



Evaluation of Chemical Compounds and their Relationship to the Breaking Point after adding Chlorine to Water

Estabraq Ali Hameed

Northern Technical University, Health & Medical Technical Collage- Kirkuk

ARTICLE INFO.

Article history:

-Received: 8 / 8 / 2022

-Accepted: 16 / 10 / 2022

-Available online: 25 / 12 / 2022

Keywords: Activated Carbon, Acetic acid, Ammonia, Organic Compound and sterilizing water .

Corresponding Author:

Name: Estabraq Ali Hameed

E-mail: estabraq_ali@ntu.edu.iq

Tel:

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ABSTRACT

Evaluation of the chemical compounds formed during the process of sterilizing water with chlorine is a very important point. During sterilization the water goes through three stages each stage resulting different chemical compounds. In the first stage, chlorine reacts with iron, magnesium and nitrates. In the second stage it reacts with ammonia and in the third stage it reacts with the organic compounds in the water. Chlorine in these three stages is called combined chlorine. Then it reaches the breaking point, after this point the water must be free from side chemical compounds, and chlorine after this point is called the residual free Chlorine. Drinking water samples were taken from 3 city in Kirkuk governorate, and the concentrations of magnesium, nitrate, sulfate, acetic acid derivatives, as well as the halomethane group in addition to some physical determinants were evaluated.

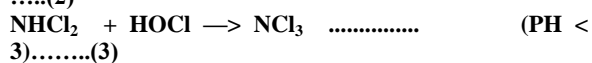
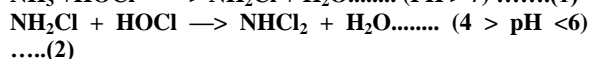
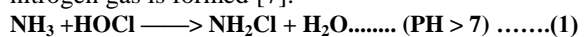
There were deviations in some chemical concentrations when comparing the results with the last Iraqi specification NO. 417. The deviations that appeared in some concentrations were treated by using two chemical methods, the first using activated carbon and the second using aluminum chloride polymer. The importance of the study is to ensure the effectiveness of chlorine by eliminating chemical compounds dangerous in the water.

1. Introduction

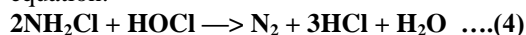
Disinfection of drinking water with chlorine provides water that is free from pathogens, for example bacteria, viruses and other germs. There are many diseases that can be transmitted with water, such as typhoid, cholera, dysentery as well as schistosomiasis [1] The health benefit of sterilization is offset by the appearance of dangerous side chemical compounds as an accidental product of chlorine sterilization [2]. The process of adding chlorine to water divided into stages, (the first acts as an oxidizing agent), where oxidizes all of (iron, manganese, sulfate, as well as nitrates) and others and in this stage the added chlorine is broken down by reducing agents . Many studies deal with creating a second-order parallel reaction model that contains fast and slow reactions to describe the kinetics of chlorine decomposition under the conditions of distribution [3]. The Nanotechnology Technology is one of the methods recently used to get rid of heavy elements such as

iron and manganese and other metals in the water [4]. Recent studies express if the water contains iron, manganese, ammonia and nitrate or any organic matter will react with the added chlorine and give a deviation in the curve that is proportional to those reactants and the degree of their cocentration in water. In the second stage and when Continuously adding chlorine, its reaction begins with ammonia and organic matter to form Chloramines or Halomethane Compounds, as well as Haloacides and Chlorine Compounds, and in this stage the chlorine called (combined residual chlorine) [5]. Several studies have concluded that the chloramine formed at this stage is possible that it acts as a sterile agent, but it is less effective than free chlorine [6]. In stage three Continuing to add chlorine to water leads to a decrease in residual chlorine due to the start of the oxidation process of monochloroamine compounds to dichloroamines and trichloroamines, and the process

continues until the oxidation is completed and nitrogen gas is formed [7].



the appearance of di- and trichloramine, with a longer contact period required for the reaction to take place [8]. If the amount of ammonia in the water is sufficient, the reaction will be constant, but if the amount of chlorine added is large, then chloramine will break down to nitrogen [9], as in the following equation:



After that reach the point of refraction, which is the lowest point that chlorine reaches, and then the residual free chlorine begins to appear, which increases with the increase in the added dose of Chlorine . Free residual chlorine depends on temperature, contact time, chlorine dose, and pH, amount of substances, and impurities that may be present in the water [10]. Forms of free residual chlorine are hypochlorous acid and the hypochlorite ion OCl^- & HOCl . HOCl is more effective in the sterilization process than the hypochlorite ion OCl^- . If the medium is more acidic. The HOCl acid increases and if the medium is closer to the base, the hypochlorous ions increase. The hypochlorous ion OCl^- carries a negative charge and most germs in the water carry a negative charge on its surface, so the hypochlorite ion is repelled by the surface of germs, while hypochlorous acid can easily penetrate killing germs and other microscopic organisms [11]

Nitrification is a major concern as chloramine is used as a secondary sterilizer in the chlorinated water distribution system, and studies have shown the formation of odors from ammonia and amino acids in the presence of chlorine during water treatment . Discussing the breakpoint or breaking point where the ammonia was treated and examining the cause and types of the resulting odor, as the smell changes according to the acidic function . A study revealed the presence of a strong odor that differs from the smell of the remaining free chlorine, and this happened after the chlorination of ammonia in the source water [12]. Where the odor production was affected by the pH rate and the Chlorine dose added to the water, where the substance causing extreme relief was determined by using a chromatography mass spectrometer. Gaseous, as it has been shown that trichloramine or dichloramine is the main cause of odor [13]. The smell varies according to the type of amino acid, and a recent study showed the possibility of aliphatic and aromatic stamides found in natural water or used as chemical aids in water treatment [14]. Currently, anion exchange resin absorption technique is used, followed by electrolysis, as a new sterilization method to control secondary compounds resulting from sterilization of drinking water [15]. The most important compounds associated with the

chlorination process are the tri-halomethane group that causes cancerous diseases and many pathological disorders, as well as halo-acid halogenated and the formation of chloramine compounds, after oxidation of all of (iron, manganese, sulfate and nitrite) present in the water by adding chlorine as a sterilizer to the water and after it The reaction was done with ammonia and the existing organic compounds. We reach the point of refraction, which is the lowest point that chlorine reaches, and then the residual free chlorine begins to appear, which increases with the increase in the added dose of chlorine [16]. Free residual chlorine depends on temperature, contact time, chlorine dose, and pH, amount of substances, and impurities that may be present in the water [17]. Forms of free residual chlorine are hypochlorous acid and the hypochlorite ion OCl^- & HOCl . HOCl is more effective in the sterilization process than the hypochlorite ion OCl^- . If the medium is more acidic, the HOCl acid increases, and if the medium is closer to the base the hypochlorous ions increase. The hypochlorous ion OCl^- carries a negative charge and most germs in the water carry a negative charge on its surface, so the hypochlorite ion is repelled by the surface of germs, while hypochlorous acid can easily penetrate killing germs and other microscopic organisms [18]. Activated carbon is one of the methods of treatment Increases in measured values that have proven effective in removing organic ingredients and sterilizer residues in water improving water taste and preserving osmotic films also exchangers Ionic [19]. This method is based on the adsorption process and the effectiveness of this method in removing the total organic matter (TOC) reaches 80%. Alum and ferric chloride are used in the enhanced coagulation method. This method has demonstrated its ability to remove solids and many elements. Recently, poly Aluminium Chloride (PACL) has been used which has proven to be very effective in this field [20].

2-Materials and working methods

2.1 Measurement of the acidic function (Ph) and the free residual Chlorine.

The pH function was measured for 6 drinking water models and for the months of the following year (February, March, May, June, July and August) for Al-Wasiti city in kirkuk by using a pH meter and measuring the remaining free Chlorine by using a Spectrophotometer (721). These tests were carried out in Al-Karunji laboratories for the production of water and juices .The values are shown in Table No. 1.

2.2 Measuring the Electrical Conductivity, Turbidity, Total dissolved salts, Magnesium, Sulfates, Nitrates and Nitrites.

Three samples of treated water were taken Al-Wasiti, Ninety and AL-Tatran and raw water samples were taken from the Lower Zab River. Magnesium, sulfate, nitrates and nitrites were measured using a Spectrophotometer. The results are shown in Table

(2) and compared with Iraqi Standard No. 417 of 2001. Samples of raw water took from the Lower Zab River and (3) models from the city (Al-Tayaran, Ninety and Al-Wasiti) and measured their different characteristics. The results are shown in Table (2), and the results are compared with the Iraqi standard. The free residual chlorine, combined chlorine and total chlorine were measured for four water models using a (Spectrophotometer) and the values are shown in table (2). These tests were carried out in Al-Karunji laboratories for the production of water and juices .

