STUDY OF THE FORMATION OF STABLE HIGH CONCENTRATED MONOCHLORAMINE SOLUTIONS

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Abstract. Disinfection is a very important step in the water treatment independent on the water application. Chlorination is the practice adopted in many industries, but chlorine can cause environmental damage and health hazards in the industry. A less aggressive agent to the environment is desirable to be found. The objective of this work is to prepare stable monochloramine solutions without any residual of chorine. The inorganic chloramine is less effective as a disinfection agent than free chorine but is capable to reduce the total population of bacteria to an acceptable level. For the synthesis of rich monochloramine solutions many are the variables that need to be considered, such as the reagent ratio, pH and temperature. Since the monochloramine solution is very unstable several others precautions should be taken for keep its concentration stable during the experiments. To find out the best way to prepare monochloramine solutions several experiments were carried out to verify the hypochlorite consumption using solutions with excess of hypochlorite or ammonium chloride, according to the stoichiometry of the reaction. Additional experiments were conducted to study the effect of monochloramine evaporation on the concentration of the chloramine solution. The results of this work reveal that an excess of ammonium chloride is necessary to avoid residuals of chlorine and the pH should be higher than 8. Also, the influence of evaporation on the decrease of monochloramine concentration has greater importance than that due to chloramine decomposition, room light and/or temperature.

Keywords: Water Disinfection, Reverse Osmosis, Polyamide Membranes, Chloramines

1. Introduction

Disinfection is a very important step in the water treatment, as much human consumption as industrial use, and normally is used in the end of the treatment. Its reason is to promote the death of the microorganisms and to oxidate the remaining organic substance of the previous treatment stages. The methods normally used for the disinfection are the ultraviolet radiation, ozonization or addition of oxidant agents such as chlorine, chlorine dioxide, hydrogen peroxide, chloramine, among others.

Ozone and ultraviolet radiation present a high cost and difficulties of control in the dosages. Also they do not offer a residual effect to assure disinfection in the water distribution system.

The chlorination is the alternative normally used in the conventional water treatment processes, however the free chlorine is responsible for the halogen compound formation, in special the trihalomethanes (THM) which are considered mutagenic and cancer risky. Moreover, in systems of water treatment, that use the reverse osmosis, aqueous chlorine can cause damage on polyamide membranes, which is a common RO membrane barrier layer material.

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Leung and Valentine (1994) affirm that the use of chloramines are the least expensive among the major alternative drinking water disinfectants, when compared with chlorine dioxide and ozone, especially in a large scale water treatment facility.

However, the effect of the chloramines and the chlorine dioxide on polyamide membranes are still not well known, and deserves be studied, since this disinfection agent could represent a good alternative to the substitution of chlorine in the water disinfection resulting in higher water quality and minor environmental impact.

In order to verify the effect of chloramines in the water treatment that comprises polyamide reverse osmosis membranes is necessary first to know how to prepare and how to deal with the chloramine solutions.

Since the chloramine solutions were found very unstable the objective of this work is to study the behaviour of this solutions and to define the optimum conditions (pH, temperature, reagents concentration, etc.) to prepare stable and very concentrated (80ppm) chloramine solutions. The results obtained will be then used to evaluate the influence of chloramines on polyamide reverse osmosis membranes in future works.

1.1. Physical and Chemical Properties of Chloramines

According to Vikesland, Ozekin and Valentine (2001) inorganic chloramines include monochloramine, dichloramine and trichloramine, however, monochloramine is the predominant chloramine species under the conditions typically found in drinking water treatment.

Gash (2002) affirm that the disinfection performance of the monochloramines is superior that dichloramines, trichloramines and organic chloramines, but they present a lower disinfecting performance that ozone, chlorine dioxide and free chlorine.

Butterfield (1948), Brodtmann and Russo (1979), cited in the document of USEPA (1994), affirm that inorganic chloramines have been considered poorer disinfectants than hypochlorous acid, since nearly 25 times as much chloramine as free chlorine was required to obtain a 100% kill of the microorganisms, with equivalent contact times. The same authors also conclude that dosages between 1.5 and 1.8mg.L^{-1} produced 100% kills of the pathogenic bacterial species and reduced the total population of bacteria for acceptable range.

