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Estimation of short-term chlorine demand and its correlation with available iron in drinking water
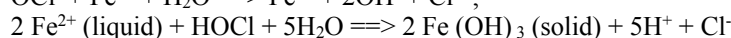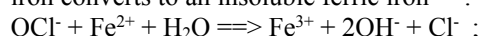
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Abstract
This study describes the effect of iron on chlorine demand and the efficiency of chlorination in drinking water. To find out the association between short term chlorine demand and available iron, 15 raw water samples were analysed for iron as well as other physicochemical parameters and then dosed with 7.8 mg/l & 3.9 mg/l of chlorine respectively. In chlorinated water samples, chlorine demands were estimated at 30 minutes and 24 hours of contact time respectively. It reveals that chlorination of water containing higher iron concentration lowers the amount of residual chlorine causing elevated chlorine demand and this may happen more rapid within 30 minutes of addition of chlorine to water than that of 24 hours. Data point of all analysed sample suggests that the concentration of available iron in drinking water is positively correlated (r >0.6; *p*<0.05) with chlorine demand.

Keywords: chlorination; chlorine demand; correlation; drinking water; iron; residual chlorine.

1. Introduction
Water disinfection through the process of chlorination is commercially economic and cost-effective [1]. It is also a well-known method worldwide to maintain microbiological quality of drinking water and to reduce the risk of contracting waterborne diseases [2]. However, the amount of chlorine that should be added for effective disinfection depends on the chlorine demand of water. Generally, chlorine is added to water as chlorine gas (Cl_2) or as a solution made from either sodium hypochlorite (NaOCl) or calcium hypochlorite (Ca [OCl]$_2$) in the form of hypochlorous acid (HOCl) or hypochlorite ion (OCl$^-$) [3]. The amount of chlorine required for a particular water sample during chlorination depends on the impurities present in raw water and the process of disinfection is measured by the characteristics of disinfectant, microorganism and environmental factors [4] and subsequently, the effectiveness of this process depend on raw water quality; disinfectant dosage; disinfection types; and contact time [3]. Dychdala [5] demonstrated that chlorine control the growth of micro-organism, reacts with organic nitrogen compounds produced from the decomposition of organisms and their wastes to form compounds with little or no disinfecting ability, effectively decreasing the concentration of available chlorine and results the chlorine demand. According to Clark [6] there are three factors commonly responsible for chlorine consumption in water distribution system: (a) reactions with biofilm (b) reactions with inorganic and organic chemicals in the bulk aqueous phase; and (c) consumption by the corrosion process. Chlorine is also a non-selective oxidant and so mostly reactive with a wide variety of compounds having reduced valence state (e.g. ammonia [NH_3], sulfide [S^{2-}], manganese (II), iron (II), sulfite [SO_3^{2-}], Br$^-$, iodide [I$^-$], nitrite [NO_2^-]) [7-8]. In aqueous solution, it oxidizes ammonia (NH_3) to form chloramines (at Cl_2 to NH_3 ratios less than 8:1) [9]. During the time of chlorination, iron reacts with chlorine (in the form of hypohlorite or hypochlorous acid) in water [7] and soluble ferrous iron converts to an insoluble ferric iron [10].

$$OCl^- + Fe^{2+} + H_2O \Longrightarrow Fe^{3+} + 2OH^- + Cl^- \; ;$$
$$2\,Fe^{2+}\,(liquid) + HOCl + 5H_2O \Longrightarrow 2\,Fe\,(OH)_3\,(solid) + 5H^+ + Cl^-$$

Kiene and Levi [11] showed that an electrochemical cell containing chlorinated water and an iron electrode can cause consumption of chlorine and which is directly proportional to the iron dissolution. Natural organic matters (NOMs) react with free chlorine to form halogenated disinfectant by-products (DBPs) such as tri halomethanes(THMs), halo acetic acids(HAAs), halonitriles(i.e. cyanogen chloride), Halophenols (i.e. 2-chlorophenol, 2, 4-dichlorophenol, 2, 4, 6-trichlorophenol), halonitromethanes (i.e. chloropicrin), haloaldehydes (i.e. chloral hydrate) [12-13].

