1 De-chlorination of drinking water by forced aeration

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7 **Abstract.** Shock chlorination is a well-known practice in swimming pools and domestic wells. One of the limitations
8 for using this technique in drinking water purification facilities is the difficulty of quickly removing high chlorine
9 concentrations in water distribution systems or production facilities. In order to use this method in the drinking water
10 industry a shock de-chlorination method should be introduced for producing microorganism and biocide free water.
11 De-chlorination using natural stagnant aeration (leaving the water to lose the chlorine naturally) is the safest known
12 method if compared with chemical and charcoaling methods. Unfortunately, stagnant aeration   is a slow process.
13 Therefore, developing a process for accelerating de-chlorination by aeration would pave the way for using shock de-
14 chlorination in drinking water industry.

16 Forced air bubbling is a possible technique for de-chlorination but there is lack of data supporting such a process. The
17 theory is that air bubbling has the advantages of higher mass transfer area, higher Reynolds number across the bubble
18 water interface, and higher mass transfer concentration gradient as the bubbling presents a continuous stream of fresh
19 bubbles. All of these factors accelerate aeration to various extents.

20

21 A 20 cm diameter, 1-meter height column provided with air sparger was designed to collect the desired data used in
22 this study. Trichloroisocyanuric acid, sodium hypochlorite and chlorine gas were the three familiar sources of chlorine
23 used to investigate their response to air bubbling.

24

25 Chlorine gas was the fastest and safest chlorine source to be dechlorinated. It dropped from 200 ppm to 0.02 ppm
26 within 4 minutes or zero ppm within 6 minutes using an air flowrate of 9 l/min.

27

28 Sodium hypochlorite decreased from 200 ppm to 0.02 ppm within 6 minutes using air flowrate of 9 l/min.
29 Trichloroisocyanuric acid found to be the chlorine source slowest to respond to de-chlorination. It decreased from 200
30 ppm to 0.02 ppm within 8 minutes using an air flowrate of 9 l/min.

31

32 Shock de-chlorination by aeration is found to be a promising method that opens up the drinking water industry and
33 could produce microorganism and biocide free drinking water.

34

35 1 Introduction

36 Chlorination of drinking water has been used as a disinfection technique for more than a century or so to produce
37 water that is safe from waterborne diseases. This method is preferred due to low cost, abundance, ease of use and less
38 need of high technology equipment. On the other hand, during the last forty years disinfectant by-products "DBPs" as
39 a new branch of study in the water industry has developed first by discovering the presence of Chloroform (Rook,
40 1974) and trihalomethanes "THMs" (Singer, 1994) in drinking water. To date some 700 or more DBPs have been
41 identified but understanding their effect on humans and the environment still needs more work (Brown et al.,
42 2011;Gonsior et al., 2014;Richardson and Postigo, 2015).

43 Liberating the drinking water industry from chlorination side effects has been approached by developing new
44 chemical, physical and hybrid techniques rather than novel methods such as plasma and solar disinfection (Kumar and
45 Pandit, 2012). All of these strategies imply economical and health disadvantages which still gives disinfection by
46 chlorine an acceptable reason for use in many places around the world.

47 One of the major advantages of chlorine is preventing bacterial regrowth if some residual level is maintained along
48 the distribution system. Recently, some European water treatment factories prevented the regrowth; i.e. producing

49 biologically stable drinking water, by optimizing nutrition levels in effluent water using pretreatment techniques such
50 as sedimentation, filtration, UV disinfection, ozone, and peroxide (Lautenschlager et al., 2013;Simoes and Simoes,
51 2013).

52 Shock chlorination is a well-known disinfection process normally used in swimming pools, springs and wells. In all
53 these applications the water reservoir is kept without use for a certain time for natural de-chlorination. The
54 concentration of chlorine and contact time for killing all or most of the contaminants varies depending on initial and
55 desired microorganism concentration and the chemical nature of water that may interfere with the chlorination process
56 (LeChevallier et al., 1981;Virto et al., 2004;Virto et al., 2005;Helbling and Vanbriesen, 2007). The rare information
57 about time-concentration needed may be due to the wide nature of reservoirs that make any generalized study difficult.
58 Furthermore, it is easy to estimate the parameters in simple laboratory experiments. De-chlorination of water by
59 aeration is also a well-known process but it driven naturally by leaving water in an open vessel for about 24 hours.
60 This process is used mainly for domestic needs such as de-chlorinating water for fish aquariums. In such applications
61 the time is available and the amount of water is small. In such cases there is no serious need for forcing the
62 dechlorination.

63 Contemporary drinking water production and distribution systems should be as biocide and microorganism free as
64 possible without forgetting the economical aspect. The need for residual biocide for preventing regrowth is decreased
65 with the development of new techniques (Lautenschlager et al., 2013;Simoes and Simoes, 2013). Therefore, the idea
66 of shock chlorinating and de-chlorinating potable water may be an acceptable approach for producing high quality
67 drinking water.

68 In this study the ability of pumped air for de-chlorinating drinking water was investigated. Such information is needed
69 for the process design of drinking water facilities. The information should help in calculating the dimensions and
70 operating conditions of continuous chlorination and de-chlorination equipment.

71 **2 Hypothesis**

72 According to Fick's law:

73 $J= -D\frac{\partial C}{\partial x}$ (1)

74 Where:

75 J: is the diffusion flux ($\frac{mole}{m^2.s}$)

76 D: is the diffusion coefficient ($\frac{m^2}{s}$)

77 C: is the concentration gradient ($\frac{mol}{m^3}$)

78 x: is the length vertical to m^2 in D and C above (m)

79 (Li et al., 1965) rearrange equation (1) dimensionally to get:

80 $\frac{dn}{dt} = k_L\,a(dC)$ (2)

81 Where:

82 n: is the moles of gas transferred (mole)

83 t: is the time (s)

84 k_L: is the mass transfer coefficient (m/s)

85 a: is the mass transfer area (m^2)

86   Therefore, to increase the moles of chlorine transferred, both of mass transfer area (a) and the concentration gradient
87   (dC) should be increased. Forced aeration is suggested to increase them both.

2.1 The role of aeration in increasing the mass transfer area

89   Chlorine is transferred from water to air through a contact area between air and water. In stagnant aeration the chlorine
90   is only transferred from the upper surface of the water. Increasing the air water interface will increase chlorine transfer
91   and decrease the time to reach the desired level of dechlorination.

92   Consider a cube of water with dissolved chlorine of a length of (r).

93   Assume that the upper face of the cube is the mass transfer area for chlorine; which equals to A=r^2 as happens in
94   stagnant aeration.

95   Assume also there is a spherical air bubble of radius (r) inside the cube as in figure (1A). The surface area of this
96   bubble will be $4\pi r^2$.

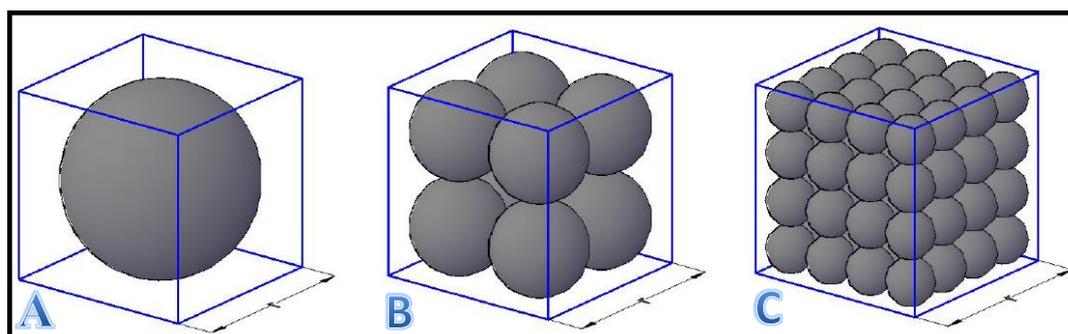



Figure 1: Hypothesis graphical illustration

99   The total surface area available for mass transfer will be the sum of upper face plus the bubble surface areas (r^2 +
100   $4\pi r^2$). The percentage increase in surface area can be expressed as:

