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Chlorine Removal with Activated Carbon Using Bubble Column

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ABSTRACT

Bubble column slurry reactor was used for the measurements of gas adsorption and ion-exchange in this work. Adsorption of chorine (dissolved in water) on activated carbon was carried out in the same reactor. The effect of gas flowrates u_G 0.016 m s^{-1}-0.027 m s^{-1} which covers the boundaries of the following four regimes: bubbly flow, first transition, second transition, and coalesced bubble and solid concentrations were investigated. In addition of studying the pH which gives an indication for Hypochlorous Acid HOCl, the most active sanitizer form of Free Chlorine. These design guidelines provide a good starting point for system of removing chlorine from water at activated carbon concentration 20 gm/L, gas velocity 0.023 m/s and contact period of time more 17 minutes.

Keywords: Activated carbon; chlorine removal; slurry bubble column.

ازالة الكلورين في عمود كاربون منشط

الخلاصة

استخدم العمود الفقاعي الثلاثي الاطوار لحساب امتزاز الغاز وكذلك تحول الايونات. وفيه يتم امتصاص الكلور المذاب بالماء بواسطة الكاربون المنشط المحمل داخل الانبوب. حسب كل من تأثير سرعة جريان الغاز (الهواء) والتي تغطي اطوار الجريان الفقاعي والانتقالي 1,2 وتكسر الفقاعات 0.016-0.027 م/ثا وتأثير كمية الصلب لكل لتر ماء بالاضافة الى حساب التغيير في قيمة الاس الهيدروجيني والذي يعتبر مؤشر لتحول ايونات OCl^- الى HOCl .

من خلال التجارب تقدم نقطة البداية لتصميم منظومة ازالة الكلور من المياه وذلك عند تركيز الكاربون المنشط 20 غم/لتر ، سرعة غاز 0,023 م/ثا وفترة زمنية اكثر من 17 دقيقة.

الكلمات المفتاحية: كاربون المنشط، ازاله الكلور، العمود الفقاعي ذو الحبيبات الصلبة المعلقة.

INTRODUCTION

Municipalities routinely began using chlorine to treat drinking water starting in 1908 with Jersey City, NJ. Its use has helped to virtually eliminate diseases like typhoid fever, cholera and dysentery in the US and other developed countries. Globally the World Health Organization (WHO) estimates that 3.4 million people in underdeveloped countries die every year from water-related diseases. Use of chlorine in water can produce an undesirable taste;

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therefore, many consumers prefer to remove it. Disinfection by products (DBPs) may also unintentionally form when chlorine and other disinfectants react with natural organic matter that is in the water. To reduce DBP formation, many municipalities are switching to monochloramine [1].

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. 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 [2].

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. 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 membranesand should be removed [3].

Tory L. Champlin *et. al* identify effective treatment methods for removing chloramines, both chlorine and ammonia, while reducing natural organic matter from the chloraminated water. Although possible technologies exist, including granular activated carbon (GAC), their effectiveness to remove chloramines (i.e., chlorine and ammonia) is not well documented. Essential for converting from chloramines to free chlorine is the removal of ammonia. If ammonia were to remain, chloramines would once again be formed by the addition of chlorine intended to provide free chlorine residual [4].

USEPA's maximum residual disinfection levels (MRDLs) are four mg/L for chlorine; however, chlorine may cause problems that activated carbon can help resolve. The addition of chlorine to disinfect water is accomplished by one of three forms: chlorine gas (Cl_2), sodium hypochlorite solution (NaOCl) or dry calcium hypochlorite, $Ca(OCl)_2$ [5].

The addition of any of these to water will produce hypochlorous acid (HOCl). This disassociates into hypochlorite ions (OCl^-) to some degree. (The reaction is summarized below).

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \qquad \text{….(1)}$$

$$HOCl^- \rightarrow H^+ + OCl^- \qquad \text{…..(2)}$$

The ratio of hypochlorous acid and hypochlorite ion in water is dependent upon pH level and, to a much lesser degree, water temperature. The ratio of hypochlorous acid and hypochlorite ion at various water pH and temperature is shown in Table 1 [6].

