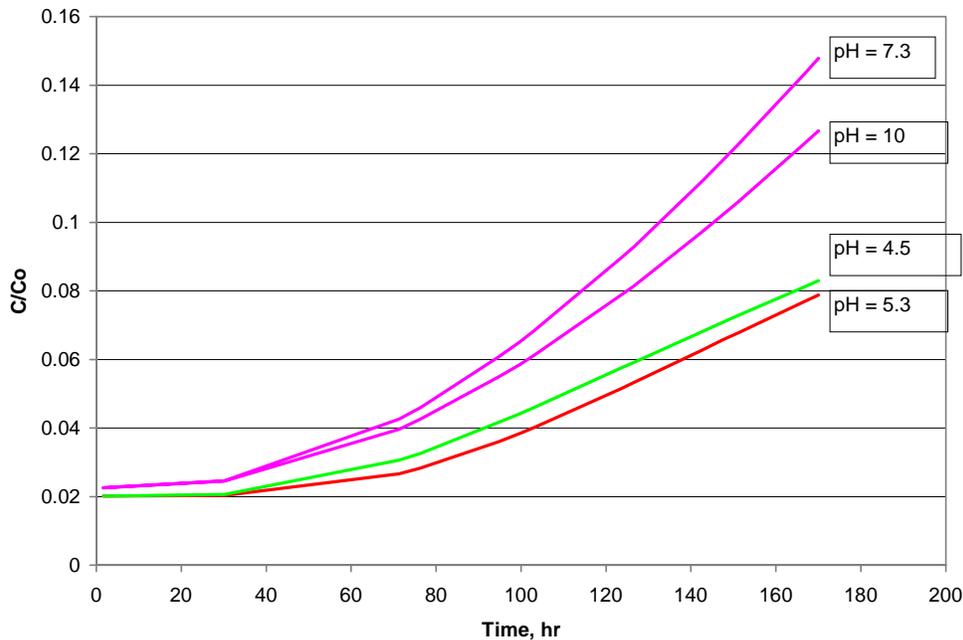
**Figure 2. Chloramine Breakthrough Curves
5 gpm/ft², 1 minute EBCT, 12X40 anthracite carbon**



In a second test, four columns were filled with 8 inches of the 12X40 mesh anthracite carbon and run at a product flow rate of 83 mL/min, reducing the superficial velocity to 4 gpm/ft² and increasing the EBCT to 1.25 minutes. CO₂ was injected at different flow rates to two columns to lower the pH to 4.5 and 5.3. NaOH was injected into the feed of the third column to raise the pH to 10 and nothing was injected into the feed of the fourth column so that the pH remained at 7.3. The results are shown in Figure 3 again plotted as C/C₀ vs. run time.

Taking breakthrough as $C/C_o = 0.05$, breakthrough occurred at about 80 hours for the columns with a feed pH of 7.3 and 10, and at about 120 hours for the columns with a feed pH of 4.6 and 5.3. There is little difference between the columns with a feed pH of 4.6 and 5.3 just as there is little difference between the columns with feed pH values of 7.3 and 10.

Figure 3. Chloramine Breakthrough Curves
4 gpm/ft², 1.25 minute EBCT, 12X40 anthracite carbon



Kinetics

In this test, four different carbons were loaded into each column – a 12X40 mesh anthracite, a 12X40 mesh bituminous, a 12X30 mesh coconut shell, and a 10X30 mesh lignite. They were all run at the same EBCT of 30 seconds and superficial velocity of 3.9 gpm/ft². The objective of this test was not to observe initial breakthrough but to record steady state removal when reaction kinetics dominate the removal. The columns were run at neutral pH until a steady state condition was achieved, i.e. the feed and product concentrations on all columns changed very little for several hundred hours. Then the pH was adjusted and again steady state was achieved. Table 1 shows the steady state values for C/C_o for each type of carbon at each pH condition.