101   % surface area increase due to aeration $= \frac{New\ mass\ transfer\ area}{Original\ mass\ transfer\ area} \times 100$

102   Or % surface area increase due to aeration $= \left(\frac{r^2 + 4\pi r^2}{r^2} \times 100 \right) = 1357\%$

103   Assume also there are 8 bubbles of a radius (0.5r) inside the cube as in figure (1B). The total percentage increase in
104   surface area will be:

105   % surface area increase due to aeration $= \left(\frac{r^2 + 8\left(4\pi\,(0.5r)^2\right)}{r2} \times 100 \right) = 2613\%$

106   Finally, assume there are 64 bubbles of radius (0.25r) inside the cube as in figure (1C). The total percentage increase
107   in surface area will be:

108   % surface area increase due to aeration $= \left(\frac{r^2 + 64\left(4\pi\,(0.25r)^2\right)}{r2} \times 100 \right) = 5127\%$

109   Or in general, % $surface\ area\ increase\ due\ to\ aeration = \frac{r^2 + x^3\left(4\pi\left(\frac{r}{x}\right)^2\right)}{r2} \times 100$

110 Where: x is the number of bubbles that lined adjacently along the length of cube line (r). Or it is the cubic root of the
111 bubbles inside the tubes.

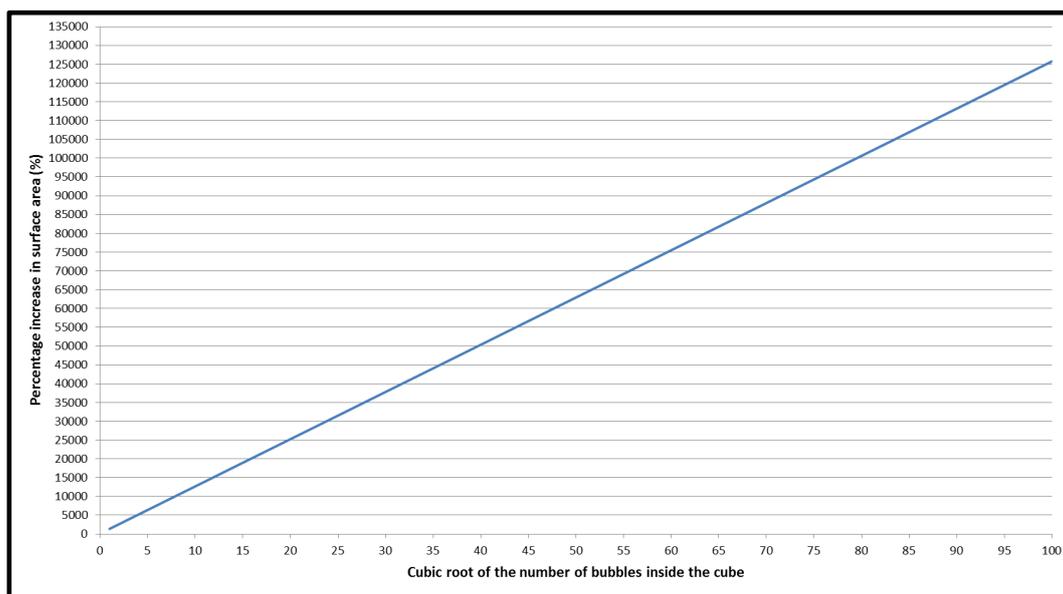
112 Simplifying by eliminating (r) to get:

113 $\% \; surface \; area \; increase \; due \; to \; aeration = 1 + \; x^3 4\pi \left(\frac{1}{x}\right)^2 \; \times 100$

114 Or:

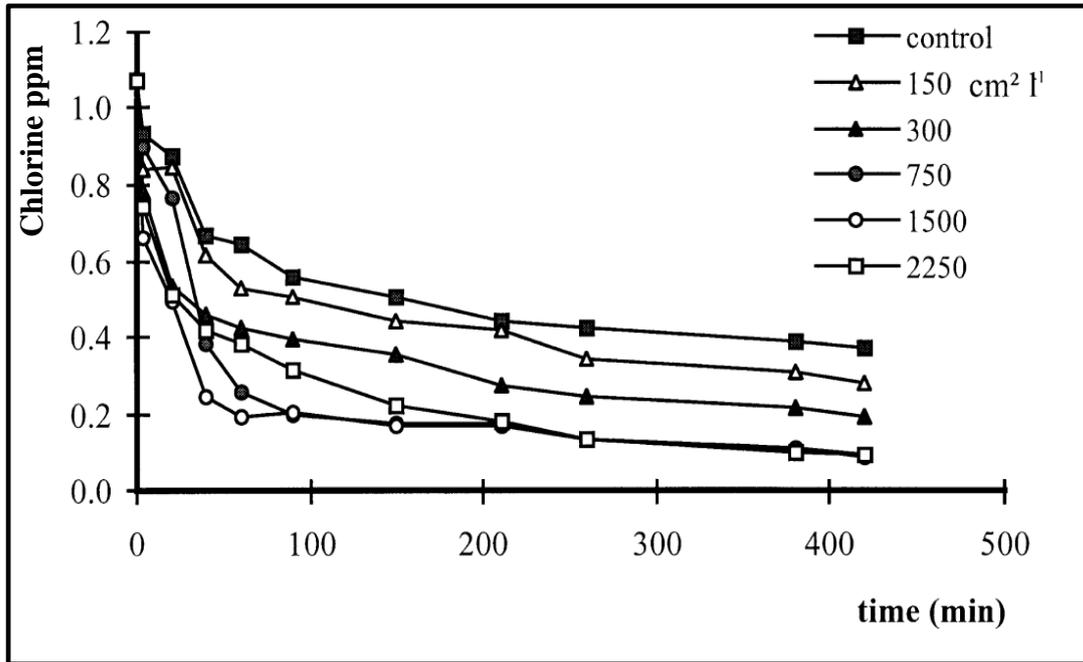
115 $\boxed{\% \; surface \; area \; increase \; due \; to \; aeration = (1 + \; 4\pi x) \; \times 100}$

116 This equation is valid for fully packed water cubes with bubbles. As spaces among bubbles increases the error margin
117 increases. Also it is valid for bubbles of equal volume; hence, every variation in bubble size range will also increase
118 the error margin.

119 This equation can be represented graphically to get the plot in figure 2.

121 Figure 2: The graphical representation of the relation between the number of bubbles inside a cube and the
122 percentage increase in surface area

123 (Lu et al., 1999) made a set of experiments investigating the effect of the ratio of surface area to volume (S/V) of
124 chlorinated water on chlorine decay. They suggested that a 1500% increase in surface area will reduce chlorine level
125 to a value of approximately one fifth of its original level. These tests as well as the conclusion in figure 2 encourage
126 the use of air bubbling for dechlorination.

127 **2.2 The role of aeration in increasing concentration gradient**
128 When a fresh air bubble rises through chlorinated water, the chlorine is transferred from water to air bubble driven by
129 concentration gradient (dC). The bubble at the surface of the sparger has the least chlorine concentration, hence greater
130 concentration gradient.

131 The average velocity of a rising bubble in water column is approximately (20-30) cm/sec (Sharifullin and Luebbert,
132 2001;Chen, 2004). Therefore, the chlorine will not have that time to reach saturation in the bubble then the
133 concentration gradient continues to be in its maxima. The more bubble velocity the more concentration gradient.

134

135   Figure 3: Effect of surface area to volume on chlorine mass transfer rate. (Lu et al., 1998)

136 **2.3   Effect of turbulence**
137 The relation between Reynolds number, boundary layer thickness and mass transfer rate were intensively outlined. At
138 higher Reynolds number boundary layer thickness increases, hence lower resistance to mass transfer. The higher
139 decrease in mass transfer resistance occurs when Reynolds number jump from laminar to turbulent flow regime.
140 Therefore, many mass and heat transfer applications that need high transferability designed to aim for turbulent
141 Reynolds number such as car radiators and air conditioners (Incropera and Dewitt, 2007;Bird et al., 2007).
142 Neglecting the jet effect and turbulence resulting from air effluent the sparger, for an air bubble rising in a column by
143 buoyancy only, Reynolds number can be expressed as (Scheild et al., 1999):

144 $Re_b = \frac{\rho_L u_b d_b}{\mu_L}$

145 Where:

146 Re_b: is Reynolds number for a bubble rising in a liquid (dimensionless).

147 ρ_L: is the liquid density (kg/m^3).