It is important to understand the ratio of hypochlorous acid and hypochlorite ion in water. First, it has been estimated that hypochlorous acid is almost 100 times more effective for disinfection than hypochlorite ion. Secondly, activated carbons more readily remove hypochlorous acid compared to the hypochlorite ion [6].

Chlorine concentrations greater than 0.3 ppm in water can be tasted. Activated carbon is very effective in removing free chlorine from water. The removal mechanism employed by activated carbon for dechlorination is not the adsorption phenomena that occur for organic compound removal [7].

Dechlorination involves a chemical reaction of the activated carbon’s surface being oxidized by chlorine. There are reactions when hypochlorous acid and hypochlorite ion react with activated carbon (shown below).

$$\text{Carbon} + HOCl \rightarrow C^{*}O + H^{+} + Cl^{-} \qquad \ldots.(3)$$

$$\text{Carbon} + OCl^{-} \rightarrow C^{*}O + Cl^{-} \qquad \ldots..(4)$$

$C^{*}O$ represents the oxidized site of activated carbon after reacting with chlorine; the chlorine has been reduced to chloride ion (Cl^{-}). These reactions occur very quickly [7].

Table (1) Percentages of HOCl and OCl $^{-}$ [1]

	% HOCl	**% OCl^{-}**	**% HOCl**	**% OCl^{-}**
pH	**0°C**	**0°C**	**20°C**	**20°C**
4	100.0	0.0	100.0	0.0
5	100.0	0.0	97.7	2.3
6	98.2	1.8	96.8	3.2
7	83.3	16.7	75.2	24.8
8	32.2	67.8	23.2	76.8
9	4.5	95.5	2.9	97.1
10	0.5	99.5	0.3	99.7
11	0.05	99.95	0.03	99.97

EXPERIMENTAL WORK

Chlorine removal with activated carbon applied by using transparence Plexiglas bubble column in a 0.08 m I.D and 1.8 m high with liquid level 1.5 m. bubble column equipped with a porous distributor. Air was used as the gas, while taped water used as liquids Figure 1. Taped water with chlorine was aerated at pressures, P = 0.1-0.3 MPa and u_G 0.016 -0.027 m s^{-1} with ambient temperature 18-19 deg. C, the boundaries of the following four regimes were visually identified: bubbly flow, first transition, second transition, and coalesced bubble. As the pressure increases to P = 0.3 MPa in liquid, all four transition velocities shift to higher superficial gas velocity, u_G. In addition, the existence of a chain bubbling regime was detected, whereas in solid liquid at P = 0.3 MPa and u_G 0.027 m s^{-1}, both laminar and turbulent chain bubbling subregimes were identified. It was found that in solid-liquid under ambient pressure, the transition velocities occur earlier than in liquid.

The pH sensor readings vary from 0 mV for a neutral pH of 7 to about -60 mV for a pH of 8. For the recommended pH of 7.4, the reading is about -25 mV. It should be recognized however that the pH readings vary slightly from electrode to electrode. This is why pH testers and controllers always include a pH calibration adjustment. Calibration can be made with a Phenol Red test kit.

A colorimetric kit supplied by Hach company was used to monitor dechlorination in the field. The kit can measure free or combined chlorine residuals at concentrations of 0 to 4.5 mg/L with a detection limit of 0.1 mg/L. In this method, a pre-measured amount of reagent is added to the water sample of 10 cm^3, mixed well, and the sample analyzed for chlorine concentration. A liquid crystal detector indicates the chlorine concentration in solution based on the intensity of the color formed.

