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Treatment of waste water by ozone produced in a dielectric barrier discharge

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Abstract This study focuses on the application of dielectric barrier discharge (DBD) at atmospheric pressure to generate ozone for the treatment of waste water. Waste water samples from domestic source, dairy industry and paint industry were collected and various parameters of the samples before and after the treatment were measured. Treatment time of 20 minutes was used for all types of samples. Our results showed that ozone treatment significantly increased dissolved oxygen (DO); reduced chemical oxygen demand (COD), fecal coliform, heavy metals and total solids (TS), but the changes in pH and conductivity were not statistically significant.

Keywords dielectric barrier discharge – ozone treatment – waste water – pH – DO – COD – fecal coliform

INTRODUCTION

Waste water is a complex solution which may contaminate the human environment, i.e. air, water, food, land and shelter. The common sources of water pollution can range from purely natural to several man-made sources of domestic and industrial waste water [1, 2]. Wastes from different industries are more dangerous since they contain xenobiotic compounds which are not bio-degradable, thus persist for longer time and can be transported through rivers to other parts of the country. The waste released from these sources into rivers will ultimately lead to water pollution. Also, polluted rivers act as breeding ground for various disease causing agents and the smell from the polluted river sometimes becomes unbearable. Thus, waste water released from various sources should be treated before it is released into rivers.

There are various methods of treatment, some of which are activated sludge method, chemical coagulations, chlorination etc. One of the emerging technologies is the use of ozone which is an industrially accepted application of electrical discharges for treatment of water and waste water [3]. In a DBD (dielectric barrier discharge) reactor the electrical discharge takes place between electrodes where at least one of the electrodes is covered with a thin layer of dielectric material [4]. The dielectric material used is a type of insulator and is made of ceramic, glass, PVC etc.

When an AC voltage is applied across the electrode, discharge is generated with the production of UV. Electrical discharges taking place in an air or oxygen environment convert oxygen into ozone. In addition to ozone, electrical discharges in air produce a variety of chemically active species, such as O_3^*, N_2^*, N^*, OH^*, O_2^*, O^*, O^{+2}, N^{+2}, N^+, O^+ [5]. These species are short lived and decay before ozone enriched air gets into the water where it oxidizes various organic and inorganic chemicals and converts them into simpler forms that become easily decomposed in the atmosphere.

Ozone is 12.5 times more soluble in water than oxygen, leading to better mixing in water treatment [6]. Other advantages of ozone over conventional chlorination process are: (i) no need to store and handle toxic chemicals; (ii) by-products with no known adverse effects on health or the environment; (iii) can safely destroy a broader range of organic contaminants; (iv) helps in removal of colour, odour and suspended solid materials; (v) far more efficient in killing bacteria, viruses, spores and cysts; (vi) also oxidizes and precipitates iron, sulphur, and manganese so they can be filtered out of solution. Ozone is very reactive because it has redox potential +2.07 V whereas chlorine has only +1.36V [6].

EXPERIMENTAL SETUP

Ozone is produced by a coaxial dielectric barrier discharge system (Fig. 1). The discharge is generated using a high voltage (0-50 kV) power supply at 50 Hz manufactured by Nepal Engineering Eakarat Co. Pvt. Ltd. The rms input voltage applied to the electrodes can be varied between 0 to 21kV. The voltage applied for

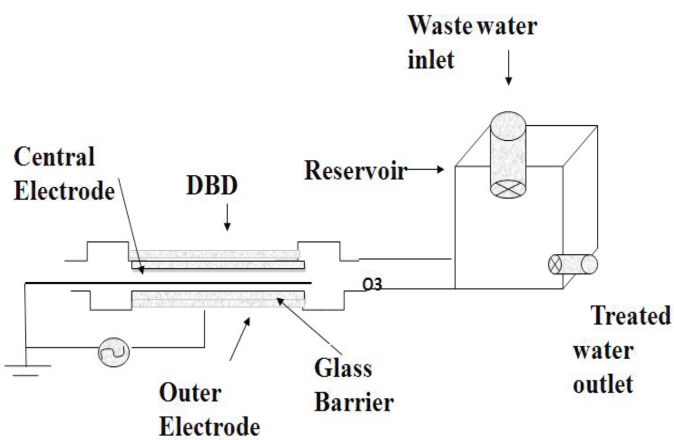

Figure 1. Schematic diagram of ozonation system.

our experiment was 14 kV with a current limiting resistance of 8MΩ.