148 d_b: is the diameter of bubble (m).

149 μ_L: liquid viscosity ($Pa.s$).

150 Values of Re_b over 500 are considered as turbulent (Lau et al., 2012). Assuming the average bubble size along the
151 column is 1 cm and the average velocity is 25 cm/s, Re_b gives the value of 2500. With this Reynolds number there is

152 a big leap in chlorine transfer from water to bubble when using forced aeration instead of conventional stagnant
153 aeration.

3. Materials and methods

3.1 Aeration system

156

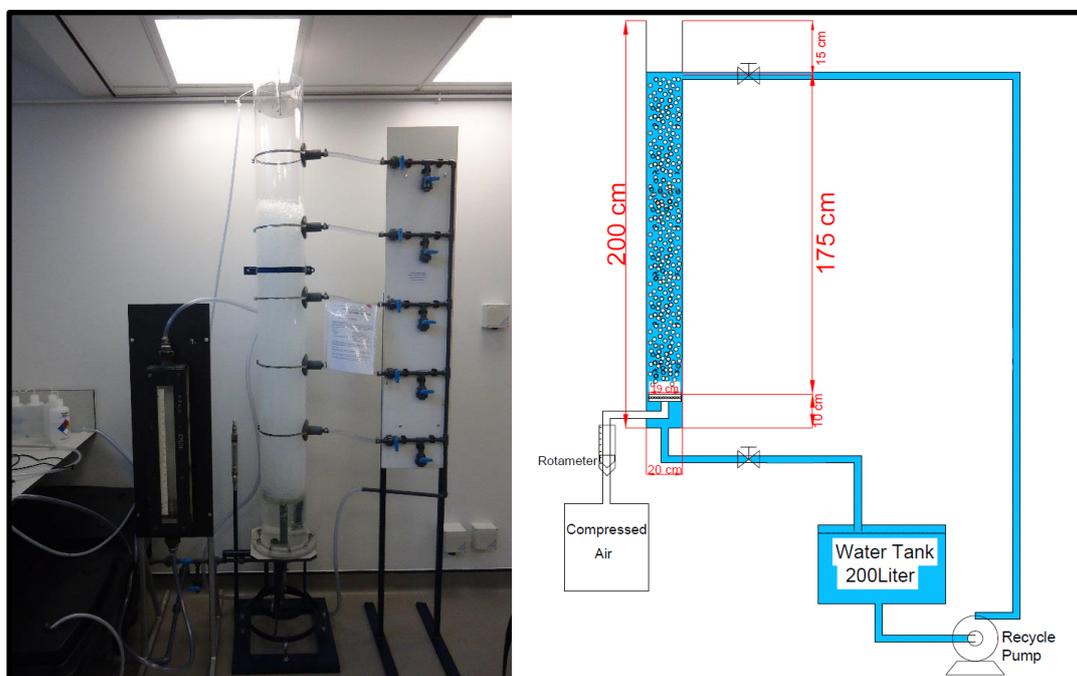



Figure 4: Experimental set up

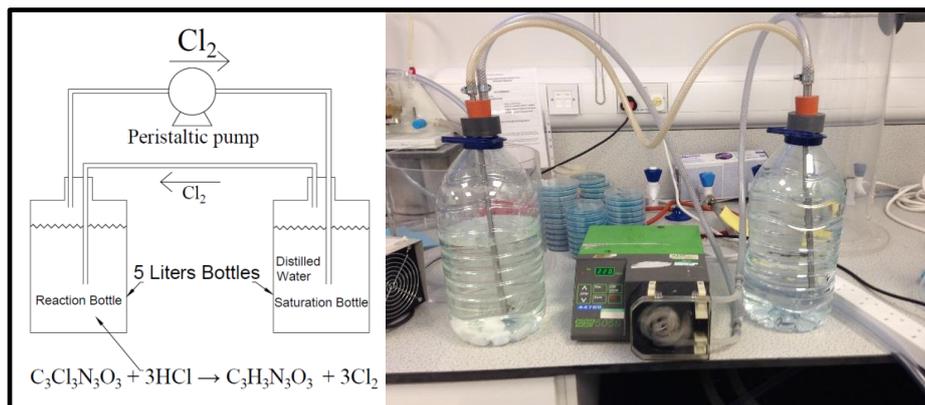
158 A compact aeration column system consists of 1 m long was designed and built. The main part is a transparent Perspex
159 (Poly (methyl methacrylate)) tube, 20 cm inside diameter. A ceramic sparger, 19 cm diameter, with 50 microns' holes
160 size is fixed 10 cm above the column base. The sparger is joined to a 15 mm diameter tube connected to a compressor
161 with a rotameter (10-900 l/min) or (0-10 l/min) depending on run demands. A 200-liter tank is installed beside the
162 system to collect distilled water from a still and provide a reservoir to the column. The working capacity of column is
163 approximately 50 liters and 63 liters when totally filled. The assembly is fixed on a steel rig (Figure 4).

3.2   The Chlorine
165 Three chlorine sources were used in this work:

166 1-   Trichloroisocyanuric acid tablets obtained from Acti.

167 2- Sodium hypochlorite obtained from SIGMA-ALDRICH (assay of 10%).
168 3- Chlorine gas: This is synthesized in the lab through reaction between trichloroisocyanuric acid and hydrochloric
169   acid (37 M); obtained from SIGMA-ALDRICH, according the following equation:
170 $$C_3Cl_3N_3O_3 + 3HCl \rightarrow C_3H_3N_3O_3 + 3Cl_2$$
171 The produced chlorine gas is dissolved in distilled water using the system in figure 5. A peristaltic pump (Watson
172 Marlow, Model - 505S, range 2 - 220 rpm) was used for transferring chlorine gas from the reaction bottle to saturation
173 bottle then circulating it back to the first bottle.

174 The reaction is implemented under standard atmospheric conditions. 100 grams of trichloroisocyanuric acid tablets
175 were placed in the reaction bottle then 5 litters of distilled water were added. Then 20 ml HCl was added to the
176 mixture and left till the water turns yellow. Using more or less amounts of the chemicals is not dangerous as the
177 reaction is not fast especially with the presence of this relatively large water amount. Finally, the peristaltic pump is
178 started to transfer the released chlorine gas from reaction bottle to saturation bottle. The increase in chlorine
179 concentration in the saturation bottle can be estimated roughly by yellowish water, it is recommended to take samples
180 every short period of time (say 10 minutes) for analysis until the desired concentration is reached.