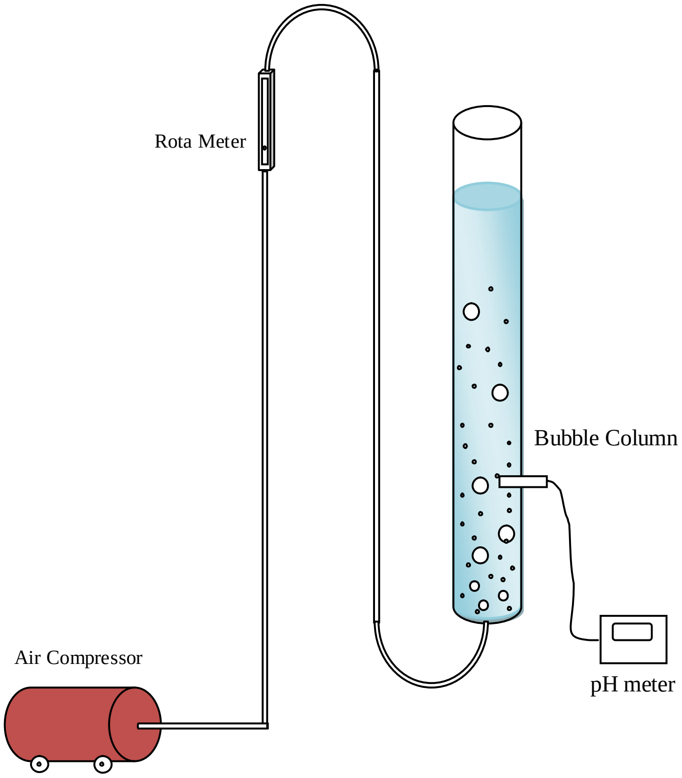


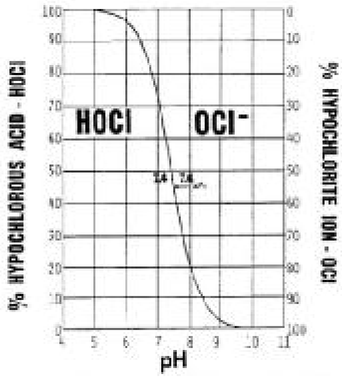
Figure (1) Bubble column with activated carbon

RESULTS AND DISCUSSION

Activated carbon (AC) is generally used in water treatment for removing free chlorine and / or organic compounds. Removal of organics from potable water could be to prevent common organic acids such as humic or fulvic from reacting with chlorine to form trihalomethanes pH represents the acidity or basicity of the water on a logarithmic scale that represent the concentration of hydrogen ions H^+ in the water. pH is very important to water chemistry because the hydrogen ions are small and very active and therefore affect most chemical reactions in water.

Most important, pH affects the dissociation, and therefore the effectiveness, of Hypochlorous Acid HOCl, the most active sanitizer form of Free Chlorine, as shown in curve Figure 2.

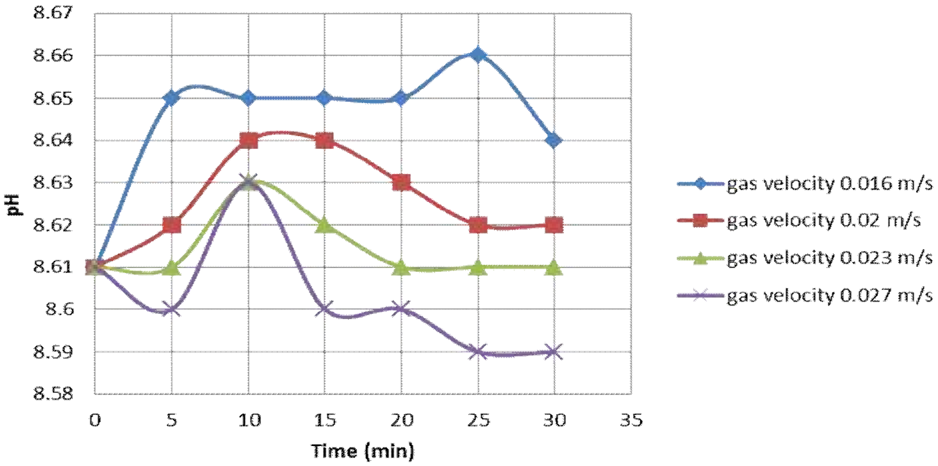
At a pH of 7.5, Free Chlorine is about 50% HOCl . At higher pH values, HOCl dissociates into the ionic form OCL^- which is a less active sanitizer.



