The Quality of Drinking Water between Ozone Sterilization Technology and Home Treatment System in Kirkuk Governorate

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Abstract. This research deals with three sources for supplying pure drinking water and within the limitations. The first source is drinking water disinfected with chlorine, the second is domestic and imported water sterilized with ozone, and the third source is water for household systems. In this research, the models’ physiochemical specifications were evaluated and compared with the modern Iraqi standard number 417. The first source results showed deviations in the values of turbidity, hardness, chlorine, and bromine. The deviations in the values were treated through an improved coagulation technique using ferric chloride. As for the second source results, they were within the specifications except for the deviation in the value of the sulfate ion for one of the models, and that deficiencies in the treatment processes caused the presence of the sulfate ion in a high percentage. Despite the different types of the third source systems, it gave good results, except for an increase in the percentage of chlorine and bromine, which needs periodic treatment, as the dose of chlorine during sterilization and removal of the bromide ion from raw water are joints of great importance and have environmental and health implications.

Keywords. Drinking water, Sterile ozone water, Household systems water.

1. Introduction

Providing drinking water has become a complicated matter due to the large number of pollutants that reach it in various ways and cause many serious health problems. It was discovered during the seventies of the last century that the disinfection of chlorinated drinking water leads to the formation of several chlorinated organic substances that may lead to many diseases, such as methane trihalides, acetic acid halides [1]. Therefore, it was believed that ozone sterilization (O₃) was a promising alternative to chlorine in closed containers, homes’ drinking water treatment systems, and some special applications. However, it became clear that some drawbacks appear through measuring some of the determinants [2]. Many types of research and studies dealt with evaluating drinking water and determining its chemical and physical properties. Whether it is within the permissible limits globally and locally and the most important of these specifications is turbidity, one of the problems that chlorinated drinking water suffers from. Water containing colloidal particles and plankton are dealt with through coagulation and settling [3]. The most commonly used coagulants are aluminum sulfate
(alum), ferric chloride, and poly-aluminum chloride. Research has proven the superiority of poly-aluminum chloride over alum in reducing the problem of turbidity [4]. As for the elements, their presence in raw water and then in drinking water causes many health problems. Among the most dangerous of these pollutants are the heavy elements [5]. Most of the filter plants that use chlorine as a sterilizer and oxidizer do not have a chemical treatment stage to remove the toxic elements [6]. The presence of iron and manganese at concentrations more than the international and local standards’ permissible limit leads to many diseases and human suffering. Therefore, many researchers studied the pollution of rivers and the concentration of heavy elements [7-9]. Other researchers studied modern methods of purifying water contaminated with heavy elements using natural detectors with nanotechnology [10]. The research studies also dealt with pH, electrical conductivity, dissolved solids, hardness, and sulfates [11] [12]. There are two significant determinants in drinking water are the concentration of bromine and chlorine, as it is necessary to confirm when using chlorine in sterilization to add 2-5 mg/liter of it for a contact period of not less than 30 minutes, as the excess of free chlorine is not less than 0.3 mg/liter at the farthest point in the distribution network [13]. As for bromine, which consists of oxidation of the bromide ion present in source water [14], it is considered a very dangerous determinant when present in water. It interacts with natural organic matter and forms carcinogenic side compounds [15]. Among the techniques used to purify water and make it drinkable is ozone. The first use of ozone for purposes other than sterilization was in the United States of America, such as removing color or controlling taste and smell. However, since the application of the Surface Water Treatment Act and the proposed Sterilization By-products Act (DBP), the use of ozone has increased in the United States of America [16]. Ozone is a colorless gas, and its pungent odor can be distinguished at low concentrations ranging from 0.02 to 0.05 ppm, which are lower than levels that harm human health; and ozone gas is highly corrosive, and it is non-toxic. Ozone is a potent oxidizing agent; it comes after the free hydrogen root (H +). It is one of the chemicals usually used in water treatment to oxidize several organic and inorganic compounds in water. These interactions with organic and inorganic compounds cause the need for ozone-treated water, which must be met during that process before it produces a residual quantity that can be measured [17]. Research and studies have shown that the need for ozone is related to the following:

- Interaction with natural organic matter (NOM) in water, as the oxidation of these substances, leads to the formation of aldehydes, organic acids, Aldehydes, and ketones [18].
- Interaction with synthetic organic compounds (SOC), as some of the synthetic organic compounds can be oxidized and become mineral under appropriate conditions, and until these compounds are entirely converted to minerals, oxidation with the hydroxyl root must be the predominant method as in the case of advanced oxidation [19].
- The bromide ion oxidation (Br–) leads to hypobromos acid formation, hypopromite ion, bromine ion, bromine organic matter, and bromoamines [20], as shown in Figure 1.
- Carbonate and bicarbonate ions are expressed in alkaline matter, where hydroxide roots are taken, and carbonate roots are formed. These reactions are essential for advanced oxidation processes in which the free radicals form.

Studies have shown the advantages of ozone technology in water purification, including [21]:

- Ozone is more effective than chlorine, chlorine amines, and chlorine dioxide in inhibiting viruses, hidden spores, and Giardia.
- Ozone oxidizes iron, manganese, and sulfides. As the iron converts from (+2) to ferric (+3) and manganese from (+2) to (+4), the oxidized forms of iron and manganese are deposited in the form of hydroxides.
- Ozone can sometimes help filter and remove turbidity. Being a potent oxidizing agent, it can achieve sterilization with short contact time and lower concentration.
- Ozone limits the color, taste, and odor, as ozone destroys and oxidizes the compounds that cause taste and odor, as it is a powerful oxidizer.
- Ozone is one of the most effective chemical disinfectants, so it requires little contact time.
In the absence of a bromide ion, no halogenated byproducts are produced for the sterilization process.

- The only residual ozone breakdown is dissolved oxygen.
- Ozone activity as a biocide is not affected by PH changes.

**Figure 1.** Ozone oxidation reactions.

The disadvantages of using ozone as a way to sterilize drinking water, they are according to studies [21]:

- Byproducts of the sterilization process, especially bromates, are formed in the presence of the bromide ion, aldehydes, and ketones. The use of ozone in sterilization leads to bromine transformation into bromate, which is a potential carcinogen [22].
- The cost of primary ozone units is high. However, the ozone water treatment systems consist of four main components: gas filling system, ozone generator, ozone tank, and surplus gas shattering system. These components require a high cost of operation and maintenance.
- Ozone generation requires high energy and must be generated on-site.
- Ozone is corrosive because it is a powerful oxidizing agent, as it automatically dissolves, generating free hydroxyl radicals.
- We need biologically active filters to remove available organic carbon and biodegradable side sterilization products, such as slow sand filters, fast filters, and active granular carbon.
- Ozone decomposes rapidly at elevated pH and high temperatures.
- Ozone does not provide residuals.
- Ozone requires a high level of maintenance and skilled operators.

Some studies and researches dealt with the physiochemical and microbial characteristics of bottled and sterilized water with ozone produced locally or imported. Local models showed an increase in the application of health requirements, and imported models showed failure rates in applying the physiochemical requirements [19]. Also, many studies have shown that a percentage of the water samples on the market and sterilized with ozone are not valid for human consumption, as they contain microbial contaminants as the total number of aerobic bacteria ranged between (0-300) cells per 100 ml and the number of fecal coliform bacteria between (0-5) cells Per 100 ml [23]. Concerning home treatment systems, or what is known as household filters, they are used in the treatment and purification of drinking water to remove or reduce impurities and pollutants, which improves the quality of water for various purposes. Its specific characteristics exceed the limits of permissible concentrations. Among the reasons that led to the deterioration of the quality of the water reaching the consumer are [24]:

- The production capacity does not match the actual need of the population.
- Not using the optimal dose of alum or using alternatives.
- Not giving the required dose of chlorine.
- Deficiency in maintenance work.
Blackouts.
- Overrun water networks.
- Furthermore, the large number of dead spots in the network finally contributes to mixing stagnant water with the prepared water.

