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Kinetic of Disinfection reaction by Sodium Hypochlorite Solution

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Abstract

The present studier aims to study the kinetic of reaction at different experimental conditions depending on coliform bacteria concentration and hypochlorite ion. The effects that had been investigated were different of sodium hypochlorite doses, contact time, pH and temperature (20, 29, 37) ^{o} C. The water samples were taken from Al-Wathba water treatment plant in Risafa side of Tigris River in Baghdad. The biological tests included the most probable number (M.P.N) for indicating the concentration of coliform bacteria with different contact times and the total plate count (T.P.C) for indicating the amount of colonies for general bacteria. The iodimetry method (chemical test) was used for indicating the concentration of hypochlorite ion with different contact times. Different models were examined to fit the experimental data including the kinetics power law (first and second order) and Selleck model. It was found that the Selleck model fitted well the experimental data in which degree of Selleck model was equal to two and the rate constants was 1.3791 x 10^{-5} L / (mole min) at 20^{o} C, 3.0806 x 10^{-5} L / (mole min) at 29^{o}C, and 5.738 x 10^{-5} L / (mole min) at 37^{o} C.

Keywords: Selleck model, coliform bacteria, disinfection, sodium hypochlorite, and chlorine

1- Introduction

Disinfection process is very important for killing the microorganisms that remain in the water after treatment. There are different types of disinfectant reagents used to disinfect drinking water such as, chlorine (Cl_2), chloride dioxide (ClO_2), ozone (O_3), chloramines (NH_2Cl), sodium hypochlorite (NaOCl), calcium hypochlorite ($Ca(OCl)_2$) and lithium hypochlorite (LiOCl) [1][1]. Typically, disinfection is applied as a final stage in the water treatment. The determined disinfectant amount added firstly should achieve its effect directly leaving sufficient amount of residuals for the next disinfection through the distribution system to ensure microbial regrowth [2].

Boccelli et al. [3] reported that these effects of disinfectant are quite beneficial, although Kopfler et al. [4] mentioned that the disinfection by-products (DBPs) which result from the side reactions between the disinfectant and natural organic matters (NOMs) could be carcinogenic. However Bielmeier et al. [5] during their genetic work on animals, proved development of some cancers of liver, stomach and renal failure. Chlorine is one of the most widely distributed elements on earth, it is not found in a free state in nature. Instead, it exists mostly in combined-ion with sodium, potassium, calcium and magnesium. Elemental chlorine is a heavy gas of greenish-yellow color, with a characteristic irritating and pen-etrating odor. Chlorine must have been known to all chemists for many centuries, but only in 1809, Sir Humphrey Davy concluded that chlorine gas was an element and because of its characteristic yellow-green color, propose the name. Chlorine gas (Cl_2) is used for drinking water disinfection due to its high oxidation potential, low cost, and excellent disinfection effectiveness, but the disadvantages of using free chlorine is a high and non selective reactivity leading to produce undesirable products. Free chlorine can rapidly react with NOMs in water by oxidation, addition and substitution reactions to form DBPs [6].

When chlorine is added to the water, it undergoes the following reactions [1]:

$$Cl_2 + H_2O \rightarrow HOCl + HCl \qquad (1)$$

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

The dissociation of Cl_2 depends on the pH value and the equilibrium between HOCl and OCl^- is maintained even through HOCl is constantly consumed through its germicidal function. It appears that the disinfecting efficiency of chlorine decreases with an increasing in pH and vice vers, which is parallel to the concentration of undissociated hypochlorous acid [1].

Disinfection by sodium hypochlorite (NaOCl) is the oldest and most widely used of active chlorine compounds in chemical disinfection due to its powerful germicides, free of poisonous residuals, easy to handle, and most economical to use. Sodium hypochlorite solutions range in concentration from 1% to 15%, with 1% to 5% available chlorine products employed for domestic use [1]. Sodium hypochlorite solution is a clear liquid which can be fed through solution feed equipment without fear of clogging. It is normally diluted to 1% solution before application; it tends to lose strength if exposed to sunlight for long time before use [7].

