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The Effects of Operating Variables on Efficancy of Water Disinfection by Sodium Hypochlorite Using Al-Wathba Wastewater

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Abstract

The aim of this investigation was to study the impact of various reaction parameters on wastewater taken from Al-Wathba water treatment plant on Tigris River in south of Baghdad, Iraq with sodium hypochlorite solution. The parameters studied were sodium hypochlorite dose, contact time, initial fecal coliform bacteria concentration, temperature, and pH. In a batch reactor, different concentrations of sodium hypochlorite solution were used to disinfect 1L of water. The amount of hypochlorite ions in disinfected water was measured using an Iodimetry test for different reaction times, whereas the Most Probable Number (MPN) test was used to determine the concentration of coliform bacteria. Total Plate Count (TPC) was utilized in this study to count the number of colonies of common bacteria. Reaction variables that were examined showed that the increase in temperature, pH, and reaction time caused the concentration of Coliform bacteria to decrease, which in turn caused an accumulation-related increase in OCl^- concentration. The optimum values of temperature and reaction pH were determined to be 8 and 29^o C respectively. The kinetics of the reaction was examined in this study, and the results showed that Selleck model's order of reaction is two, with rate constants of $1.3791x10^{-5}$, $3.0806x10^{-5}$, and $5.738x10^{-5}$ L/(mole min) at 20^o, 29^o, and 37^o C, respectively.

Keywords: Water disinfection, Sodium hypochlorite, Most Probable Number Test, Selleck Model.

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1- Introduction

Disinfection process is necessary for get rid of microorganisms that still in the treated water [1, 2]. Several kinds of chemical substances have been used as disinfectants, such as; chlorine gas (Cl_2), chloride dioxide (ClO_2), ozone (O_3), chloramines (NH_2Cl), calcium hypochlorite ($Ca(OCl)_2$), lithium hypochlorite (LiOCl), and sodium hypochlorite (NaOCl) [3]. Typically, disinfectants are added at the last stage in water treatment plants. Keeping a trace suspended for secondary disinfection in the distribution system to stop any microbial regrowth should be considered when determining the appropriate amount of disinfectants to kill all the organisms in water [4, 5]. However, it must be remembered that the process of disinfecting water also exposes consumers to some health risks due to some unfavorable side reactions occur in water [6]. This is demonstrated in the work of Zazouli et al. [7], in which they show how these reactions can result in the production of Disinfection By-Products (DBPs) from the Natural Organic Materials (NOMs) that are already present in the water [8]. The carcinogenic effects of DBPs on humans many researchers [9 - 13] who proved the relation between DBPs and some cancers and renal failure.

Chlorine element is available in nature as combined-ion with calcium, magnesium, potassium, and sodium [14]. Chlorine is considered as one of the most popular water disinfectants due to its relatively low cost, high disinfection-activity, and perfect oxidation potential [15]. On the other hand, using chlorine gas has the drawback of having low reaction selectivity, which results in undesirable byproducts. Chlorine gas can rapidly oxidize NOMs producing DBPs in water [16]. Free chlorine concentrations in drinking water typically range from 0.2 to 2.0 mg/L, although they can reach 5.0 mg/L for restoring a water distribution system that is in need of repair or for treating water that has a high level of biological contamination [17]. The fact that chlorine is a poisonous gas that can cause death if it is concentrated enough must be mentioned. The chlorine gas water disinfection process is demonstrated in the reactions below [18]:

$$\mathrm{Cl_2} + H_2\mathrm{O} \rightarrow \mathrm{HOCl} + \mathrm{HCl} \quad (1)$$

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$$HOCl \leftrightarrow H^+ + OCl^- \quad (2)$$

The decay of Cl_2 is controlled by the equilibrium between HOCl and OCl^-. Acidity (pH) value plays an important role in effecting the equilibrium process acquiring [19]. The disinfection-activity of chlorine is reduced with the raising in pH value and the amount of the unassembled hypochlorous acid [18]. NaOCl was used in water disinfection field due to its proven germicides control, capability to combat a wide spectrum of microorganisms, nonpoisonous, nontoxic byproducts, easiness to handle, and low cost. NaOCl solution for domestic use is mostly between 1% to 5% in dilution of 1% to 15% stock [18]. Since NaOCl is a clear liquid, it can be injected into the reactors as a solution; however, NaOCl has a stability issue that causes its concentration to decrease over time when exposed to sunlight [20, 21]. When Sodium hypochlorite dilute in a pure water, chemical reaction occurs as it shown in Eqs. 3 and 4, knowing that pH controls the amount of HOCl and the OCl^- ion produced from the HOCl decaying [22]. Low pH shifts the NaOCl reaction towards producing HOCl [23]. Producing OCl^- is assisted by the use of NaOCl to disinfect drinking water. According to Bolyard et al. [24], NaOCl industrialization and storage can result in the production of OCl^-. It is understood that OCl^- can generate $ClO_3^=$, as shown in Eq. 5 below [25]:

$$NaOCl + H_2O \rightarrow NaOH + HOCl \quad (3)$$

$$HOCl \leftrightarrow H^+ + OCl^- \quad (4)$$

$$3\ OCl^- \rightarrow 2\ Cl^- + 3\ ClO^= \quad (5)$$

Corrosion is another issue that coexists with DBPs problem that is caused by high chlorine concentrations in drinking water disinfection. Corrosion takes place in the pipeline network that transports drinking water from projects to homes [26]. The corroded nature of chlorine acid and chlorite with metals, results in placement and distortion of its surface and from then stripping the layers of metal in a cumulative effect over time [27]. This causes an additional infection to the drinking water, which needs an increase in the amount of free remaining chlorine in water for the secondary disinfection process. This will also lead to an additional increasing in the erosion problem and the amount of DBPs together [28]. In order to avoid any interaction of secondary reactions brought on by the corrosive nature of the NaOCl, which could affect the accuracy of the results, glass beakers, tubes, and bottles were used in this work.

Coliform bacteria can enter to the human body through consuming infected food and drinks [29]. Due to the fact that coliform bacteria are among the organisms that can contaminate wastewater, as well as their affordability and ease of use in water analysis, coliform bacteria have come to be used as a quality standard for water disinfection processes [30]. Coliform consume glucose and convert it to acetic acid, D-lactate, L-lactate, and ethanol for energy [31]. This work was aimed to study the different variables that can affect the water disinfection quality and also the reaction kinetics for sodium hypochlorite as a water disinfectant, using E Coli bacteria in wastewater, through Selleck method instead of Harriet methods as other works did. This work focused on the interaction that takes place between the effect of concentration of E Coli bacteria in a particular way with the influence of OCl^- concentration during the course of the reaction process by examining the effect of changing pH, temperature, and initial concentrations of bacteria and sodium hypochlorite. The possibility of accelerating water disinfection processes by raising the temperature of the treated water, especially in projects that aim to treat and disinfect small amounts of water, can be realized by studying the reaction mechanism of the chlorination wastewater process and calculating the rate constants for different temperatures. For large wastewater treatment plants, the process can be accelerated in summer since the water naturally originates from warm sources. This lowers the cost of energy consumption and increases process efficiency by shortening the duration of the water chlorination process.

2- Experimental Work

From the general diagram in Fig. 1, a sequence of the experimental work steps can be observed.

2.1. Chemical Materials

Sodium Hypochlorite (NaOCl) (97% Across organics), Lauryl Tryptose Broth (LTB) (99% Merck), Starch (98% Sigma-Aldrich), Potassium Iodide (KI) (99% Sigma-Aldrich)

2.2. Samples Collection

Wastewater samples were brought from Al- Wathba Water Treatment Plant. Samples were rounded by ice to suppress the bacterial activity and transported next day to the laboratory.

2.3. Wastewater Disinfection Reaction

NaOCl solution was used to disinfect treated water. The variables studied were initial concentrations of fecal coliform bacteria, reaction temperature, reaction pH value, reaction time, and NaOCl solution doses. 1% NaOCl solution was used to treat 1L, of wastewater in a batch reactor, with various doses being injected each time.

2.4. Biological and Chemical Tests

Samples were tested biologically (MPN. and TPC) and chemically (Iodimetry) for various reaction times. MPN test been accomplished initially (t = 0 minute) for one set of five tubes with different dilutions (10^{-1}, 10^{-2}, 10^{-3}). One ml of each dilution was injected into the L.T.B. media in each set, while 20 ml of the samples injected into the triple concentration L.T.B. media set for different reaction times. Fig. 2 demonstrates how to distinguish between the contaminated and healthy L.T.B tubes for MPN test. On the other side, 25 ml of water sample was tested by titration with the starch for Iodimetry test, KI was used as an indicator [32].

