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Investigating use of chlorine dioxide for pre-treatment of raw water from polluted sources at Morton Jaffray Water Treatment Works, Harare, Zimbabwe

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ABSTRACT

Raw water quality deterioration has affected capabilities of Conventional Water Treatment Processes (CWTP) in many countries. CWTP used at Morton Jaffray Water Treatment Works (MJWTW) in Harare have proven ineffective due to pollution. The study investigated the use of chlorine dioxide (ClO_2) as an alternative pre-treatment chemical. Its effectiveness was compared to that of calcium hypochlorite ($Ca(ClO)_2$) used at MJWTW. Grab raw water samples from MJWTW were collected between January and March 2020 and pre-treated with ClO_2 and $Ca(ClO)_2$ followed by jar tests with alum to determine pre-treatment effectiveness. Parameters analyzed included electrical conductivity (EC), total dissolved solids (TDS), total solids (TS), turbidity, chemical oxygen demand (COD), pH and total algae counts (TAC). The raw water had mean TDS (264 mg/L), TS (440 mg/L), turbidity (7.1 NTU), COD (85 mg/L), pH (7.9) and TAC (28.4×10^6 cells/mL). The optimum alum dosage without pre-oxidation was 80 mg/L. Pre-oxidation with 0.075 mg/L ClO_2 reduced alum dosage to 60 mg/L. This ClO_2 dosage was compared to a $Ca(ClO)_2$ dosage of the same concentration and strength at 5 and 15-minutes contact time before alum dosage at 60 mg/L. The treated water quality parameter levels proved better performance for ClO_2 compared to calcium hypochlorite.

Key words: calcium hypochlorite, chlorine dioxide, Morton Jaffray Water Treatment Works, pre-treatment, raw water, water quality

HIGHLIGHTS

- Raw water quality deterioration in Lake Chivero has complicated treatment and treatment costs.
- Chemicals currently used have become ineffective including calcium hypochlorite, which creates risk of formation of carcinogenic compounds.
- Chlorine dioxide was considered an an alternative as it has been used widely elsewhere, enhances coagulation compared to calcium hypochlorite, and thus is likely to be economic.

INTRODUCTION

There has been a global trend of deterioration of water quality for potable water sources (Biswas & Totajada 2019). Increased pollution of water sources has been due to both industrial and urban population rapid growth along with associated anthropogenic activities. Poor institutional, regulatory and management aspects have also led to poor catchment management, thus resulting in pollution (Afroz *et al.* 2014). Polluted water sources pose a major challenge during potable water treatment (Dlamini *et al.* 2016) including increased costs of treatment (Amrose *et al.* 2020) and risks of water borne diseases due to poor drinking water quality (Praveen *et al.* 2016).

There are emerging problematic pollutants, namely algae and other compounds of concern including trace organics and pesticides (Pal *et al.* 2010). The presence of algae in drinking water has many challenges including odour and taste (Matilainen *et al.* 2010). Algae is also known to release toxins such as cyanobacterial toxins, which have been linked to illnesses in various regions throughout the world (WHO 2020). Moreover, algae also increases the turbidity of water, and if not removed can promote regrowth of pathogens in water supply

networks leading to waterborne disease outbreaks (Levy *et al.* 2016; USGS 2020). For instance, *vibrio cholerae* exploit high water turbidity to hide from the effect of water treatment agents (Bwire *et al.* 2020).

The deterioration in raw water quality has complicated drinking water treatment, especially in developing countries where the conventional water treatment systems are still the most preferred and feasible technology as highlighted by Treacy (2019). Conventional water treatment processes and use of traditional chemicals such as chlorine have been linked to toxin release and formation of disinfection byproducts (Hu *et al.* 2018). Conventional water treatment processes are now failing to deal with the high levels of pollution including emerging pollutants such as algae (Ghernaout *et al.* 2010). Improvements in potable water treatment processes have been necessitated by presence of emerging pollutants in the raw water including algae (Choi *et al.* 2006). However, there has been slow progress in advancing techniques for improving water treatment systems in many developing countries due to many factors that include lack of capital and low skills capacity (Brame *et al.* 2011). There is therefore need to find alternative and feasible processes and chemicals to deal with the emerging pollutants and enhance performance of conventional treatment systems in developing countries in the mean time (Khan *et al.* 2020).

Coagulation is a critical step in the removal of turbidity during conventional water treatment (Bongiovani *et al.* 2014; Abebe *et al.* 2016) and it is done before filtration (Vieno *et al.* 2006). Algae has to be removed during the initial stages of water treatment processes, especially during coagulation-flocculation and sedimentation, to reduce impact on subsequent processes (Hu *et al.* 2014). During drinking water treatment, pre-treatment is carried out for a variety of purposes including reducing solids and algae, taste and odor control, control of manganese and iron, improving coagulation performance and disinfection (Yang *et al.* 2013). Pre-treatment reduces the loading to subsequent processes inclding coagulation-flocculation and sedimentation.

Forms of pre-treatment in water treatment include microstraining, dissolved air flotation, pre-oxidation with chemicals such as chlorine and application of algicides such as copper sulphate (Ghernaout *et al.* 2010). Chlorine dioxide has been used to pre-treat water and remove algae (Gordon & Rosenblatt 2005). Ozone can also be used to pre-treat water and reduce algae (Hu *et al.* 2014). Activated carbon has been widely used to reduce other compounds including taste and odor (Bertone *et al.* 2018). Membrane filtration can also be used for pre-treatment of water to specifically reduce dissolved solids and suspended solids (Lee *et al.* 2000). Aeration or gas stripping is also another pre-treatment method for removing taste and odor causing substances in drinking water (Taricsk *et al.* 2009). Pre-sedimentation can also be used to reduce solids and in so doing enhances flocculation and coagulation (Ahamad *et al.* 2014).