Johnson et al. (2002) suggest the preparation of monochloramine solutions adding sodium hypochlorite (NaOCl) in a solution contend ammonium chloride (NH4Cl) under vigorous stirring. Monochloramines are produced according to Equation (1).

$$OCl^- + NH_4^+ \rightarrow NH_2Cl + H_2O \tag{1}$$

Monochloramines in the presence of hypochlorite excess can undergo a succession of reactions that result in the formation of dichloramine, trichloramine and nitrogen gas. However, the addition of an excess ammonium chloride is necessary to minimize the hypochlorite concentration and the by-product formation.

Jafvert and Valentine (1992), cited for Vikesland, Ozekin and Valentine (2001), affirm that chloramines are inherently unstable at neutral pH values, even without the presence of reactive inorganic or organic substances, and they auto-decompose by a complex set of reactions that ultimately result in the oxidation of ammonia and the reduction of active chlorine.

The document of USEPA (1994) relates that the distribution of mono-, di- and trichloramines are dependent of pH, temperature and of the ratio between ammonium and hypochlorite concentration.

Hand and Margerum (1983) conclude that the decomposition of dichloramine is 5 orders of magnitude slower in neutral solutions that contain ammonium ion, because hypochlorite ion reacts rapidly with ammonia and hence it is not available to form trichloramine.

Gray, Margerum and Huffman (1979) affirm that monochloramines are the only chloramines formed when pH of ammonia containing water is superior that 8 and the molar ration of hypochlorite to ammonia is minor that 1. When the molar ration of hypochlorite and ammonia is superior that 1 or at lower pH values, dichloramines and trichloramines are preferentially formed. At pH values lower than 5.5 monochloramines slowly decompose into dichloramines.

2. Materials and Methods

2.1 Reagents

The chloramine solutions were prepared with analytical ammonium chloride from Nuclear (Brazil) and commercial sodium hypochlorite, 10 to 12% v/v, supplied for Laborpeq.

Before start of the preparation of chloramine solution, the correct concentration of the sodium hypochlorite solution was evaluated with absorbance measurements in the wavelength 293nm.

Analytical sodium hydroxide solution, from Nuclear, was used to adjust pH of the chloramine solutions to values superior that 8.

2.2 Analytical Methodology

The chloramine solutions were prepared in order to form predominantly monochloramine and small amounts of dichloramines can be present naturally due to the reaction or the decomposition of monochloramines. Thus to calculate the individual concentration of the species was necessary to measure the same sample in two different wavelength.

The wavelengths used were the maximum ultraviolet absorption of monochloramine in water (245nm) and the isobestic point for a mixture of mono- and dichloramine at 231nm. These points present respectively a molar absorptivity of 320 and 445$mol^{-1}.L^{-1}.cm^{-1}$ for monochloramine and 208 and 591$mol^{-1}.L^{-1}.cm^{-1}$ for dichloramine, according to Valentine, Brandt and Jafvert (1986).

Sodium hypochlorite concentration was evaluated using the absorbance measurements at wavelength of 293nm, that presents a molar absorptivity of 350$mol^{-1}.L^{-1}.cm^{-1}$ in water.

Quartz cells with a 1.00cm path length and Varian Cary 300 spectrophotometer UV were used for the absorbance measurements. This equipment is connected to a computer provided with Cary WINUV software.

An unidentified product of the chloramine decomposition is the main interference of this method. This product absorbs in the same wavelength range of chloramine and presents a higher molar absorptivity. According to Leung and Valentine (1994) and Valentine, Brandt and Jafvert (1986) the interference of this unidentified product is only considered significant for solutions that were prepared for more than 50 hours.

2.3 Experimental Methodology

The main objectives explored in the experiments were how to prepare monochloramines solutions without any residual of chlorine, and which factors influence the variation of the chloramines concentration.

In the initial tests, it was observed that sodium hypochlorite concentration decreased due to an evaporation process. For this reason, the Experiment 1 was performed to evaluate if the decrease of the monochloramine concentration could be due to evaporation.

In this experiment a solution with a known concentration was prepared and divided in two portions. One sample was kept in an open bottle and the other in a closed bottle. After the chloramine concentration was determined for each sample in intervals of half-hour during 4 hours. The monochloramine formation reaction was performed with a molar excess of 20% of ammonium chloride.