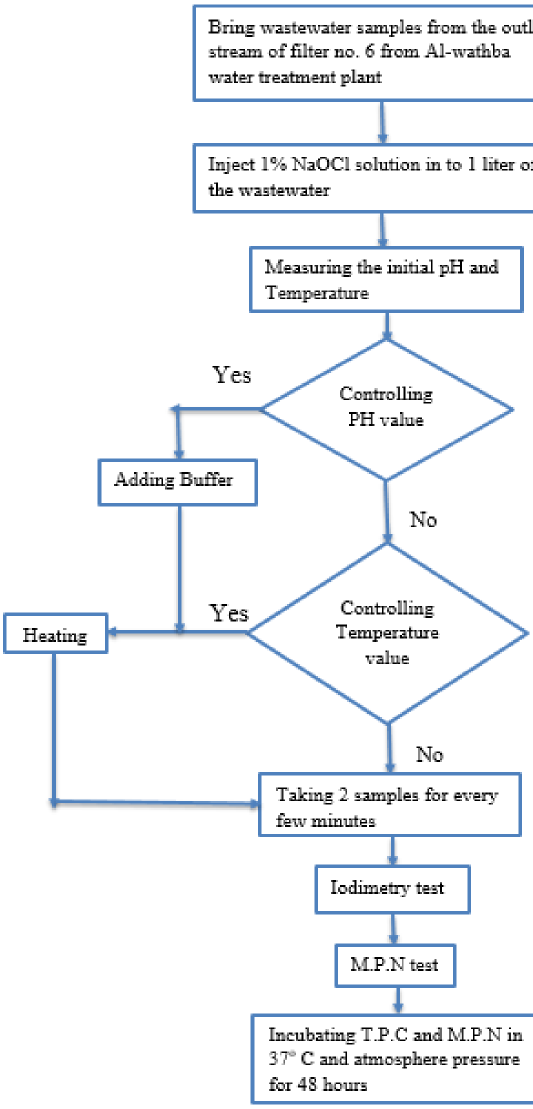

Fig. 1. Flowchart Diagram, Illustrating the Steps in the Experiment's Wastewater Disinfection by Sodium Hypochlorite

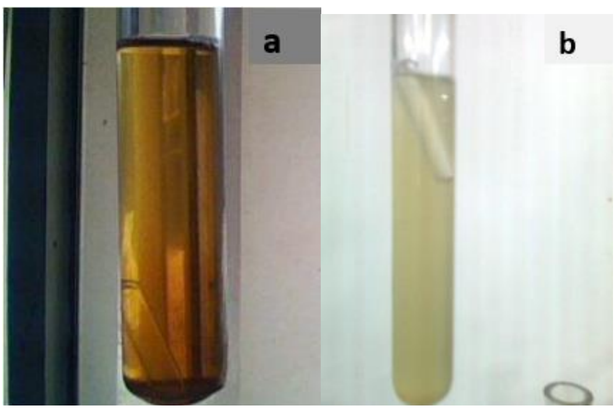

Fig. 2. MPN Tubes Test, (a) Positive LTB Tube, (b) Negative LTB Tube

2.5. Incubation Process

The initial MPN tubes (contact time = 0) test and Petri dish for the T.P.C test incubated in a Memmert incubator for two days at 37ºC, while the sets of MPN test for 5, 15, 30, 60, 90, and 120 minutes of reaction time incubated in the same incubator at 37ºC for 24 hour [32].

3- Results and Discussion

3.1. Most Probable Number and Iodimetry Tests

The Most Probable Number (MPN) method is used to determine the concentration of viable microorganisms in a sample by replicating liquid broth growth in ten-fold dilutions. It is frequently applied to the estimation of microbial populations in agricultural products, waters, and soils [33]. When samples contain particulate matter that obstructs plate count enumeration techniques, MPN tests are particularly helpful. In order to determine whether the water is safe to drink in terms of the amount of bacteria present, MPN is most frequently used to test the quality of water [34]. Fecal contamination of water is indicated by a class of bacteria known as fecal coliforms [35]. In contrast, the presence of large numbers of fecal coliform bacteria would indicate a very high probability that the water could contain disease-producing microorganisms making the water unsafe for consumption. The presence of very few fecal coliform bacteria would indicate that water probably contains no disease-causing microorganisms [36]. While iodimetry test is a technique for volumetric chemical analysis that uses a redox titration to determine the point at which elementary iodide appears or vanishes, this absorption will cause the solution's color to change from deep blue to light yellow, estimating active chlorine ion concentration.