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DBPs formation reactions are relatively fast and result in the consumption of chlorine and eventually decrease the concentration of chlorine with time [7, 14-15]. Therefore, it can be seen that several factors are accountable for the estimation of chlorine demand. Warton *et al.* [16] defined short-term chlorine demand (0–4 h) and long-term chlorine demand (4–168 h). In this study, we also used the term "short-term chlorine demand", because we only measured free chlorine demand for particular dosage (i.e 7.8 mg/l and 3.9 mg/l) at 30 minutes and 24 hours of exposure instead of several more hours, days or weeks. The main focus of this study was to estimate the short-term free chlorine demand with respect to the consumption of chlorine with particular exposure time and to find out the extent of correlation particularly in between chlorine demand and available iron along with other physicochemical parameters in drinking water collected from a rural community in Bangladesh.

2. Methods
2.1 Raw waters
Raw water samples were collected from a rural community of Kishoreganj district in Bangladesh which is 130 kilometers away from the Dhaka Metropolitan City. Fifteen untreated drinking water samples were collected into high density polyethylene containers maintaining 4 °C to 10 °C temperature in the cool box and transported to the laboratory within 24 hours of collection with the logistic support of International Centre for Diarrhoeal Diseases Research, Bangladesh (ICDDR, B). Then Samples were immediately processed for the measurement of pH using a pH meter (Orion 2star, benchtop pH meter, Thermo Scientific, USA), turbidity using a turbidity meter (Oakton, T-100 Turbidimeter, Singapore), temperature and conductivity using a conductivity meter (Hach, sension5 conductivity meter, USA), residual free chlorine (method described below) and thereafter prepared for chlorine dosing. All experiments were carried out in the environmental laboratory of ICDDR, B.

2.2 Chlorine dosing procedure
Sodium hypochlorite solution (Clotech, Global heavy chemical, bd.) containing 5.25% of free available chlorine was used as the chlorinating agent. All water samples (including chlorine demand free deionized water for the control run) were dosed with 7.8 mg/l and 3.9 mg/l of chlorine respectively for the particular contact time of 30 minute and 24 hour respectively. The aim of the dosing was to produce a residual concentration of ≥ 0.5 mg/l as chlorine after the desired exposure time (at least 30 minutes contact time) at pH <8.0 [17]. PH of all analysed water samples were maintained within the range of 6.0 to 8.0 throughout the entire experiment and was determined using a portable pH meter (Hach, sension1, USA). Chlorination was conducted in 300 ml chlorine demand free glass stoppered bottles and after being dosed with chlorine, samples were stored headspace-free at 20 °C in the dark [18].

2.3 Residual free chlorine measurement
Residual free chlorine of the water samples were measured at 30 minutes and 24 hours of exposure following the standard DPD (N, N-diethyl-p-phenylenediamine) ferrous titrimetric method [19]. All reagents used in this experiment were ACS analytical grade.

2.4 Chlorine demand calculation
Chlorine demand was calculated by subtracting the residual chlorine concentration from the concentration of chlorine dosed at a fixed contact time, after correction for blanks. The chlorine demand obtained in this way was quoted for a given chlorine dose, contact time, temperature and sample pH [19]. Following expression was used for the calculation of chlorine demand in water samples: Chlorine demand = Chlorine added concentration (mg/l) – Chlorine residual measured concentration (mg/l).

2.5 Determination of iron
In this study the concentration of total iron was determined following standard phenanthroline method. 50 ml (or a portion diluted to 50 ml volume if sample contains more than 4.0 mg/L of iron) of sample water plus 1 ml of hydroxyl amine hydrochloride (10 g dissolved in 100 ml deionised water) plus 2 ml of concentrated (37%) hydrochloric acid were taken in a 250 ml Erlenmeyer flask and were heated until the volume is reduced to 15 to 20 ml. Then after cooling to room temperature 10 ml of ammonium acetate buffer (125 g of ammonium acetate dissolved in 75 ml deionised water and 350 ml glacial acetic acid) and 4 ml of 1, 10-phenanthroline monohydrate (0.1 g dissolved in 100 ml deionised water) were added and finally diluted to 100 ml mark with deionised water. After 15 minutes, absorbance was taken at 510 nm using a UV-V is spectrophotometer (Varian, Cary 50, Australia) after correction for blank. The concentration of total iron was determined in milligrams per litre in the sample from the absorbance by reference to the calibration curve prepared by using a suitable range of iron standards containing the same amounts of phenanthroline, hydroxylamine, and ammonium acetate buffer as the sample [19].

