

Physicochemical and Microbiological Analysis of Drinking Water Treated by Using Ozone

(Analisis Fisikokimia dan Mikrobiologi Air Minimum yang dirawat dengan Ozon)

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ABSTRACT

This study focused on the application of a Dielectric Barrier Discharge (DBD) unit to produce highly oxidizing ozone molecules for the treatment of drinking water. The samples of water were collected from three different sources, namely tap, stone spout and tube-well in the Kathmandu valley. Various physical, chemical and micro-biological analyses were carried out to both the ozone treated and untreated samples of water for comparison. Our results indicated that ozone does not alter the physical characteristics, namely pH, conductivity and turbidity of water but it has significant effect on the chemical properties such as nitrate concentration, total hardness, calcium hardness, Fe(II) and Fe(III) concentration. It was observed that ozone efficiently precipitates ferrous ion into ferric ion and is effective in the removal of fecal coliform, a key element for various water related health problems in most of the developing countries. It is shown that the treatment with ozone leads to a significant reduction in the number of fecal coliform in the samples of drinking water from tap, stone spout and tube well with p values 0.00182, 0.026 and 5.8×10^{-15} , respectively at 0.05 level of significance.

Keywords: Dielectric barrier discharge; ozone; water treatment

ABSTRAK

Kajian ini berfokus kepada kegunaan molekul ozon yang dihasilkan daripada nyahcas dielektrik berpenghadang (DBD) untuk membersihkan air minimum. Sampel air dari paip air, batu spout dan perigi tuib di Lembah Kathmandu telah dirawat dengan ozon. Pelbagai analisis ciri-ciri fizikal, kimia dan mikrobiologi telah dilakukan ke atas sampel air sebelum dan selepas dirawat dengan ozon. Hasil analisis menunjukkan bahawa rawatan ozon tidak mengakibatkan perubahan kepada ciri-ciri fizikal seperti nilai pH, kekonduksian dan kekeruhan tetapi membawa kesan terhadap ciri-ciri kimia seperti kepekatan nitrat, keliatan keseluruhan, keliatan kalsium, kepekatan Fe(II) dan Fe(III). Ozon didapati sangat berkesan untuk menukarkan ion ferus kepada ferik dan berjaya menghapuskan koliform feses yang merupakan satu masalah penting tentang kebersihan air yang dihadapi oleh kebanyakan negara membangun. Hasil kajian ini menunjukkan bilangan koliform feses dalam air dapat di kurangkan secara berkesan dengan rawatan ozon, ia itu nilai p untuk sampel air minum dari paip air, batu spout dan perigi tuib adalah 0.00182, 0.026 dan 5.8×10^{-15} , masing-masing pada aras tekal bernilai 0.05.

Kata kunci: Nyahcas dielektrik berpenghadang; ozon; perawatan air

INTRODUCTION

Water becomes contaminated by pathogens such as coliform group bacteria, salmonella and dysentery causing bacilli. The human faecal material carried in sewage is often dumped into the rivers and lakes that may lead to water contamination. Therefore water supply has to be regularly checked from the microbial point of view. According to a World Health Organization (WHO) report in 2007, 1.1 billion people lack access to an improved drinking water supply and 1.8 million people die from diarrheal disease each year. Nepal has the poorest quality drinking water and sanitation for its population in South Asia, although rich in fresh water resources. Contamination by fecal coliform bacteria is the major reason contributing to the poor water quality in Nepal.

Conventional methods for the purification of water are either expensive, or have limited efficiency. After many years of using chlorine in water disinfection, it has been concluded that its use in potable water treatment can be harmful for human health. So, there is a growing need for an effective method of water treatment. The area of water purification by ozone synthesis is an industrially accepted application of electrical discharges (Bubnov et al. 2004; Chang & Wu 1997; Eliasson et al. 1987). The major advantages of the ozonation process for water treatment are that there is no need to store and handle toxic chemicals, by-products of ozonation do not have any known adverse effects on health or the environment, ozone is a stronger and faster-acting oxidant, ozone can safely destroy a broader range of organic contaminants and helps in the removal of colour (Rajeswari et al. 2001), odour and suspended solid

materials. Moreover, ozone is highly efficient in killing bacteria, viruses, spores and cysts (Malik et al. 2001).

