

## Chlorine Demand and Water Pollutants of Pond and River Water

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### Abstract

*Bacteriological impurities due to pathogenic bacteria, organic and inorganic contaminants in water may pose health risks and unfit for drinking purpose. Chlorination is a popular disinfectant which kills and removes a broad spectrum of pathogenic microorganism and prevents the regrowth of harmful bacteria and viruses. Residual chlorine, Chlorine demand, alkalinity and pH were measured to characterize the water quality of pond, Bagmati, Bishnumati and Dhobikhola rivers. The effects of pH, chlorine dose and contact time on chlorine demand were determined by using starch iodine method. The sample water from Bishnumati and Dhobikhola rivers were turbid and black in colour whereas Bagmati river water was grey and pond water was turbid and white in colour. The pH of water sample ranged from 6.13 to 8.27. Bagmati river water was slightly basic (pH=8.27) while Bisnumati river water was slightly acidic (pH=6.13). The alkalinity of pond water was very low (60 ppm) while that of Bagmati river water was very high i.e., 494 ppm. The alkalinity of Dhobikhola river water was 310 ppm and that of Bisnumati river water was 190 ppm. The preliminary analysis showed that the river water was highly polluted and pond water was comparatively less polluted.*

*The analysis of chlorine demand reveals that the disinfection of chlorine was medium at the pH range 6 to 9. The pH (6.13-8.27) of pond and river water indicated that hypochlorous acid and hypochlorite ion both actively participate on disinfection of water. The results reveals that highly turbid water from Bishnumati river had high chlorine demand (23.40 ppm) and it took about 60 min for disinfection. The chlorine demands of Dhobikhola river and Bagmati river water were 20 ppm (contact time: 50 min) and 12.30 ppm (contact time: 30 min), respectively. Pond water was less turbid and had chlorine demand of 0.18 ppm (contact time: 15 min). It attributes that high chlorine demand took long contact time for disinfection. The grey and black colour of water and high chlorine demand implied that the river water was severely polluted. This study concludes that the river water contains high amounts of organic/inorganic and pathogenic contaminants which increases contact time to consume large amount of chlorine for disinfection of polluted water hence are not applicable in any domestic consumptions.*

**Keywords:** Chlorine demand, Contact time, Water pollution.

### Introduction

Kathmandu valley is one of the most populated cities of Nepal. The population of Kathmandu is near about 2 million<sup>1</sup>. Well, pond, river, tap etc., are the main sources of water in Kathmandu. Nowadays, the water sources in Kathmandu are polluted at alarming rate due to the industrial effluents, hospital discharge, municipal waste, drainage disposal etc. The bacteriological impurities such as pathogenic

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bacteria and organic contaminants in water pose health risks and unfit for its use hence water quality is the great public health concern. However, the poor peoples in Kathmandu are using pond and river water directly without any treatment or purification for cooking, bathing, drinking etc. Without investigation and treatment, the use of such polluted water may create severe health related problems. The water containing pathogenic bacteria generates water borne diseases including diarrhoea, typhoid. World Health Organization estimates that 3.4 million people, mostly children, die every year from water related diseases<sup>2</sup>. In Nepal, the total cases of diarrhoea was 1,398,106 and among them 206 diarrhoeal death occurred in the fiscal year 2064/2065<sup>2</sup>. Water borne infectious diseases not only cause loss of life and illness but also have negative effects on the economy related to medical expenses and productivity<sup>3</sup>.

Hence, to protect people from water borne disease, treatment of water is necessary before its use. According to World Health Organization (WHO), potable water should be odorless, tasty and free from any kind of microorganism and chemical substances. Among the various oxidants/disinfectants, chlorine and chlorine compounds are most widely used disinfectant to get rid of pathogenic bacteria from drinking-water treatment because of its favorable effects, reasonable cost, and much longer residual effects. Chlorine is powerful oxidizing agent, able to penetrate cells and on vital cellular substances, to kill microorganisms<sup>4,5</sup>.