Co-axial type of electrode made up of aluminum was used in the experiment. The outer electrode was made of wrapping an aluminum foil over a polycarbonate tube which was used as dielectric material in this case. The inner electrode was made of aluminum wire of length of 22 cm and diameter of 0.4 cm. The length of the outer electrode was 20 cm and that of the dielectric material was 24 cm. The outer and inner diameters of the dielectric material were 1 cm and 0.7 cm respectively. The inner electrode was connected to the output of the power supply and the outer electrode was grounded.

When a high voltage was applied across the electrodes, a strong electric field was created and discharge was generated. For the purpose of producing ozone, air was pumped into the electrode gap by an air pressure pump, at the rate of about 300cm^3/min. The concentration of the ozone output from the generator was determined by the standard iodometric method [7].

SELECTION OF SOURCES OF WASTE WATER

Samples of waste water from various sources located in the Bhaktapur Industrial sector of Bhaktapur, Nepal were collected.

Waste water from household/domestic sources

Waste water from residential, commercial, institutional and similar facilities are referred to as domestic waste water. Domestic sewage consists of organic as well as inorganic substances which may include protein, carbohydrate, fats as well as grits, salts and metals in varying proportions. A significant amount of heavy metals like copper, manganese, cobalt, lead, etc may also be present in significant proportions. In our experiment the discharge from various households (excluding discharge from sewerage system) was considered.

Dairy industry

The dairy industry is generally considered to be the largest source of food processing waste water in many countries. In general, wastes from the dairy processing industry contain high concentrations of organic material such as proteins, carbohydrates, and lipids, high concentrations of suspended solids, high biological oxygen demand (BOD) and chemical oxygen demand (COD), high nitrogen concentrations, high suspended oil and/or grease contents, and large variations in pH, which necessitates ‘specialty’ treatment so as to prevent or minimize environmental problems [8].

Paint industry

Acrylics and styrene-butadiene polymers are mainly used in water-based paints for interior and exterior use. Other materials that paints may contain include organic and inorganic pigments which have varying degrees of toxicity. Cadmium, lead, chrome and nickel-containing pigments may still be added to some paints. Zinc chromate which is added to metal primers has now been found to be strongly carcinogenic and will no longer be produced. Plastic polymers and solvents with very slow rates of biodegradability, and solvents that contain aromatic hydrocarbons may also be present. These wastes are strongly eco-toxic and should not be allowed to enter any water systems [9].

EXPERIMENTAL PROCEDURES

Different physical, chemical and microbiological parameters (Table 1) were investigated for both treated and untreated samples of waste water. The analytical procedures were performed using standard methods [10].

RESULTS AND DISCUSSION

Ozonated water samples were titrated with sodium thiosulphate to find out the concentration of dissolved ozone. The concentration of dissolved ozone increased with the increase in treatment time (Fig. 2). Since cost of treatment is also one of the important factors, a suitable treatment time for effective treatment has to be chosen. It was found that 20 minutes treatment was sufficient to produce observable effects for all the tests carried out in this work. The qualities of the waste water samples were then analyzed both before and after ozone treatments using ANOVA test (at 0.05 level of significance).

Removal of colour

When ozone was bubbled into samples of waste water from domestic, dairy and paint industries, only a slight change in colour of the water samples was observed visually. Surface waters are generally coloured by natural organic materials such

Table 1. Parameters selected and method of analysis.