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When NaOCl hydrolyzes in pure water solution, the reactions in equations (3) (4) occur indicating that the ratio of HOCl / OCl$^-$ depends on the pH of the solutions, with low pH favoring the formation of HOCl and vice versa, [8]. The use of sodium hypochlorite solutions for disinfection was also reported to introduce chlorate ion into drinking water. Under some conditions, the strength of hypochlorite can significantly decline in just a few days. In fact, stability is one of the major issues that must be addressed in operating with sodium hypochlorite.

Bolyard et al. [9] found that chlorate ions can be formed during the manufacture and storage of hypochlorite solutions. Hypochlorite ions are known to disproportionate in basic solution to produce ClO_3^- as it shown in equation (5): [10]

$$\mathrm{NaOCl} + \mathrm{H_2O} \rightarrow \mathrm{NaOH} + \mathrm{HOCl} \qquad (3)$$

$$\mathrm{HOCl} \leftrightarrow \mathrm{H^+} + \mathrm{OCl^-} \qquad (4)$$

$$3\,\mathrm{ClO^-} \rightarrow 2\,\mathrm{Cl^-} + \mathrm{ClO3^=} \qquad (5)$$

Coliform bacteria can transferred to human by drinking water or food that had been contaminated with them. Coliform bacteria are used as an indicator for contamination of drinking water because coliforms may be associated with the sources of pathogens contamination and the analysis of drinking water for coliform are relatively simple, economical, and efficient [11]. The exceptions of using coliform as an indicator is when there is any availability of diseases-production organisms, especially protozoa so The suible treatment for any can kill all coliform bacteria in the water [12].

Coliform are shown to produce amount of D-lactate, ethanol, and acetic acid plus traces of L-lactate from glucose [13].

This work was aimed to study the kinetics of the disinfection reaction and finding the suitable kinetic model that fit the experimental data.

2- Experimental Work

The experimental work includes disinfection process for treated water using sodium hypochlorite (NaOCl) solution. Different experimental conditions were investigated as listed below:

1- pH values of (6.5, 7.4, 8),
2- Doses of sodium hypochlorite (NaOCl) solution (5, 10, 20) ppm,
3- Contact times (0, 5, 15, 30, 60, 90, 120) min., and
4- Temperature (20, 29, 37)° C

Batch reactor with magnetic stirrer was used for disinfection process in which one liter of a glass beaker was used for making the reactor. Different doses of 1% NaOCl solution were added to one liter of treated water. Samples were taken from the disinfected water for each contact times for the biological and chemical tests.

The biological tests included the most probable number (M.P.N) for indicating the concentration of coliform bacteria with different contact time and the total plate count (T.P.C) for indicating the amount of colonies for general bacteria at time = 0. The iodimetry method (chemical test) was used for indicating the concentration of hypochlorite ion with different contact times.

M.P.N test at time = 0 had been performed using three dilutions (0.1, 0.01, 0.001), for each dilution one set of five tubes of single L.T.B media had been used, 1ml of each dilution had been injected in each tube of its tubes set. For other times of contact, 20ml of the sample had been injected in each tube of the five triple L.T.B media tubes. For the iodimetry test, 25ml of water sample had been used by adding KI to get light yellow color titration was done by using starch until the color change to blue then titrated by sodium thiosilfet until the color became invisible [14].

2.1. Sample Collection

The water samples were taken from Al-Wathba water treatment plant in Risafa side of Tigires River, they were from the second sedimentation tank of Al-Kefah line project so the samples were with no chlorine addition and with a turbidity range NTU (4.5-18), pH values between (7.36-7.66), electrical conductivity EC (684-939 µs/cm) and for temperature the range is (14.5-18°C) . The samples were kept in ice at temp.= 0, to prevent bacteria from division. Samples had been transformed during 24 hour to the laboratory.