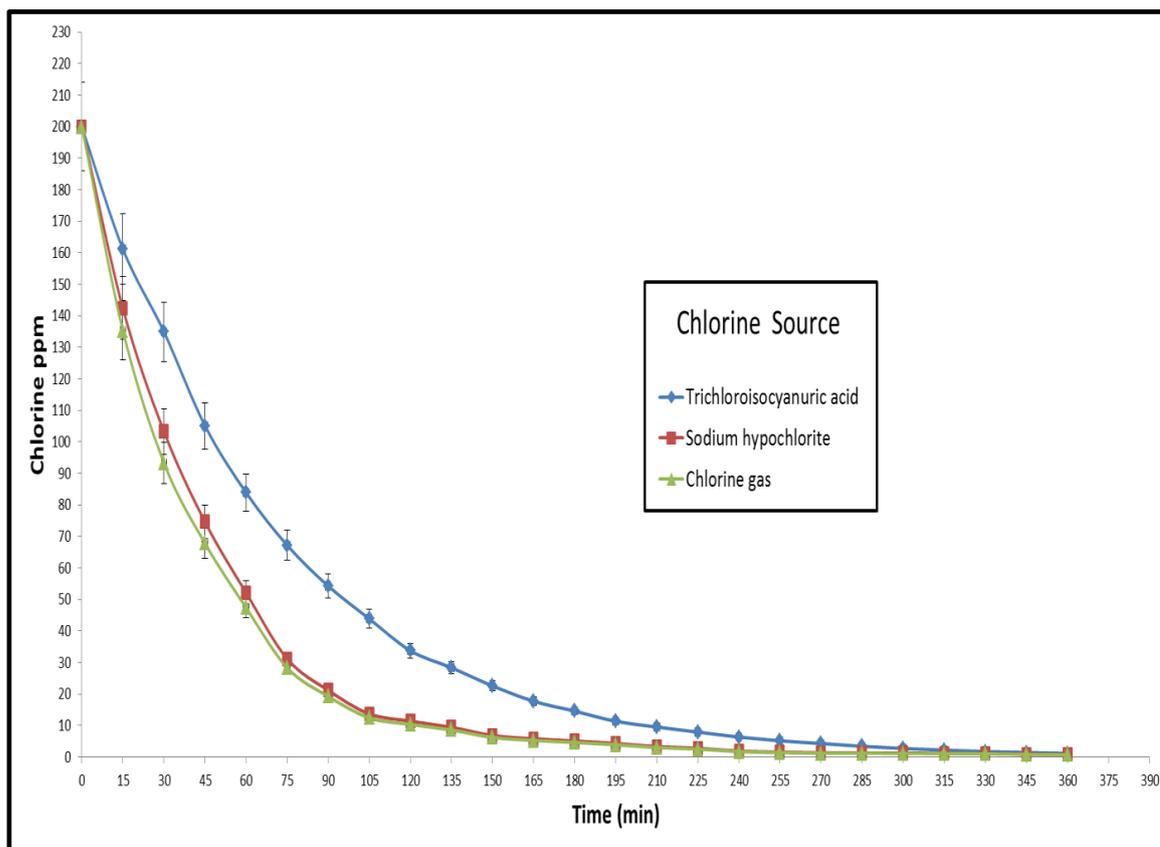
181 **3.3   Chlorine meter**
182
183 Two chlorine meters were used in this study. The first was exact®Z Obtained from Industrial Test Systems, Inc. (ITS).
184 The second was ExStik® obtained from EXTECH instruments, model number of CL200. Both meters are self-
185 calibrated. In addition of that they are provided with standards for external calibration.
186

188 Figure 5: Chlorine production and water chlorination system

189 **3.4   pH meter**
190 The pH meter used in this work obtained from AZ® with the model number of 8685. The device was calibrated using
191 three pH standard buffer solutions of the values of 4.0, 7.0 and 10 obtained from VWR international and
192 manufactured by MERCK MILLIPORE.

193 **3.5   Experimental procedure**
194 1- Prepare 5 litters of 2000 ppm chlorine water solution in a separated bottle.
195 2- Fill the column with 45 liters of distilled water.
196 3- Add saturated chlorine solution obtained from step 1 gradually to the column with mixing to get 200 ppm.
197 4- Start air pumping at 1 l/min.
198 5- Start taking samples every 1minute for low range or 2 minute for high range, for 30 minutes for analysis.
199 6- Stop air pumping and drain the system.
200 7- Repeat steps 1 through 6 for every new air flowrate.
201 8-

202 **4.   Results**
203 Results were expressed by measuring chlorine decay in ppm as a response of pumping time in minutes and air flowrate
204 in l/min. Two ranges of air flowrates were investigated; the first was a high range (10 – 50) l/min with an interval of
205 10 l/min while the second was (1-9) l/min with an interval of 1 l/min which represented the fine tune of the first range.

206 **4.1 Chlorine decay without air pumping (control)**

207 For the control chlorinated water was put in the column with the same concentration used in the full experiments and
208 left to evaporate naturally. The obtained results are summarized in figure 6.

209

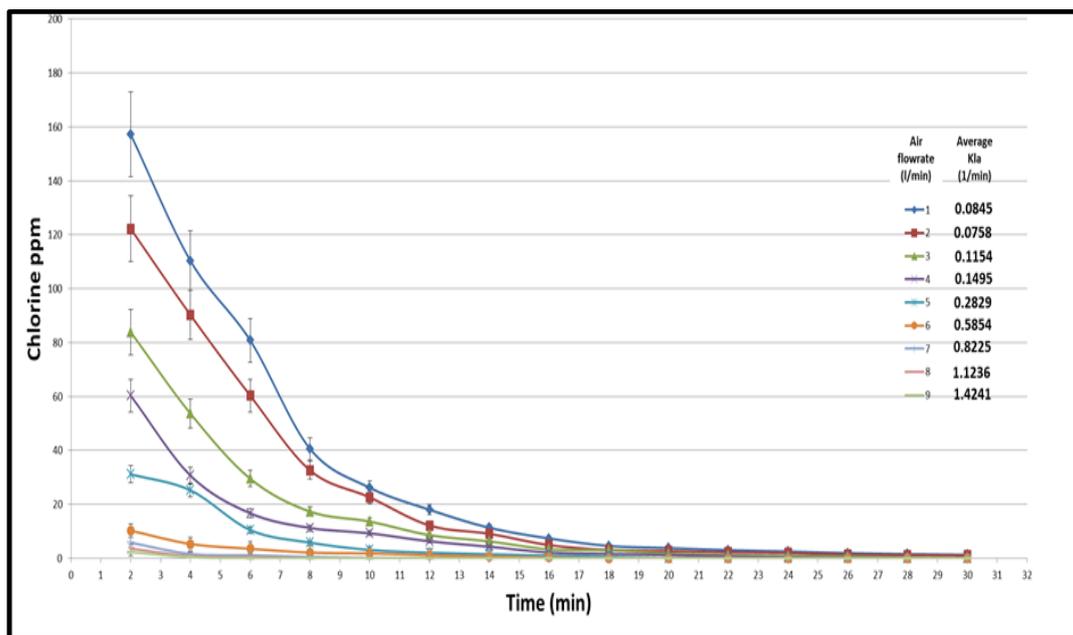
210   Figure 6: Natural stagnant aeration rate (control)

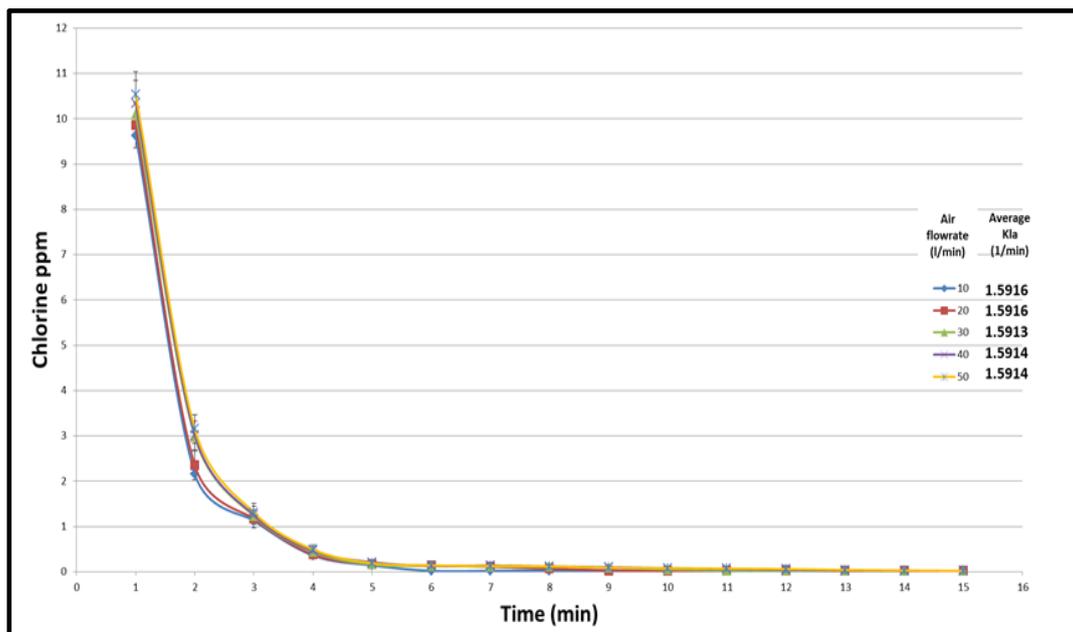
211   4.2 De-chlorination of chlorine obtained from trichloroisocyanuric acid