The ozonation process can be made more competitive by improving the energy efficiency and ozone yield of the ozone generator, developing better ozone-water contactors, and/or catalyzing the chemical reactions of ozone (Kuraica et al. 2004; Malik et al. 2001). The oxidation of organic pollutants in water is an attractive method of treatment because it finally results in conversion of the innocuous materials with no secondary disposal requirements (Sunka et al. 1999).

When air is passed through the DBD, the interaction of high energy electrons with the oxygen molecules within the inter electrode space may give rise to the dissociation of oxygen molecules. The atomic oxygen combines with another oxygen molecule to form ozone which when passed through water can induce changes in the chemical or biological properties of water. The present paper reports on the investigation of these changes induced by ozone treatment.

EXPERIMENTAL SETUP

The experimental setup used in this study is shown in Figure 1. A high frequency (10-30 kHz) and high voltage (0-20 kV) power supply (Shrestha et al. 2007) was used to power the discharge in the air gap between a wire-cylinder annular electrode system. The central electrode is made of steel wire and the outer electrode is made from an aluminum film wrapped around a glass tube of internal radius 3 mm and thickness 1 mm. For the production of ozone by DBD, air was pumped into the reactor at the rate

of about 300 cm³ per min by an air pressure pump. The concentration of ozone dissolved in water was determined by using the iodometric titration method (Moris 1977). The concentration of ozone as a function of treatment time is presented in Table 1. The treatment was carried out by bubbling ozone to the bottom of the beaker containing the sample of water. For this study, the treatment time was 20 min for each sample. Each water sample had a volume of 100 mL.

The chemical analyses of the samples were made in the Aquatic Ecology Center at the Department of Environmental Science and Engineering and the microbiological analysis were made in the Department of Biotechnology, School of Science at Kathmandu University. pH and conductivity analyses were made by using digital pH meter and conductivity meters respectively. The turbidity of the samples was analyzed on the basis of optical property (Tyndal effect) in which the light is scattered by the suspended particles present in water. It was measured using a turbidity meter and was expressed as Nephelometric Turbidity Unit (NTU). Brucine absorption method was employed for the analysis of Nitrate concentration (APHA 1995).

Titration was used for the analysis of total hardness and calcium hardness of the water samples in which the known volume of samples were allowed to react with known concentration of EDTA in the presence of selective indicator to form a complex of Ca(EDTA)²⁻. The concentration of total hardness and calcium hardness were then calculated using the formula given by (1) and (2), respectively:

$$\text{Total hardness [mg / L]} = \frac{(\text{Volume of EDTA used [mL]} \times (\text{Normality of EDTA}) \times (32.196))}{\text{Volume of aliquot taken [mL]}} \quad (1)$$

$$\text{Calcium [mg / L]} = \frac{(\text{Volume of EDTA used [mL]} \times (1) \times (1000) \times (0.40))}{\text{Volume of aliquot taken [mL]}} \quad (2)$$

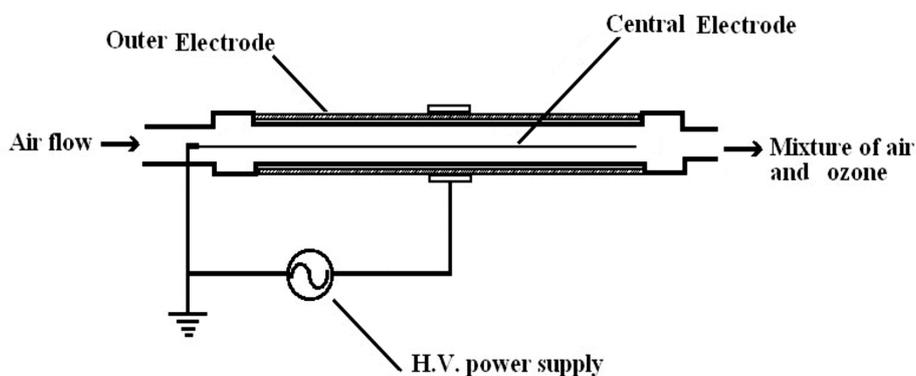


FIGURE 1. Experimental setup of DBD system for the ozone generation

TABLE 1. Concentration of ozone dissolved in water as a function of treatment time