Two experiments were conducted to verify if all sodium hypochlorite is consumed in the monochloramines formation reaction, so called Experiment 2 and Experiment 3. In Experiment 2, a 20% molar excess of ammonium chloride was used and the chloramine concentration was measured each minute during a period of 45 minutes. In Experiment 3, a 20% molar excess of sodium hypochlorite and the chloramine concentration was measured each 5 minutes, during 65 minutes.

3. Results and Discussion

As it was mentioned in the introduction, the component of interest among the inorganic chloramines is the monochloramine, which is the predominant chloramine species, in the conditions typically found in water treatment processes. Besides, the monochloramine presents the greater disinfecting action among the chloramines.

Sodium hypochlorite is used to prepare monochloramine solutions, after the formation reaction the monochloramine should be the predominant specie and the solution must be free of chlorine, which presents a harmful effect on polyamide membranes.

To reach these criteria it was developed a methodology to prepare stable monochloramine solutions free of chlorine. According to Gray, Margerum and Huffman (1979), the pH higher than 8 seems to be the more suitable to maintain the concentration of monochloramine solutions.
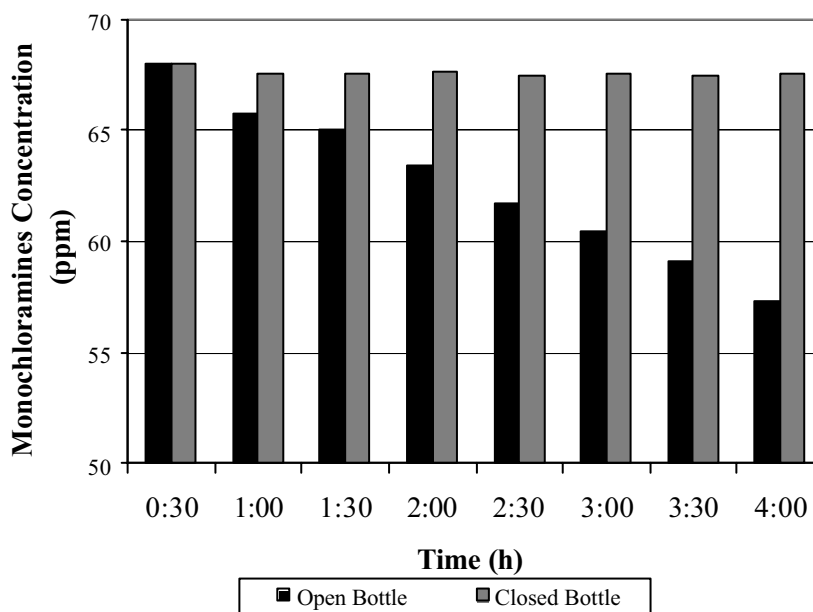
Fig. 1. Monochloramine concentration versus time to the Experiment 1.

The results of Experiment 1 are shown in the Figure 1, it can be seen that monochloramines concentration in closed bottle was kept constant during all experiment, however, in the open bottle the concentration decreased continuously. These results indicate that monochloramines are released to the environment by a simple evaporation process.

The objective of Experiment 1 was not only to verify the volatility of monochloramines, but also to alert about the existence of this phenomenon and to demonstrate its significance when experiments are performed.

Kumar, Shinness and Margerum (1987) have affirmed that trichloramine is very volatile (its vapor pressure is 150mmHg at room temperature) and it is easily lost from aqueous solution, but any reference was found in literature about monochloramine volatility.

The sample conditions were as follow: alkaline pH, excess of ammonium chloride, room light and temperature. The monochloramine concentration in the closed bottle was almost constant during all the experiment this result indicates that factors such as the monochloramine decomposition, room light and temperature have a small influence on the decrease of the monochloramine concentration when compared with that observed in the open bottle due to evaporation.

The objective of the Experiment 2 was to evaluate the time necessary for the total consumption of the sodium hypochlorite with an excess of ammonium chloride. The results shown in Figure 2 demonstrate that the monochloramine concentration remained constant during the experiment and presented a conversion of 99% of monochloramine and 1% of dichloramine in the initial 5 minutes of reaction. The sodium hypochlorite concentration cannot be evaluated, however for the stoichiometric results its concentration is null or insignificant.

