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Using Of Ozonation Method for Filtertion of Mineral Water

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Abstract

In this reseach, two samples of mineral water found in Northern Mahabad, west Azarbaigan, with hardnesses of 36, 42 mg/l ($CaCO_3$) are investigated (.Kanisepi South Region, and Minerals of the Tutankhach Village Northern Region).
Then, different amount of Ozone gas is injected into mineral water and biological and chemical changes are observed.The used Ozonator can produce 25 mg Ozone per hour. To determine the amount of Ozone gas. We used iodometry method. By injection of 1.25 mg/l we achieved complete removal of diatomaceae in sample **1** and up to 99 percent in sample 2. Both complete removal of chlorophyceae in 1.1 mg/l complete removal of BOD_5 sample **1** in 1.1 mg/l Ozone and in sample (2 in 1 mg/l Ozone complete removal).We had 65 percent reduction of COD by injection of 1.2 mg Ozone for sample **1** and 68 percent for sample **2**.Complete disinfection is done in both samples by injection 0.5 mg per liter. In this method clean water is achieved because no chemical is used and we don’t need to provide chemicals. So, Ozonation can be introducd as the best method for filtration of water.
DO: Dissolved Oxygen
BOD: Biological Oxygen Demand
COD: Chemical Oxygen Demand

Keywords: Ozonation, Filtration, Disinfection, Mineral water, clean water.

Introduction

Water is one of the most significant compounds in the life of all living beings. The human being, for example, may survive up to three weeks without eating and in moderate climates may tolerate three days of a water free life. It is therefore that water is among the essential needs for the survival of the living beings and its protection and maintenance is necessary. Undoubtedly, the access to clean water is required. Although there are abundant water resources on the planet, not all of them are usable for human beings. One of the problems in this regard is that water is not merely used for drinking. For instance, it is applied as a suitable detergent and an industrial solvent. This may lead to the pollution of surface waters. Since water resources are restricted, they should be recovered. In spite of the fact that there are more water resources in Europe than most other places in the world, the Europeans make serious efforts to treat and recover these watershemical precipitation, coalescence, inverted osmosis and adsorption was used for water treatment. Application of these methods did not result in the total removal of pollutants.

In fact, these pollutants are moving from solid to liquid and liquid to liquid phases and they may not be easily separated from water, since some of them may even have some reactions when exposed to water. Coalescence, filtration, and chlorination may really destroy microbic ingredients. However, organic destructive materials resulting from industrial sewages may exist in water. In the 1980's, it was found that the increase of chlorine in the sewages containing chain of organic materials create cyclic compounds and increase the pollution scale. Taking into account the above facts, it is mentionable that the drinking water resources are not very expensive [1].

One of the most useful methods for the destruction of pollutants in the world is the use of chemicals with high oxidation powers. Chlorine and different* compounds, electro oxidation, coalescence with electricity or ultraviolet light and different peroxides are some strong oxidants. All these materials convert insoluble organic compounds to soluble forms and even proper quantities of water and carbon dioxide may be obtained through these reactions. The result of each reaction is the oxidation of organic materials. Due to their stability and resistance to oxidation, some of these materials may be converted to smaller stable compounds. Consequently, different water treatment stages are required for enhancement of water quality. One of the most significant issues regarding the oxidition materials is that they should not be pollutant themselves. Now that water is extensively used in intensively populated areas, inorganic waters in remote places are seriously taken into account. Due to long distance of these waters from the urban and industrial centers, they may be used only after filtration and disinfection. These waters, however, may be exposed to serious threats from the pollutants. The final solution is thus treatment and control polluted waters with a safe and proper method [2].

Results and discussions

In this research, the effects of ozone on the inorganic waters around Mahabad are examined for biological and chemical purposes.

1.The impact of ozone on the removal or reduction of biochemical oxygen demand (BOD)
2.The impact of ozone on the removal or reduction of chemical oxygen demand (COD).
3. Effects of ozone on the algae existing in mineral waters.
4. Effects of ozone on the reduction of microbial ingredients of mineral waters.
5. In this study, an ozonator with the production capacity of 25 mg of ozone per hour was used. Two springs of mineral water with the relative hardness of 36 & 42 mg/liter were used for this purpose (since they change in different seasons of the year) [3].