When chlorine is added to water, at first some of the chlorine reacts with organic materials and metals in the water this is called chlorine demand of the water. The remaining chlorine concentration after the chlorine demand accounted is called residual chlorine. The chlorine demand of a water sample is the difference between the concentration of chlorine added to the sample and the concentration of the chlorine residual that remains at the end of a specified contact time. The chlorine demand is highly influenced by water quality because chlorine readily reacts with many compounds, including ammonia (NH<sub>3</sub>), nitrate (NO<sub>3</sub>), natural organic matter (NOM), iron (Fe), manganese (Mn) and many others<sup>8,9,10,11</sup>. Abdullah et al. (2009)<sup>8</sup> showed that chlorine demand increased with increased in concentrations of NH<sub>3</sub>-N, increased in pH, and increased in ultraviolet (UV) absorbance in the water. Powell et al. (2000)<sup>12</sup> observed that chlorine demand increased with increase in temperature and total organic carbon (TOC). These studies attribute that the chlorine demand depends on concentration of organic and inorganic pollutants hence, measurement of chlorine demand can determine the water quality i.e., amount of pollutants present in the water.

On the other hand, high concentration of chlorine such as about 2 to 3 ppm creates unpleasant taste and odor in water. Further, disinfection by chlorine shows problems such as the production of trihalomethane (THM) from its reaction with natural organic matter (NOM) in water<sup>4,6</sup>. Even though residual chlorine generates unpleasant taste and odor in water, it is necessary to maintain an appropriate chlorine concentration in water from finished water to prevent the re-growth of harmful bacteria and viruses within the distribution system. The concentration 1.5 to 2.0 ppm of free residual chlorine is essential in drinkable water<sup>6</sup>. WHO specifies desirable concentration of chlorine in drinking water should be around 0.2 – 0.5 ppm for 30 minute of contact in all points in the supply and about 1.0 ppm in the treatment plant<sup>7</sup>.

The objectives of this study is to measure water quality parameters such as temperature, colour, pH, alkalinity and residual chlorine of water from different sources and finally determining the water quality of pond and river water by analyzing chlorine demand of those water in more detail.

## **Experimental Methods**

### **Sample collection and storages**

Water samples were collected from different sources in Kathmandu valley. The jar water, tap water, tanker water, spring water and rain water were collected from the Kirtipur for the preliminary analysis. Samples were collected during rainy season (May 2017). The pond water was collected from Bhanjanganal which is used by local people for daily consumption. The river water were collected from Bagmati river water, Dhobikhola river water and Bisnumati river water. Pond water sample and river water samples were collected by dipping 5 litre bottle in the edge of pond and river and stored in cool place. Analysis of thus collected samples water was carried out as soon as possible. Temperature and pH were measured on the spot during sampling for all samples. The collected samples of pond water and river water were used to determine pH, alkalinity. The chlorination of water sample was done by using Piyush water (0.5% chlorine solution) available in local market. From the chlorinated water residual chlorine was measured and chlorine demand was calculated.

### **Measurement of different parameters of water sample:**

The pH of well water sample was recorded directly with the help of pH meter. The pH meter was calibrated with the help of standard buffer solutions of pH 4.2 and 9.0. Alkalinity of water was determined by the titration of water sample against a standard acid using phenolphthalein and methyl orange as indicator.

### **Chlorine demand**

The iodometric titration method is used for the determination of chlorine. Chlorine will liberate free iodine from potassium iodide (KI) solutions. The liberated iodine is titrated with a standard solution of sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3$ ) with starch as the indicator. 200 mL water sample was taken in 250 mL BOD bottle and standard chlorine water solution of 200 ppm strength was added to a series of portion of the samples using increment of 1-2 ppm chlorine. After 30 minute contact time residual chlorine was determined. For the determination of the residual chlorine 2 mL of acetic acid was added followed by 25 mL KI solution (25 % solution prepared freshly each time) to each of the bottle. Instantly each of the bottle was titrated with standard solution of sodium thiosulphate (0.00357 N) using starch solution as indicator.

### **Effect of pH on chlorine demand**

The effect of pH on chlorine demand was studied by performing starch iodine titration method. Where chlorine residual were determined at fixed dose of chlorine for the number of different sample in which 50 mL buffer solution [without chlorine demand] were added and pH of samples were fixed as 3.8, 4, 5, 5.3, 6, 7, 8, 9, 10, 11.

### **Contact time**

The chlorine demand of different water sample were determined with the increment of time and relations between contact time and chlorine demand were studied.