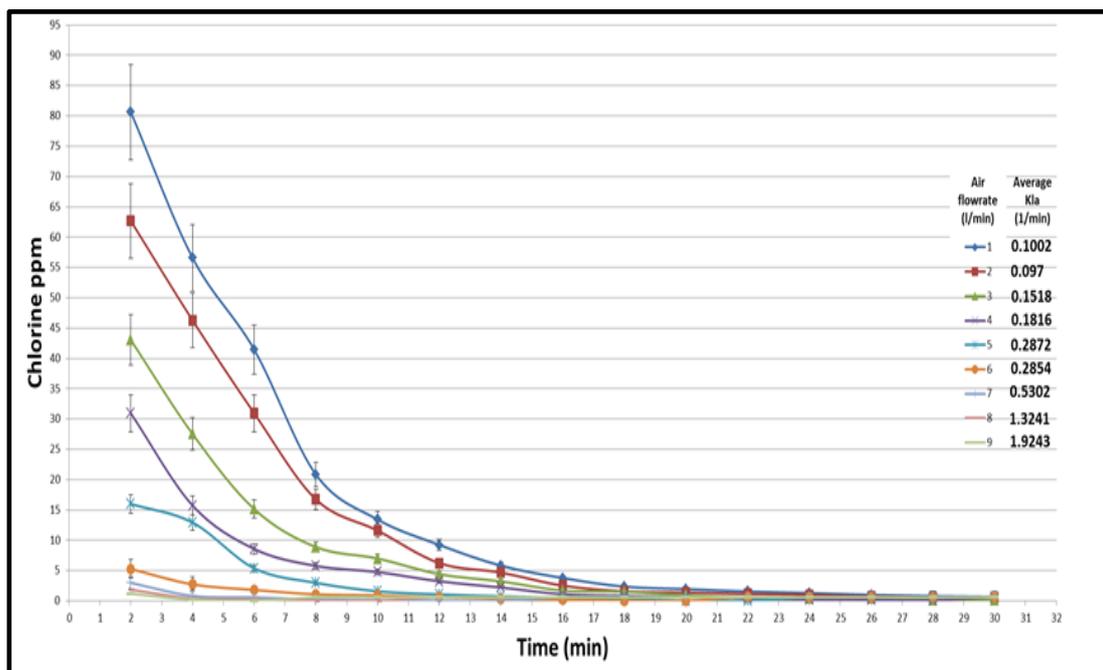
212   In this set the saturated chlorine solution in step 1 in 3.5 was prepared using trichloroisocyanuric acid (200 ppm). The
213   obtained results are summarized in figures 7 for low and 8 for high ranges of air flowrates.
214

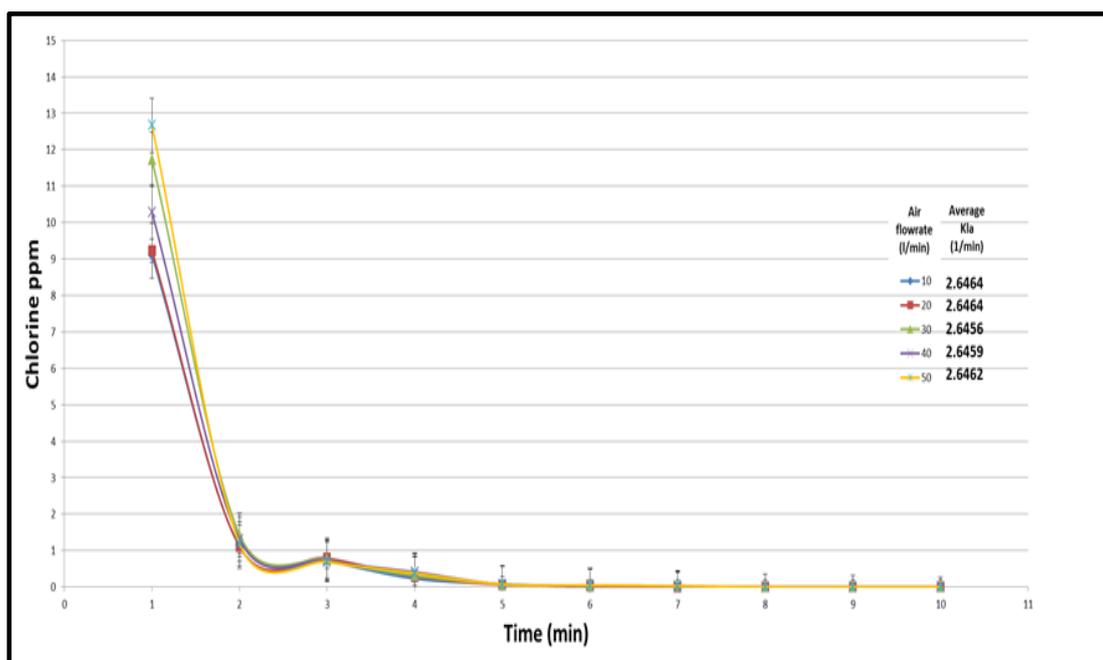
215   4.3   De-chlorination of chlorine obtained from Sodium hypochlorite
216   In these experiments the saturated chlorine solution in step 1 in 3.5 was prepared using sodium hypochlorite (200
217   ppm). The results are summarized in figures 9 for low and 10 for high air flowrates.

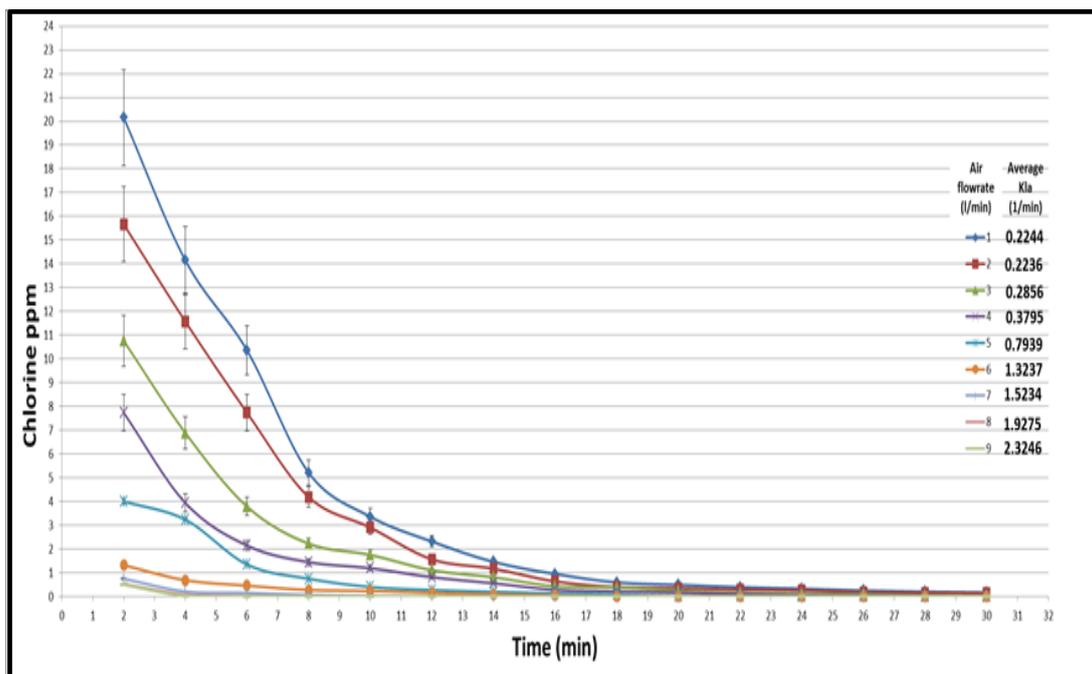
218   4.4   De-chlorination of chlorine obtained from Chlorine gas
219   In this set the saturated chlorine solution in step 1 in 3.5 was prepared using chlorine gas prepared using the system
220   in figure 5 and following step 3 in 3.2 (200 ppm). The obtained results are summarized in figures 11 for low range
221   and 12 for high air flowrates.