Volume of water for treatment (ml)	Treatment time (min)	Concentration of ozone (mg/L)
100	1	0.36
100	5	1.92
100	10	14.48
100	15	24.36
100	20	31.2

Concentration of the ferrous (Fe^{2+}) ions and ferric (Fe^{3+}) ions were measured by spectrophotometric method. To determine the ferric ion concentration, 25 mL of standard iron(III) ion solution was taken in 50 mL volumetric flasks and 0.5 mL of the thiocyanate solution and 3 mL of 4M nitric acid was added to it and diluted with distilled water to the mark. A blank solution was prepared using the same quantities of reagents except iron(III) ion solution. The measured portions of standard iron(III) thiocyanate solution were diluted with distilled water to prepare five solutions of different concentrations. The absorbance of different standard solution and sample solutions of iron(III) was determined at 480 nm. The absorbance was plotted against concentration of the solution, i.e. a calibration curve was plotted. The amount of iron(III) in the sample was then calculated from calibration curve. Similarly, to determine ferrous ion concentration 10 mL of standard iron (II) solution (containing not more than 0.5 mg of iron) was taken in a 50 mL volumetric flask. Five milliliter of hydroxyl ammonium chloride (10%) solution and acetate buffer was added to it. 10-Phenanthraline solution (4 mL) was added to it and was diluted after 5-10 min using proper blank solution. The absorbance of other standard solution and the sample was measured in similar way to develop the calibration curve from which the amount of iron(II) in the sample was calculated.

The total colonies of coliform in untreated and treated samples were determined by membrane filtration method in which 100 mL of the sample was filtered slowly through the membrane filtration unit upon which a sterile membrane filter was placed. The water was pumped down using a pump. After all the water was filtered the membrane was placed in a Petri dish containing absorbent pad soaked in Lauryl broth. Then Petri dish was then incubated at 44.5 °C. After 24 h yellow colored colonies were counted as CFU/100 mL as expressed in (3):

$$\frac{\text{count}}{100 \text{ ml}} = \frac{\text{count on filter}}{\text{Volume of water filtered}} \times 100. \quad (3)$$

RESULTS AND DISCUSSION

PH ANALYSES

The experimental results for pH analyses of untreated and treated samples of water from the three different sources are depicted in Figure 2. In the case of water from tap, the mean value of pH was found to be 6.76 before treatment and 6.79 after treatment indicating a negligible change in pH. Similarly, for the sample from stone spout, the mean value of pH was found to be 6.28 before treatment and 6.51 after treatment showing a slight increase in pH after treatment. For sample from tube well, the mean value of

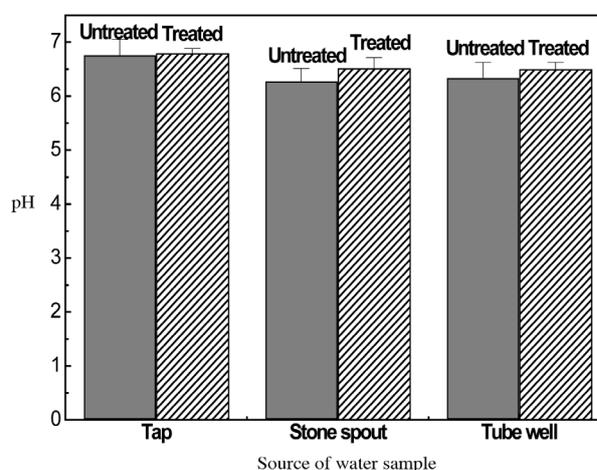


FIGURE 2. pH of untreated and treated water samples

pH was found to be 6.33 before treatment and 6.50 after treatment also with slight increase in pH after treatment. Figure 2 also indicates that pH of water from tap is found to be close to the neutral value of 7 as compared to other two sources of water.

From Figure 2, there appears to be no significant change in the pH values of water from the three sources of water tested before and after treatment. In the case of tap water, there is no change in the pH at all but in the

case of stone spout and tube well, there is a little effect of ozonation and in both the cases pH is found to increase and is within the guideline range of 6.5-8.5 for drinking as indicated by WHO. The increase in pH of water can be attributed to the accumulation of H_2O_2 during the treatment.