Parameters	Unit	Method/Instrument used
Color		Visual
Total Solids	mg/L	Gravimetric method
Conductivity	µS/cm	Conductivity meter (Hanna probe, HI 98107)
pH	scale	pH meter (Hanna probe, HI 98303)
Dissolved oxygen	mg/L	Winkler's method
Chemical oxygen demand	mg/L	Reflux method
Manganese	mg/L	UV-Visible Spectrophotometer
Chromium	mg/L	UV-Visible Spectrophotometer
Fecal coliform	CFU/100 mL	Membrane filtration method

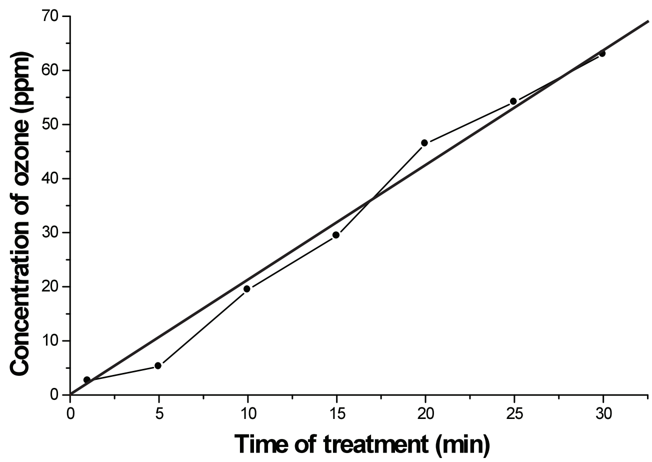

Figure 2. Concentration of ozone dissolved in waste water after different treatment times. —— Linear fit

as humic, fulvic and tannic acids. These compounds are produced from the decay of vegetative materials and have conjugated carbon-carbon double bonds. Ozone is effective in breaking organic double bonds. As more of these double bonds are eliminated, the colour disappears.

Colour in dairy waste water is usually whitish because of high content of milk and organic compounds. In the case of water from paint industry, colour is usually of different types depending upon the pigment used. The main chemical used is 'chrome' which is a combination of chromium ion. Manganese is also commonly used as pigment.

Ozone causes structural change in organic compounds especially humic material causing rapid decrease in colour [11]. The yellow-brown humus can be oxidized, producing a clear product [12]. Ozone oxidizes both the organic compounds as well as heavy metals. It is very effective in breaking the hydrocarbons, which create colour and is widely used in different applications where colour has to be removed or made less noticeable.

Total solids (TS)

TS load is mainly due to organic or inorganic constituents that include salts of various metals as well as sand, grits etc. TS in the three types of samples before and after the treatment are shown in Figure 3.

Domestic waste water shows high TS because it contains a variety of waste from organic to inorganic of different sizes. In an average domestic waste water, total solids are about half organic and half inorganic, and about two-thirds in solution (dissolved) and one-third in suspension.

In the case of dairy waste water, the value is lower than domestic source but

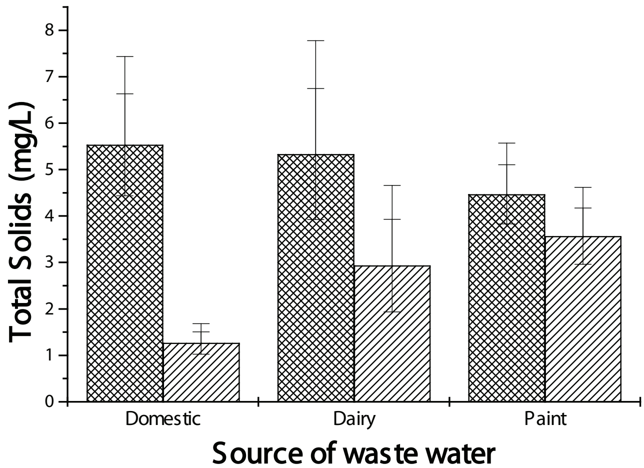

Figure 3. TS before and after treatment. :Untreated
: Treated

greater than paint waste water because it mainly contains high organic compounds mostly milk and less chemicals except those used as preservatives.