Home treatment systems are of many types and accessories, and they may have excellent or low-quality filters. However, one of the most important techniques used in these systems is the reverse osmosis technology, a purification process using membranes and isolating pollutants. This process is different from nature and depends entirely on the physical properties of water. The water is transferred from a concentrated liquid solution to the least concentrated and then the least concentrated by a semi-permeable membrane, where pressure plays an essential role in the reverse osmosis process [25]. The second technique used in these home systems is the ultraviolet ray technique. This short electromagnetic ray effectively kills types of bacteria and viruses, as these rays destroy the DNA of the bacterial cell [26]. This research aims to address three essential stages, which are evaluating drinking water, physically and chemically, for several residential areas in Kirkuk Governorate, and then treat the deviation with values using the enhanced coagulation technique in the second stage. The third stage is the treatment of drinking water for the same residential areas using household filters. We conducted physiochemical tests for drinking water after passing through household filters to determine the qualitative variables, and then an evaluation of some types of bottled and ozone-disrupting water present in the local markets of those residential areas in order to come up with a conclusion on determining the best source for providing clean drinking water within limits permitted internationally and Iraqi specifications.

2. Experimental work

2.1. Used devices
The used devices are pH meter for pH estimation, conductivity device for measuring total dissolved salts, hardness measurement by titration with EDTA solution, Turbidity device for measuring turbidity, spectrophotometer for measuring the concentrations of sulfate, manganese, iron, chlorine, and bromine. And the Jar Test coagulant evaluation technique.

2.2. Evaluating the physical and chemical specifications of drinking water
Drinking water samples were taken from four residential areas in the Kirkuk governorate. Their physical and chemical characteristics were evaluated, represented by pH, turbidity, total dissolved salts, hardness represented by calcium bicarbonate, sulfate ion, manganese, iron, chlorine, and bromine. Hardness was also assessed by titration with EDTA solution. After these tests were carried out, it was compared with the values specified by the latest Iraqi standard number 417 for 2001 to determine the extent of their compliance with the permissible parameters. Table 1 shows the values of previously determined drinking water specifications.

2.3. Treatment with enhanced coagulation of drinking water for values with deviations
The enhanced coagulation method refers to modifying the standard coagulation technique [27], to achieve the highest removal of natural organic matter (NOM). This method depends on the acidity value (pH) and the dose of coagulant added. The coagulants commonly used are alum because of its ability to remove solids and remove phosphorous from water. We have used ferric chloride instead of alum because of the latter contains aluminum, as increasing the concentration of aluminum in water to more than the permissible limit by 0.2 mg/lit is considered dangerous, so we focused on the use of ferric chloride as a coagulant with concentrations ranging between 20 - 35 ppm. Moreover, ferric chloride was evaluated as a coagulant using the jar test technique, depending on the coagulant’s pH and dose. Table 2 shows the values that were treated in this way.

2.4. Evaluation of drinking water after treatment with home treatment systems
It was necessary to conduct laboratory analyzes of the drinking water entering the household systems to determine its validity and the effectiveness of these systems. These systems are used to treat
drinking water by physical, chemical or biological means to remove or reduce impurities and pollutants from the water, which improves the water quality. The four samples A*, B*, C*, D* of previous drinking water were passed through household filters. The same physical and chemical specifications were evaluated to know the changes taking place, noting that the household systems whose effectiveness was evaluated differed. Table 3 shows the values after passing through these filters.

2.5. Evaluating the physiochemical parameters of ozone sterilized bottled drinking water models
Eight models of bottled and sterilized drinking water with ozone were approved in the local markets of Kirkuk Governorate (local and imported). We gave them the symbol (1,2,3,4,5,6,7,8), as they were chosen randomly. Their physical and chemical characteristics were evaluated, such as pH, turbidity, hardness, total dissolved salts, sulfates, manganese, iron, bromine, and chlorine. After that, it was compared with the concentrations specified in the latest Iraqi standard 417. Table 4 shows the results.