## **Results and Discussion**

### **Physical parameters of water sample**

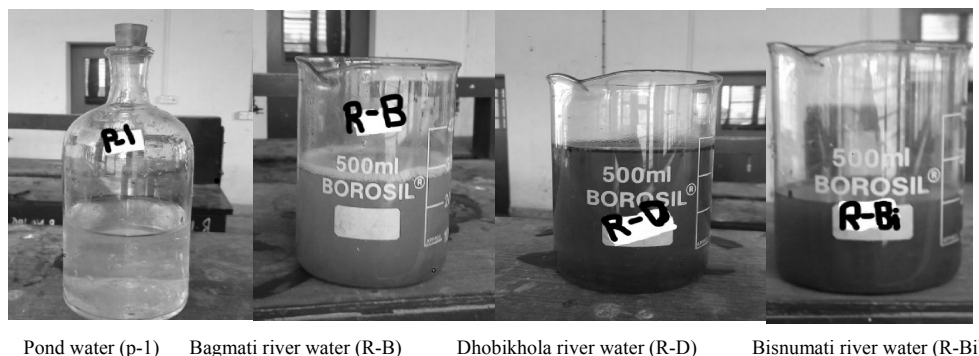
Temperature influences the water quality. High temperature limits oxygen dispersion into deeper waters, contributing to anaerobic condition which leads to increase bacteria levels. Indirectly, the high

summer temperature can cause high chlorine demand because bacteria usually grow better in warmer water. Table 1 showed the observed temperature of water sample. The temperature of pond and river water was 27 °C and that of Jar water, City supply and Tank water was about 26 °C.

**Table 1: Water quality parameterization**

Water sample	Temperature (°C)	Colour	pH	Residual Chlorine (ppm)	Alkalinity (ppm)
Jar water	26	Colourless	6.80	0.41	-
City supply	26	Colourless	6.90	0.30	-
Tanker water	26	Colourless	7.3	0.0	-
Pond water	27	Turbid	6.13	0.0	60
Bagmati river	27	Grey	8.27	0.0	494
Dhobikhola river	27	Black	6.79	0.0	310
Bishnumati river	27	Black	6.62	0.0	190

The colour of water varies with the ambient condition in which that water was present. Small quantities of water appeared to be colourless, however, the suspended and dissolved particles in water influenced the colour of water. Hence, water colour can indicate physical, chemical and bacteriological conditions. The colour of the water sample observed in this study was tabulated in Table 1. Table 1 showed that the Jar water, Tanker water, City supply water were colourless whereas pond water was slightly turbid and white in colour and river water were not colourless but grey and black in colour. The colour of water sample indicated that the pond and river water were polluted, they might contain dissolved inorganic/organic contaminants, soil, pathogenic bacteria etc<sup>13</sup>. The photographs of pond and river water were shown in Figure 1. The photograph also showed that river water were highly polluted than pond water.



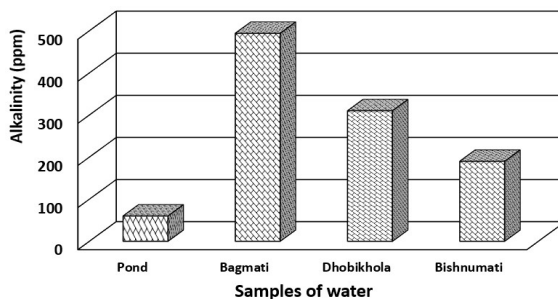
**Figure 1: Water samples from pond and rivers**

pH measures the activity of hydrogen ions [H<sup>+</sup>]. High and low pH indicate the water quality. The water with a low pH (<6.5) could be acidic, soft and corrosive similarly water with a high pH (>8.5) could be basic, hard and corrosive in nature. Low pH kill fish and aquatic animals by stressing animal system and causing physical damage but bacteria can survive even at pH 2.0. Further, pH affect the effectiveness of chlorine application. It is considered that normally at pH 7.3, 50% of the chlorine present will be in the form of HOCl and 50% in the form of OCl<sup>-</sup>. At low pH, effectiveness of chlorine is

dominated by HOCl species however, at high pH it is dominated by hypochlorite ion (OCl<sup>-</sup>) species<sup>14, 15</sup>. The pH of different water samples measured in this study was tabulated in Table 1. The value of pH obtained were within the range 6.5 to 8.5, recommended by WHO (1996) for drinking water. The Table 1 showed that the pH of Bagmati river (8.27) water was slightly alkaline as compared to other river water (6.62 and 6.79). The pH of the water sample attributes that disinfection of chlorine will be effected by both HOCl and OCl<sup>-</sup>.