Lastly, waste water from paint industry mainly contains chemicals and pigment which are very small in size and are found in dissolved state.

The maximum tolerance limit of industrial effluents into inland surface water according to CBS2008 for TSS is 50 mg/L. All three sources of waste water under study have TSS value lower than the tolerance limit. For TDS, there is no maximum tolerance limit given.

Oxidation of dissolved organic materials by Ozone results in polar and charged molecules that can react with polyvalent aluminum or calcium to form precipitates. Since the precipitates are heavier they tend to settle down faster. Thus, after treatment the value of TS decreases.

Analysis of pH

Figure 4 shows the pH of different samples before and after the treatment. According to CBS2008, the maximum tolerance limit of industrial effluents into inland surface water for pH is 5.5 to 9. The waste water from all the sources studied has pH well below the prescribed values.

The pH of waste water from dairy was less than that of the samples of domestic and paint sources because in dairy, most of the compounds used are organic which include amino acids, carboxylic acid which are slightly acidic in nature and hence the pH is lower. Although in all cases the difference after treatment is not statistically significant, a point to be noted is that all the values are moving toward neutral point, i.e. pH 7 which means neither acidic nor basic.

Literally pH refers to the concentration of hydrogen ions within any solution.

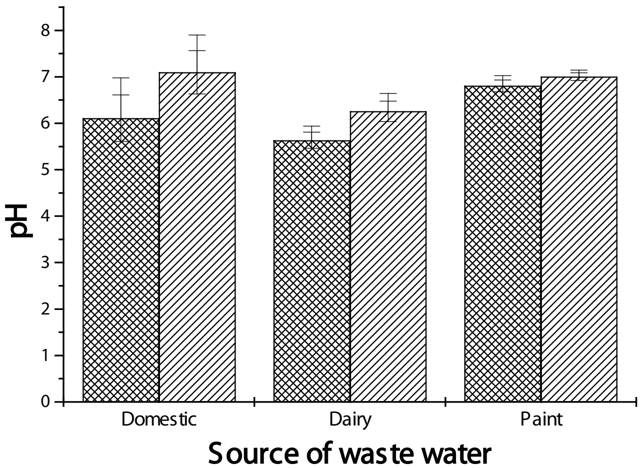

Figure 4. pH before and after treatment. : Untreated
: Treated

Low pH values are connected with high concentrations of hydrogen ions and vice versa. Generally, water with a pH above 7 is much less likely to dissolve heavy metals than water with a pH below 7, and precipitates are formed at higher pH levels since ozone oxidizes the free ions in the solutions to form different salts and the pH value was increased after treatment. Also, there is a negative correlation between dissolved oxygen and hydrogen ion concentration. Since ozone decomposes in water to give oxygen molecules, the pH tends to increase.

Analysis of conductivity (µs/cm)

Electrical conductivity is used as an indication of the amount of total dissolved salts, or the total amount of dissolved ions in water. Conductivity of the samples before and after the treatment is shown in figure 5. As the current is the rate of flow of electric charges, the presence of higher concentration of dissolved ions in the sample leads to higher conductivity. The values of conductivity for all the samples of waste water after treatment do not show large variations.

Ozone in water oxidizes the heavy metals and organic compounds to a form that can be filtered so the total salt concentration is not heavily reduced and hence the conductivity of the solution does not change significantly. Earlier work also reported no significant change in conductivity after ozonation [13].

Analysis of dissolved oxygen (DO)(mg/L)

DO in the case of waste water from paint industry is much greater than dairy source because in dairy and domestic wastes, much of the constituents in them are organic compounds which are degradable by micro-organisms and consume oxygen during degradation.