3. Results and discussion

3.1. Discussing the results of drinking water tests for four residential areas in the kirkuk governorate
From the observation of the values in Table 1, we find that all samples’ acidity values are within the permissible limit, as the Iraqi Standard 417 of 2001. Specified the pH values (8.2-6.5), while the turbidity values were all within the permissible limit except for a deviation in the value sample C, where the test value was 17.9mg / lit is higher than the permissible concentration which determined (5 NTU). High concentrations of turbidity in the water are mainly due to the type and concentration of the coagulant used. Therefore, research and studies have directed towards using alternatives to reach acceptable concentrations and ensure water quality [28].
As for the total dissolved salts, all the samples were within the permissible limit of (1000 mg/lit). The hardness test results of all the models were within the permissible limit (500 mg/lit), except for model C, the concentration was (560mg / lit). The reason for the presence of hardness in the water may be the presence of calcium, magnesium ions, and other elements in concentrations greater than usual due to pollution [29]. Concerning sulfate, manganese, iron, and all four drinking water samples, it is permissible, and there is no deviation in values. The chlorine values, or the so-called free chlorine, are imposed at a concentration of (0.3mg / l) at the farthest point of distribution. From this, we conclude that there is a limitation in the amount of chlorine dose for the samples A, B. By referring to Table 1, the bromine values were high in the C and D samples and higher than the permissible in the local and international specifications, as the highest permissible limit is 0.01mg / lit and the presence of high concentrations of free bromine in drinking water is a dangerous reflection, which indicates The presence of the bromide ion in the source water, which has been oxidized by chlorination, in turn from free bromide, or what is called bromine, and in turn, it may turn into the bromate compound that causes cancerous diseases [30].

Table 1. It shows the physiochemical values of drinking water for four residential areas in Kirkuk governorate.

| Test type           | A     | B     | C     | D     | The values are in Iraqi standard 417 |
|---------------------|-------|-------|-------|-------|--------------------------------------|
| PH                  | 8.1   | 7.1   | 7.2   | 7.4   | 8.5-6.5                              |
| Turbidity (NTU)     | 0.01  | 3.8   | 17.9  | 1.23  | 5                                    |
| T.D.S (mg/l)        | 147   | 255   | 490   | 290   | 1000                                 |
| Hardness ,CaCO₃ (mg/l) | 55   | 140   | 580   | 135   | 500                                  |
| SO₄²⁻ (mg/l)        | 36    | 63    | 70    | 66    | 250                                  |
| Mn (mg/l)           | 0.016 | 0.003 | 0.0   | 0.004 | 0.1                                  |
| Fe (mg/l)           | 0.0   | 0.0   | 0.2   | 0.00  | 0.3                                  |
| Chlorine (mg/l)     | 0.1   | 0.37  | 1.82  | 0.82  | 0.3                                  |
| Bromine (mg/l)      | 0.0   | 0.0   | 0.057 | 0.045 | 0.01                                 |
3.2. Discuss the results of tests for enhanced coagulation with ferric chloride

From observing the values in Table 2, we find that there are deviations from the maximum permissible limits as a value in drinking water. The model C test results were higher than the permissible limit for testing turbidity and very close to the permissible concerning hardness. We also treated total dissolved salts for the same model to determine the effectiveness of this technique in reducing these specifications. From the values in Table 2, we note the apparent decrease of these concentrations after the enhanced coagulation process, which indicates that the use of ferric chloride as a coagulant is better than alum in addition to the fact that the first consists of iron in its chemical composition, and the second from aluminum and this is better because of aluminum. It represents a health risk because it is concentrated in the brain and causes many diseases, such as Alzheimer’s if its concentration is higher than the permissible level.