2.2. Incubation Procedure

The initial M.P.N test tubes at time = 0 and the Petri dish of T.P.C test were kept in the incubator (Memmert) at 37^{0}C for 48 hour, while the M.P.N tubes for other time contact times 5, 15, 30, 60, 90, and 120 min were kept in the same incubator at 37^{0}C for 24 hs [14].

3- Results and Discussion

3.1. Results for M.P.N Tests - Effects of Ph Values

Three pH values of 6.5, 7.4, and 8 were used to investigate the effect of solution acidity on the disinfection process by hypochlorite solution. Fig. 1, Fig. 2 and Fig. 3 show the decay in fecal coliform bacteria for higher values of pH, i. e, 7.4 and 8. It can be seen that the decay in the concentration is more rapid for larger values of pH. This was interpreted by Styler and Rumsey [13]. They showed that when the pH value of the water increased from 6.5 which is the ideal value, that will lead to increasing in amount of food intake by the coliform bacteria from the media and that casing increases in producing lactic acid and acetic acid as food west product for the glucose sugar that been consumed by the bacteria as food from the media, the increasing in the amount of acetic acid and lactic acid will lead to reduce in the value of pH of the media. On the other hand, these results revealed a decrease in the (N/N_o) ratio with the increase in the dose of NaOCl solution due to increase in the HOCl concentration and OCl^- concentration, since the affinity of the pathogens killing were also increased, similer effects were reported by Rajput and Polprasert [8].

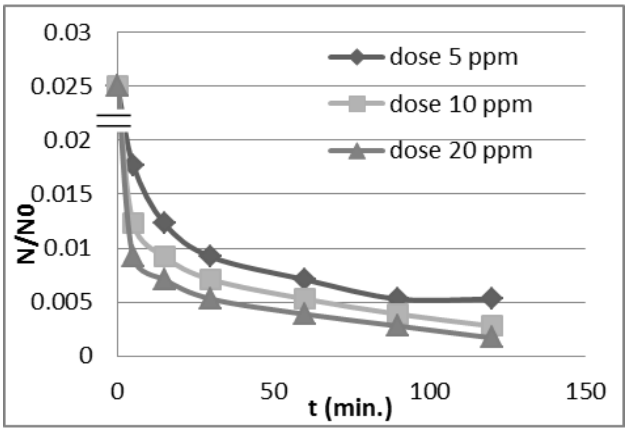

Fig. 1. Decay of fecal coliform concentration with time N_o = 1300 coliform/l, TPC = 51 Colony, pH = 6.5 and temp.= 29° C

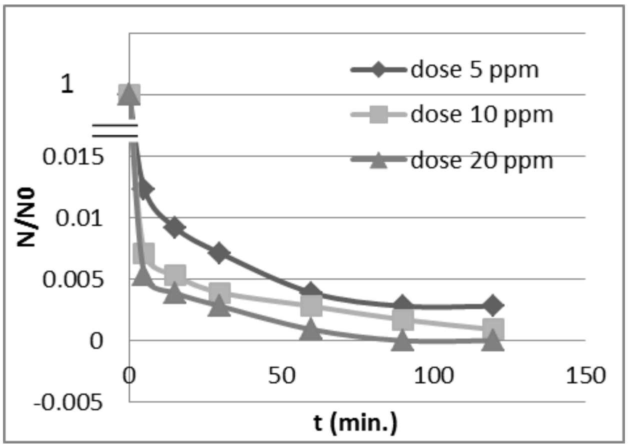

Fig. 2. Decay of fecal coliform concentration with time N_o = 1300 coliform/l, TPC = 51 Colony, pH = 7.4 and temp.= 29° C