CONDUCTIVITY ANALYSES

Figure 3 shows the results of the analysis of conductivity of untreated and treated samples of water from the three sources. For tap water, the mean value of conductivity was found to be 76.28 $\mu\text{S}/\text{cm}$ before treatment and 77.38 $\mu\text{S}/\text{cm}$ after treatment indicating a slight increase in its value. For water from stone spout, the mean conductivity was found to be 526.8 $\mu\text{S}/\text{cm}$ before treatment and 525.7 $\mu\text{S}/\text{cm}$ after treatment and in the case of water from tube well, the mean value was found to be 456.6 $\mu\text{S}/\text{cm}$ before treatment and 454 $\mu\text{S}/\text{cm}$ after treatment. Conductivity of all samples was very low compared to standard value i.e. 1500 $\mu\text{S}/\text{cm}$ reported by the National Drinking Water Quality Standard (NDWQS) of Nepal.

It was evident from the figure that tap water has the lowest conductivity as compared to the other two sources of water. It was also observed that there was no significant change in conductivity of water from the three sources before and after treatment. Conductivity is directly related to the amount of salts dissolved in water and ozonation does not contribute to addition of extra ions. Patrick et al. (2007) have reported that conductivity remains at stable values before and after treatment, which agrees with our present result.

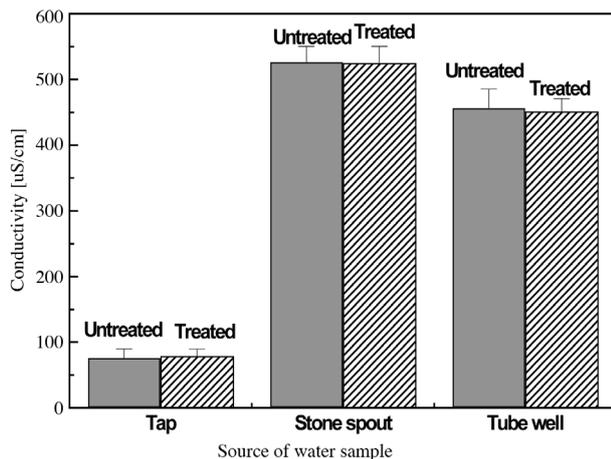


FIGURE 3. Conductivity of untreated and treated water samples

TURBIDITY ANALYSES

Results of turbidity analyses of untreated and treated samples of water are shown in Figure 4. For tap water, the mean value of turbidity was measured to be 2.94 NTU

before treatment and 2.86 NTU, after treatment indicating a small reduction in the value. In the case of water from stone spout, the mean value was found to be 1.4 NTU and 1.1 NTU, respectively before and after treatment. Likewise, for water from tube well, the mean value of turbidity was found to be 75.8 NTU before treatment and 72.2 NTU after treatment. For all samples there is a small reduction in turbidity after treatment. This is an indication that ozone helps in the removal of suspended materials from water. The mean values of turbidity for the samples of tap and stone spout are below the reported value but water from tube well exceeds the standard value, which is 5 as given by NDWQS. Figure 4 also indicates that the turbidity of water collected from tube well was found to be much higher compared to the other two sources of water.

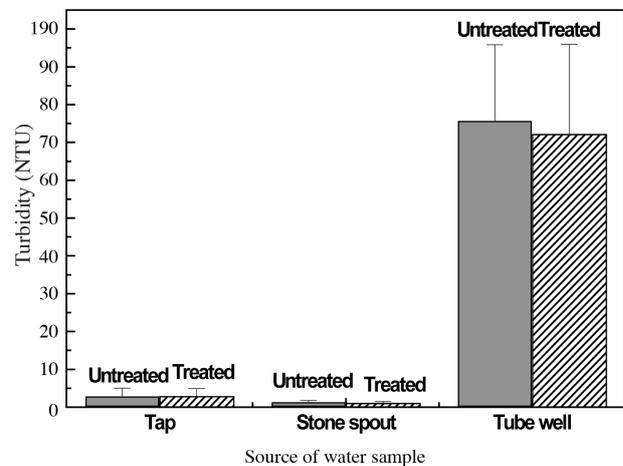


FIGURE 4. Turbidity of untreated and treated water sample

NITRATE CONCENTRATION

Figure 5 shows the results of analyses of nitrate concentration of untreated and treated samples. For tap water, the mean value of nitrate concentration was found to be 0.44 mg/L before treatment and 4.80 mg/L after treatment showing a remarkable increase after treatment. Similarly, for water from stone spout, the mean value was found to be 16.40 mg/L before treatment and 19.3 mg/L after treatment indicating an increase in the concentration of nitrate. For tube well water the concentration of nitrate was found to increase from 2.6 mg/L to 6.90 mg/L after treatment. The mean values of nitrate for all the samples are below the recommended value i.e. 50 mg/L as given by NDWQS.