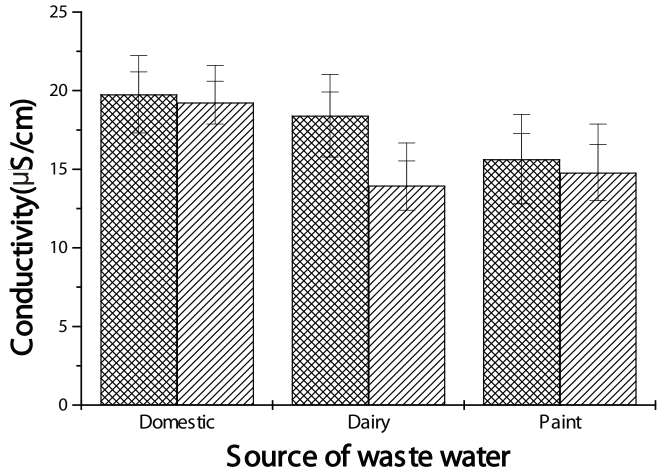

Figure 5. Conductivity before and after treatment. ▩: Untreated ▨: Treated

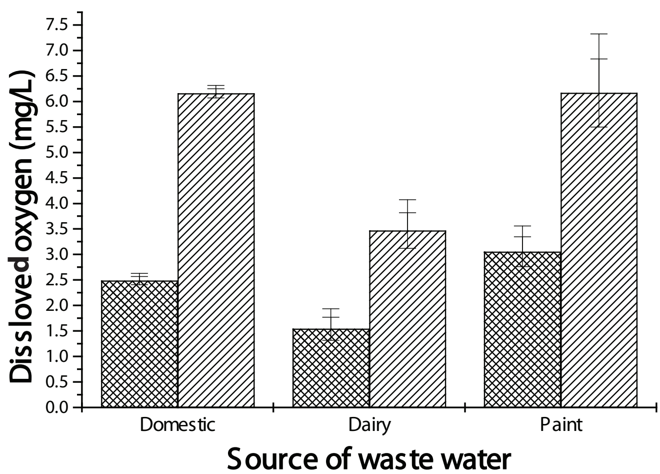

Figure 6. Concentration of DO before and after treatment. ▩ : Untreated ▨ : Treated

According to USEPA, 1972 the minimum DO levels required for protection of aquatic life is 5.8 to 6.8 [2]. After treatment, the values are found to reach or even become higher than the given limits (Fig. 6). Normally, oxygen is not a very soluble gas and the dissolved oxygen concentrations in waste waters are very low. When micro-organisms and an available food supply are present, dissolved oxygen will be consumed.

Ozone is more soluble than oxygen in water and since it is unstable, it decomposes to oxygen in minutes in aqueous media. Use of oxygen feed gas results in treated effluent dissolved oxygen levels as high as 40 ppm [12]. Neutral

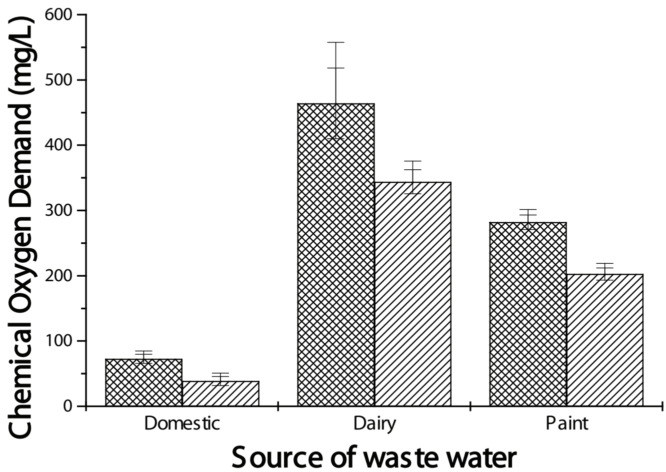

Figure 7. COD before and after treatment. ▩: Untreated ▨: Treated

salts and hydroxylations accelerate this decomposition, which in pure aqueous solution occurs as: $O_3 + H_2O \rightarrow HO_3^+ + OH^-$; $HO_3^+ + OH^- \rightarrow 2HO_2$; $O_3 + HO_2 \rightarrow HO + 2O_2$andHO $+ HO_2 \rightarrow H_2O + O_2$.