Figure(2) Ionization curve of HOCl as a function of pH [6]

EFFECT OF GAS VELOCITY

Figure (3) shows the effect of the gas velocity on the pH with time and zero concentration of activated carbon and Figure (4) shows the effect with presence of activated carbon (5 gm/L)



Figure(3) Effect of the gas velocity on the pH with time and zero concentration of AC.

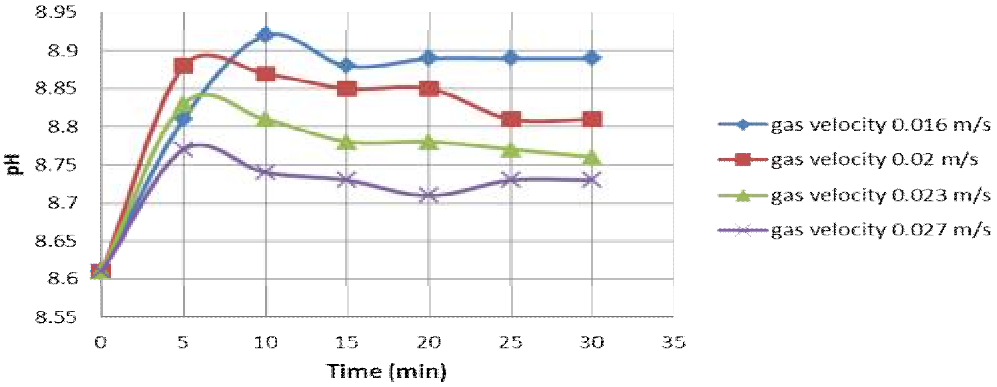
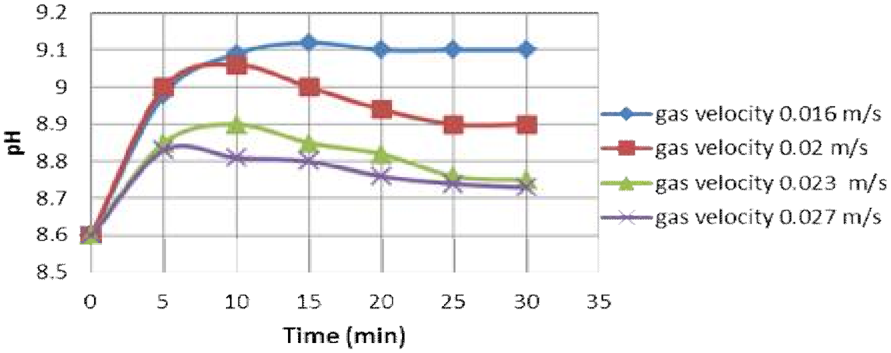
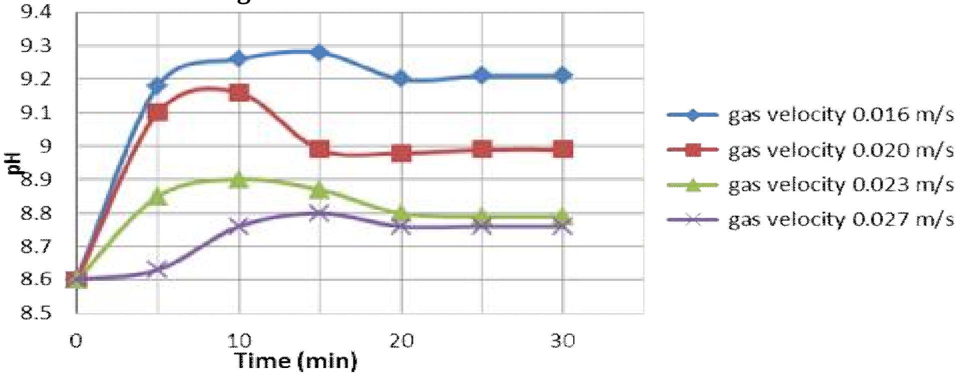