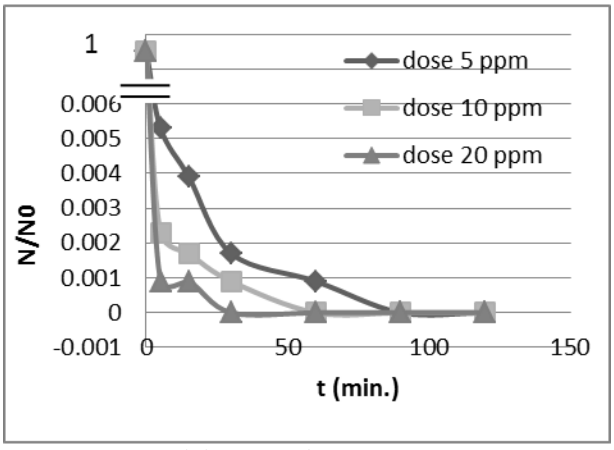

Fig. 3. Decay of fecal coliform concentration with time N_o = 1300 coliform/l, TPC = 51 Colony, pH = 8 and temp.= 29° C

3.2. Effect of Temperature

Disinfection experiments were carried out at different temperatures which were 37, 20, and 29° C to examine the effect of temperature on the rate of disinfection reaction.

From Fig. 4, Fig. 5 and the previous Fig. 2 it can be noticed that the ratio of fecal coliform bacteria concentration to its initial concentration (N/N_0) was lowered when the temperature was increased due to increasing the rate of reaction [15].

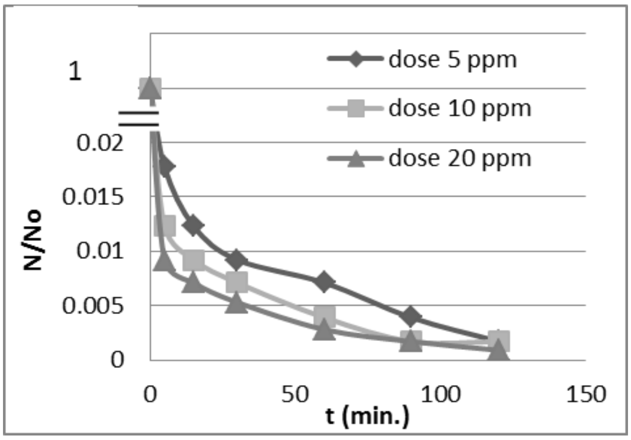

Fig. 4. Decay of fecal coliform concentration with time N_o = 1300 coliform/l, TPC = 51 Colony, pH = 7.4 and temp.= 20° C

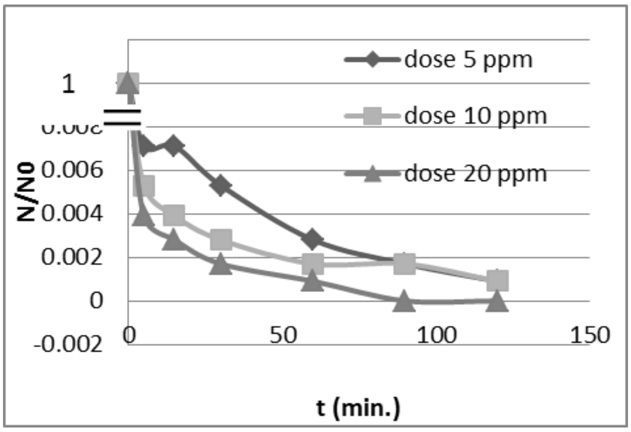

Fig. 5. Decay of fecal coliform concentration with time N_o = 1300 coliform/l, TPC = 51 Colony, pH = 7.4 and temp.= 37° C

3.3. Results for Iodimetry Tests - Effects of Ph Values

Increasing pH values from 6.5 (Table 1) to 7.4 (Table 2) and to 8 (Table 3) leads to sharp decrees in the number of coliform bacteria, reducing the consume of HOCl in which it needed for the pathogens killing process and that lead to increasing the amount of accumulated hypochlorite ion (OCl^-) in water. hypochlorite ion (OCl^-) is producing from the decay of HOCl as it shown in equation (4).