Water from stone spout was found to have highest concentration of nitrate ions. In all the cases, the concentration of nitrate was found to increase consistently after the treatment. Ozone, being a strong oxidizing agent, converts nitrite or other nitrogenous compound in the water into nitrate by direct oxidation.

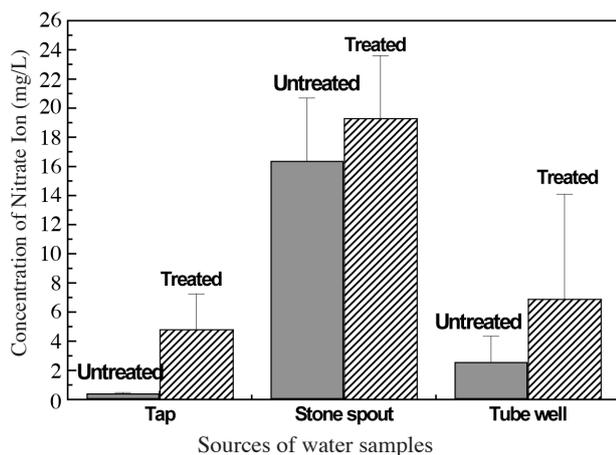


FIGURE 5. Concentration of nitrate ions in untreated and treated water samples

TOTAL HARDNESS

Figure 6 shows the total hardness of untreated and treated samples of water from the three sources. Tap water was found to have a mean value of total hardness of 26.52 mg/L before treatment and 21.61 mg/L after treatment whereas for the sample from Stone spout, the mean value was found to be 49.50 mg/L before treatment and 45.05 mg/L after treatment. In both of these samples the total hardness of water was found to decrease after the treatment. However, in the case of water from tube well, there was slight increase in the total hardness from 107.64 mg/L before treatment to 108.43 mg/L after treatment.

Hardness of water samples from tap and stone spout lie between 0-50 mg/L, thus are soft water. On the other hand, hardness of water from tube well lies between 100 and 150 mg/L and thus it has slightly higher hardness (Gupta 2000).

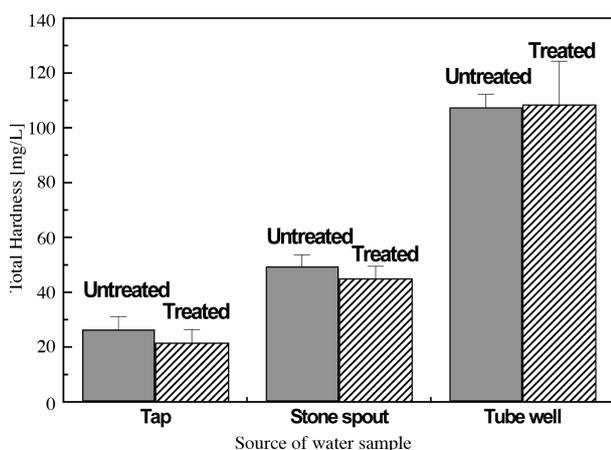


FIGURE 6. Total hardness of untreated and treated water samples

CALCIUM HARDNESS

We also analyzed the calcium hardness of the samples in addition to the total hardness. The results of the analysis are presented in Figure 7. The mean value of calcium hardness for tap water was found to be 14.74 mg/L before treatment and 10.33 mg/L after treatment indicating a decrease in the calcium hardness. Similarly, for stone spout sample, it was 39.36 mg/L before treatment and 36.34 mg/L after the treatment. Unlike the total hardness, the calcium hardness was found to decrease after the treatment in the case of water from tube well. The mean value was found to be 41.99 mg/L before treatment and 37.36 mg/L after treatment. It is evident from Figure 7 that calcium hardness of water from tap is many times lower compared to that of water from tube well and stone spout. Also, in all the cases there is decrease in calcium hardness after the treatment.