Weil and Morris (1949) concluded in their studies that the rate of monochloramine formation is so fast that determination of rates between pH 6.5 and 10 is almost impossible. At pH 8.5 the rate of the formation reaction reaches a maximum. These data are in accordance with the results obtained in the Experiment 2.
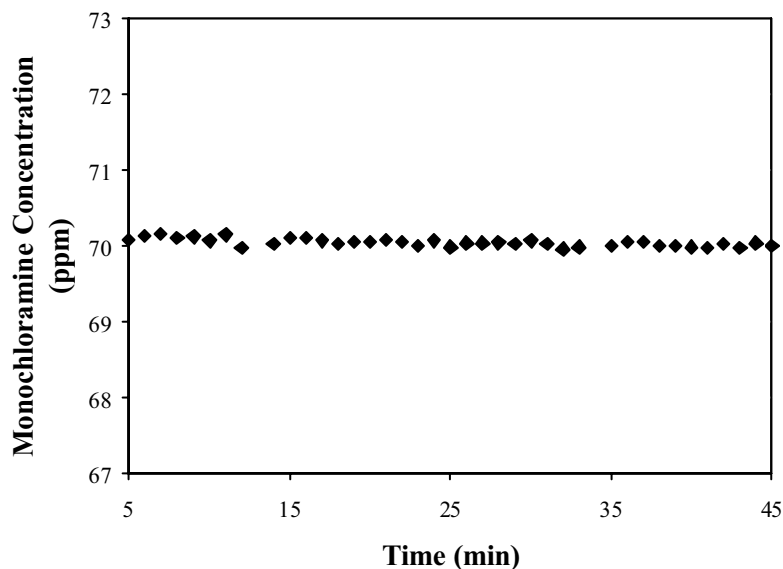

Fig. 2. Monochloramine concentration of the Experiment 2.

Experiment 3 was similar to Experiment 2 but with an excess of sodium hypochlorite. In the results shown in Figure 3 can be observed that the monochloramine concentration presents an exponential decrease, and after about 1 hour of experiment the concentration decline becomes smoother. The initial monochloramine concentration was next to the stoichiometric value and the dichloramine concentration was practically constant and very low during all experiment, as it is shown in Figure 4.

Jafvert and Valentine (1992) also performed similar experiments and their results are in accordance with the results of Experiment 3. The same authors measured the sodium hypochlorite concentration during the experiments and also verified exponential decrease of its concentration until complete consumption. This sodium hypochlorite reduction was associate to the decrease of the monochloramine concentration until to a constant value.

In Figure 5 is shown the absorbance specter after 65 minutes of running Experiment 3. The molar absorptivity in 231, 245 and 278nm are respectively 340.3, 452.1 and 82.0mol^{-1}.L^{-1}.cm^{-1} while those measured by Valentine, Brandt and Jafvert (1986) are respectively 320, 445 and 89mol^{-1}.L^{-1}.cm^{-1}. This result is consistent for a mixture of mono- and dichloramines when monochloramine is the majority component.