Thus, forms of pre-treatment are mainly chemical and non-chemical (physical) processes. Non-chemical methods that include microstraining, dissolved air flotation and utra-filration (or membrane filtration), aeration and pre-sedimentation require significant investment in new or retrofitting of civil and electro-mechanical works (Sharma & Vairavamoorthy 2009). Therefore, they may be suitable when the original design incorporates these to avoid retrofitting. Chemical methods require less structural and mechanical equipment investment (Kawamura 2000). Changes or modification of application of chemicals including alternative chemicals require minimal retrofitting on existing water treatment plants. As a result, the application of alternative or new chemicals has been common and popular as this has a low capital demand, and thus they can be easily integrated on existing water works (Somani *et al.* 2011).

According to Pereira *et al.* (2008), chlorine is the most widely used pre-oxidant in water treatment. However, Yin *et al.* (2020) state that when chlorine is used in water treatment it can react with halides and natural organic matter in raw water to produce numerous carcinogenic halogenated disinfection by-products (DBPs). The disadvantages of the application of copper sulphate and microstraining and dissolved air flotation in the removal of algae are the creation of toxicity, risk of some of the algae forms not being removed and difficulties in sludge handling respectively (Ghernaout *et al.* 2010). Ozone pre-oxidation may cause physiological stress or cell membrane damage resulting in release of intracellular organic matter into the bulk water (Hu *et al.* 2014) thus increasing turbidity. This is further supported by Amirsardari *et al.* (1997) who stated that in some studies, turbidity removal during coagulation was unaffected by pre-ozonation.

Among the different chemical agents that can be used as alternatives to chlorine for water treatment, chlorine dioxide has received considerable attention (Jonnalagadda & Nadupalli 2014). Chlorine dioxide is a powerful, selective oxidant and broad-spectrum biocide thus pre-oxidation of water with chlorine dioxide improves coagulation and extends filter runs (Gordon & Rosenblatt 2005). As a pre-oxidant, it is used as an alternative to

chlorine for the control of trihalomethane formation (Jonnalagadda & Nadupalli 2014). Chlorine dioxide does not result in formation of DBPs when conventional water treatement processes are used (Al-Fatlawi 2014). As compared to other pre-oxidants, chlorine dioxide is effective over a wide range of pH (Gordon & Rosenblatt 2005). When it comes to anti-mycobacterial effect on protozoa and viruses, chlorine dioxide is superior to chlorine at equal concentrations (Taylor et al. 2000). In Italy and Germany chlorine dioxide is used as a primary oxidant and disinfectant (Lenntech 2020). On the African continent the Botswana government adopted the use of chlorine dioxide in water treatment as a measure towards improved water distribution in remote areas (Parker 2016). The continued deterioration in raw water quality due to algae is straining the water treatment process at Morton Jaffray Water Treatment Works (MJWTW) as this has resulted in filter clogging and a high chemical demand (Hoko & Makado 2011). Consequentially, there is poor quality of drinking water in Harare (Madungwe & Sakurigwa 2007). Nhongo et al. (2018) has reported formation of trihalomethanes as well as general deterioration of water quality in the Harare drinking water supply system. As a result of poor water quality of raw water some USD 2–4 million is required for water treatment chemicals in Harare when the plant is fully operational (Nhongo et al. 2018; ZPP 2019). The poor quality of drinking water has negatively affected customer perceptions, leading to low willingness to pay (Dandadzi et al. 2019). Contaminated drinking water has also been linked to cholera outbreaks in 2008/9 (Chirisa et al. 2015) and 2018 (WHO 2018).

Initiatives to develop other raw water sources in unpolluted catchments, for instance the construction of Kunzwi Dam, east of Harare, has failed to take off since the early 1990s due to financial constraints (Hoko & Makado 2011). Given this situation, there is need for a feasible water treatment technology which is effective and low cost in the short-term. Thus, this study therefore investigated the feasibility of using chlorine dioxide as an alternative chemical for pre-oxidation in place of calcium hypochlorite, which is currently being used at Morton Jaffray Water Treatment Works with a view to reduce the amount and cost of chemicals used at the plant. The study is divided into four sections which are introduction, materials and methods, results and discussions, and conclusion and recommendations.

MATERIALS AND METHODS

Study area

Background on Harare

Harare is the capital city of Zimbabwe and lies in the upper Manyame sub-catchment (Figure 1). Harare is the industrial and commercial hub of the country (Tsiko & Togarepi 2012). Harare Province urban has a population of 1,883,938 based on an interim demographic survey of 2017 (ZimStat 2017). In Harare, the informal sector contributes 58% of employment through flea markets, social markets, home industries and guarded car parks (Chekenya 2017). The informal sector is a product of a coping mechanism to economic downturn and rising unemployment (Njaya 2014).

Background on water supply in Harare

Water supply for Harare and surrounding towns is the responsibility of the City of Harare (Ndunguru & Hoko 2016). Lakes Chivero and Manyame are the two principal sources of raw water for Morton Jaffray Water Treatment Works (Muisa et al. 2011). The Zimbabwe National Water Authority (ZINWA) is responsible for management of these raw water sources (Ndedzu et al. 2012). Lake Chivero, the main source of Harare, has a history of pollution dating back to the 1960s (Dlamini et al. 2016). Nutrients from treated sewage effluent have resulted in the proliferation of water hyacinth and algae in the lake (Nhapi et al. 2002; Chawira et al. 2013).