The use of ozone gas has a history of half a century. Ozone was first discovered by Schonbein in 1840 through the electrolysis of sulfuric acid. It was first used by Martenec in 1886 for disinfecting water. Before the mass production of chlorine gas and the examination of its biochemical and chemical properties in World War 1, Ozone was used in refining the sewages. Ozone was replaced by chlorine, following the emergence of chlorine gas since cholrine was relatively cheap and easly accessible. In the1980's, it was found that chlorine gas converts chained compounds to cyclic ones. This problem led to the return to ozone-based method. Its reliable application resulted in the discovery of other applications of ozone for the oxidation of quite dangerous metals iron and manganese in drinking waters [4].

Ozone Properties

Physical Properties

Ozone is a gas with 1.5 times of the Oxygen density. It is in fact one of the allotropes of oxygen and considered a poisonous gas, with a boiling point of 112^{0C} and is quite unstable. This gas is more stable in the gas from compared to its liquid state. It has no color or smell in gas state and is dark blue in liquid state [5].

Chemical Properties

Most of ozone reactions are rooted in the nucleophilic double bonds and this nucleus demand results in the ozone oxidation property. There are different mechanisms for the analysis of this gas, but it is widely acceptable that the hydroxide ion act as a catalyst in the ozone analysis in water solvent, which may be shown in the following manner:

$$O_3 + OH^- \longrightarrow O_2^- + HO_2$$

$$O_3 + OH^- \longrightarrow HO_4^-$$

$$O_3 + 2OH^- \longrightarrow O_2 + 2O^- + H_2O$$

Ozone usually absorbs the infrared visible light and absorbs the ultraviolet light in certain wavelengths of maximum 2500^{0A}.The solubility of the Ozone in water is 12 times that of the oxygen[6].

Ozone Reactions

Ozone reactions may be examined in three ways:

1. Initiators.
2. Inhibitors; and synergistic.
3. Synergists [7].

Initiators:

These compounds should be peroxide like materials, which are produced in the nature media (O_2^{2-}). Inorganic compounds such as peroxides, hydroperoxides, hydroxides and organic compounds such as formic acid may produce such materials. Ultraviolet rays may also produce such ingredients. Consequently, when it is cloudy, the skin is more prone to burning compared to sunny weather.

Inhibitors

Inhibitors are materials, which may consume hydroxyl ion and prevent the reproduction of anion peroxides. Inhibitors are materials such as secondary alcohols, which consume hydroxyl radical.

Synergists

All organic and inorganic materials, which may produce hydroxyl or anion peroxide are considered as synergists of ozone reactions. These synergists include compounds such as aryl, formic acid, and glyoxylic acid and primary alcohols [8].

Measuring the Ozone Gas

Measuring Ozone in the Liquid State

Since ozone is highly powerful oxidants, the applicable method shall be carefully selected. Otherwise, the reagents used are easily oxidized by ozone and other reagents resulted from the ozone analysis are easily oxidized. Therefore, in different analysis methods, including colorimetric or electrochemical ones, other oxidants also engage in the determination of the ozone volume in the analysis method and result in the existence of the ozone volume. In fact, the entire density of oxidants is usually measured and thus the result is much higher than the real volume of the ozone gas. Consequently, this error may be reduced by taking the following steps:

1- Sampling should be done carefully avoiding any mixtures and in closed tubes.

2- In order to prevent ozone loss, we directly add the gas.

3- The interval between sampling and measuring has to be short.

4- Since the manual work is prone to errors, the automatic tool-based methods are preferred [9].

Colorimetric Method (IndigoTriSulphate)

The above method was used by Beade & Hogen for the control of water pollution and is quite exact, selective and quick.

Peroxide hydrogen ions, manganese, chloride and products of ozone breakup and otheroxidations have less engagement in this method. The ozone volume should be selected in a manner that between 20-90 percent of the reagent is discolored. The stock solution is prepared using strong phosphoric acid and indigo potassium tri-sulphate.The said solution has a stability of four months in the darkness.

Iodometry

Iodide ion in the potassium iodide solution is oxidized with iodine. The acidity of the said solution shall be adjusted to lower than 2 for the ozone measurement potassium iodide is used. Thus, the ozone consumption amounts may be determined since ozone releases iodine as a result of the following reaction: The iodine level is specified by the Sodium Thosolphate and the ozone volume is proportional to the released iodine volume.