The residual chlorine measured in water samples from different sources was tabulated in Table 1. The residual chlorine in drinking water indicates that chlorine added in water was sufficient to inactivate the bacteria and some viruses that cause water borne diseases. The measurement of residual chlorine can indicate the potability of water because the presence of residual chlorine indicates that there is free chlorine available to inactivate organisms which cause water borne diseases. The residual chlorine of 1.5 to 2.0 ppm in concentration is essential in drinkable water to kill germs and prevents the regrowth of harmful bacteria and viruses till its use<sup>6</sup>. Table 1 showed that Jar water and City supply water have the residual chlorine of 0.41 ppm and 0.30 ppm, respectively. Tank water, pond water and river water had no chlorine residual. The result showed that the Jar water and City supply water was treated before its distribution and it contains enough residual chlorine to prevent regrowth of harmful bacteria and viruses hence they are potable<sup>7</sup>. However, water from other sources are not potable hence must be analysed in more detail and must be treated before its use.

Alkalinity is another parameter which indicates the water's ability to neutralize acids. It results primarily from dissolving limestone or dolomite minerals in the water. It measures the presence of carbonate, bicarbonate and hydroxyl ions in water. It is again important because it acts as a stabilizer for pH or buffers against rapid changes in pH of water. Water with low level of alkalinity (< 155 PPM) is more likely to be corrosives<sup>13</sup>. Fig. 2 shows the alkalinity of different water samples. Alkalinity of pond water was much lower than that of river water. There are a great variation in alkalinity value of river water. It was found that alkalinity of Bagmati river water (494 ppm) was higher than Dhobikhola river water (310 ppm) and Bisnumati river water (190 ppm). The alkalinity of Bisnumati river water was lower than Dhobikhola river water. Measurement of pH also attributed similar result i.e., the Bagmati river water was more alkaline than pond water and Bishnumati river water was less alkaline than Dhobikhola river water. Low alkalinity of pond water indicates that there were less amount of calcium and magnesium ions. The high alkalinity value of Bagmati river water attributed that the water was highly contaminated with alkaline pollutants such as soil, chemicals from runoff, waste from aquatic animals and decaying organic material<sup>16</sup>.

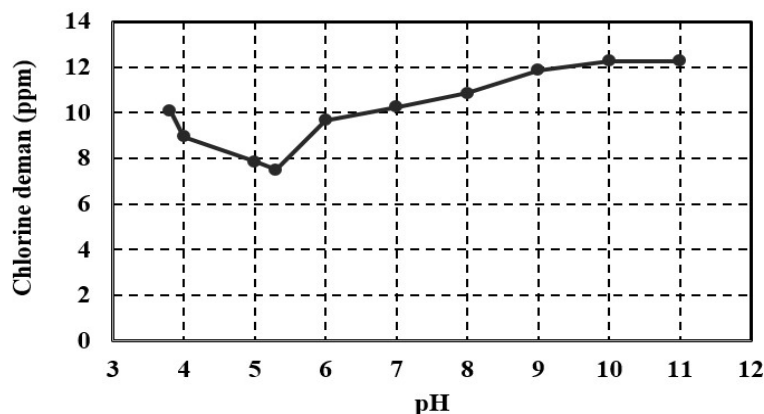


**Figure 2:** Alkalinity of water samples collected from pond and rivers.

From the preliminary result, it was considered that the Jar water and City supply water were potable and pond water and river water were polluted. The colour and turbidity indicated that they may contain inorganic and organic contaminants as well as pathogens. So further detail analysis is necessary to characterize the water quality of pond and river water. Therefore, pond and river water were further parameterized by measuring the chlorine demand.