Raw water abstracted from Lake Chivero and Lake Manyame is treated at Morton Jaffray Water Treatment Works (MJWTW), as in Figure 2, which consists of three units; that is, Old Works or Number 1 (160 ML/day), Number 2 Works (227 ML/day) and Number 3 Works (227 ML/day) with a combined design capacity of 614 ML/day (Muisa et al. 2011). The operating capacity of the treatment plant has been as low as 200 ML/day at times and this has been attributed to shortage of water treatment chemicals needed to treat the polluted raw water and breakdowns. The water treatment process flow at MJWTW is described by Hoko & Makado (2011), as follows (Figure 2): first powdered activated carbon is added to remove organics and smells whilst H_2SO_4 acid is added to lower pH in the mixing chamber at the inlet. The water then flows into a distribution chamber and thereafter into clarifiers. $Ca(ClO)_2$ (pre-oxidation agent), hydrated aluminium sulphate (coagulant) and activated silica (coagulant aid) are added to each channel leading into a clarifier. The water then flows into
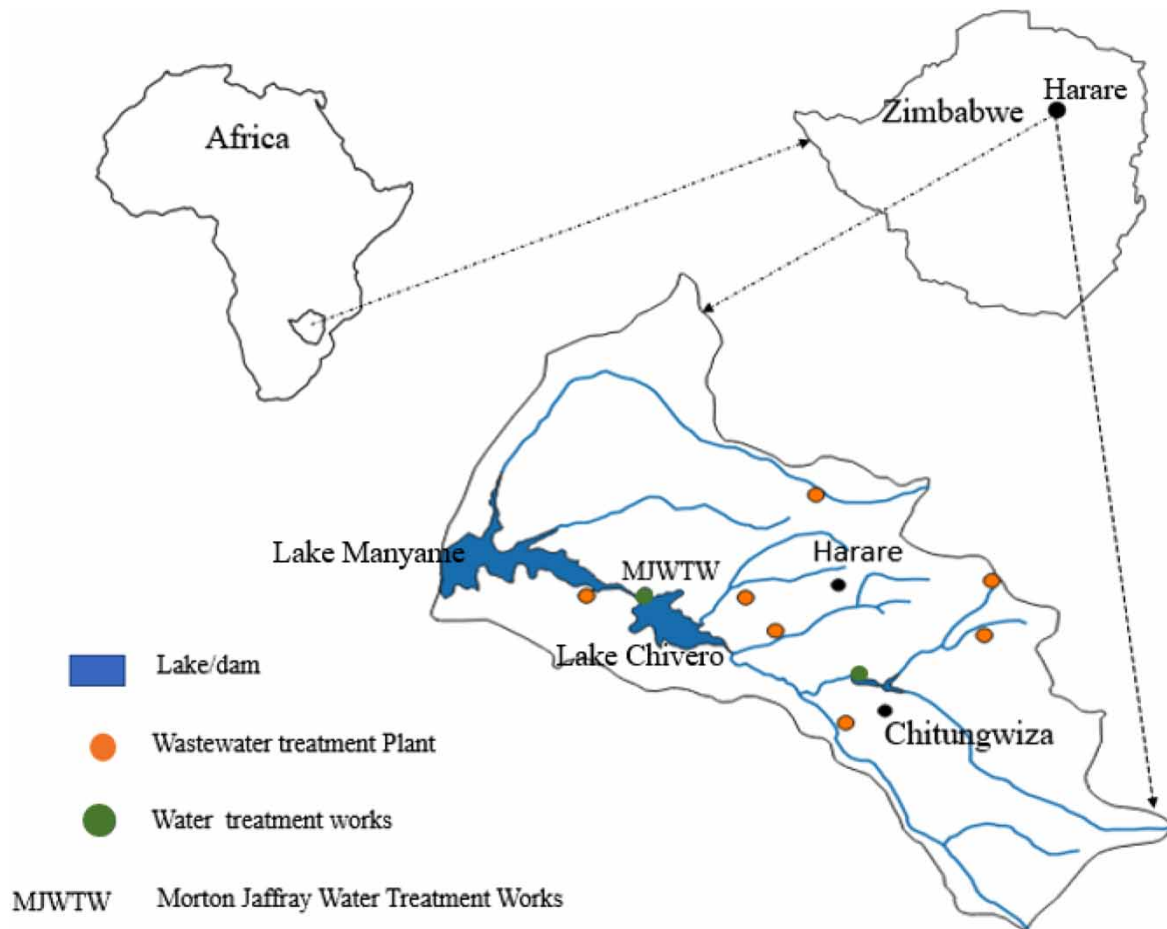
Figure 1 | Upper Manyame sub-catchment map showing location of Morton Jaffray Water Treatment Works.

sedimentation tanks followed by rapid sand filters. From the filters, the water then passes through the chlorine and lime dosing chamber for post disinfection and pH correction. This treatment process has not been able to deal with the high pollution load into the water sources, resulting in poor treated water quality (Dandadzi et al. 2019). Pollution of raw water has created complications in water treatment including high chemical demand (7–8 chemicals), filter clogging and frequent backwashing requirement (Hoko & Makado 2011). There has been evidence of algae re-growth in the water distribution system (Dandadzi et al. 2020), and also formation of trihalomethanes in the water distribution system of Harare (Nhongo et al. 2018).

Study design

Selection of study area

The eutrophic state of Lake Chivero has resulted in the chemicals needed for treatment increasing from three to seven (Nhongo et al. 2018). Thus, the cost of water treatment has significantly increased and the treatment process has become unsustainable as there is no full cost recovery tariff (Makwara & Tavuyanago 2012). Moreover, the current chemicals being used at MJWTW have failed to treat the water to drinking water standards (Dandadzi et al. 2020). This has resulted in a water supply system characterized by poor water quality, severe water rationing and reoccurrence of water-borne diseases outbreaks such as cholera and typhoid (Chirisa et al. 2015). Regrowth of algae in the distribution system has been reported by Dandadzi et al. (2020). It is therefore important to study how pre-oxidation using chemicals such as chlorine dioxide can help to reduce the cost of water treatment and also improve the quality of treated water.