Since ozone is formed by addition of oxygen atom to oxygen molecule, when it reacts chemically it releases or decomposes back to oxygen and causes the dissolved oxygen content to increase rapidly. It had been reported that this was one of the principal reasons of choosing ozone as disinfectant in Indiana [11].

Analysis of chemical oxygen demand (COD)(mg/L)

The maximum tolerance limit for COD of industrial effluents discharged into inland surface water, according to CBS, 2008 is 250 mg/L. In the case of the samples of waste water from domestic and paint industry, COD was higher than the given limit and treatment by ozone brought the levels below the limit. However, the COD value for dairy industry waste is very high. Although COD decreased after treatment, the value was still well above 250 mg/L (Fig. 7).

This suggests that for waste water from dairy industry the treatment time is not sufficient and has to be increased. DO in the case of waste water from paint industry was much greater than samples from dairy industry but waste water from paint industry showed high COD. This is because, although COD refers to oxygen required to break down organic compound by potassium dichromate, ozone being a strong oxidizing agent may also oxidize chemicals present in the paint. Ozone readily attacks carbon-carbon double bonds, certain carbon-nitrogen double bonds, and nucleophiles such as amines and selinides. Other bonds, such as carbon-hydrogen, react favourably with ozone but only in the absence of competition from the above [12]. Oxidation of organic compound by ozone and

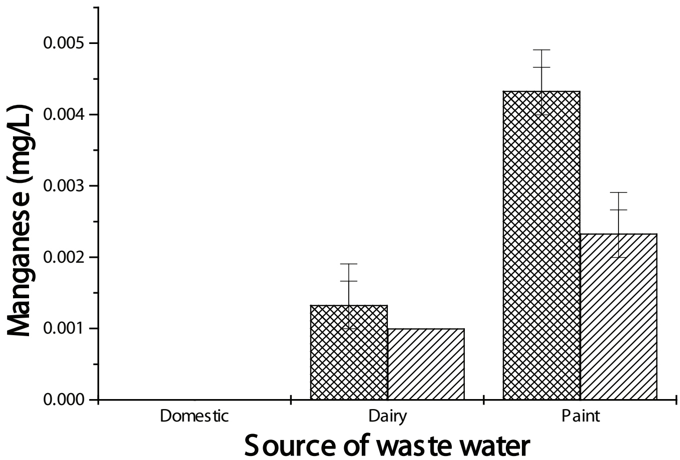

Figure 8. Concentration of Manganese before and after treatment. ▩: Untreated ▨: Treated

generation of oxygen decreases the demand for oxygen and reduces the COD level.

Analysis of heavy metals (mg/L)

Manganese. Manganese was not found in domestic waste water. Manganese in paint is used as a pigment and hence its concentration is higher than in samples from dairy waste. Normally, manganese is not added in dairy products hence its presence in the waste water is probably due to contamination. But in both cases the concentration is very low (Fig. 8).

Manganese in water is usually present in dissolved form. After ozonation, the ozone oxidizes the metal ion into higher oxidation state, i.e. +4 state and getsprecipitated. Oxidation of manganese occurs as follows: $Mn^{+2} + O_3 + 2H_2O \rightarrow Mn^{+4} + O_2 + 2OH^-$.

Chromium. In the samples from paint industry the concentration of chromium is higher because it is the colour forming agent used in paint. The maximum tolerance limit of industrial effluents into inland surface water according to CBS, 2008 for Cr is 2mg/L, and in all sources of waste water the concentration of chromiumis is fairly low (Fig. 9).

Ozone oxidizes the transition metals to form $Cr(OH)_3$ which is in colloidal form which is then easily separated by filtration. Other metals such as arsenic (in the presence of iron), cadmium, chromium, cobalt, copper, lead, manganese, nickel, and zinc can be treated in a similar way. Ozone does not remove iron or manganese from water, but it can facilitate their removal. Once these metals are oxidized, they can be easily filtered.