2.6 Statistical analyses
Data analyses were performed using SPSS software for windows (Version 16.0, Inc., Chicago, IL, USA). Arithmetic mean, standard deviation, maximum, minimum were analyzed following basic descriptive statistics. Paired samples T-test was used to determine the significant differences between variables and within variables and significant criteria level was set at $p \leq 0.05$. Correlation among the studied parameters was analyzed using Pearson's correlation matrix analysis which was applied to measure the strength of association between variables. Correlation coefficients(r) and *p* values were computed from the correlation matrix.

3. Results and discussion
3.1 Iron and other physicochemical parameter of raw waters
Before the chlorine dosing steps, raw waters were analysed for the determination of iron and other physicochemical parameters. **Table 1** shows the results of these parameters where iron concentration was ranged from 0.01 to 6.4 mg/L with statistical mean of 1.43 mg/L, pH was ranged from 6.53 to 7.21 mg/L with an average of 6.85, water temperature was ranged from 22.5 to 27.3 ℃ with a mean of 25.21 ℃.

Table 1: Physicochemical quality parameters of collected raw water samples

Sample ID	Iron (mg/L)	Residual chlorine (mg/L)	pH	Temperature (°C)	Turbidity (NTU)	Conductivity (µS/cm)
S-01	6.13	<0.03	6.90	26.0	4.80	375
S-02	3.82	<0.03	7.12	25.0	2.65	287
S-03	0.01	<0.03	6.60	26.5	0.35	250
S-04	0.81	<0.03	6.85	24.5	1.23	206
S-05	0.45	<0.03	6.53	27.3	0.25	190
S-06	0.24	<0.03	6.82	25.0	0.70	184
S-07	0.17	<0.03	6.78	26.5	0.90	201
S-08	6.40	<0.03	7.21	26.0	3.50	175
S-09	0.38	<0.03	6.82	24.0	0.85	162
S-10	0.01	<0.03	7.10	22.5	0.28	209
S-11	0.12	<0.03	6.93	26.3	0.81	155
S-12	2.13	<0.03	6.56	23.2	1.92	190
S13	0.15	<0.03	6.95	26.4	0.41	227
S-14	0.63	<0.03	6.81	25.0	0.75	125
S-15	0.01	<0.03	6.85	24.0	0.34	186
Mean	1.43	-	6.85	25.21	1.32	208.13
Minimum	0.01	-	6.53	22.50	0.25	125
Maximum	6.40	-	7.21	27.30	4.80	375
STDEV	2.21	-	0.20	1.38	1.34	60.31

Residual free chlorine of all 15 raw water samples were below the detection limits (<0.03 mg/L). Two important physical parameters such as turbidity and conductivity were ranged from 0.25 to 4.80 NTU and 125.0 to 275.0 µS/cm respectively. Average values for turbidity and conductivity were found 1.32 NTU and 208.13 µS/cm respectively. Within 15 water samples, 4 samples contained iron beyond the acceptable limit (>1.0 mg/l) recommended by Bangladesh standard for drinking water [20]. All other analysed parameters were within the range of guideline values.

3.2 Chlorine demand and chlorine consumption
After dosing with chlorine all water samples including blank and control were subjected to estimate the short-term chlorine demand. **Table 2** shows the data of free chlorine demand for 30 minutes and 24 hours contact times respectively after the decay of initially dosed chlorine. For the particular chlorine dose of 7.8 mg/l at 30 minutes contact time, chlorine demand of all samples was ranged from 1.22 to 6.11 mg/l with an average of 3.12 mg/l. On the other hand for 3.9 mg/l chlorine dose at same contact time it was ranged from 1.09 to 3.75 mg/l with an average of 2.54 mg/l. In case of 7.8 mg/l dose at 24 hours of contact time, chlorine demand ranged from 1.93 mg/l to 6.66 mg/l with statistical mean of 3.92 mg/l. However, for 3.9 mg/l dose at 24 hours of contact time, a number of samples consumed the total amount of initially added chlorine leaving insufficient residual free chlorine to achieve chlorine demand.