2.3 Evaluation of the Concentration of Halogen Derivatives of Acetic acid

Concentrations of dichloroacid and trichloroacide were in three city in Kirkuk (Al-Tayaran, Ninety, and Al-Wasiti), by the method of Gas Gromotography, Table No. (3) Shows the values of each of these two compounds resulting from the chlorination process obtain.

2.4 Determination of TOC value and evaluation of Tri halo methane group concentrations.

The absorbance was measured by the (UV) for raw water model at a wavelength of 254nm [21] and the absorbance was calculated by applying equation (A) to obtain the TOC value:-

$$TOC(Mg/L)=33 \times UV_{254}(cm^{-1}) + 0.673 - 0.673 + 0.085 \dots (A)$$

Equation (B) is applied to find out what is expected to be formed from tri Halo methane THMFP according to the value of (TOC) calculated for raw water:-

$$THMFP=43.367 \times TOC + 4.549 + 2.6 \dots (B)$$

2.5 Treatment method using two methods of activated carbon and enhanced coagulation

A glass column is filled with a layer of activated carbon and a layer of gravel and sand, and then a sample of treated water from the Al-Tayaran city is passed through it. The turbidity and total dissolved salts have already been measured. After passing this model in the column, the measurements are repeated and the difference between the two readings is calculated, as well as the removal in the amount of TOC that is expected to be formed from the carcinogenic group (THMFP) Polycarbonate. Aluminium sulphate coagulant was used to remove organic compounds and turbidity, by dose between 5-20 ppm. Evaluate the efficiency of this method in removing contaminants and treating diffraction in concentrations [22].

3. Results and Discussion.

3.1 Result of pH and Free Residual Chlorine.

Table 1: pH and Free residual chlorine

Months	pH	Free residual Chlorine (mg/L)
2	7.61	0.8
3	7.90	1.3
5	8.10	2.8
6	7.66	0.98
7	7.42	0.67
8	7.0	1

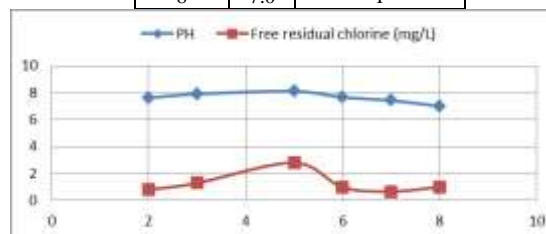


Fig.1: pH and Free Residual Chlorine

The results showed that the residual free chlorine value is affected by the change of pH, as the higher the value of the residual free chlorine increases but the relationship remains unclear. Iraqi Standard No. 417 of 2001 specified the value of the residual free chlorine in the distribution network not less than 0.3 mg / L and all values fall within the permissible standard limits [22] as shown in table 1& fig1.

3.2 Evaluating the conductivity, turbidity, and total dissolved salts concentrations, as well as measuring the concentrations of magnesium, sulfates, nitrates and nitrites for four models that represent a raw water sample and three models of water for Al-Wasiti , ninety and Tayaran. It is noted that the conductivity value is within the permissible limits according to Iraqi specifications. Table 2 shows the concentrations of conductivity, turbidity, total dissolved salts, magnesium, sulfates, nitrates and nitrites for four models that represent a raw water model and three models of treated water for Al-Wasiti, ninety and aviation. All values are noted within the permissible limits according to Iraqi specifications. The results showed high values of turbidity in the raw water, and it was within the permissible limit for the treated water. The magnesium component of raw water that was oxidized in the first stage was higher than the permissible limits of (mg/ L 50). As for the rest of the samples. they are within the permissible limit and this indicates the effectiveness of chlorine in getting rid of these compounds and dangerous elements that are present in the water.