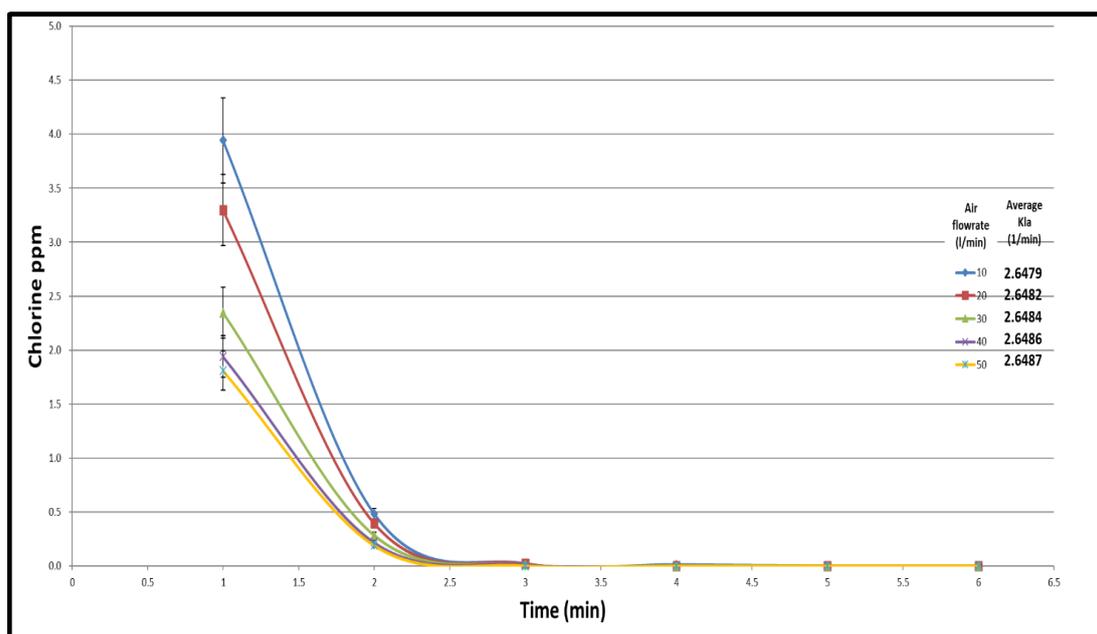
222   4.5   Effect of air flow rate on mass transfer coefficient (K_la)
223   The average values of Kla are plotted against air flow rate. Figures 13 for low and 14 for high flowrates summarize
224   the results.
225

226

227   Figure 7: Effect of low range air flowrate on chlorine decay when using trichloroisocyanuric acid as chlorine source

228

229   Figure 8: Effect of high range air flowrate on chlorine decay when using trichloroisocyanuric acid as chlorine source

230

231   Figure 9: Effect of low range air flowrate on chlorine decay when using sodium hypochlorite as chlorine source

232

233   Figure 10: Effect of high range air flowrate on chlorine decay when using sodium hypochlorite as chlorine source

234

235   Figure 11: Effect of low range air flowrate on chlorine decay when using chlorine gas as chlorine source

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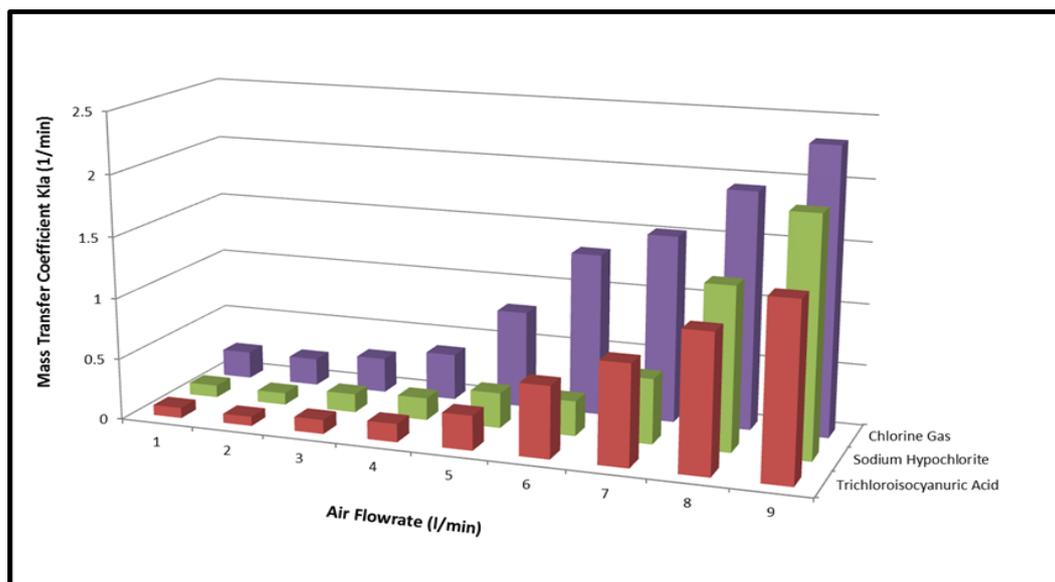
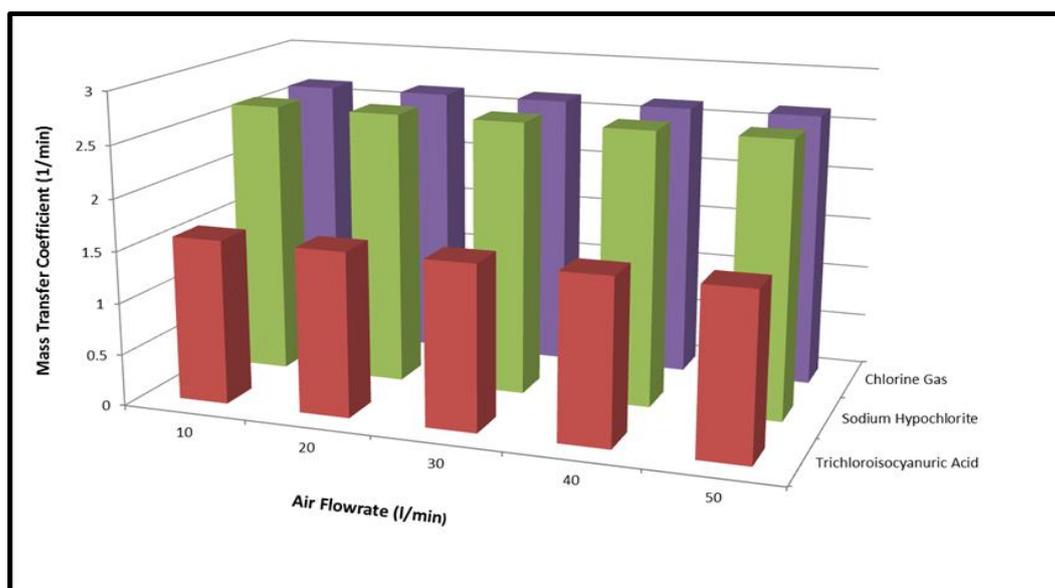
237   Figure 12: Effect of high range air flowrate on chlorine decay when using chlorine gas as chlorine source

238
239   Figure 13: Effect of air flowrate on mass transfer coefficient K_la (Low range flowrate)
240

241
242   Figure 14: Effect of air flowrate on mass transfer coefficient K_la (High range flowrate)
243
244   **4.6 Effect of chlorination on water pH**
245   Along all the experiments of the three chlorine sources, pH was monitored to give the results in figure 15.