3.1.1 Effects of Initial Coliform Bacteria Concentration

The impact of the initial bacterial concentration of fecal coliform bacteria on the process of water disinfection was examined using two concentrations (1300 and 2200 coliform/L). For various bacterially contaminated samples, the decaying in fecal coliform bacteria is shown in Fig. 3a and Fig. 3b, by comparing the results of 2200 coliform bacteria at a constant pH of 7.5 with the results of 1300 coliform bacteria. It can be seen that the decay exhibits a decrease in the number of coliform bacteria to its initial number (N/N_o). Based on the decrease in this ratio, it can be indicated that the order of the reaction between NaOCl and water is higher than one, and this is going in agreement with Asami et al.'s [37] opinion. Others like Lister [38] stated that the order of this reaction was near two. Fig. 4a shows that for the 2200 coliform/L, the amount of OCl^- produced by the decomposition of NaOCl in water is consumed less by the coliform bacteria compared to the concentration of 1300 coliform/L. This is demonstrated by that the amount of OCl^- which increased after 60 minutes for the dosage of 20 ppm NOCl in Fig. 4b. This is associated with the complete consumption of the coliform bacteria at 20 ppm shown in Fig. 3b. Without the coliform bacteria present in the water, the hypochlorite ion produced by the decay of NaOCl will continue to accumulate in the water, increasing its concentration.

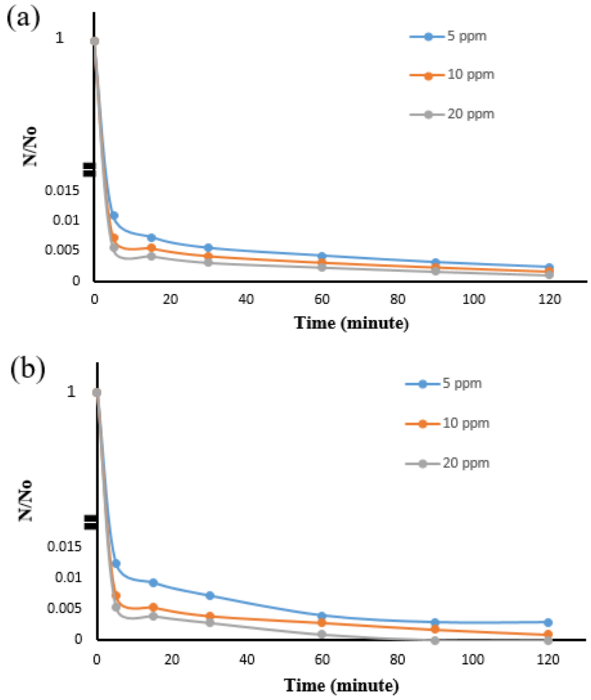

Fig. 3. Concentration of Coliform Bacteria with Reaction Time at pH = 7.5 and Temperature = 29^o C, (a) No = 2200 coliform/L and TPC =98 colonies, (b) No = 1300 coliform/L and TPC = 51 Colonies

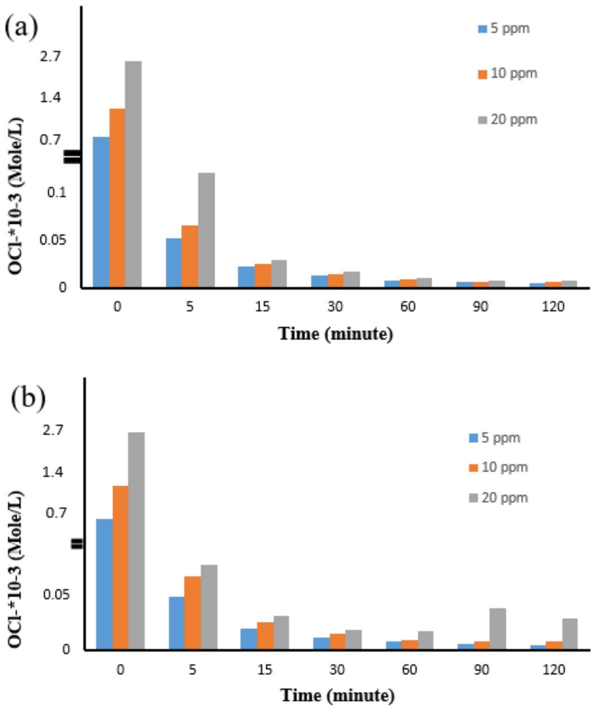

Fig. 4. Concentration of OCl^- with Reaction Time for pH = 7.5, and Temperature = 29^o C, (a) No = 2200 Coliform/L and TPC =98 colonies, (b) No = 1300 coliform/L and TPC = 51 Colonies