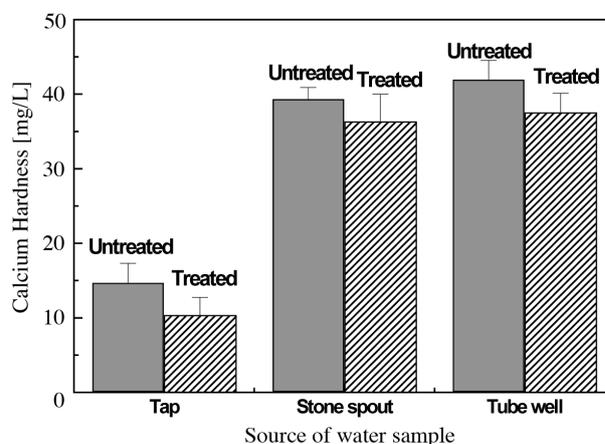


FIGURE 7. Calcium hardness of untreated and treated water samples

FERROUS ION (Fe^{2+}) CONCENTRATION

The other chemical parameter studied in our work was the concentration of ferrous ions (Fe^{2+}) in water. Figure 8 shows the results for ferrous concentration of and effect of ozone treatment in the concentration untreated and treated samples of water from three different sources. In the case of water from tap, the mean value of ferrous ion concentration was found to be 3.32 mg/L before treatment and 1.92 mg/L after treatment. Similarly, for water from stone spout, the Fe^{2+} concentration before treatment was 6.12 mg/L and after treatment was 5.58 mg/L. For tube well water, it was 18.91 mg/L before treatment and 16.37 mg/L after treatment. It is also evident from Figure 8 that ferrous ion concentration of water from tube well is very high as compared to water from stone spout and tap. After treatment the Fe^{2+} concentration was found to decrease in all samples. Iron in its ferrous state has charge of 2+. When ozone is passed through the solution containing ferrous

salts, it contributes the oxygen atom that reacts with the Fe^{2+} to give ferric salt and hence concentration of Fe^{2+} decreases. The change in the concentration of Fe^{2+} ions should be analyzed in connection with the change in Fe^{3+} ion concentration as discussed in the following section.

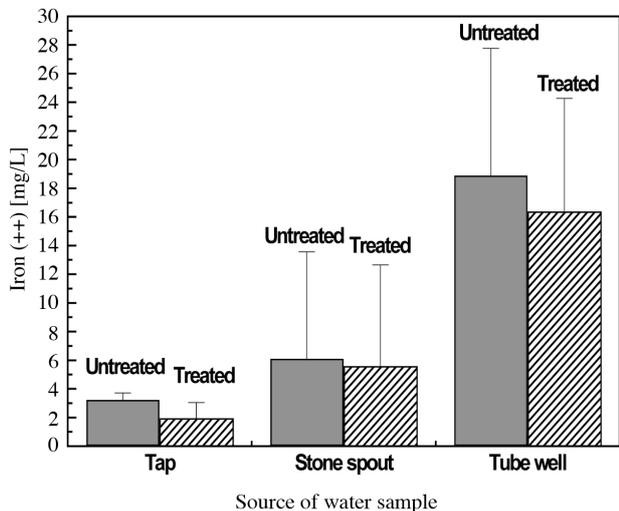


FIGURE 8. Concentration of Iron (2+) in untreated and treated water samples

FERRIC ION (Fe^{3+}) CONCENTRATION

Analysis of ferric ions (Fe^{3+}) was also carried out for all samples before and after the treatment in ozone and the results are plotted in Figure 9. It is observed that for water from tap, the treatment causes an increase of ferric ion concentration from 0.72 mg/L to 1.04 mg/L. Likewise, for sample from stone spout Fe^{3+} ion concentration increases from 0.72 mg/L to 0.82 mg/L after the treatment. Similarly, for tube well sample, the ferric ion concentration is found to increase from 5.44 mg/L to 7.3 mg/L due to ozonation.