| Test type                      | Before treatment | Before treatment | The values are in Iraqi standard 417 |
|--------------------------------|------------------|------------------|-------------------------------------|
| Turbidity (NTU)                | 17.9             | 3.91             | 5                                   |
| T.D.S (mg/l)                   | 580              | 150.2            | 1000                                |
| Hardness ,CaCO₃ (mg/l)         | 490              | 320              | 500                                 |

3.3. Discussing the results of drinking water tests after treating it with household filters

After evaluating sterilized drinking water with chlorine physically and chemically for four residential areas in Kirkuk, the same samples were passed on to household filters to treat them from pollution and remove unwanted elements. The results were shown in Table 3, and for the tests for each of the pH, turbidity, hardness, total dissolved salts, sulfate ion, iron, manganese, chlorine, and bromine. From the results, we noticed that these filters were able to reduce turbidity, salts, hardness, sulfates, and iron and manganese elements. However, bromine and chlorine’s problem remained. It is necessary to control chlorine’s dose in the raw water and conduct a bromide ion test for the source water before performing any desalination process.

| Test type                      | A*    | B*    | C*    | D*    | The values are in Iraqi standard 417 |
|--------------------------------|-------|-------|-------|-------|-------------------------------------|
| PH                             | 8.0   | 7.6   | 7.1   | 7.6   | 8.5-6.5                             |
| Turbidity (NTU)                | 0.01  | 0.02  | 0.02  | 0.33  | 5                                   |
| T.D.S (mg/l)                   | 28    | 106   | 68    | 26.7  | 1000                                |
| Hardness ,CaCO₃ (mg/l)         | 0.0   | 30    | 80    | 55    | 500                                 |
| SO₄⁻ (mg/l)                    | 0.00  | 21    | 63    | 62    | 250                                 |
| Mn (mg/l)                      | 0.00  | 0.003 | 0.00  | 0.002 | 0.1                                 |
| Fe (mg/l)                      | 0.00  | 0.00  | 0.00  | 0.00  | 0.3                                 |
| Chlorine (mg/l)                | 0.00  | 0.26  | 0.3   | 0.65  | 0.3                                 |
| Bromine (mg/l)                 | 0.00  | 0.00  | 0.00  | 0.045 | 0.01                                |

3.4. Discussing the results of the physicochemical tests of the ozone sterilized bottled water

In this part of the research, many ozone sterilized drinking water samples packed with plastic bottles were tested and available in the local markets. Those above physical and chemical specifications were evaluated. It was noted that all measurements were within acceptable concentrations except for the sulfate ion concentration in sample 6, where the test result was 410 mg/lit, and this is a negative indicator that must be paid attention. Modern methods of removing it can be followed; its presence leads to kidney disease and other health repercussions.
Table 4. Represents the physiochemical values of ozone sterilized drinking water models.

| Test type                  | 1    | 2    | 3    | 4    | 5    | 6    | 7    | 8    | The values are in Iraqi standard 417 |
|----------------------------|------|------|------|------|------|------|------|------|-------------------------------------|
| PH                         | 6.7  | 6.5  | 6.8  | 7.1  | 7.3  | 7.8  | 7.9  | 8.1  | 8.5-6.5                             |
| Turbidity (NTU)            | 0.01 | 0.01 | 0.01 | 0.02 | 0.02 | 0.01 | 0.02 | 0.01 | 5                                   |
| T.D.S (mg/l)               | 102  | 106  | 97   | 167  | 155  | 147  | 300  | 147  | 1000                                |
| Hardness, CaCO3 (mg/l)     | 30   | 50   | 50   | 65   | 45   | 85   | 110  | 55   | 500                                 |
| SO4= (mg/l)                | 0.00 | 0.00 | 3    | 20   | 30   | 210  | 43   | 36   | 250                                 |
| Mn (mg/l)                  | 0.002| 0.001| 0.002| 0.00 | 0.002| 0.001| 0.00 | 0.016| 0.1                                 |
| Fe (mg/l)                  | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.3                                 |
| Chlorine (mg/l)            | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.1                                 |
| Bromine (mg/l)             | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01                                |