3.1.2. Effect of pH Values

Effects of three different pH values (6.5, 7.5, and 8) were examined on the effectiveness of water disinfection by NaOCl, Fig. 5a and Fig. 5b. It is shown that the increase in pH values caused a reduction in the concentration of coliform bacteria. This is in line with the finding of Mcfadden et al. [39]. The pH values were reduced from the ideal pH at 7.5 (Fig. 3b) to 6.5 (Fig. 5a), increasing the amount of bacteria capacity for feeding, which provides a suitable environment for bacteria to multiply, and this can be seen through the increase in the lactic acid and acetic acid that produced as a result of bacteria's feeding. It is shown also that the rise in sodium hypochlorite solution caused drop in coliform bacteria concentration, concentration of hypochlorous acid and hypochlorite ions, which are responsible of destroying germs during the disinfection process which is inconsistent with Cotter et al. [40].

Increasing pH values leads to an increase in OCl- concentration, as shown in Fig. 6. Although the effect of the accumulation of OCl^- is more effective in the results even when the alkaline environment reduces the decaying capacity of NaOCl, this fact causes the impact and momentum into the accumulated amount of OCl^- to be reduced at high pH values, yet not preventing it. This resulted in a higher OCl^- concentration at pH 8 as shown in Fig. 6b comparing with pH 6.5 and 7.5 (Fig. 6a, and Fig. 4b), which sharply reduced the number of coliform bacteria (Fig. 5b). This will reduce the need for HOCl consumption during the pathogens' killing process and caused OCl^- to accumulate in the disinfected water, as shown in the Eq. 4.

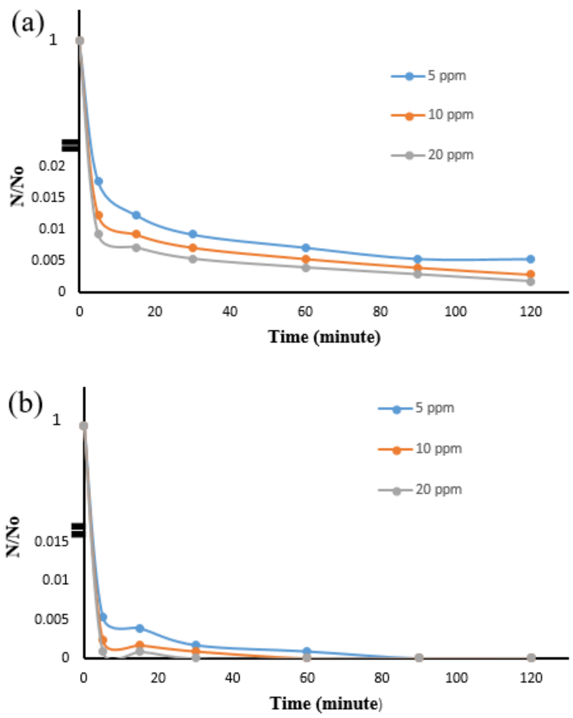

Fig. 5. Concentration of Coliform Bacteria with Reaction Time at No = 1300, TPC = 51 Colonies, and Temperature = 29^o C, (a) pH = 6.5, (b) pH = 8