Table 2: Chlorine demand of water samples dosed with 7.8 mg/l & 3.9 mg/l of chlorine after 30 minutes and 24 hours of contact time respectively at 20 °C and pH <8.0.

Sample ID	Chlorine demand (mg/l) at 30 minutes		Chlorine demand (mg/l) at 24 hours	
	7.8 mg/l dose	3.9 mg/l dose	7.8 mg/l dose	3.9 mg/l dose
S-01	5.35	>3.75*	6.66	>3.70*
S-02	3.60	3.25	4.20	3.63
S-03	1.22	1.15	2.03	1.77
S-04	4.75	3.55	5.40	>3.70*
S-05	1.25	1.09	2.45	1.84
S-06	2.51	2.25	3.36	3.00
S-07	1.71	1.25	2.24	1.76
S-08	6.11	>3.75*	7.11	>3.70*
S-09	4.73	3.48	5.38	>3.70*
S-10	1.35	1.15	1.93	1.80
S-11	2.85	3.10	3.33	3.47
S-12	3.50	3.17	4.40	>3.70*
S13	2.15	1.95	2.75	2.42
S-14	2.80	2.55	3.75	3.33
S-15	2.85	2.65	3.85	3.50
Mean	3.12	2.54	3.92	2.65
Minimum	1.22	1.09	1.93	1.76
Maximum	6.11	3.75	7.11	>3.70*
STDEV	1.54	1.00	1.62	0.81

*Insufficient data of residual chlorine to achieve actual chlorine demand

For both the cases of different dose and contact time, chlorine demands were significantly different (p <0.01). It is found that chlorine consumption was higher within 0 to 30 minutes of contact time than in between 30 minutes to 24 hours and their

mean differences were statistically significant ($p<0.01$) **(figure 1)**.
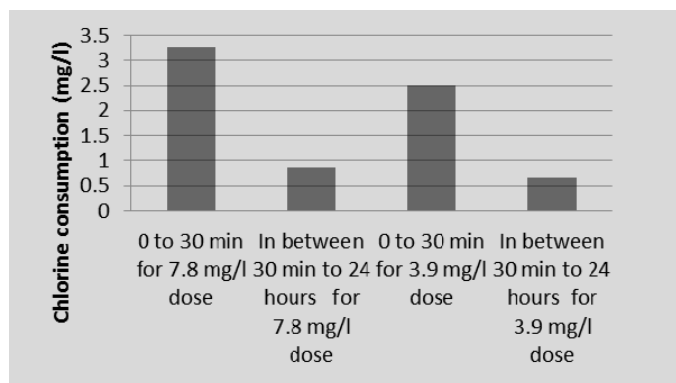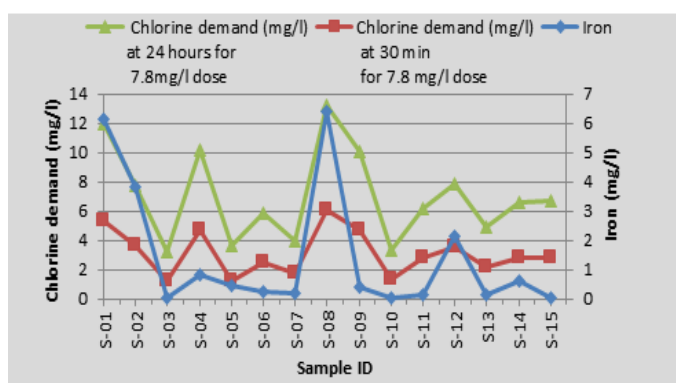

Fig 1: Comparison of chlorine consumption within 0 to 30 minutes and in between 30 minutes to 24 hours of addition

It suggests that reactions of chlorine with available substances in raw water can take place more swiftly at the very beginning and then become slower with time.

3.3 Correlation Analysis
Correlation analysis of iron and other physicochemical parameters were carried out to show the relationship between them. Pearson's correlation was used to find out correlation between two parameters. The relationship between chlorine demand and concentration of available iron in drinking water was examined. Correlation analysis reveals that concentration of iron is significantly correlated with chlorine demand ($p<0.01$). Chorine demand was found to be positively correlated with iron in the cases of 7.8 mg/l dose at 30 minutes (r= 0.750) and 24 hours (r=0.786) of exposure time respectively **(figure 2)**. Similarly in the case of 3.9 mg/l dose at 30 minutes contact time, chlorine demand showed significant positive correlation with iron (r=0.625 & $p<0.05$) **(figure 3)**.