Selection of parameters to be analyzed

Parameters analyzed included electrical conductivity (EC), total solids (TS), total dissolved solids (TDS), turbidity, chemical oxygen demand (COD), pH, and total algae count (TAC). EC is an indirect measure of dissolved solids (Rusydi 2018). Addition of chemicals during water treatment increases total dissolved solids (Wilson
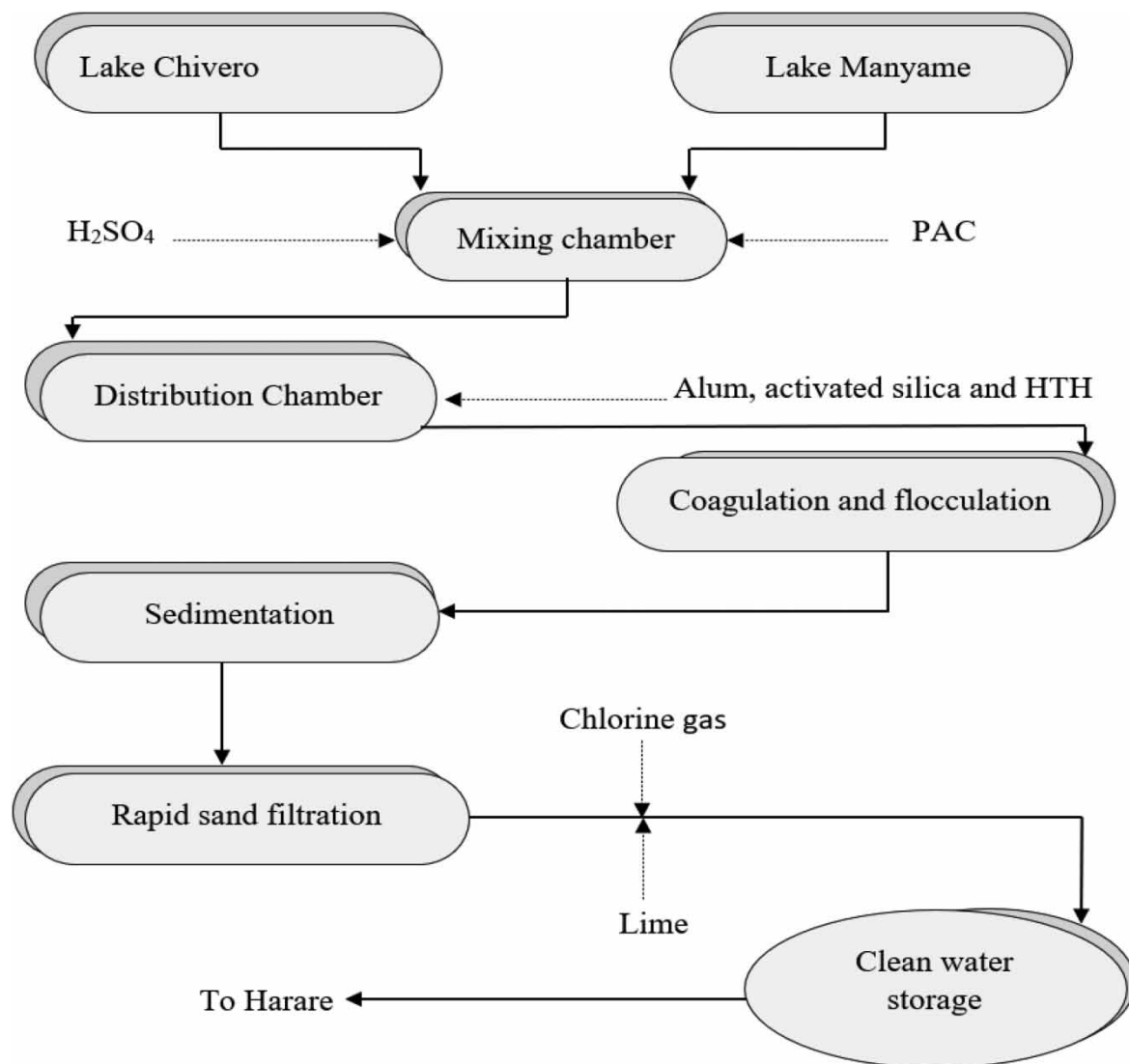
Figure 2 | Morton Jaffray Water Treatment Works flow scheme (adapted from Hoko & Makado 2011).

et al. 2014). TDS and TS have a strong positive correlation with turbidity (Iqbal *et al.* 2004). Turbidity is used to monitor source water quality, the effectiveness of coagulation and clarification and filtration in water treatment plants (WHO 2017a). The quality of water in an urban set up is prone to contamination from point-sources of pollution such as municipal wastewater carrying large amounts of solids and organic matter, which is inferred from the chemical oxygen demand (Bojarczuk *et al.* 2018). It has been established that pH affects coagulation, as different coagulants have different optimum pH values (EPA 2017). pH and turbidity are some of the critical parameters measured when a Jar test is carried out (Langlais & Degremont 2010). Algae is common in polluted raw water sources and is one of the causes of odours in potable water; some species produce toxins including hepatotoxic peptides, cytotoxic and neutotoxic alkaloids (Falconer 1999). Algae impede coagulation and filtration, causing colouration and turbidity in treated water if not removed completely (WHO 2006).