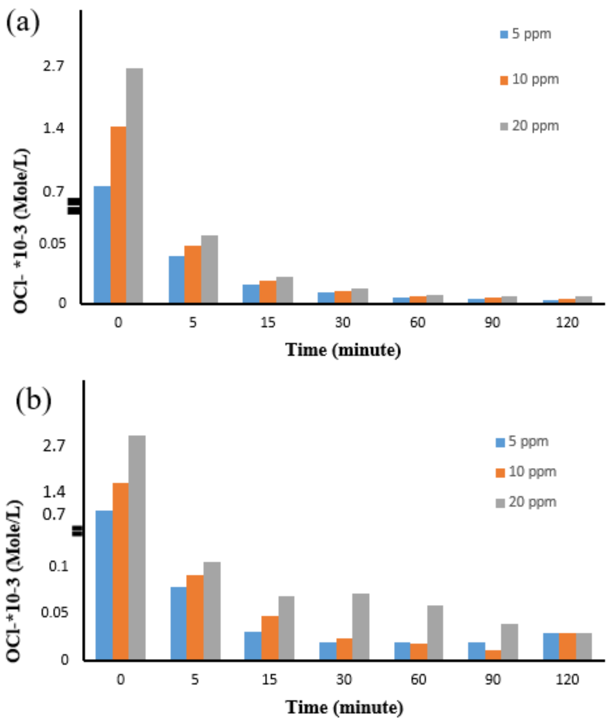

Fig. 6. Concentration of OCl$^-$ with Reaction Time for N_o = 1300 coliform/L, TPC = 51 Colonies, and Temperature = 29^o C, (a) pH = 6.5, (b) pH = 8

3.1.3. Effect of Temperature

Different reaction temperatures; 20, 29, and 37 ^{o}C were tested in this work. It was noticed that when the temperature of reaction is increased, coliform bacteria amount is reduced, this is due to the increasing in the rate of reaction [42], Fig. 7a, Fig. 3b and Fig. 7b. The NaOCl disinfection reaction's second order nature can be demonstrated by the opposite relationship between temperature and the availability of coliform bacteria's residuals. Because the rate of reaction has increased due to the rise in reaction temperature, as shown in Fig. 8a and Fig. 8b, the amount of OCl$^-$ at 5 minutes of contact with the NaOCl in the reactor at 20° C is less than the amount at 29° C. This agrees with Adams' finding [26], who had noted that increasing the reaction temperature could actually accelerate sodium hypochlorite's conversion to hypochlorous acid and hypochlorite ions.

3.2. Reaction Kinetics

Kinetics of NaOCl disinfection was studied in this work. Different kinetic models have been tested. Harriet Chick model was tried to fit the reaction data for the pH = 7.5 and 29^o C reaction with the 1300 initial coliform concentration in one litter of treated water [43]. The model was tested for first and second reaction order for the same NaOCl disinfection reaction data as shown in Fig. 9a and Fig. 9b.

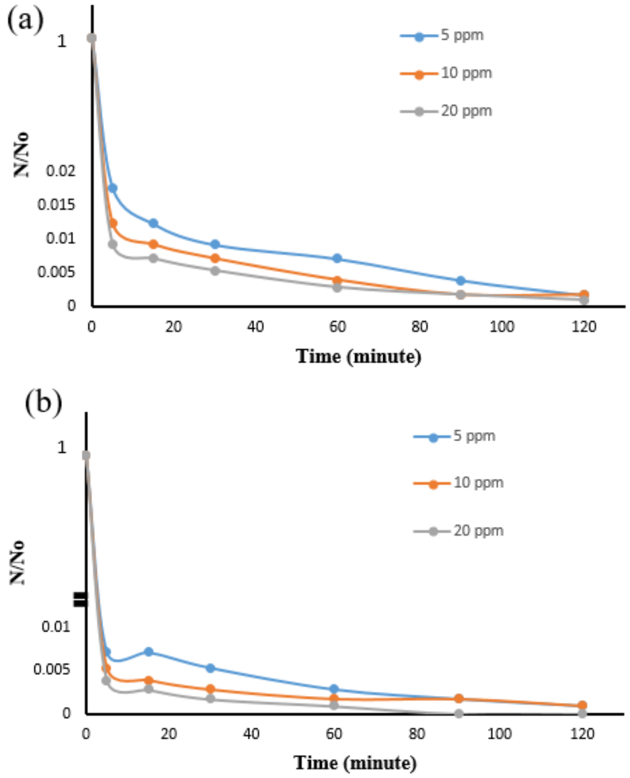

Fig. 7. Concentration of Coliform Bacteria with Reaction Time at No = 1300, TPC = 51 Colonies, and pH= 7.5, (a) Temperature = 20^o C, (b) Temperature = 37^o C