4. Conclusion
i. Drinking water tests for the four residential areas in Kirkuk Governorate showed that all models’ acidity values (pH) are within the permissible limit. At the same time, there are deviations in the values of turbidity, hardness, as well as in the concentrations of chlorine and bromine from the permissible limit, except for the C model, and that the presence of high concentrations of turbidity in water, it is mainly caused by the type and concentration of the coagulant used. The presence of hardness in the water is the presence of ions of calcium, magnesium, and other elements in concentrations greater than usual due to pollution. As for the concentration of sulfate, manganese, and iron, there is no deviation in their values. As for free chlorine, there is a limitation in the amount of chlorine dose for models A and diffraction for models C and D.

ii. The use of ferric chloride as a coagulant is better than alum, in addition to the fact that the first consists of iron in its chemical composition, and the second from aluminum and this is better because aluminum represents a health risk because it is concentrated in the brain and causes many diseases such as Alzheimer’s if its concentration is higher than the permissible.

iii. Household filters are very suitable to reduce the percentage of turbidity, salts, hardness, and sulfates and iron and manganese elements. However, the bromine and chlorine’s problem remains, as it is necessary to control the dose of chlorine in the raw water and conduct a bromide ion test for the source water before performing any desalination process.

iv. Regarding bottled and sterilized water with ozone, all measurements were within acceptable concentrations except for the sulfate ion concentration. This is a negative indicator that must be paid attention to and modern methods that can be followed in its removal presence leads to kidney diseases and other health repercussions.

5. Recommendation
i. Not all bottled and sterile water is free of compounds that have an environmental and health impact on citizens

ii. Not all bottled and sterile water is free of compounds that have an environmental and health impact on citizens.

iii. Ensure the use of alternatives to chlorine sterilization, such as ozone sterilization, UV sterilization, and other methods, emphasizing achieving the required goal of providing safe drinking water free of side compounds and within standard specifications.

iv. It is necessary to work first on raw water in bottled water or water entering the systems installed in homes. Therefore, the raw water must be completely bromine-free. Tighter control is required to conduct this analysis before entering the water to the home sterilization station. A modification of the bromine ion must be made in the final product.

v. The acidity (pH), organic matter, temperature, and contact time must be controlled to reduce the formation of side-effects with a harmful effect.
vi. It is imperative to continuously evaluate the water throughout the year to find appropriate solutions for all deviations in values through various treatment methods.

vii. Focus on the number of additives from the coagulant to reduce the compounds that cause turbidity and soil.

viii. Attention to the amount of chlorine added as a sterilizer and oxidizer, if filtered water in the city is used as the water inside the ozone sterilization systems.

ix. We observed high concentrations of bromine by evaluating bromine concentrations as the values indicated that attention should be paid to and stopped at this problem, which can be solved using bromine-free sources as much as possible.

x. Intensive surface water treatments are necessary, and a fundamental change in sterilization practices must be made, with the specification always modified and new specifications introduced to meet the high standards.

xi. The necessity of tightening control over the water in the market, developing related laboratories, and introducing other analyzes in addition to simple traditional analyzes such as pesticide analysis and dangerous organic groups.

xii. Educating workers by enrolling in courses and conferences, looking at research and publications, and supplying stations with competencies that can analyze and interpret each value of what it means and what its implications are.

xiii. Maintenance of stations and water distribution pipelines, as the presence of refraction or interference, maybe the reason behind the presence of many dangerous compounds such as sulfates.

xiv. Require factories and water filling units to comply with the bromate ratio requirement, not exceeding 0.01 mg/L.

xv. Ignorance of industrial methods, health technology, lack of training, and lack of control leads to the fact that most bottled water factories depend on making ozone in large quantities to eliminate microbiological problems, forgetting how dangerous this is for individuals.

xvi. The need to spread awareness among citizens that not all bottled drinking water is safe and not harmful, as most laboratories do not examine toxins and viruses that cause intestinal diseases, so water must be boiled before using it, especially for patients and children suffering from diseases and a lack of immunity.

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