Table 1. Hypochlorite ion concentration for different contact times, N_o = 1300 coliform/l, TPC = 51 Colony, pH = 6.5 and temp.= 29° C

Time min.	$OCl^{-}*10^{-3}$ mole/L dose 5ppm	$OCl^{-}*10^{-3}$ mole/L dose 10ppm	$OCl^{-}*10^{-3}$ mole/L dose 20ppm
0	0.67	1.35	2.7027
5	0.0402	0.0494	0.0579
15	0.0165	0.0193	0.0224
30	0.0097	0.0112	0.0131
60	0.0056	0.0065	0.0077
90	0.0044	0.0051	0.0062
120	0.0033	0.0046	0.0059

Table 2. Hypochlorite ion conc. with different contact time, N_o = 1300 coliform/l, TPC = 51 Colony, pH = 7.4 and temp.= 29° C

Time min.	$OCl^{-}*10^{-3}$ mole/L dose 5ppm	$OCl^{-}*10^{-3}$ mole/L dose 10ppm	$OCl^{-}*10^{-3}$ mole/L dose 20ppm
0	0.67	1.35	2.7027
5	0.0494	0.0671	0.0784
15	0.0193	0.0261	0.0311
30	0.0112	0.0155	0.0185
60	0.0077	0.0092	0.0171
90	0.0062	0.0079	0.0167
120	0.0046	0.0073	0.0161

Table 3. Hypochlorite ion conc. with different contact time, N_o = 1300 coliform/l, TPC = 51 Colony, pH = 8 and temp.= 29°C

Time min.	$OCl^{-}*10^{-3}$ mole/L dose 5ppm	$OCl^{-}*10^{-3}$ mole/L dose 10ppm	$OCl^{-}*10^{-3}$ mole/L dose 20ppm
0	0.6711	1.35	2.7027
5	0.0784	0.1109	0.2057
15	0.0307	0.0479	0.0686
30	0.0185	0.0239	0.0611
60	0.0184	0.0171	0.058
90	0.0183	0.0114	0.0387
120	0.0180	0.0113	0.0289

3.4. Effect of Temperature

It can be noticed from (Table 4) and (Table 5) that the concentration of OCl^{-} after 5 minutes of reaction at a temperature of 20° C (0.018 x 10^{-3} mole/ L) is much lower than that at 37° C at the same operating conditions (0.0494x10^{-3} mole/ L).

This can be explained as increasing the reaction temperature will increase the rate of reaction, in which Montgomery [16] showed that the decaying process of the NaOCl solution to HOCl and OCl^{-} is increased with the increasing in the temperature.

Table 4. Hypochlorite ion concentration for different contact times, N_o = 1300 coliform/l, TPC = 51 Colony, pH = 7.4 and temp. = 20° C

Time min.	$OCl^{-}*10^{-3}$ mole/L dose 5ppm	$OCl^{-}*10^{-3}$ mole/L dose 10ppm	$OCl^{-}*10^{-3}$ mole/L dose 20ppm
0	0.6711	1.3514	2.7027
5	0.018	0.022	0.024
15	0.007	0.008	0.012
30	0.004	0.006	0.006
60	0.003	0.003	0.004
90	0.002	0.0028	0.0038
120	0.0019	0.0023	0.003

Table 5. Hypochlorite ion concentration for different contact times, N_o = 1300 coliform/l, TPC = 51 Colony, pH = 7.4 and temp. = 37° C

Time min.	$OCl^{-}*10^{-3}$ mole/L dose 5ppm	$OCl^{-}*10^{-3}$ mole/L dose 10ppm	$OCl^{-}*10^{-3}$ mole/L dose 20ppm
0	0.6711	1.3514	2.7027
5	0.125	0.144	0.171
15	0.042	0.057	0.068
30	0.024	0.034	0.045
60	0.017	0.026	0.032
90	0.0015	0.015	0.0173
120	0.0014	0.014	0.017

3.5. Kinetics of Disinfection Reaction

In the present work, experimental data were used to demonstrate the kinetics of the disinfection reaction when using sodium hypochlorite solution as a disinfectant.