$O_3 + 2I^- + H_2O \longleftrightarrow I_2 + 2OH^- + O_2$

$I_2 + 2S_2O_3 \longleftrightarrow 2I^- + S_4O_6^{2-}$

Considering the above reactions, it is possible to conduct the tests of BOD_5, COD and microbe culture to observe ozone effects on these waters. However, since the amounts of water in these springs change during the year, the ratio of required ozone gas will change, too [10].

Iodine Measurement in the Gas State

Ozone may also be measured in the gas state. However, ozone can be extracted from the solution indirectly by an inert gas. In the gas state it can be measured by absorption methods, such as UV and colorimetry. It can also bere introduced in the solution and measured by color indicators.

Ozone Production

The raw material for production of ozone is oxygen gas.The general reaction of ozone production has a negative enthalpy, which is an exothermic reaction. Every reaction, which may release radical oxygen, may have the required qualifications for the ozone gas production. The energy resources for this reaction may be found in following forms [11].

1- Electronic; and
2- Light

Ozone in Comparison to other Oxidants

Observing the application of this simple and effective compound is followed by the comparison to other oxidants. Taking into account the negative effects of chlorination, the application of ozone gas is really preferred, since higher costs of this method is compensated by the use of ozone through precipitation of iron and manganese, the control of smelling and taste, as well as its discoloration property and contribution to coalescence[12].

The ozone oxidation potential is 2.07 volts under acidic conditions and 1.24 volts in alkali conditions.

In the following table (1), a comparison is made between different oxidants.

Taking into account the above table, the ozone gas may have positive effects on water purification. According to the experimental taken from the ozone efficiency, different uses of ozone gas are mentioned hereunder:

1.Promotion of the coalescence process (since even after the ozonation, other particles exist in this state in the emulsion form and their mass is increased for clotting and since ozone has a radical reaction, loaded and ready-for-clotting particles are produced).

2. Oxidation of the organic pollutants (such as aromatic,phenyl,and different organometallic compounds such as insecticides.These compounds, are more stable since they have aromatic rings and the analysis of these materials shall be done with stronger oxidants).

1. Oxidation of pollutants with high molecular weights (these materials mainly form points and resins, whose cracking is done by strong oxidants)

2. Not straying microbes and algae (a powerful oxidant may destroy microbes and algae and destroy their structure, which may have a significant role in disinfecting drinking waters).

3. Oxidation of inorganic ingredients, such as manganese and iron (some inorganic ingredients are soluble in water, but with

the change of their oxidation state, they may be precipitated).
However, considering the type of pollutants, ozone should be introduced at a suitable time to increase its efficiency [13].
In this study, two springs in the vicinity of Mahabad were examined.

Ozonator

The ozonator used in this study may produce a quantity of 25 mg of ozone per hour. Pure oxygen is used for the production of ozone, but before the entry of oxygen to the ozonator. Silica gel is capable of drying the oxygen gas. However, the silica gel container should be occasionally changed; since the container gets saturated after a while and loses its drying property.
For the proper diffusion of ozone inside water, a diffuser is used, which is in the form of a porous stone and make the complete contact of ozone inside the water. All the joint used in this study are made of resistant glass.
Moreover, in order to measure the ozone amount, the iodometry method is used to determine the excess ozone. The remaineting ozone from the reaction is conducted to two vessels containing potassium iodide with certain thicknesses. Then by titrating potassium iodide with sodium thiosolphate, the volume of ozone used is determined.
In order to dry the oxygen gas, suitable drying filters are used and where there is a probability of the pollution of gas with the chemical compounds, filters with containing active carbon ingredients in granule form are used. Otherwise, ozone gas itself may produce pollution and more gas would be used, which leads to more errors.

Experimental

Ozone Measurement

Ozone and strong oxidants may oxidize potassium iodide in water solutions and release iodide. In this case, the released iodine may be titrated with sodium thiosolphate. The corresponding equations are given below [14].

Determination of Coliform Number

These microbes, which are called coliforms, are generally aerobics and in voluntary conditions, they are capable of being anaerobic. Coliforms are negative, spore-free and rod shaped. They may survive in suitable media containing lactose at 35^{0C} for 48 hours and produce carbon dioxide because of fermentation.