#### **Effect of pH on chlorine demand**

Chlorine, whether in the form of pure chlorine gas, sodium hypochlorite or calcium hypochlorite, dissolves in water to form hypochlorous and hydrochloric acids. The hypochlorous acid (HOCl) is a weak acid partially dissociates to hydrogen ion ( $H^+$ ) and hypochlorite ions ( $OCl^-$ ). The equilibrium between undissociated hypochlorous acid and hypochlorite ions depends on pH. Thus any free chlorine or hypochlorite ion ( $OCl^-$ ) added to water would immediately form either HOCl or  $OCl^-$  and that was controlled by the pH value of the water<sup>14, 17</sup>. This is extremely important since HOCl and  $OCl^-$  differ in disinfection ability. HOCl has a greater disinfection potential than  $OCl^-$ . At high pH ( $> 8$ ) the dissociated forms predominate and below pH 6, the hypochlorous acid is very poorly dissociated<sup>18</sup>. The effect of pH on chlorine demand in river water was determined using water sample from Bagmati river, which was shown in Figure 3.

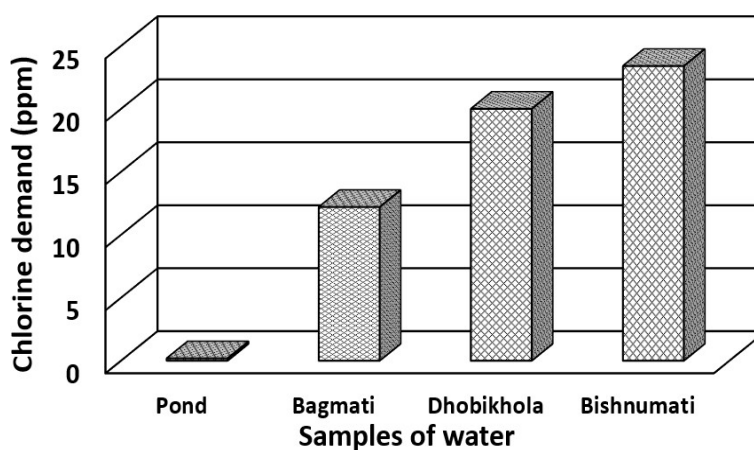


**Figure 3:** *Effect of pH on chlorine demand of Bagmati river water*

The Fig. 3 showed that the chlorine demand was about 10 at pH 4 and decreased to about 7.5 at pH 5, which was the minimum chlorine demand. Further increasing the pH, the chlorine demand increases slowly and remains almost constant above pH 10. It clearly indicated that the disinfection of chlorine is more effective at pH 5.3 and medium between pH 6 and 8 but less effective above pH 9. At pH 5.3, hypochlorous acid was more dominated and in between pH 6 and 8, both hypochlorous acid and hypochlorite ions act effectively, however above pH 9 hypochlorite ions were dominated for disinfection<sup>18</sup>. The results reveal that chlorine disinfection was more effective between pH 4 to 6. As shown in Table 1, the pH of pond and river water varies between 6.6 and 8.2. Hence, it was considered that the HOCl as well as  $OCl^-$  both will act as disinfectant species hence, effectiveness of chlorine will be medium and will remain almost constant at observed pH (6.2- 8.27) of pond and river water.

### Chlorine demand

Chlorination of water is the most widely used method of disinfection nowadays because it kills and removes a broad spectrum of pathogenic microorganism responsible for water borne diseases<sup>6, 11, 19</sup>. The amount of chlorine applied is related to the demand of the source water, which is the amount of chlorine needed to satisfy all chemical reactions. Chlorine demand generally increases with increasing concentrations of inorganic matter, organic matter, bacterial count, conductivity etc.<sup>20</sup>. Turbidity can have great effect on the chlorine demand of the system as it is composed of both inorganic and organic matters. Total organic carbon (TOC), which is associated with turbidity, exerts a very large chlorine demand<sup>12</sup>.



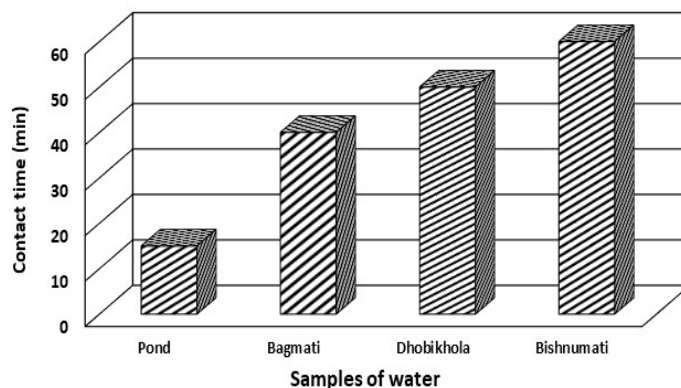
*Figure 4: Chlorine demand of water samples from pond and rivers*