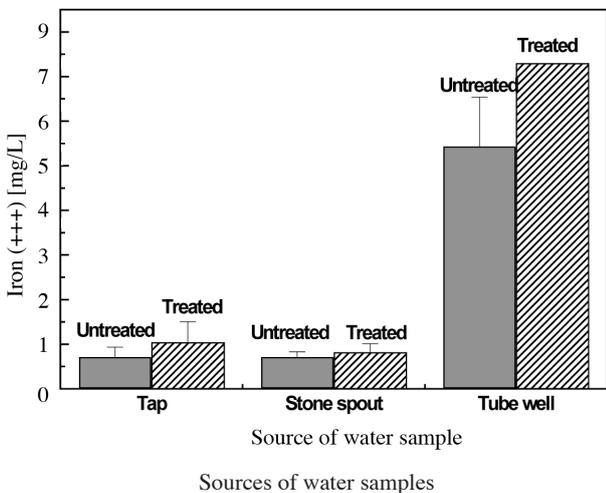


FIGURE 9. Concentration of iron (3+) in untreated and treated water samples

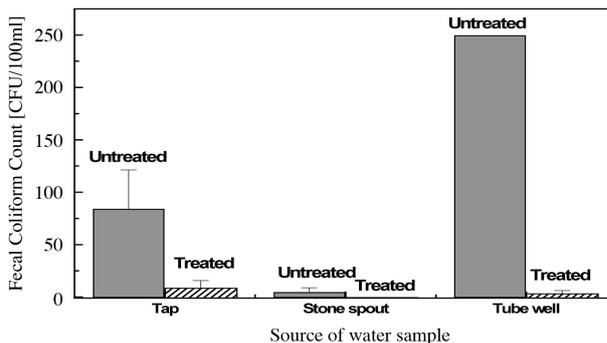


FIGURE 10. Fecal coliform count in untreated and treated water samples

The results also indicate that ferric ion concentration of water from tube well is much higher compared to water from stone spout and tap. After treatment Fe^{3+} is found to increase in all samples. This can be attributed to the oxidation of Fe^{2+} as indicated by the reduction of ferrous ion concentration as discussed in the last section. It is important to note that ferrous salts are soluble in water whereas ferric salts are insoluble.

FECAL COLIFORM

In addition to the investigation of physical and chemical parameters, we also studied the effect of ozonation on coliform content in the water samples. Results of fecal coliform analyses are shown in Figure 10. The most notable result is that samples collected from stone-spout contained smallest number of coliform per 100 mL of the sample. For all samples, there was a remarkable decrease in the coliform count after the treatment.

In the case of water from tap, the mean value of fecal coliform count was found to be 84 CFU per 100 mL before treatment and this was reduced to 8 CFU per 100 ml after treatment. In the case of water from stone spout, the mean value was found to be 5 CFU per 100 ml before treatment it was almost completely removed after treatment. In the case of water from tube well, the mean value was found to be 250 CFU per 100 mL before treatment and it was reduced to 4 CFU per 100 mL after treatment. It is obvious that the effect of coliform reduction is most significant in the case of tube well, where the fecal coliform count was reduced from 250 CFU per 100 mL to a very small number. The coliform count in stone spout shows a direct reduction to zero by ozone treatment.

McNair and Leshner (1963) had studied the effect of ozone on the survival and permeability of *Escherichia coli* cultured in the logarithmic phase or resting. The treatment was carried out with various concentrations of ozone in saline solution. Approximately 2×10^7 molecules of ozone per bacterium was able to kill 50% of the cells. It was postulated that the primary attack of ozone was on the cell wall or membrane of the bacteria, probably by reaction with the double bonds of lipids, and that leakage or lysis of the cells depended on the extent of that reaction.

Our earlier work (Subedi et al. 2009) on the analysis of water subjected to direct treatment in DBD also indicated a remarkable decrease in coliform after the treatment.

CONCLUSION

Results of ozone treatment of water samples collected from various sources showed a significant reduction in the number of coliform bacteria. No remarkable effect on pH and conductivity was observed. Ozonation of water led to the conversion of ferrous ions present in water to ferric ions as indicated by the corresponding changes in their concentrations. This indicated that ozonation can be a useful method to separate iron content from water. Further investigations about the effects of ozonation on different physical, chemical and biological parameters of drinking water are in progress.

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