Mono- and dichloramine also absorb in the main peak of absorbance of the sodium hypochlorite, 293nm. In this wavelength it was not observed a significant alteration that should indicate the presence of sodium hypochlorite, the results are displayed in Figure 5.
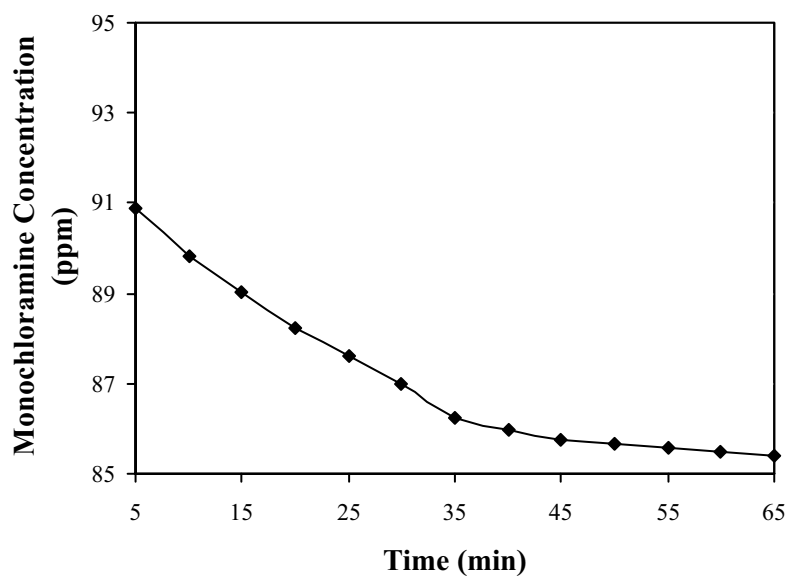
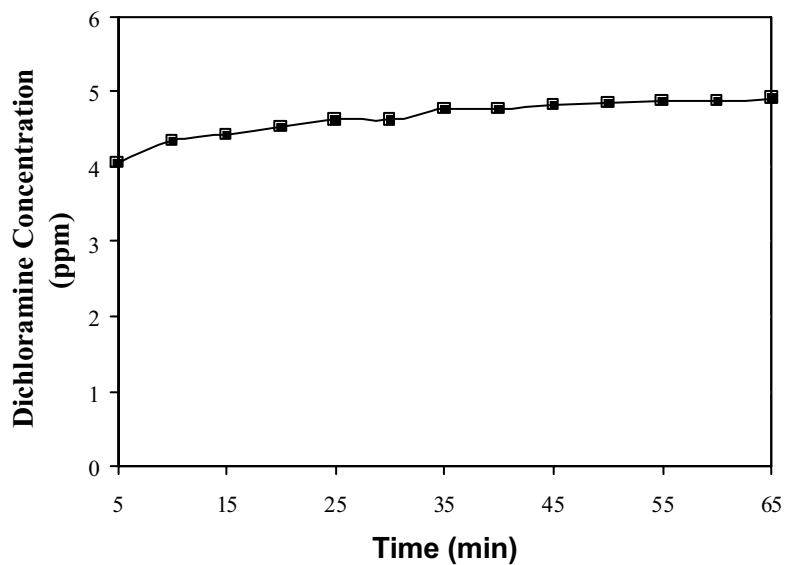**Fig. 3.** Monochloramine concentration in the Experiment 3.

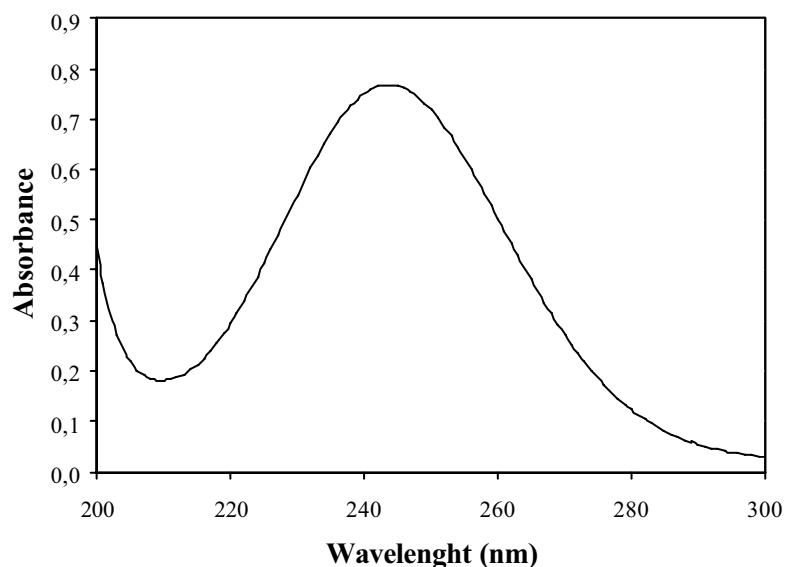**Fig. 4.** Dichloramine concentration of the Experiment 3.

Fig. 5. Absorbance specter of the Experiment 3.

4. Conclusions

This work demonstrates that for the preparation of a rich monochloramine solution without any residual of chorine is necessary to have the following conditions: pH superior than 8 and an excess of ammonium chloride.

The presence of an excess of sodium hypochlorite causes a consumption of monochloramines until the extinguishing of the sodium hypochlorite. This result guarantees that all the solutions were chlorine free.

The main cause of decrease of the monochloramine concentration is the evaporation. It is necessary a closed system to keep the concentration constant. The monochloramine decomposition, room light and room temperature do not modify the monochloramine concentration significantly when these effects are compared with the evaporative effect.

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