Fig 2: Relationship between iron and chlorine demand of collected water samples dosed with 7.8 mg/l of chlorine with 30 minutes and 24 hours of contact time.

Chlorine consumption within zero to 30 minutes showed strong positive association (r=0.750 & $p<0.01$) with available iron in water **(figure 3),** but in between 30 minutes to 24 hours no significant correlation ($p>0.05$) with iron were found which

indicates that iron may play an important role in chlorine consumption within 30 minutes than in between 30 minutes to 24 hours.
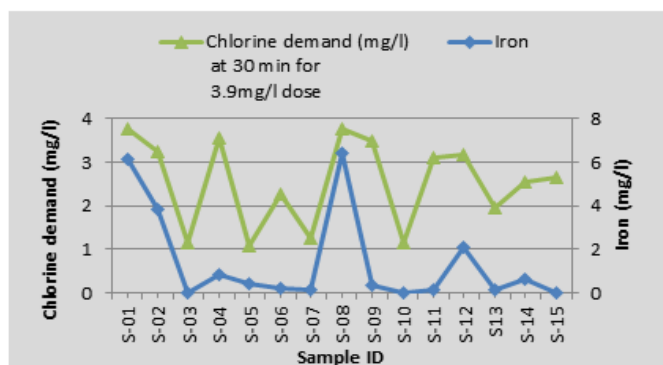
Fig 3: Relationship between chlorine demand and iron of collected water dosed with 3.9 mg/l of chlorine with 30 minutes of contact time.

Significant positive correlation of chlorine demand was also found with turbidity in the cases of 7.8 mg/l dose at 30 minutes (r= 0.770, $p<0.01$) and 24 hours (r=0.798, $p<0.001$) of exposure time respectively **(figure 4)**. Similarly in the case of 3.9 mg/l dose at 30 minutes contact time, chlorine demand showed significant positive correlation with turbidity (r=0.679 & $p<0.01$).
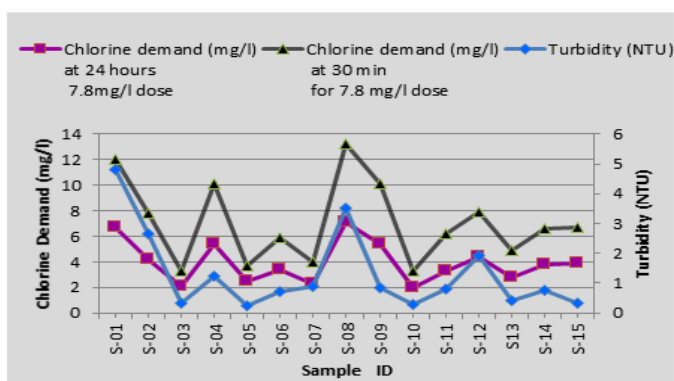
Fig 4: Relationship between chlorine demand and turbidity of collected water samples dosed with 7.8 mg/l of chlorine with 30 minutes and 24 hours of contact time.

LeChevallier [20] also found that chlorine demand is positively correlated with turbidity in water where disinfection efficiency was negatively correlated with turbidity. It is also stated that if the turbidity causing particles react with chlorine, this can result in chlorine demand [3]. So from this point of view, we can also say that iron may participate as the turbidity causing particle in the form of ferric hydroxide which can consume free chlorine in water and thereafter results in chlorine demand. The association of chlorine demand with iron at 30 minutes contact time for 7.8 mg/l dose can be described by a linear equation as: Chlorine Demand = 2.366 + 0.523 × Iron.

4. Conclusion
Chlorine demand of water depends on various physicochemical factors present in water body as well as its surrounding environment. It varies from sample to sample. Within all other organic and inorganic pollutants in water, iron is one of the most important parameter that is responsible for the consumption of chlorine. As a result it interfere the effectiveness of chlorination of water in a large extent. Iron plays an important role in decreasing the concentration of free residual chlorine within 30 minutes of addition of chlorine in water. So this study suggests that high iron containing water

requires elevated amount of chlorine to maintain the efficiency of disinfection.

6. References

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