Fig. 6 shows the relationship between the fecal coliform ratio (N/N_o) and contact times after disinfection by NaOCl for 1300 fecal coliform bacteria, T.P.C= 51 of bacteria colonies respectively, for first order of Harriet Chick model [16].

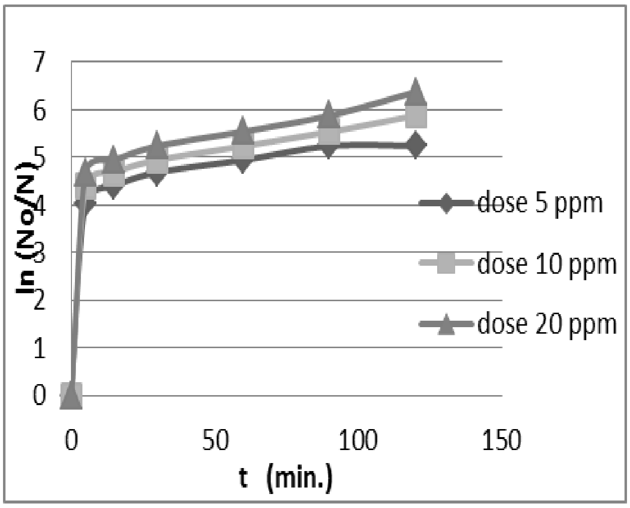

Fig. 6. First order model for coliform concentration ratio to its initial concentration vs. contact times N_o = 1300 coliform/l, TPC = 51 Colony, pH = 6.5 and temperature= 29° C

Harriet Chick first order model failed to unfit straight line. Another trial was made to fit the experimental data to the second order reaction model. Fig. 7 shows the response to the second order model as it is shown in equation 6 using integral method [15], it shows that the second order power law model was unable to fit the experimental data of the reaction of sodium hypochlorite with water and this is in agreement with the results of Gordon et al. [17].

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

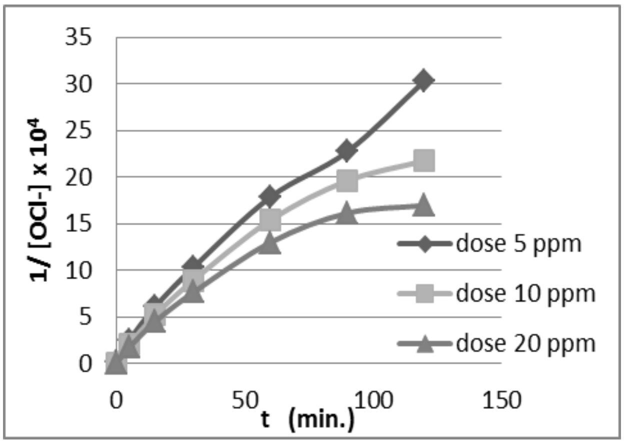

Fig. 7. Second order model for hypochlorite ion concentration vs. contact times N_o = 1300 coliform/l, TPC = 51 Colony, pH = 6.5 and temperature= 29° C

The general power low formula which is shown in equation 7 had been tested using 0.1% error percent Microsoft Visual Basic program to fit the experimental data for coliform bacteria concentration decay with time by integral method. The coliform bacteria concentration and contact times were applied in the program. The formula had failed to fit well the experimental data due to the variation in values of rate constant (k) and reaction's order (n) [15].

$$-rN = -dN/dt = k\,Nn \qquad (7)$$

The failure of using first and second order models and the formula $r_N = -k\,N^n$ led to try the "Selleck model" which was used earlier by Selleck (1978) to describe chlorine inactivation of coliform bacteria in wastewater effluent. Although the Selleck model was initially derived for chlorine inactivation of bacteria in wastewater, it is an empirical model and therefore applicable to any chemical disinfectant, organism and test water [18]. Selleck model can be expressed as

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

The calculations were done by using a less or equal 9% error percent of Microsoft Visual Basic Program to fit the experimental data of the present work for OCl^- and fecal coliform bacteria concentrations.