Experimental design

Overview. The study investigated the effectiveness of two oxidizing agents for pre-treatment of raw water before coagulation and flocculation. At present, calcium hypochlorite ($Ca(ClO)_2$) is often used as a pre-oxidizing agent at Morton Jaffray Water Treatment Works. Zhu *et al.* (2012) highlighted chlorine dioxide (ClO_2) as a powerful oxidizing agent that has high bactericidal activity, and more stable and effective than calcium hypochlorite. Thus the study investigated opportunities for use of ClO_2 as an alternative pre-oxidizing agent.

Laboratory experiments using raw water from the inlet at Morton Jaffray water treatment works were carried out to (i) determine the raw water quality, (ii) determine optimum pH and dosage of alum, (iii) determine the

optimum combination of ClO_2 and alum dosage, and (iv) to compare the performance of ClO_2 to $Ca(CIO)_2$. The outline of the steps for each experiment is as follows.

(i) Determination of raw water quality. For most water quality parameters except algae, grab samples from the raw water feed into the treatment plant were collected in 6 campaigns for the duration of the study (January to March 2020) in 25 liter plastic containers. Samples for algae analysis were collected in three campaigns by grab sampling from the raw water feed pipeline. The samples for all water quality parameters were collected from the same point at MJWTWs that was considered by Hoko & Makado (2011). For each campaign, the raw water quality was determined by measuring electrical conductivity, TDS, TS, turbidity, COD, pH, and total algae.

(ii) Determination of optimum pH and alum dosage. A single bulk raw water sample collected from the inlet of MJWTW was used to determine the optimum pH and alum dosage for the experiments. The raw water sample was adjusted to varying pH values using sulphuric acid (H_2SO_4) as is the practice at MJWTW. The alum dosage was determined by carrying out jar tests at varying dosages as recommended by Langlais & Degremont 2010) after adjusting pH to 6.11, 6.52, 6.79, 7.34 and 8.30 using H_2SO_4 acid. Alum is reported to work well in the pH range 6–7 (EPA 2017).

A Stuart Scientific Flocculator SW1 was used for the jar test experiments. Parameters measured to assess the performance of each dosage after the jar tests were pH and turbidity as these are deemed to be key in assessing the efficiency of a coagulant (Budd *et al.* 2004). For each experiment run at the adjusted pH, the jar with the lowest alum dosage giving a turbidity of 1 NTU or less was taken as the best performing jar. A comparison was then made across the best performing jars for the different intial pH values to determine the optimum alum dosage (A_o) and its coressponding intial pH (pH_o).

(iii) Determination of optimum combination of alum and chlorine dioxide. Jar tests were carried out to determine the optimum combination of chorine dioxide and alum. In these experiments, four raw water samples collected within the same week on different days were first pre-treated by chlorine dioxide and a contact time was allowed before alum was added. The contact time of chlorine dioxide before addition of the coagalant (alum) was simulated by first applying the chlorine dioxide into the raw water while the flocculator mixers were set to 15–20 rpm and a length of time equal to the desired contact time before addition of alum was allowed to lapse. After the contact time lapse, alum was then added and the flocculator mixer speed adjusted to 200 rpm for one minute to simulate rapid mixing. The speed of the mixers was then reduced to 15–20 rpm for 15 minutes following which the mixers were switched off and settlement allowed for 30 minutes as per the standard procedures for the flocculation test (Langlais & Degremont 2010). Hang-Bae *et al.* (2001) and Shehata *et al.* (2002) performed Jar tests to investigate the efficiency of different coagulants to remove algae. Hoko & Makado (2011) also performed Jar tests to investigate the efficiency of algicides in a study which investigated application of algicides followed by coagulation by alum.

The optimum alum dosage (A_o) obtained from the procedure in the previous section was taken as the maximum dosage in experiments to determine the optimum combination of chlorine dioxide and alum. The rationale for this is that the addition of a pre-oxidising agent should result in reduction of alum dosage since most organics and algae are expected to have been oxidised by the oxidant, resulting in less alum being required for coagulation (Yan *et al.* 2019). Typical doses for pre-oxidation with chlorine dioxide range from 0.07 to 2 mg/L (Shams *et al.* 2011). In our study, experiments were carried out with four varying chlorine dioxide concentrations from 0.05 to 0.20 mg/L. No pH correction of the raw water was made as the pH value obtained after addition of chlorine dioxide was found to be in the range of 6–7, which is suitable for alum coagulant (EPA 2017).

For each of the four chlorine dioxide dosages selected, the optimum alum dosage of A_o (referred to above) was applied into the first jar and in the other five jars alum was applied in decreasing concentrations. This was repeated for different dosages to determine the optimum dosage. For these experiments, alum was dosed 5 minutes after chlorine dioxide. Parameters considered for determining the optimum combination of alum and chlorine dioxide included TDS, TS, turbidity, COD and pH. After running each jar test experiment for a selected chlorine dioxide dosage, and measuring pH and turbidity along with observing floc properties, the best performing jar for each chlorine dioxide dosage was determined. TDS, TS, COD were then also measured only for the best performing jar for each chlorine dosage. The optimum combination of alum and chlorine dioxide (**A_{co}, C_{co}**) was determined from the best performing jars for each chlorine dioxide dosage based on comparison of overall performance taking into account all parameters considered.