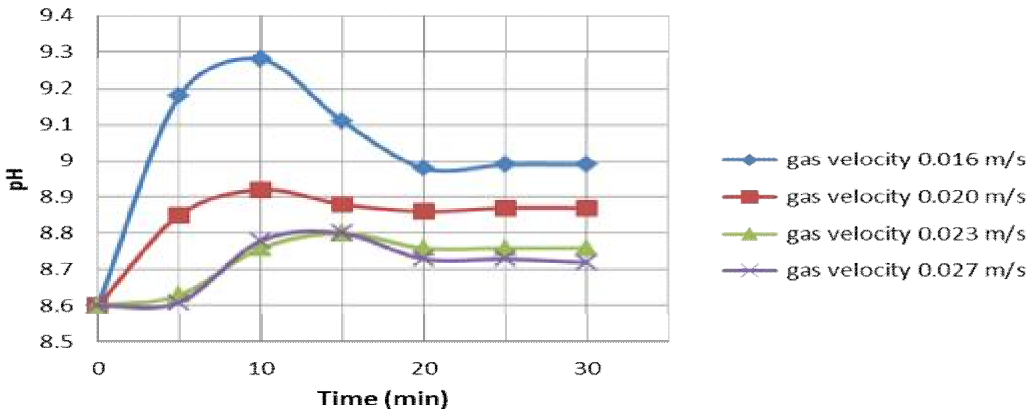
Figure (4) Effect of the gas velocity on the pH with time and 5 gm/L of AC.



Figure(5) Effect of the gas velocity on the pH with time and 10 gm/L of AC.



Figure(6) Effect of the gas velocity on the pH with time and 15 gm/L of AC.



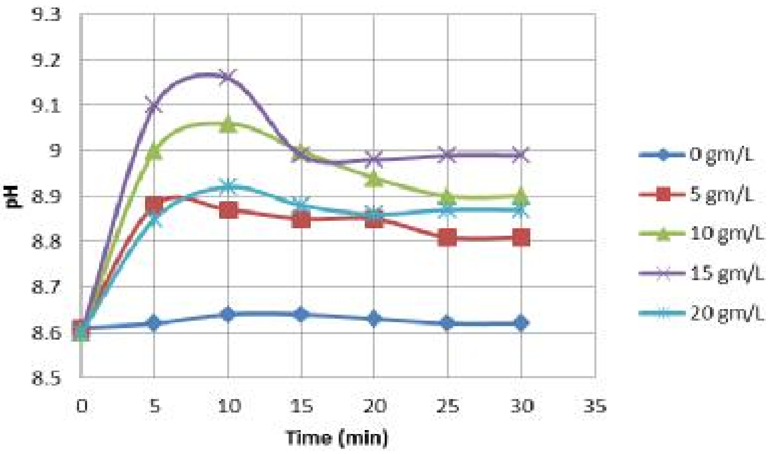
Figure(7) Effect of the gas velocity on the pH with time and 20 gm/L of AC.

Figures 3 through 7 showed that increasing then lowering in the pH of the water to an activated carbon bubble column could extend the time before breakthrough of chloramine occurs. Experimental results yielded breakthrough time after approximately 10 minutes then lowering the pH. 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.

EFFECT OF ACTIVATED CARBON CONCENTRATION

Figure (8) shows the effect of the activated carbon concentration on the pH with time and taking constant selected velocity at 0.020 m/s.



Figure(8) Effect of the activated carbon concentration the PH with time at gas velocity 0.020 m/s.

The pH of the water can increase due to the addition of alkaline (basic) chemicals such as liquid chlorine (Sodium Hypochlorite NaOCl), dry chlorine (Calcium Hypochlorite $Ca(OCl)_2$) or make-up water. It can decrease with the addition of Chlorine Gas (Cl_2), body perspiration, acid rain or make-up water.

Acids are used to decrease the pH of the water, usually liquid muriatic acid (Hypochloric Acid HCl), dry acid (Sodium Bisulfate $NaHSO_4$) or Carbon Dioxide CO_2 gas. Bases like caustic soda (Sodium Hydroxide NaOH) or dry soda are used to raise the pH.