246

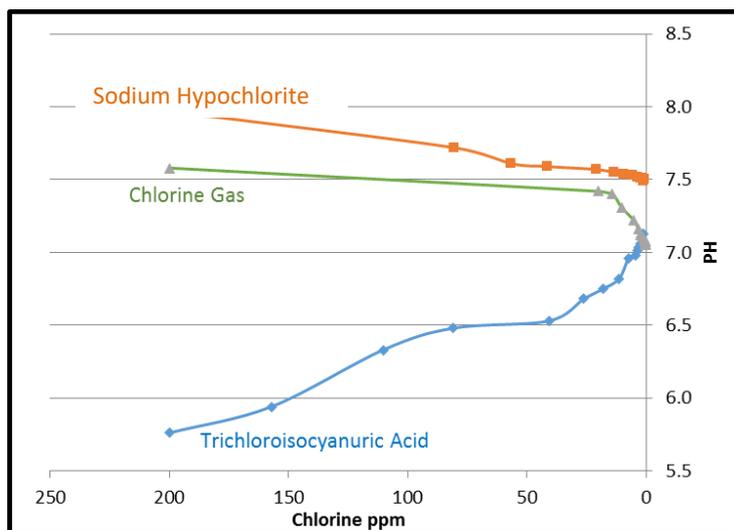
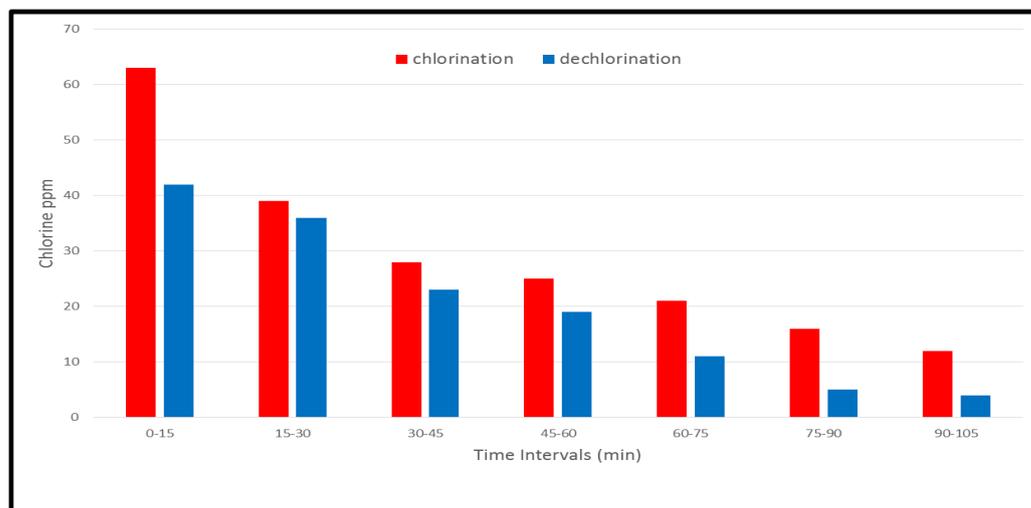



Figure 15: pH variation in shock chlorination for the three chlorine sources

248   **4.7 Shock chlorination rate**
249   Results are expressed as ppm reduction for dechlorination and ppm increase for chlorination during the same time
250   intervals. Every bar is the net difference between one reading and the next one.

251   To make a fair comparison, the chlorination values near to zero ppm are compared with the dechlorination values near
252   200 ppm because at these two values the driving forces are at their maxima. Figure 16 shows the results. It is shown
253   that the chlorination is faster than dechlorination rate by an average of 25%.

254

255   Figure 16: Comparison between chlorination and dechlorination rates

256

5. Discussion

The main aim of this study was to investigate increasing the release of dissolved Chlorine from water by increasing the mass transfer area, concentration gradient and turbulence using aeration. This hypothesis is supported and data for such a process is given.

Chlorine is widely used in water industry. Changing this technique would cost a lot (Fawell, 2014;Powell, 2010). Therefore, it is better to keep using disinfection by chlorination and trying to avoid the disadvantages.

The perfect drinking water system should be, free of biological contaminants and free of chemicals, especially biocides. The results show that shock chlorination and shock dechlorination by aeration can produce such water. The proposed purification process aims to kill the entire microorganism load with a high dose of chlorine then removing this chlorine by aeration.

The findings of this study pave the road for using shock chlorination followed by shock dechlorination for producing high quality drinking water. Dissolved chlorine can easily be removed from water by forced aeration as it provides three advantages on stagnant aeration. First is the significant increase in mass transfer area as shown in figure 2. Second is the increase in mass transfer boundary layer turbulence between air bubble and bulk water. The third is the increase in mass transfer concentration gradient along water-bubble interface.

In this study, three sources of chlorine were examined for their response to dechlorination by aeration. The first was trichloroisocyanuric acid which is used frequently in swimming pools due to its reaction with water to produce cyanuric acid which is considered as a chlorine stabilizer that prevent chlorine from volatizing that may result from high surface area with respect to water mass in swimming pools (Harnvajanawong et al., 2004). The second is sodium hypochlorite (bleach). It is the most used chlorine source in all applications as a result of its abundance, cheapness and ease of use. The third was chlorine gas.

With all three chlorine sources the general trend is relatively fast chlorine removal from water but they do differ slightly in removal rate, the final steady concentration and how fast they reach this steady concentration. For trichloroisocyanuric acid the chlorine removal was optimum at 9 l/min of air and needed 6 minutes to reach the minimum steady concentration. For the low flowrate range the results obeyed the hypothesis that assumes more air pumping lead to faster chlorine removal. For the high range over 10 l/min the removal rate did not increase as a response to air flowrate increase. This because of "the column effect"; that is, in a column, at high air flow rates there will be a bubble "traffic jam" along the water column and bubbles increase in size as they rise. These two factors drive bubbles to be adjacent to each other reducing the total surface area for mass transfer as well as losing the turbulence along the bubble-water interface. Therefore, at higher air flowrates further increasing air flowrate had two counteractive effects; first, is increasing the three driving forces of aeration "increasing surface area, increasing turbulence, and increasing concentration gradient" while the opposite is "the column effect". The more the air flowrate, the more the domination of column effect and the less chlorine transfer.

It was concluded that in an air-water bubbling system the column effect should not start effectively before 50 l/min (Hassan and Edyvean, 2015) but in this work it started after 10 l/min. This is because the relatively high concentrations of trichloroisocyanuric acid and sodium hypochlorite seem to work as frothers which stimulate the column effect at lower air flow

It was also noticed that in aerating trichloroisocyanuric acid the chlorine removal is lower when compared with sodium hypochlorite and chlorine gas. Furthermore, the chlorine concentration did not reach zero even with a long aeration time and stuck on 0.02 ppm. This because of the stabilizing effect of cyanuric acid that is produced from the reaction of trichloroisocyanuric acid and water (Harnvajanawong et al., 2004).

Using trichloroisocyanuric acid in shock chlorination would give many problems and limitations. Concentration of cyanuric acid, formed when trichloroisocyanuric acid is added to water, above 30 ppm leads to a phenomenon called "chlorine lock" in which cyanuric acid locks the ability of chlorine to kill bacteria. hypochlorous acid is another product from trichloroisocyanuric acid and water which decreases the pH to a level unacceptable for drinking water (Harnvajanawong et al., 2004).

303   For the sodium hypochlorite solution, the dechlorination was faster than trichloroisocyanuric acid rather than the
304   ability for reaching zero chlorine level. It seems that the acidic pH; not the presence of cyanuric acid alone hinders the
305   dechlorination.

306   Shock chlorination using trichloroisocyanuric acid and sodium hypochlorite is known in the treatment of swimming
307   pools and domestic wells. Using either of them is not a recommended practice in drinking water production for many
308   reasons. First, is because of corrosion, especially when the construction material is cast iron. Second, is the difficulty
309   of lowering chlorine level across the distribution system naturally. Third, there will be reaction residuals lead to a
310   significant unacceptable effect on water pH away from the neutral value of 7. Therefore, using chlorine gas is the
311   recommended method for shock chlorination and shock dechlorination because there will be no residual chemicals
312   after the dechlorination.