The average value of n in the model was found to be equal 2 as it is shown in Fig. 8, Fig. 9, and Fig. 10.

Table 6. The values of k for different temperature

Temperature in °C	K in L / (mole . min)
20	1.3791×10^{-5}
29	3.0806×10^{-5}
37	5.738×10^{-5}

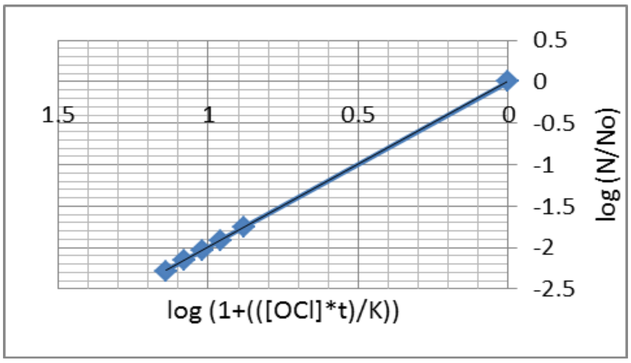

Fig. 8. Selleck model for hypochlorite ion concentration vs. fecal coliform concentration N_o = 1300 coliform/l, TPC = 51 Colony, pH = 6.5 and K=3.0806×10^{-5} L / (mole min)

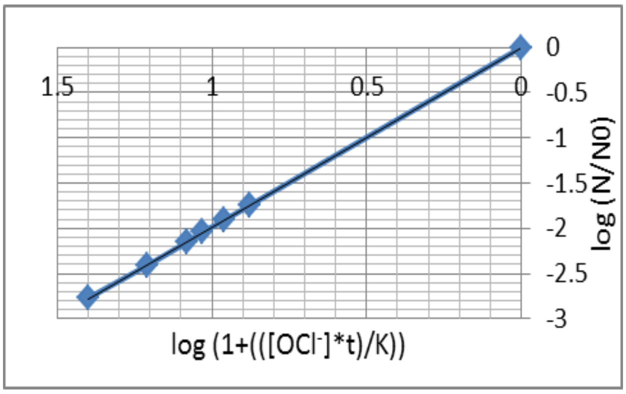

Fig. 9. Selleck model for hypochlorite ion concentration vs. fecal coliform concentration N_o = 1300 coliform/l, TPC = 51 Colony, pH = 7.4 and K=1.379×10^{-5} L / (mole min

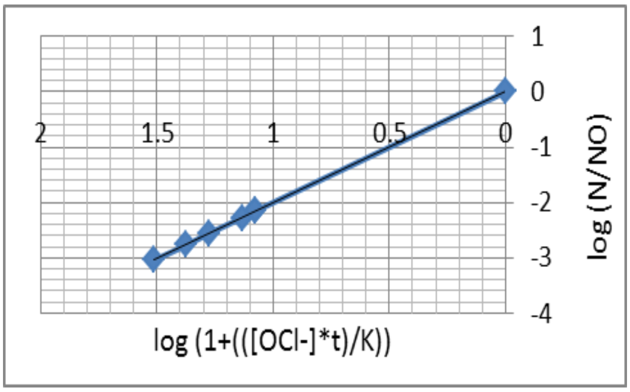

Fig. 10. Selleck model for hypochlorite ion concentration vs. fecal coliform concentration N_o = 1300 coliform/l, TPC = 51 Colony, pH = 7.4 and K=5.738×10^{-5} L/ (mole)

4- Conclusions

The following conclusions can be drawn from the present work

1- The reaction between sodium hypochlorite solution (NaOCl) and water is fast in which Coliform bacteria concentration is reduced sharply in the first five minutes.
2- When pH value rises above 6.5, the coliform bacteria concentration is reduced. The best optimum pH value of the disinfection reaction is 8 according to the range used in this study.
3- Rate of disinfection increases with the increasing in the reaction temperature up to 37° C.
4- The power low kinetic model (first and second order) fails to fit the experimental data, while Selleck kinetic model fit well the experimental data with a value of reaction order equal 2

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