(iv) Comparison between chlorine dioxide and calcium hypochlorite. A single bulk raw water sample was used in comparing the effectiveness of the two oxidants. Jar tests were carried out at a contact times of 5 and 15 minutes using either chlorine dioxide or calcium hypochlorite $Ca(CIO)_2$ for pre-oxidation followed by application of the optimum alum (A_{co}) dosage determined in the previous section above. Chlorine dioxide has been found to be effective in inactivation of pathogens at a contact time of 5–15 minutes (Pearson & Swartz 1992; SUEZ 2020a). The optimum chlorine dioxide (C_{co}) determined above was applied in the first set of experiments whilst in the other set of experiments, $Ca(CIO)_2$ of same strength and concentration was added. All six jars for each experiment were dosed with the same dosage of either chlorine dioxide or calcium hypochlorite followed by alum to increase reliability of results. Average results for each experiment were then determined from the results of all six jars. Parameters measured to assess the effectiveness of these two oxidants after the jar tests included TDS, TS, turbidity, COD, pH, and total algae count.

Methods of water quality analysis

Samples were analyzed at the University of Zimbabwe Biological Sciences and Civil Engineering Water Laboratory according to standard methods suggested by APHA (2012) for all the parameters studied (Table 1).

Table 1 | Methods and equipment used for water quality analysis

Parameter	Analytical method	APHA method number	Equipment brand
Electrical conductivity (20 °C)	Conductimetry	2550	Hanna (HI 98704)
Total dissolved solids	Gravimetric	2540C	Genlab Oven & Sartorius BP221S
Total solids	Gravimetric	2540B	Genlab Oven & Sartorius BP221S
Turbidity	Nephelometry	2130B	Hanna (HI 9803)
Chemical oxygen demand	Closed reflux with colorimetric reactor	5520D	Camlab 16500–10 reactor
pH (20 °C)	Potentiometry with combined glass	$4500\text{-}H^+$	Hanna
Algae	Microscopy	(Hemocytometer method)	Celestron CM800

RESULTS AND DISCUSSION

Raw water quality

The physical and chemical parameters for Lake Chivero water (Morton Jaffray Water Treatment Works raw water feed) determined during the study period are presented in Table 2.

Table 2 | Summary of Lake Chivero raw water quality for 13 January–12 March 2020

Parameter	Number of samples (n)	Range	$\mu \pm \sigma$	CV
Electrical conductivity (μS/cm)	6	440–528	476 ± 17.8	3.7%
Total dissolved solids (mg/L)	6	215–295	264 ± 27	10.2%
Total solids (mg/L)	6	321–447	440 ± 5.0	1.1%
Turbidity (NTU)	6	6.4–8.4	7.1 ± 0.67	9.4%
Chemical Oxygen Demand (mg/L)	6	65–90	85 ± 7.1	8.4%
pH	6	6.8–8.3	7.9 ± 0.63	8.0%
Total algae (count/mL)	3	$(7.3\text{–}42.0) \times 10^6$	$(28 \pm 18.2) \times 10^6$	65%

Note: $\mu =$ mean; $\sigma =$ standard deviation; CV $=$ coefficient of variation.

The raw water electrical conductivity (EC) ranged between 440 and 528 μS/cm with a mean of 476 μS/cm. The EC values had low variability (CV = 3.7%). The mean raw water EC obtained in this study was comparable to 540 μS/cm obtained by Muisa *et al.* (2011) for the same source

The total dissolved solids (TDS) ranged from 215 to 295 mg/L with a mean of 264 mg/L. TDS showed low variability as the coefficient of variation (CV) was 10.2%. The TDS concentration for lake water is typically found in the range 50–250 mg/L (Bhateria & Jain 2016). Thus, the TDS obtained in this study can be described as moderately high.

Total solids (TS) concentration ranged from 321 to 447 mg/L with a mean of 440 mg/L. The coefficient of variation was low (1.1%). The TS range obtained in this study is relatively lower than 220–2,096 mg/L obtained by Nhongo *et al.* (2018) for Morton Jaffray Water Works raw water between February and April 2015. The total solids concentration in surface water is usually above 500 mg/L (Sawyer *et al.* 2003). Thus, the TS concentration obtained in this study can be described as moderately low.

The raw water turbidity range was 6.4–8.4 NTU with a mean of 7.1 NTU. The turbidity values showed low variability as the coefficient of variation was 9.4%. The mean turbidity found in this study was comparable to 5.81 NTU obtained by Nhongo *et al.* (2018) for Morton Jaffray Water Works raw water between February and April. Turbidity of surface waters can vary widely (1–200 NTU) depending on season and land use of the surrounding catchment (Sharma & Bhattacharya 2017). Thus, the mean raw water turbidity in this study is in the lower band of the suggested surface water turbidity range. This relatively low raw water turbidity could be due to the near-quiescent conditions that allow settlement in lakes.

The COD ranged from 65 to 90 mg/L with a mean of 85 mg/L. The variability in COD was relatively low as the CV was 8.4%. The mean COD obtained in this study was higher than the 30 mg/L stipulated by EU for raw water to be treated by conventional water treatment processes (EU 1975).

The pH values ranged from 6.8 to 8.3 with a mean of 7.9. The pH values had a low variability as the coefficient of variation was 8.0%. The pH of water has an effect on the speciation of contaminants and also choice and performance of a coagulant (Wang *et al.* 2010). Moreover, pH has an effect on the effectiveness of disinfection by chlorine (Fiset *et al.* 2013). Optimal pH for coagulation when using alum is 6–7 and when using iron-based coagulants it is 5.5–6.5 (EPA 2017). Coagulation is more effective at low pH due to a strong ionic solution, which promotes amalgamation (Saritha *et al.* 2017).