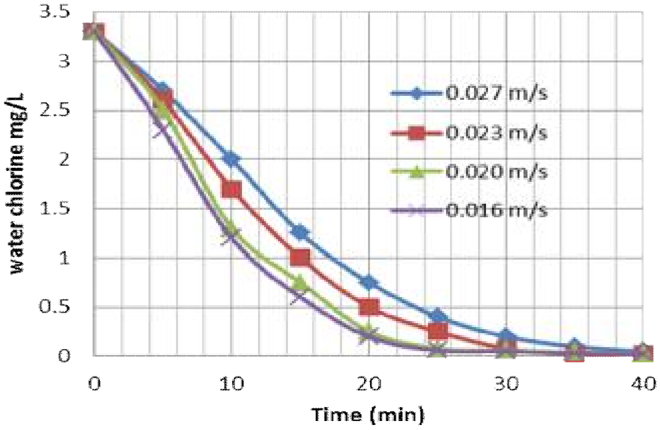
The addition of pH correction chemicals used to be done manually or with a chemical feeder. It is now done on demand with automatic controllers.

A chemical controller monitors the pH of the water with an electronic sensor consisting of a glass pH electrode.

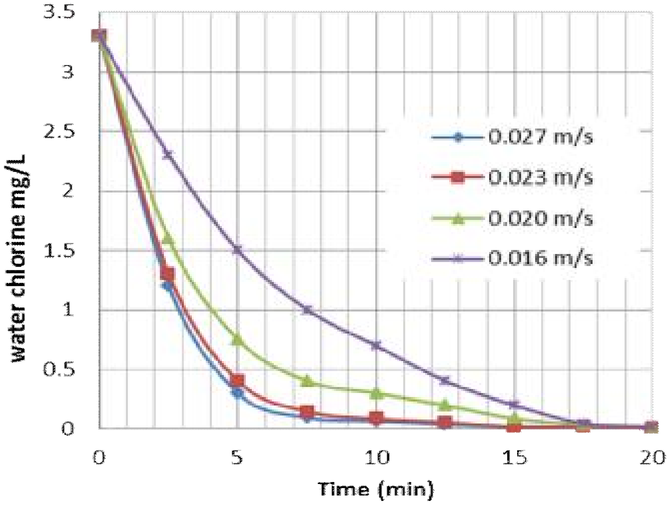
CONTENT OF CHLORINE

Figure 9-10 shows the effect of concentration of activated carbon for deferent gas velocities along with time it shows the effect of time and solid concentration of AC more obvious than gas velocity.

Increasing contact time allows greater amounts of contaminant to be removed from the water, contact is improved by increasing the amount of AC in the Bubble column slurry reactor (abbreviated as BCSR) and reducing the flow rate of air through the BCSR.



Figure(9)Effect of the exposure time on the content of chlorine With 5 gm/L of activated carbon.



Figure(10)Effect of the exposure time **on the content of chlorine With 20 gm/L of activated carbon.**

These Figures 9-10 gives the guidelines of design provide a good starting point for activated carbon concentration 20 gm/L, gas velocity 0.023 m/s and contact period of time more 17 minutes. 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.

CONCLUSIONS

Chlorine Removal**:** AC catalyzes removal of free chlorine with little consumption or degradation of the carbon during the process. This ability, however, requires tremendous surface area and organics in the water will gradually adsorb onto the carbon particle, blocking or occupying pores. This leads to gradual loss of dechlorination ability and the need to replace the carbon. Such carbon can be replaced and this is frequently done; however, reprocessed carbon should only be used in waste water applications.

These test results show that changhing 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 with run time after 10 minutes (breakthrough) and gas velocity 0.023 m/s.

Dechlorination occurs very rapidly with AC concentration 20 gm/L than 5 gm/L nearly to half its time required. One advantage of carbon for dechlorination is its low operating cost once installed and virtual “fail safe” operation. A disadvantage, however, is that once the chlorine is removed in the top one inch or so of the media.

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