Table 2. Turbidity, EC, TDS, Mg, SO₄ &NO₄ for the raw & treated water

Test	Raw water	AL-Tayran	Ninety	AL -Wasti	Iraqi standard specification
EC μ ohms/cm	379	356	359	364	1500
Tur. NTU	8.0	0.03	0.05	0.03	5
TDS(mg/L)	234	223	226	232	1000
Mg (mg/L)	56	40	43	33	50
SO ₄ (mg/L)	113	66	83	75	250
NO ₄ (mg/L)	46	32	33	40	50
NO ₃ (mg/L)	0.04	0.09	0.03	0.03	3

3.3 Measurement of Free, Combined and Total residual chlorine

Table 3& fig.2 shows that each of the free, combined and total residual chlorine was zero in the raw water because no chlorination was carried out and the water was not sterilized, so the concentrations were zero. The value of the residual free chlorine was less than the required limit according to the Iraqi standard for

chlorinated drinking water [23]. The low of these values indicates that the chlorine was consumed in the formation of the combined residual chlorine, which represents dichloroamines and chloro-organic compounds such as the THM group. It is noted that the value of the combined residual chlorine is higher than the free residue, which should be It accounts for 85-90% of the total chlorine added [24].

Table 3: Total chlorine, residual free chlorine and combined chlorine

TEST	AL Wasti	Ninety	AL Tayaran	Raw water
Total Chlorine (mg/L)	0.54	0.43	0.46	0.0
Free Chlorine	0.24	0.18	0.22	0.0
Combined Chlorine	0.30	0.25	0.24	0.0

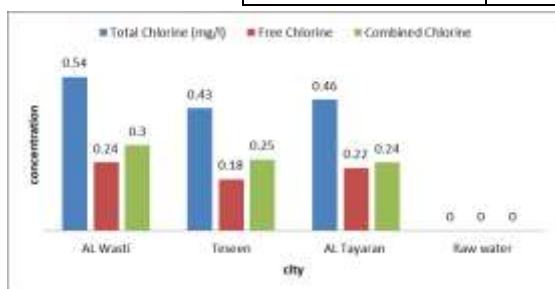


Fig. 2: Total chlorine, Residual Free Chlorine and Combined Chlorine

If the level of the combined chlorine is higher than the heat then we need better Chlorination, and this means that the nitrogen and ammonia compounds combine with the chlorine and make the sterilizer less effective and to eliminate the chloroamines the pH value must be between (7.2-7.8).

3.4 Concentrations of Halogen derivatives for acetic acid

The results showed that it is within the permissible limit for trichloroacetic acid as shown in table 4 & fig. 3.

Table 4: Dichloroacetic acid and trichloroacide

Test	AL Tayaran	Ninety	AL Wasti	Iraqi standard
Di Chloro acetic acid	0.023	0.033	0.025	0.05
Tri Chloro acetic acid	0.024	0.062	0.021	0.1



Fig. 3: Dichloroacetic acid and trichloroacide

3.5 The results of determining the expected Total Organic Carbon.

After calculating the amount of total organic carbon in the raw water, and then calculating the expected formation from the trihalo methane group, the results

are as shown in table (5). It is noticed that the values were higher than the permissible limit according to the Iraqi specifications, where the concentrations of the THM group were determined (0.15 mg / L), but in this model we noticed that the value of (THM) is (0.397), which is a high percentage of a dangerous carcinogenic compound, so it must be Conducting treatment operations to reduce the percentage of (TOC) in raw water and reduce the concentration of this health and environmentally hazardous group.

Table 6: TOC and THM_{fp}

TOC (mg/L)	THM _{fp} (mg/L)
8.95	0.397

3.6 Treatment method using Activated carbon

The turbidity and TDS of the raw water model decreased due to the passage of the column filled with activated carbon and the value of (TOC) also decreased to a good level, which leads to a decrease in the concentrations of (THM) group as shown in table (6) & fig.4.

Table 6: Turbidity, TOC and TDS before and after raw water treatment

Test	Before processing	After processing
Turbidity	8NTU	6.2
TDS	234	189
TOC	8.25	2.15

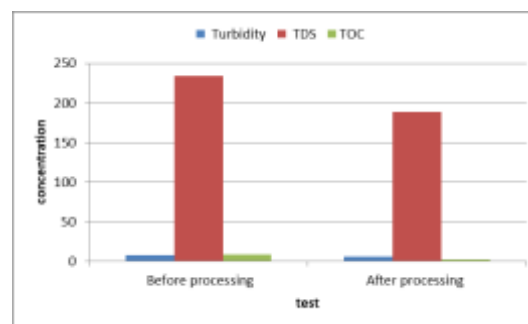


Fig. 4: Turbidity, TOC & TDS before and after raw water treatment.