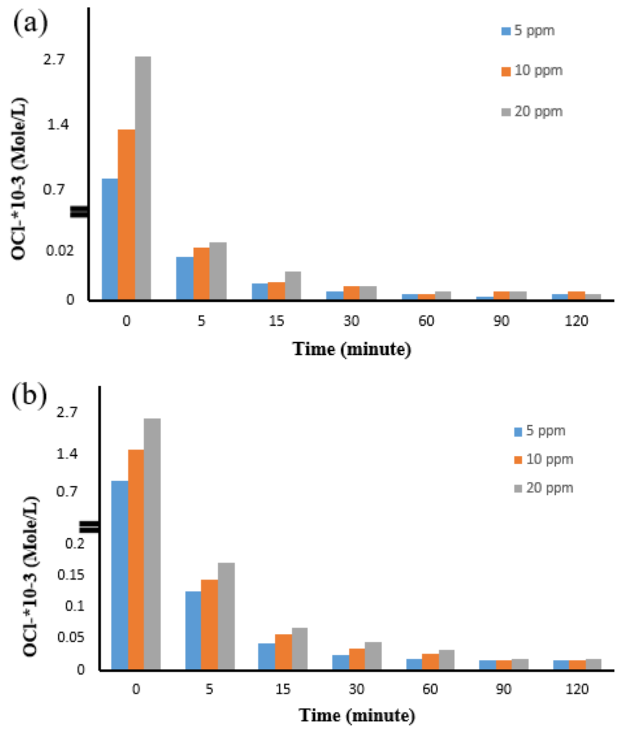

Fig. 8. Concentration of OCl$^-$ with Reaction Time for No = 1300 coliform/L, TPC = 51 Colonies, and pH= 7.5, (a) Temperature = 20^o C, (b) Temperature = 37^o C

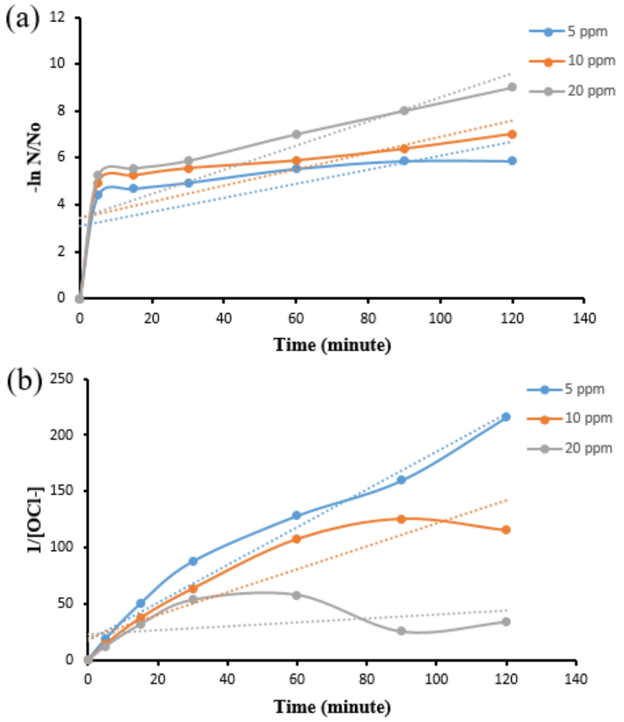

Fig. 9. Harriet Chick for the Ratio of Remaining Coliform Bacteria after Different Reaction Time, (a) First Order, (b) Second Order

The 2nd order equation is:

$$\frac{1}{[OCl]} - \frac{1}{[OCl]0} = k\,x\,t \qquad (6)$$

It is clear that the data of the NaOCl disinfection reaction cannot be fit by the first order and second order reaction of the Harriet Chick model. Wu et al. [44] showed the same conclusion in their study. The general power low (Eq. 7) has been tested in this work by using Visual Basic computer program with 0.1% error. The fluctuating in degree and rate of reaction led to indicate this model as an unsuitable for the NaOCl disinfection reaction [43].

$$-r_N = -dN/dt = k\,N^n \qquad (7)$$

At 1978 Selleck described the effect of Chlorine on coliform bacteria in wastewater by design a model (Eq. 8) that counting on the bacteria and hypochlorite ion. This makes Selleck model suitable to be applied to the data of our work.

$$\log\left(\frac{N}{N0}\right) = -n\log\left(1 + \frac{[OCl]\,x\,t}{K}\right) \qquad (8)$$

Selleck model succeeded to calculate the reaction kinetics for water disinfection by NaOCl by using Visual Basic with an 9% error, Selleck model estimated that the degree of reaction for water disinfection by NaOCl is second order (Fig. 10). The rate of reactions obtained are listed in Table 1.