Identification and Counting of Algae

Algae are living beings with a high variety. Previously, before this wide variety was not identifiable, all these creatures were called algae. Some of these species have a maximum length of 50 meters and some of them may be seen only with microscopes with magnifying power of 100. Some of them may be examined by simple magnifiers. However, currently, allthe existing species are specified and have separate names.

COD Determination

100 ml of the sample is selected and added to a flask containing glass pearls. Then because to remove from the chloride troubles, 0.2 gr of mercury sulphate is

added to the flask. After shaking, the 5 ml of the 0.25 normal solution of potassium bicarbonate is added to the flask. Then, 15 ml of strong sulfuric acid containing silver sulphateis introduced to the flask (the solution should be shaken, since the reaction is significantly exothermic, the observance of safety rules is required).

$$COD = \frac{(a-b)(N)(8000)}{C}$$

C= the sample volume in.

b= the Iron (II) sulphate and ammonia volume used.

a= volume of Iron (II) sulphate and the ammonia volume used as pilot.

N= Iron (II) sulphate and ammonia normality.

BOD_5 Determination

For determination of BOD_5 a German device is used. First, a certain volume of the sample is put in the particular vessel of the device and a soda tablet is added to it, and then the glass is capped. At the beginning, we select the zero grade for the device and put it in the incubator at a proper temperature, usually, 25^{0C}. After 5 days, the BOD_5 is recorded .

Results and Discussions

The results may be examined in three aspects:

1. Production of the ozone gas and factors influencing the optimization of its efficiency.
2. Properties of the samples under examination.
3. Results from the ozonation of samples at different temperatures.

Production of Ozone Gas and Effective Factors in the Optimization of its Efficiency

According to given the results in Table 2, the most proper rate for the oxygen gas introduction is 23 ml per second and the most proper time for the injection of ozone is between 50 to 400 seconds.The reason for selection of such a rate is that at higher rate, practically the production of ozone gas does not increase and in lower speeds, the ozone gas production shall be lowered. The reason to use 50 to 400 seconds is that outrange of this calibration curve shows a high deviation.

A reason for this may be that with the increase of oxygen gas rate, the required time for the effect of the electrical discharge on the oxygen molecules is reduced and many oxygen molecules pass the device without any change and lose the opportunity for changing to free radicals, caused by the device capacity.

Other subsidiary factors influencing the manner of ozone production are described below:

1. No vibration in the electrical current.
2. No chemical pollutants in oxygen gas.
3. No humidity in oxygen gas.
4. No change in the input gas current.

Properties of the Samples under Examination

Proper and sterilized vessels were used for sampling. After each sampling, all the vessels were completely sterilized by Iron, since the existence of any microbic element in the vessel results in very high rates of error. Even in the sampling site, the wearing of sterilized gloves was required. However, for determination of BOD_5 and COD, the sterilization is not important, but for the sake of integration in the study and the elimination of all the error factors in different stages, the sterilized vessels were used.

The point, mentioned earlier, is related to the sample time because the environmental conditions of algae and microbes constantly change and at high temperatures, that is the hot seasons, these ingredients are quite active and in rainy months and at low temperatures, the microorganism activities are low.

Consequently, for the preparation of samples under study the samples were selected concurrently and were kept in the refrigerator to be used at the time of examination. However, the refrigerator was protecting from other factors, which increase the pollution probability on the samples.

Results from the Ozonation of Samples in Different Amounts

When there is a good weather and the temperature is mild, the growth of these particles will increase and requires to remove more ozone.

The next point is related to disinfecting these waters. Since they are found in quite outside environments, these waters provide very suitable media for the growth of microbes. Considering Tables 1&2 we understand that these waters have very high pollution and injecting of 0.4 mg per liter, they may be perfectly sterilized and their coliforms removed. For comparison of the activities of these bacteria, Tables 8, 10, and 11 are recommended. They show the amounts of $BOD_{5,}$ and COD. With higher metabolisms, this particles consume more energy and it shows that the microbic activity in these waters are high. Therefore, when an increase in the BOD_5 and COD is observed, these waters are recommended to be disinfected. A look at Tables 1,2,3,4 indicates that injecting of 1 mg per liter, COD and BOD_5 may be totally removed.