The preliminary results [Fig. 1] showed that pond water was slightly turbid but Bagmati river water was highly turbid than pond water. Bisnumati river water and Dhobikhola river water were more turbid than Bagmati river water. Bisnumati river water was highly polluted/turbid than pond, Bagmati river, Dhobikhola river water. The chlorine demand of all samples was plotted in Fig. 4. The figure shows that chlorine demand of pond water was about 0.18 ppm whereas that of Bagmati river water was 12.30 ppm. Chlorine demand of Dhobikhola river water was 20.00 ppm. Bisnumati river water shows highest chlorine demand of 23.00 ppm. The colour of water samples reveals that river water contain large amount of inorganic and organic pollutants, which increase turbidity, which was responsible for high chlorine demand in Bishnumati river water. From the results it is considered that Bishnumati river water was most polluted among the observed river water in this study.

### Contact time

The contact (retention) time in chlorination is that period between introduction of the disinfectant and when the water is used. A long interaction between chlorine and the microorganisms results in an effective disinfection process. Contact time varies with chlorine concentration, the type of pathogens present, pH, and temperature of the water. The contact time of chlorination in pond and river water was plotted in Fig. 5. It was found that the contact time of Bishnumati river water was highest among all the

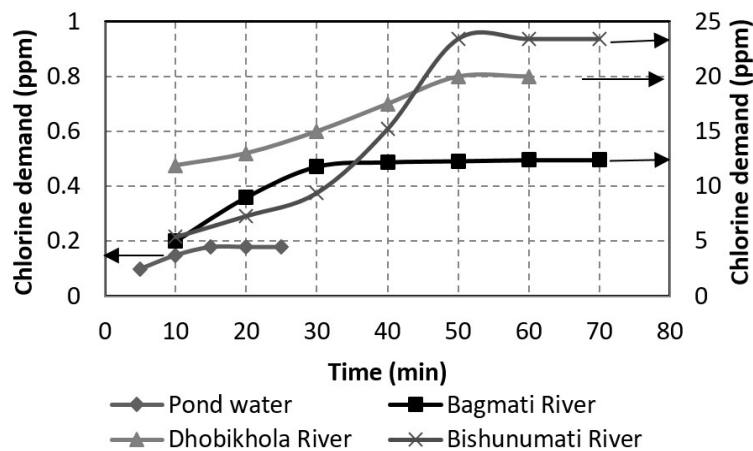
samples. The temperature and pH of all samples were almost similar, hence, the long contact time is the indications of presence of high level of pathogens.



**Figure 5:** Contact time of chlorination of pond and river water.

The variation of chlorine demand with contact time was plotted in Fig. 6. The figure shows that chlorine demand of pond water increases with time initially and becomes constant after 15 minute with chlorine demand of 0.18 ppm. This attributed that the equilibrium condition reach at about 15 min. The pond water was more or less clear and has very low chlorine demand. Hence, about 0.2 ppm chlorine dose and about 15 min is enough to kill germicides, bacteria, viruses in pond water. The chlorine demand of pond water is within the WHO standard hence can used for domestic purpose after treatment.

In the case of Bagmati river water the chlorine demand slowly increases initially and reached almost constant at about of 12.30 ppm. Figure shows that after 30 minute of contact time chlorine demand becomes constant i.e., it reaches a desired level of chlorine after 30 minute of contact time.



**Figure 6:** Variation of chlorine demand with contact time of water from Pond and river.



The chlorine demand of Dhobikhola river become constant at contact time of about 50 minute.

The Bisnumati river water shows highest chlorine demand of 23.40 ppm after contact time of 60 minute. Not only Bisnumati river, Bagmati and Dhobikhola rivers were also polluted and had high chlorine demand but less than Bisnumati river. It attributes that river water contains large amount of pathogens, they may cause various diseases like diarrhoea, fever, typhoid and many more when people or lives come in contact with these river water. WHO reported that chlorine demand greater than 5 ppm in water is dangerous for living beings<sup>7</sup>. These three rivers i.e. Bagmati, Bisnumati and Dhobikhola that had chlorine demand three to 5 times greater than 5 ppm which are dangerous for living beings and not useful for any purpose.