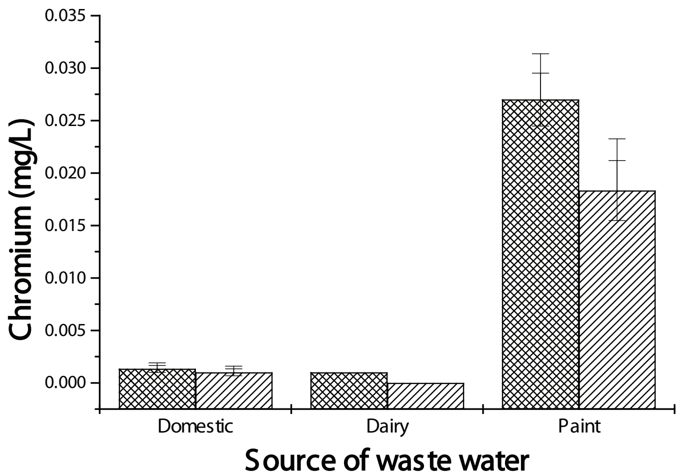

Figure 9. Concentration of Chromium before and after treatment. ▨: Untreated ▨: Treated

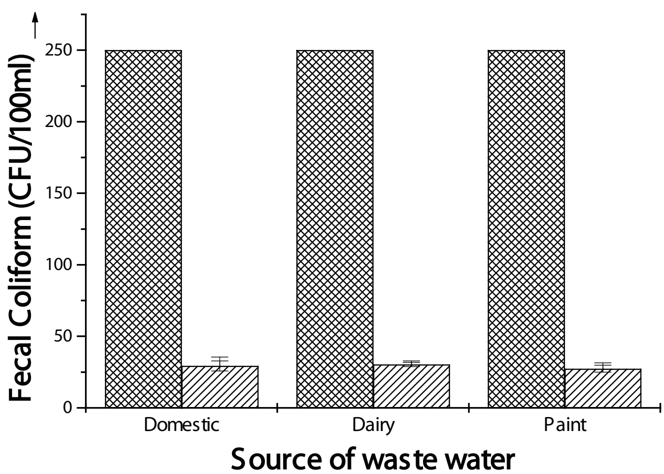

Figure 10. Fecal coliform count before and after treatment. ▨: Untreated ▨: Treated

Analysis of fecal coliform (CFU/100 mL)

The mean value of concentration of Coliform Formation Unit (CFU) per 100 mL of fecal coliform for the three replicates of samples of waste water from domestic, dairy and paint industry (Fig. 10) were Too Many to Count (TMC), i.e. more than 250 which is the maximum number of pores in the membrane filter. The heavy contamination of fecal coliform in the waste water may be due to contamination during storage.

The ANOVA test shows that ozone is a very good disinfectant. Ozone causes damage to cell membrane, nucleic acid and some enzymes. Similar result has also been reported in our earlier experiment on treatment of drinking of water [14].

It has also been reported that ozone concentration as low as 0.0l ppm is toxic to *Escherichia coli* and *Streptococcus faecalis* at pH 7.0 and 25 °C in pure systems and it is more effective than chlorination. In general, ozone dosage of 5 to 10 ppm is adequate to achieve disinfection to a plate count of 200/100 mL of fecal coliform, which is a typical waste water requirement [12].

Disinfection by ozone occurs through the rupture of the cell wall because bacteria are single cellular and their cell wall consists of lipid layer. Ozone attacks the double bond of the lipid bi-layer causing lysis of cell wall [15]. This is more efficient than chlorine which depends upon diffusion into the cell protoplasm and inactivation of the enzymes.

CONCLUSION

After 20 minutes of treatment time for all sources of waste water, ozone did not change the physical property of water significantly. However, the results indicated the increase in DO concentration and pH to some extent. Ozone also lightens the colour of waste water, decrease COD and TS. It was also observed that, ozone efficiently precipitated metals and caused substantial reduction of fecal coliform, a key element for various water related health problems in a country like Nepal. For practical application of ozonation for waste water treatment, which is expected to be carried out in large scale, the treatment time should be increased to longer than 20 minutes.

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