Table 1. Change in COD as a result of Ozonation in sample (1)

Sample	COD(mg/l)	Amount of ozone injection(ppm)	% removal
original	13.5	––	--
1	13.48	0.25	0.14
2	11.98	0.50	11.25
3	8.98	0.75	33.48
4	8.4	1	35.55
5	6.5	1.25	51.85
6	5	1.5	62.96

Table 2.Changes in COD as a result of Ozonation in sample (2)

Sample	COD(mg/l)	amount of ozone injection(ppm)	% removal
original	11.5	--	--
1	10.8	0.25	6.08
2	9.1	0.50	20.8
3	7.8	0.75	32.1
4	6.2	1	46
5	4.3	1.25	62.6
6	3.8	1.5	66.95

Table 3. Changing in BOD_5 as a result of Ozonation in sample (1)

Sample	BOD_5 (mg/l)	amount injection ozone(ppm)	% removal
original	7.8	--	--
1	6.8	0.25	12.8
2	4.8	0.50	38.46
3	2.8	0.75	64.1
4	0.9	1	88.46
5	0	1.25	100
6	0	1.5	100

Table 4 .Changes in BOD_5 as a result of Ozonation in sample (2)

Sample	BOD_5 (mg/l)	amount of ozone injection(ppm)	% removal
original	7	--	--
1	6	0.25	14.28
2	5	0.50	28.57
3	3	0.75	57.14
4	1	1	85.71
5	0	1.25	100
6	0	1.5	100

Table 5. The specifications of biological sample of Tutankhach Village (Northern Region)

Entry	Organism	Number/liter
1	Diatomaceae	285
2	Chlorophyceae	95

Table 6. The results of bacteria experments of Kanisepi sample (South Region)

Number Coliphorm (MPN/100 ML)	14
Namber E.Coli in Sample(100ML)	3.2

Table 7. The results of bacteria experments of Tutankhach Village sample (Northern Region)

Number Coliphorm (MPN/100 ML)	14
Namber E.Coli in Sample(100ML)	3.2

Table 8. Change in COD as a result of Ozonation in sample (1)

Sample	COD(mg/l)	Amount of ozone injection(ppm)	% removal
original	13.5	--	--
1	13.48	0.25	0.14
2	11.98	0.50	11.25
3	8.98	0.75	33.48
4	8.4	1	35.55
5	6.5	1.25	51.85
6	5	1.5	62.96

Table 9.Changes in COD as a result of Ozonation in sample (2)

Sample	COD(mg/l)	amount of ozone injection(ppm)	% removal
original	11.5	--	--
1	10.8	0.25	6.08
2	9.1	0.50	20.8
3	7.8	0.75	32.1
4	6.2	1	46
5	4.3	1.25	62.6
6	3.8	1.5	66.95

Table 10. Changing in BOD_5 as a result of Ozonation in sample (1)

Sample	BOD_5 (mg/l)	amount injection ozone(ppm)	% removal
original	7.8	--	--
1	6.8	0.25	12.8
2	4.8	0.50	38.46
3	2.8	0.75	64.1
4	0.9	1	88.46
5	0	1.25	100
6	0	1.5	100

Table 11 .Changes in BOD_5 as a result of Ozonation in sample (2)

Sample	BOD_5 (mg/l)	amount of ozone injection(ppm)	% removal
original	7	--	--
1	6	0.25	14.28
2	5	0.50	28.57
3	3	0.75	57.14
4	1	1	85.71
5	0	1.25	100
6	0	1.5	100

Conclusion

High amounts of COD results in the use of ozone for the oxidation of organic materials. The process leads towards the disinfection when the natural organic material in the water is reduced or oxidized. Algae and microorganisms have a direct impact on the disinfection. Consequently, COD is one of the factors, which indicates the direct impact of ozone gas on the removal of all the pollutant materials (Tables 8, 9, 10 & 11).

BOD_5 shows the amount of oxygen used. Through the total removal of the natural compounds, in accordance to Tables 10 & 11, it may be observed that with the injection of proper amounts of ozone, BOD_5 shows a decreasing trend. However, it may be noticed that the BOD_5 changes are more severe than COD. In order to describe this fact, it is mentionable that at the beginning, the inseparable materials under oxidation arechanged to separable materials and they begin exhibiting biological activiting. They may increase BOD_5 amount and then be quickly oxidized by ozone, resulting in the reduction of the BOD_5. In order to overcom this problem, the oxidation time by ozone should be increased. The longer contact, time to the destruction of the subsidiary activity of organic compounds.

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