The use of improved coagulation method with poly Aluminium Chloride (PACL) with concentrations ranging between 5, 10, 20 ppm and its effectiveness where we notice a decrease in turbidity ,TDS and TOC as shown in Table 7.

Table 7: Turbidity, TDS & TOC.

TOC After coagulation	TOC Before coagulation	TDS After coagulation	TDS Before coagulation	Turbidity After coagulation	Turbidity Before coagulation	Concentration mg/L
3.92	8.95	130	234	6.32	8.95	5
2.60	8.95	128	234	5.91	8.95	10
2.2	8.95	110	234	3.33	8.95	20

4. Conclusions and recommendations

When chlorine is combined with ammonia or organic nitrogen, such as acetic acid halides, as well as trichloromethane group many organic and inorganic side compounds, so the amount of added chlorine must be determined. The absence of halogenated side compounds with chlorine, such as the haloacid group, is not necessarily a factor encouraging the success of the sterilization process and it is free of dangerous compounds because the presence of bromine causes a shift towards the brominated compounds of acetic acid, which are not less dangerous than the side compounds resulting from the chlorination process. Many factors affect the amount of free residual chlorine, such as temperature, presence of total organic matter and contact time. The acidic function is one of the important factors affecting the formation of both free residual chlorine and combined residual chlorine. If the amount of ammonia in the water is less than the amount of chlorine added, then chloramine appears quickly, followed by the appearance of both second and trichloramine, but slowly, and this leads to the breakdown of chloramine into nitrogen. Free

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chlorine is much stronger in killing bacteria than combined chlorine therefore, it is necessary to obtain a concentration of free chlorine that is higher than that of residual combined chlorine, as free chlorine represents 85-90% of the value of the total chlorine added. Evaluating the organic products resulting from the sterilization process continuously and throughout the year. It is necessary to treat the deviations and deviations in the physical and chemical concentrations, if any, by appropriate treatment methods and to keep pace with the development in this field. Adherence to the amount of the added substance from the coagulant, because it is not necessary to increase the amount of the coagulant that leads to a large removal of the clay material, dust and silt, and it may lead to the emergence and deposition of unwanted elements in the water, for example: increasing the amount of alum formed from the element aluminum leads to the accumulation of this element in the brain Causing Alzheimer's if its percentage is above the normal limit according to Iraqi specifications [25].

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تقييم المركبات الكيميائية وعلاقتها بنقطة الانكسار بعد إضافة الكلور إلى المياه

الملخص

تقييم المركبات الكيميائية المتكونة خلال عملية تعقيم المياه بالكلور نقطة غاية بالاهمية. يمر الماء خلال تعقيمه بالكلور بثلاث مراحل كل مرحلة ينتج عنها مركبات كيميائية. حيث يتفاعل الكلور في المرحلة الاولى مع الحديد، المغنيسيوم والنترات. وفي المرحلة الثانية يتفاعل مع الامونيا وفي المرحلة الثالثة فيتفاعل مع المركبات العضوية الموجودة في المياه. ويسمى الكلور في هذه المراحل الثلاثة بالكلور المتحد. بعدها يصل الى نقطة الانكسار وهي النقطة التي بعدها يكون الماء خالي من المركبات الكيميائية الجانبية ويسمى الكلور بعد هذه النقطة بالكلور الحر المتبقي. اخذت نماذج مياه شرب عدد 3 من مناطق سكنية في محافظة كركوك وتم تقييم تراكيز كل من المغنيسيوم، النترات، السلفات، مشتقات حامض الخليك وكذلك مجموعة الهالو ميثان اضافة الى بعض المحددات الفيزيائية. وجدت هناك انحرافات وحيود بتراكيز بعض المواد الكيميائية عند مقارنة النتائج مع المواصفة العراقية الاخيرة ذو العدد 417. عولجت الانحرافات التي ظهرت في بعض بالتراكيز باستخدام طريقتين كيميائيتين الاولى باستخدام الكربون المنشط والثانية باستخدام بوليمير الالمنيوم كلورايد. اهمية الدراسة هو التأكد من فعالية الكلور بالقضاء على المركبات الكيميائية الخطرة الموجودة في المياه .