### **Conclusions**

The water quality parameterization was performed taking sample from city supply, jar water, tanker water, pond water and river water. It was found that temperature of water samples varied between 26 and 27 °C and pH varied between 6.2 and 8.27. The jar water, city supply and tanker water were colourless and pond water was turbid. The Bagmati River, Bishnumati river and Dhobikhola river water were grey to black in colour. It was found that city supply water (0.35 ppm) as well as Jar water (0.41 ppm) had sufficient chlorine residual as reported by WHO. The remaining water sample showed zero chlorine residue. The alkalinity of water was measured using pond water from Bhanjangan, Bagmati river, Bishnumati river, Dhobikhola river water samples. The alkalinity of Pond water was very low (60 ppm) while that of Bagmati river water was very high i.e., 494 ppm. The alkalinity of Dhobikhola river water was 310 ppm and that of Bisnumati river water was 190 ppm. The results of preliminary analysis showed that the city supply water and jar water were potable however, pond water and river water were not potable, because those water contains inorganic/organic contaminants.

The chlorine demand of pond water was 0.18 ppm (at contact time of 15 minute) and that of river water was higher than 12 ppm. Water of Bisnumati river was highly turbid/contaminated than Bagmati and Dhobikhola river water it was black in colour thus have high chlorine demand of 23.40 ppm and contact time of 60 min. Dhobikhola river water was highly turbid than Bagmati river water and have higher chlorine demand (20 ppm) than Bagmati river water (12.30 ppm). From this study it is concluded that the pond water can be used as a potable water after treatment but river water were highly polluted and contains a lot of inorganic, organic and pathogenic contaminants hence, can't be utilize as such in any purposes.

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### **References**

1. B. Bista, *Central Bureau of Statistics, Kathmandu, Nepal*, NPHC2011, 2014, **6**.
2. A. Khaysat, *M.E. Thesis*, Massachusetts Institute of Technology, USA, 2000.
3. P. Corso, M. Kramer, K. Blair, D. Addiss, J. Davis, A. Haddix, *Wisconsin., Emerging Infect. Dis.* 2003, **4**, 426-431.
4. J. J. Rook, *Journal American Water Works Association*, 1976, **68 (3)**, 168-172.

5. G.C. White, *Handbook of chlorination and alternative disinfections*. 3<sup>rd</sup> Ed. New York: Van Nostrand Reinhold Publisher, Inc. 1992.
6. E. F. Jaguaribe, L. L. Medeiros, M. C. S. Barreto and L. P. Araujo, *Brazilian Journal of Chemical Engineering*, 2005, **229(1)**, 41-47.
7. WHO, Chlorination concept, Fact Sheet **2.17**
8. Md. P. Abdullah, L. F. Yee, S. Ata, A. Abdullah, B. Ishak, B. and K.N. Z. Abidin, *Journal of Physics and Chemistry*, 2009, **34**, 806
9. B. Barbeau, R. Desjardins, C. Mysore and M. Prévost, *Water Research*, 2005, **39**, 2024.
10. R. M. Clark and M. Sivaganesan, *Journal of Environmental Engineering*, 1998, **124(12)**, 1203
11. L. F. Yee, Md. P. Abdullah, S. Ata, and B. Ishak, *The Malaysian Journal of Analytical science*, 2006, **10(2)**, 243-250.
12. J. Powell, J. West, N. Hallam, C. Forster and J. Simms, *Journal of Water Resources Planning and Management*, 2000, **126(1)**, 13
13. G. Gilbert, S. Bregt, T. Satoshi and W. W. Delmer, *Journal of American Water Works Association*, 1990, **1(6)**, 160-165.
14. Bitton G. *Wastewater Microbiology*, 1999, Wiley-Less, New York
15. M. J. Borucke, *Master thesis*, 2002, Massachusetts Institute of Technology
16. M. Kafle, *Master Project report*, 2016, Central Department of Chemistry, Tribhuvan University.
17. Y. Kott, E. M. Nupen and W. R. Ross, *Water Research* 1975, **9**, 869-872.
18. G. D. White., *Handbook of chlorination*, 2<sup>nd</sup> edition, Van Nostrand Reinhold Company New York, 1986.
19. M. W. LeChevallier, *Journal AWWA*, 1999, **91(1)**, 86.
20. J. M. Gile, *Thesis and Dissertation*, University of Arkansas, Fayetteville, 2013.