The total algae count in the raw water was found to be from 7.3 to 42.0×10^6 count/mL with a mean of 28.0×10^6 count/mL. The raw water total algae count showed high variability as the coefficient of variation (CV) was 65%. The total algae count range in this study was much higher than 875–6,000 cells/mL obtained by Hoko & Makado (2011) between February and April 2007. During the period of study, the water level in Lake Chivero was very low as the City of Harare had been relying on Lake Chivero only for a very long period of time as the abstraction system for the other source (Lake Manyame) was non-functional.

The raw water for Morton Jaffray Water Works is characterised by high electrical conductivity, solids concentration, chemical oxygen demand and total algae count. These high raw water parameters indicate that the raw water is from a polluted source and may thus be complicated to treat with conventional water treatment processes. Moreover, the raw pH is alkaline and requires either high coagulant dosages or addition of an acid in order to lower the pH. It can be concluded pre-oxidation of the raw water is a necessity at MJWTW. Therefore, there is need for an effective pre-oxidizing agent.

Determination of optimum pH and alum dosage (with no pre-oxidation)

Results presented here are for five experiments with different initial raw water pH adjusted by addition of H_2SO_4. Parameters considered to investigate optimum pH and alum dosage were mainly turbidity and pH. Results for settled pH and turbidity from the best jars for experiments for each of the initial pH values are presented in Figure 3 and those for the best jar for each initial pH and the corresponding alum dosage and settled turbidity are shown in Figure 4. From Figure 3, the lowest turbidity was 0.75 NTU and it occurred at an initial pH of 7.34 and a corresponding settled pH of 6.65. Therefore, the best initial pH was determined to be 7.34 since that gave the most favourable outcomes in terms of settled pH and turbidity.

Best results for settled pH and turbidity for all five experimental runs were obtained with an alum dosage of 80 mg/L (Figure 4). The lowest turbidity was determined to be 0.75 NTU. Hoko & Makado (2011) obtained turbidity values less than 1.0 NTU with an alum dose of 90 mg/L at an initial pH of 7 in similar experiments. Hence, these results are comparable to the optimum initial pH (7.34) and alum dose (80 mg/L) applied in this study. The
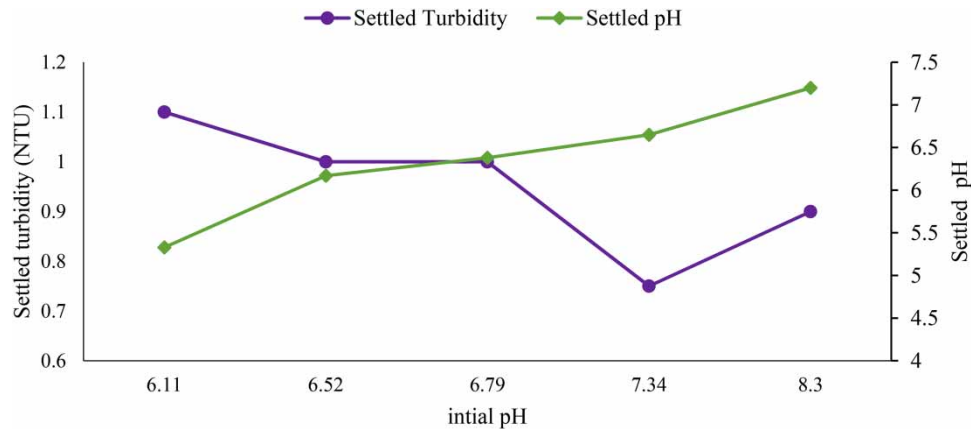
Figure 3 | Initial pH against settled turbidity and settled pH (13 January–12 March 2020).
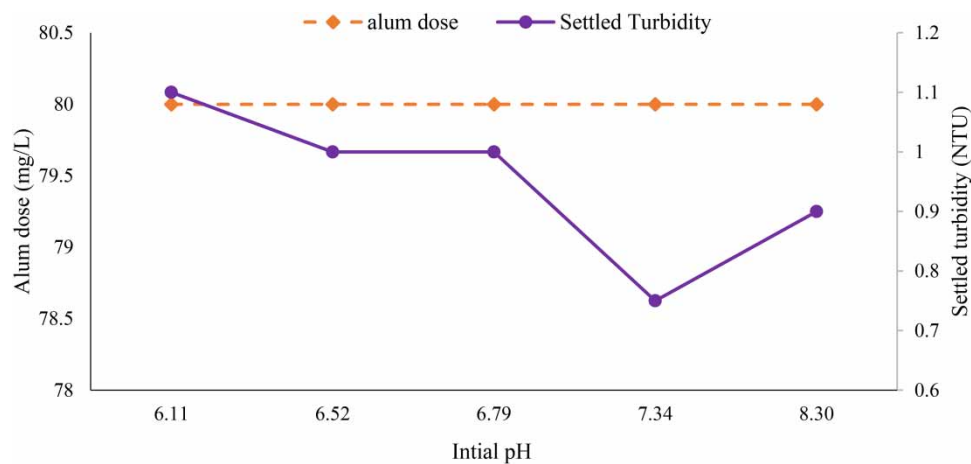

Figure 4 | Initial pH against corresponding best jar alum dosage and settled turbidity (13 January–12 March 2020).

optimum initial pH for raw water and its corresponding alum dose were 7.34 and 80 mg/L respectively, with a settled pH of 6.65 and settled turbidity of 0.75 NTU. Therefore, the raw water pH should be adjusted to a pH around 7.3 and the alum dosage to about 80 mg/L if there is no pre-oxidation of the raw water.

Determination of optimum combination of alum and chlorine dioxide

Results in this section are based on investigations to determine the optimum combination of chlorine dioxide dosage and alum. In the experiments, the highest dosage of alum was taken as 80 mg/L (obtained above); this was applied in Jar 1 and in the other jars the dosage was gradually reduced. Parameters considered for determining the optimum combination of alum and chlorine dioxide included TDS, TS, turbidity, COD and pH. The mean raw water TDS, TS, turbidity, COD and pH were 262 mg/L, 443 mg/L, 7.2 NTU, 83 mg/L and 7.85 respectively. The CV for the values of the raw water was low and below 10% for all.