Table 1. Steady State C/C_o Values at Several pH Values

pH	Anthracite	Bituminous	Coconut Shell	Lignite
4.5	0.50	0.55	0.61	0.60
5.9	0.59	0.65	0.71	0.69
7.4	0.75	0.78	0.82	0.81
9.3	0.81	0.85	0.86	0.85

DISCUSSION

Breakthrough tests showed that lowering the pH of the feed water to an activated carbon vessel could extend the time before breakthrough of chloramine occurs. Lab scale results yielded an increase in breakthrough time of fifty to one hundred percent by lowering the pH from 7.3 to 4.6. Increasing the time before breakthrough will increase the usable life of the carbon and add safety margin against premature breakthrough of chloramines. This may prove valuable in the application of pH reduction to existing equipment.

However, when designing a new system for chloramine removal it may be more appropriate to design the equipment based on reaction kinetics. Because the reactions of monochloramine with activated carbon are overall catalytic ones, design of a carbon reactor using reaction kinetics should allow for a theoretically infinite bed life for the removal of monochloramine. The reaction between dichloramine and activated carbon is not catalytic meaning that eventually the carbon will lose its capacity to remove dichloramine and breakthrough will occur. However, this has been shown to happen only after the application of over 5 grams NHCl_2 per gram of carbon.⁸ This equates to several years of typical operation.

The reactions between monochloramine and activated carbon and the reaction between dichloramine and activated carbon have been shown to be first order.⁸ That is, the removal of these species on activated carbon can be modeled using first order rate equations. It has also been shown that the process is strongly dependent on internal diffusion and not dependent on external or surface diffusion.⁹ This means that carbon particle size will have a large impact on removal whereas superficial velocity may not. Because of this, design of carbon reactors for chloramine removal can be done using a straightforward model based on first order reaction kinetics. For a tubular reactor, the removal can be described by the following:

$$V = (v_o/k) * \ln(C_o/C) \quad (11)^{10}$$

where

V = reactor volume or media volume, mL

v_o = flow rate, mL/sec

k = overall reaction rate constant, sec^{-1}

C_o = influent concentration, mg/L

C = effluent concentration, mg/L

This equation can be rearranged to give the following:

$$k = (1/\tau) * \ln(C_o/C) \quad (12)$$

where

τ = residence time, sec

Using the EBCT as the residence time and the values of C/C_o previously given in Table 1, the overall reaction rate constant can be determined for each carbon at each pH using equation (12).

Because the temperature varied somewhat for these tests, its effect on the reaction kinetics must be taken into account. To do this, the Arrhenius equation is used. This equation is given as:

$$k(T) = Ae^{-E/RT} \quad (13)^{10}$$

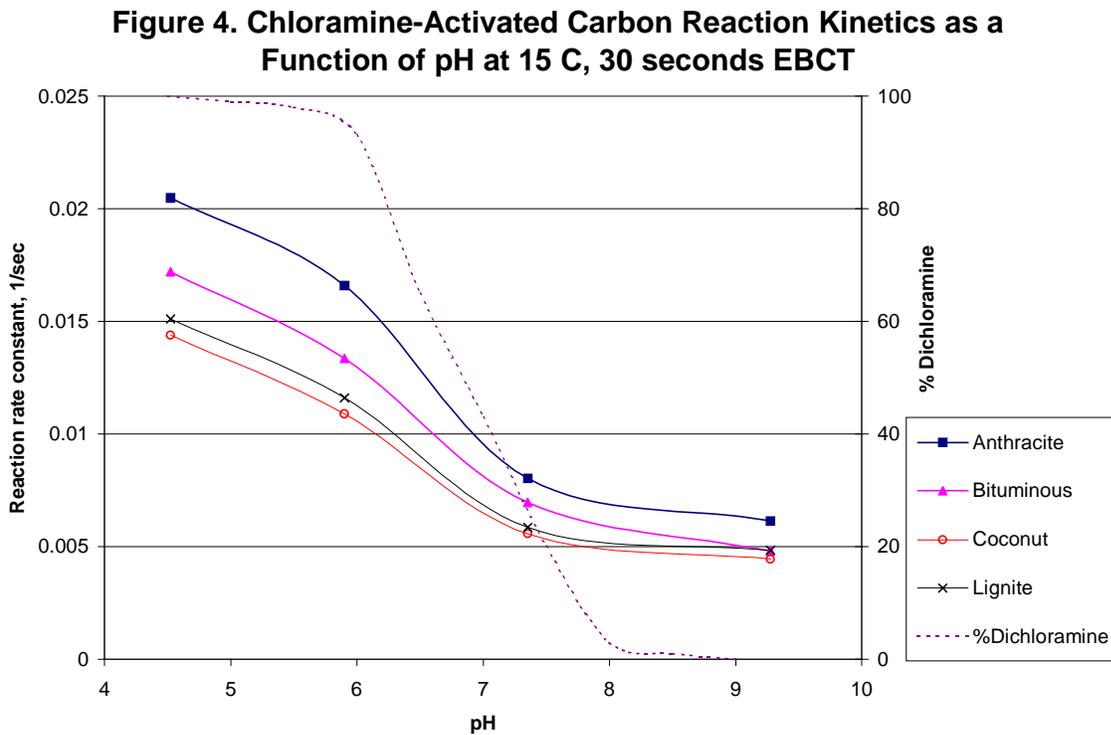
where

- k(T) = specific rate constant, sec⁻¹
- A = preexponential factor
- E = activation energy, cal/mol
- R = universal constant, 1.987 cal/molK
- T = absolute temperature, K

Using substitution equation (13) can be rearranged to give:

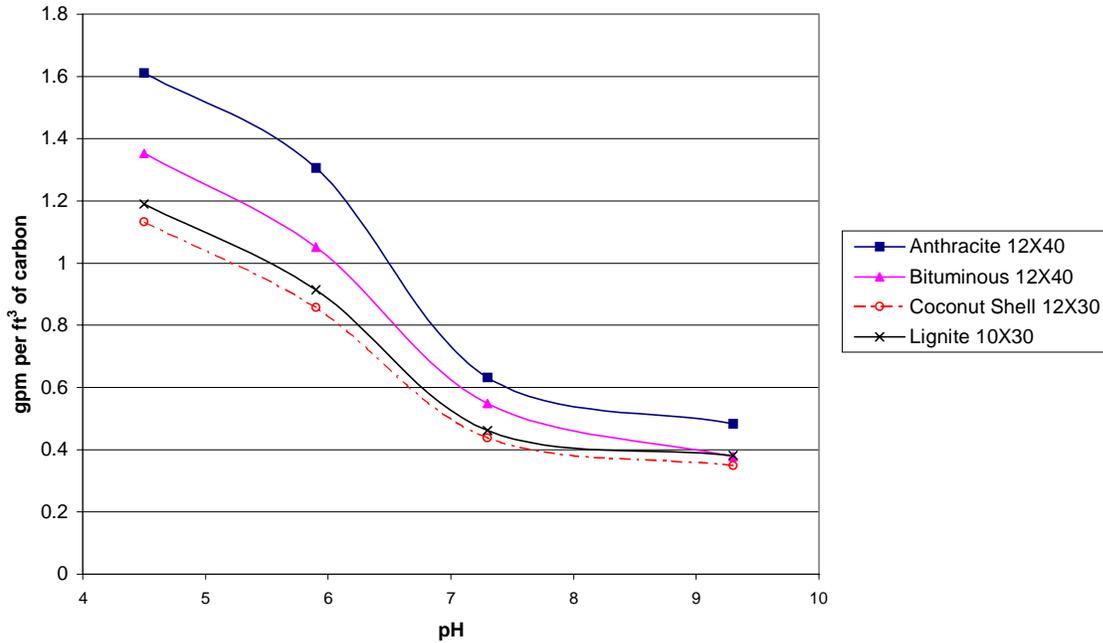
$$k(T_2) = k(T_1) * e^{E/R(1/T_1 - 1/T_2)} \quad (14)$$

The activation energy, E, for the monochloramine carbon reaction has been experimentally determined.⁹ With this, equation (14) can be used to convert all of the rate constants back to the same temperature. Figure 4 shows the rate constants calculated at 15°C as a function of pH. Shown on the second x-axis is a curve adapted from a reference² showing the percent dichloramine vs. pH under the conditions of excess ammonia.