Table 1. The Rate of Reactions

Temperature (°C)	Rate of Reaction (L *(mole min)$^{-1}$)
20	1.3791 x 10^{-5}
29	3.0806 x 10^{-5}
37	5.738 x 10^{-5}

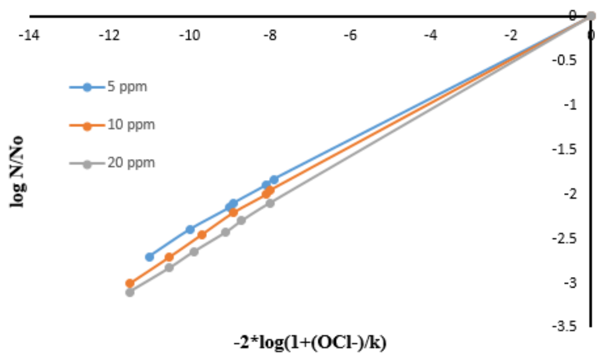

Fig. 10. Selleck Model Second Order for the Ratio of Remaining Coliform Bacteria after Different Reaction Time

4- Conclusion

The present work demonstrated that NaOCl is very effective as a disinfectant in the drinking water field, in which five minutes was sufficient to kill the majority of coliform bacteria. The study also proved that the pH value of the reaction has a great effect on suppressing the pathogens growing and increase the killing of Coliform Bacteria. Using pH value of 8 raised the disinfection process activity by killing most of the Coliform Bacteria with less amount of NaOCl and reduced the DBPs produced as side reactions of the disinfection process by chlorine. Temperature also has an important effect on the rate of reaction in addition to the coliform bacteria concentration. The rate of reaction increases with the increase in the initial bacteria concentration and temperature. The kinetics of the disinfection reaction was well represented by Selleck model in which the order of the disinfection reaction was found to be two.

Acknowledgment

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تأثير متغيرات التفاعل على كفاءة عملية تعقيم المياه بواسطة هايبوكلورايت الصوديوم باستخدام المياه المعالجة في مشروع الوثبه

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الخلاصة

الهدف من هذا التحقيق هو دراسة تأثير معاملات التفاعل المختلفة على مياه الصرف الصحي المأخوذة من محطة الوثبة لمعالجة المياه على نهر دجلة في جنوب بغداد، العراق بمحلول هيبوكلوريت الصوديوم، مثل: جرعة هيبوكلوريت الصوديوم، وقت التفاعل، التركيز الاولي للبكتيريا القولونية، ودرجة الحرارة ودرجة الحموضة. تم استخدام المفاعل الدفعي في عملية تعقيم ١ لتر من المياه بتراكيز مختلفه من الهايبوكلورايت الصوديوم. تم فحص وقياس ايونات الهايبوكلورايت في الماء المعقم باستخدام طريقه التسحيح الايودي في اوقات تفاعل مختلفة، في حين تم استخدام طريقة الاعداد الاكثر احتماليه لقياس تراكيز البكتريا القولونية. استخدمت طريقة صحون الاختبار لقياس العدد الاجمالي للمستعمرات للانواع المختلفة من البكتريا في المياه المزمع تعقيمها. أظهرت متغيرات التفاعل المختلفة التي تم فحصها في هذا العمل أن الزيادة في درجة الحرارة ودرجة الحموضة وزمن التفاعل تسببت في تقليل تركيز البكتيريا القولونية، مما أدى بدوره إلى زيادة تراكميه في تركيز ايون الهايبوكلورايت الناتج من التفاعل. في هذا العمل قد ضهر انه درجة الحراره ودرجة الحموضه المثلى للعمليه التفاعليه هي ٢٩ درجه سيليزيه و ٨ على التوالي. اظهرت دراسة ميكانيكية التفاعل في هذا العمل انه نموذج سيليك هو النموذج المثالي للتعبير عن درجة التفاعل وثابت سرعته، حيث قد ثبت ان تفاعل هايبوكلورايت الصوديوم مع الماء هو من الدرجه الثانية، بقيم ثوابت سرعة تتراوح بين 1.3791×10^{-5} و3.0806×10^{-5} و 5.738×10^{-5} لتر/(مول*دقيقة) عند الدرجات الحرارية ٢٠، ٢٩ و ٣٧ درجة سيليزية.

الكلمات الدالة: تعقيم المياة، هايبوكلورايت الصوديوم، أختبار ألاعداد ألاكثر احتمالية، نموذج سيليك.