313   Chlorination by chlorine gas is usually implemented by injecting it through water pipes. For shock chlorination this is
314   not enough even though chlorination with chlorine gas is known to be fast. Also, releasing high doses of chlorine to
315   the air through the shock dechlorination process implies a high health risk on the people that may live near water
316   treatment facilities. Therefore, a new design for recycling chlorine in shock chlorination equipment is needed. Figure
317   5 gives a preliminary idea for such design.

318   Chlorine is very corrosive substance; so it should be fully controlled to prevent the decay of the distribution system.
319   On the other hand, Chlorine level in treatment and distribution facilities should be kept acceptable. Mostly, water
320   distribution systems are made of three well-known construction materials; cast iron, concrete, and plastic. For cast
321   iron chlorine is not recommended. Concrete and plastic are less affected by corrosion (Al-Jasser, 2007). Therefore,
322   minimizing the chlorine level in water distribution system is another advantage for dechlorination.

323   Using bubble aeration has the advantage over stagnant aeration due to three physical phenomena. First is higher mass
324   transfer area. The second is higher Reynolds number through the mass transfer interface, the third is a higher mass
325   transfer concentration gradient; that is, the bubble is rising fast through the water column which leads to shorter time
326   to mass transfer then there is a higher concentration gradient. Smaller bubbles have larger mass transfer area; less
327   Reynolds number and less concentration gradient as they climb up slowly through the water column which makes
328   them to collect more chlorine inside hence there is less concentration difference between the bubble and the bulk
329   water. However, the comparison between small or large bubbles is a tradeoff and needs further investigation.

330   pH was monitored against chlorine removal for each chlorine source. For trichloroisosyanuric acid at 200 ppm chlorine
331   the pH was acidic at 5.76. as chlorine was withdrawn by aeration the pH decreased till reaching 7.13 at 1.32 ppm
332   chlorine. For sodium hypochlorite at 200 ppm the pH was 7.97 then went down 7.5 at final chlorine concentration of
333   0.68 ppm. For chlorine gas at 200 ppm pH was 7.58 then dropped down to 7.05 when the chlorine concentration
334   became 0.17. The reason behind these trends is that the continuous withdrawal of chlorine from the system leads to
335   continuous withdrawal of hypochlorous acid; hence, decreasing the acidity of the water.

336   The pH results give important limitations that should be considered when selecting a shock chlorinator. Using
337   trichloroisosyanuric acid will produce high residual of syanuric acid which raises water acidity to unacceptable levels.
338   The same is for sodium hypochlorite but is less marked and in basic direction. Sodium is also a side product of water
339   dechlorination by sodium hypochlorite but its health effect is not that dangerous as stoichiometrically the produced
340   sodium when using 200 ppm sodium hydroxide is approximately 131 ppm. Sodium is an essential component in
341   mineral water, so this sodium concentration may still acceptable. Chlorine gas is the best for use in such application
342   as its chlorination and dechlorination is nearly completely reversible.

343   Practically, when low chlorine concentration is needed for shock chlorination; say less than 30 ppm, the preferred
344   chlorinator is sodium hypochlorite because of its affordable effect on water pH. For higher chlorine levels chlorine
345   gas would be recommended but with some modifications in chlorination facilities.

346   Mass transfer coefficient is a direct reflection to the chlorine depletion rate in water. The faster the decrease of chlorine
347   ppm the greater the mass transfer coefficient is. When plotting the term $ln \frac{(C^*-C)}{(C^*-C_\circ)}$ against the time, the slope represents
348   the value of $K_l a$. The sign of $K_l a$ was negative in all points which indicate that the process represents dissolved gas
349   depletion from water to gas bubble.

K_la values are necessary for design purposes. Therefore, they should approach the reality not the values predicted by mathematics. That is, the first few points have fast chlorine decrease hence more vertical slopes while the many others have slow decrease hence more horizontal slopes. When taking the average of these slopes, the average will show horizontality which is much away from design reality and will cause an unfair or magnified equipment. To deal with that, the average slope for the range from 200 ppm to nearly 1 ppm was taken into account as this range represents the most reliable chlorine depletion rate. Within this range equipment will designed well and economically.

It is clearly noticed that K_la values are very high at higher air flowrates. This is a direct result of the increase of mass transfer area that resulting from higher number of bubbles per certain time period and water volume.

K_la values for low range air flowrates (1-9 l/min) shows an increase with respect to air flowrate for all the three chlorine sources. This is due to the parallel increase in mass transfer area that resulting from the increase of bubbles per unit volume and time. After that, when reaching 10 l/min bubbles come to be crowded inside the column and; in majority of cases, attached to each other. This attachment reducing the overall mass transfer area as bubbles will not be longer exposed to water. Over the range of 10 to 50 l/min K_la shows nearly constant values because there will be a counteractive effect between increasing the air flowrate and decreasing the mass transfer area resulting from bubble crowd.

The variation of K_la ($K_l \times a$) or (mass transfer coefficient multiplied by the mass transfer area), is a direct result of varying the mass transfer area alone. K_l is nearly constant at the same other variables such as pressure and temperature.

Every value in figures 13 and 14 is the mean of many K_la values with respect to chlorine concentration. K_la increases as the starting chlorine concentration increases. This because the term$(C^* - C)$; the transferred moles, is increasing also.

It is clear that chlorination is faster than dechlorination by an average of 25 %. The explanation behind this can be illustrated by the comparison between chlorine and air bubbles rising in water. When a chlorine bubble rises in water column, the gas that transfers across the bubble-water interface is only the chlorine. On the other hand, when an air bubble is rising along the water column, the transferred gasses across the interface are chlorine and water vapor.

The solubility of a gas in liquid and the counter action of the release of a gas from the liquid under the same conditions is governed by mass transfer rate. This depends mainly on the concentration gradient. In the chlorination process the concentration gradient continues to be the maximum level from the bottom to the top of the column while in dechlorination it starts at the maxima and decreases as it rises up. However, in chlorination the lower the concentration of chlorine in water the higher the chlorine transfer rate as a result of higher concentration gradient while for dechlorination process the higher the concentration in the water the higher the transfer rate for the same reason.

The findings of this set assumes that as the chlorination is faster than dechlorination by a factor of 25%, hence, the "air/water demand per ppm of chlorine reduction" should be reduced by the same percentage.

After chlorination the chlorinated water should reside in the column for a short time to kill the bacteria. Approximate calculations indicate that, at a chlorine level of 200 ppm, the contact time should be about 11 seconds (Wagnet et al., 2005). These calculations are proposed to work under moderate or low bacterial load and chlorine concentrations. Generalizing these figures for high chlorine levels is not fully recommended but can give a preliminary indication. Furthermore, such calculations are not for a complete kill of all the microorganisms but for a reduction to certain cfu/ml according to industrial bio-purification demands. Therefore, in designing a chlorination unit both chlorination and contact time have to be addressed.

For the low chlorine concentrations that are conventionally used in treatment processes, the dissolution time is not important as it takes little time to rise from zero to 4 ppm. However, for shock chlorination, chlorine has to rise from zero to 200 ppm. This time should be kept in mind in design calculations.

For design purposes, the chlorination unit dimensions can be assumed to be the same as dechlorination. This assumption depends on the fact that if dechlorination takes 2 minutes, the chlorination should take one minute and 30 seconds (dechlorination takes 25% more the time of chlorination) this gives 30 seconds to kill all the bacteria. If more time is needed to do so, it should be taken into account.

6. Conclusions

Forced aeration is a promising technique that can be used for removing chlorine in a fast and safe way in drinking water industry. This would enable shock chlorination followed by shock dechlorination to produce microorganism and biocide free drinking water. Chlorine gas was found to be the fastest and cleanest chlorine source to response to dechlorination by aeration followed by sodium hypochlorite and trichloroisosyanuric acid respectively.

On average, chlorination is faster than dechlorination by 25%. This gives a good tolerance and enough idea about the dimensions of a chlorination unit. The design of a chlorination unit is not that different from a dechlorination unit. As a rule of thumb, they can be the same.

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