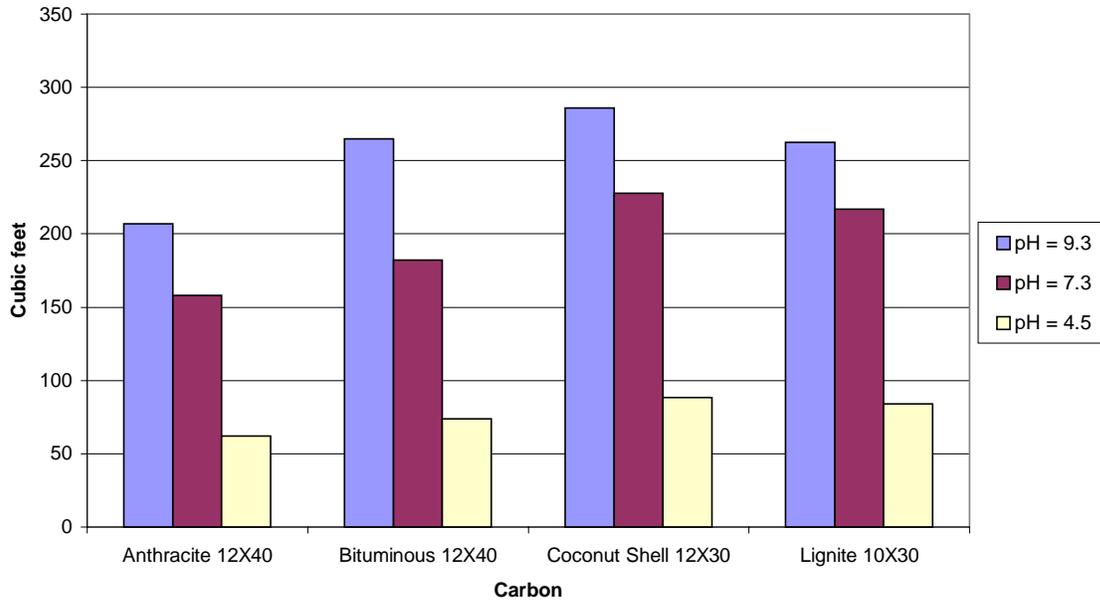
Once the rate constants are determined, design guidelines can be developed. Shown in Figure 5 are recommended flow rates based on the four carbons tested at varying feed water pH values. The feed concentration of 3 mg/L is considered typical, and the product concentration of 0.01 mg/L is essentially complete removal.

Figure 5. Design Flow Rate as a Function of Feed pH
 $C_o = 3 \text{ mg/L}$, $C = 0.01 \text{ mg/L}$, 15 degrees C



This shows that for all carbons tested, the volume needed to remove chloramine could be reduced by 75% by reducing the pH from 9 to 4.5. An example of this is shown in Figure 6 using a flow rate of 100 gallons per minute (gpm).

Figure 6. Carbon Volume Necessary to Treat 100 gpm of 3 mg/L Chloramines to 0.01 mg/L, 15 degrees C



Figures 5 and 6 also show the difference between the four carbons tested. Based strictly on volume, the anthracite showed the best kinetics followed by bituminous and lignite, which were comparable, and the coconut shell, which was slightly worse. However, these carbons had different particle sizes. Reducing the particle size for any of these carbons would improve the kinetics and further reduce the amount of carbon required.

These design guidelines provide a good starting point for system sizing. However, these may not be enough to provide a guarantee in certain situations. Other contaminants, such as organics, in the water may compete for sites on the carbon slowing the reaction kinetics with chloramines. The makeup water used for this test report consisted of 1.0 ppm TOC as C. In one study, wastewater with 20 – 30 ppm TOC was fed to carbon columns and monochloramine removal was studied.⁸ This loading appeared to reduce the kinetic rate constant by 50%. However, when water was fed to the columns with smaller, more polar organics at similar concentrations, there was no effect on the monochloramine removal.

CONCLUSIONS

These test results show that reducing the pH of a water containing chloramines will speed the reaction kinetics between the chloramine and activated carbon by converting monochloramine to dichloramine. For existing equipment, which may be undersized to treat monochloramine, this would mean better removal and longer run time before breakthrough, therefore increasing the usable life of the carbon. For carbon adsorbers designed for organic removal, which may have much longer residence times, it will add safety margin to prevent premature breakthrough of chloramines. In designing new equipment for chloramine removal, it would allow for the use of smaller equipment and less carbon to be used.

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