Results for settled turbidity and pH of the best jars for each of the four chlorine dioxide dosages considered are shown in Table 3. The lowest turbidity (0.75 NTU) and highest (1.12 NTU) turbidity were obtained with a chlorine dioxide concentration of 0.05 mg/L and 0.20 mg/L respectively. Turbidity is used for operational monitoring as it can be measured easily and accurately (WHO 2017b). Thus, based on a target settled turbidity of 1 NTU, chlorine dioxide dosages for pre-oxidation of 0.05 mg/L and 0.075 mg/L were suitable as the settled turbidity values at these chlorine dioxide dosages were lower than 1 NTU. However, selection of the optimum chlorine dioxide dosage also considered the solids concentration and chemical oxygen demand level in the settled water. Results of solids and COD levels in settled water after treatment with varying dosages of chlorine dioxide at optimum alum dosage are presented in Figure 5.

Table 3 | Settled turbidity and pH for different chlorine dioxide dosages for best jars

CIO$_2$ dosage (mg/L)	Alum dosage (mg/L)	Settled turbidity (NTU	Settled pH
0.05	70	0.75	7.42
0.075	60	0.85	6.97
0.100	60	1.10	6.78
0.200	50	1.12	6.41
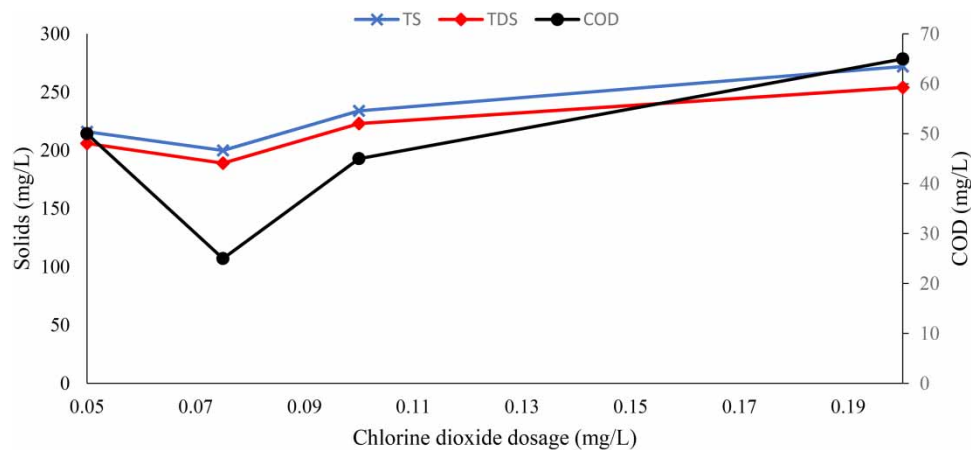
Figure 5 | Solids and COD concentrations in settled water at varying chlorine dioxide dosages for the best jars dosage (13 January–12 March 2020).

Irrespective of the oxidant used, overdosing can induce cell lysis, resulting in release of undesirable toxins or taste and odour compounds, and this can also trigger degradation of extracellular organic matter to form compounds with interfering properties including mono and dicarboxylic acids and glycaric acids (Henderson *et al.* 2007; AWWA 2010a, 2010b). Therefore, the optimum dose is that which achieves cell modification to promote algae settling without excess cell lysis (Henderson *et al.* 2007). Thus, the degradation of extracellular organic matter and release of other compounds resulting from cell lysis due to increased oxidant dosage and the resultant increase in dissolved solids from the oxidant may explain the increase in turbidity with increasing chlorine dioxide dosage in Table 3. It was observed that increasing the chlorine dioxide dosage beyond 0.075 mg/L resulted in a corresponding increase in solids and COD (Figure 5), suggesting lysing of algae cells and release of compounds (including organic matter) into the water phase. The lowest TDS and COD were obtained for a chlorine dioxide dosage of 0.075 mg/L with an alum dosage of 60 mg/L, suggesting that this was the optimum dosage to remove these parameters.

Although a chlorine dioxide and alum dosage of 0.075 mg/L and 60 mg/L had a relatively higher turbidity than that of chlorine dioxide dosage of 0.05 mg/L with an alum dosage of 70 mg/L, its performance based on TS, TDS and COD was better. Furthermore, the turbidity at 0.075 mg/L chlorine dioxide dosage was still less than 1 NTU. Therefore, based on all parameters considered, the optimum chlorine dioxide dosage was determined to be 0.075 mg/L with an alum dosage of 60 mg/L.

Comparison between chlorine dioxide and calcium hypochlorite performance

Results in this section are based on jar tests performed using chlorine dioxide and calcium hypochlorite at the same dosages of 0.075 mg/L (determined above) at retention times of 5 and 15 minutes before an alum dosage of 60 mg/L (also determined above). Assessment of the performance of the two agents was based on comparing the results of total solids, turbidity, COD and algae.

Overall, chlorine dioxide had a better performance than Ca(CIO)$_2$ for all parameters although the differences were generally not statistically significant ($p > 0.05$) based on a t-test at 95% confidence interval. However, Ca(CIO)$_2$ has the risk of creating Disinfection By-Products (DBPs) such as carcinogenic trihalomethanes (Yin *et al.* 2020). It was also established that increasing the contact time did not significantly improve the performance

of both oxidizing agents ($p > 0.05$). The discussion on the performance of the two oxidizing agents for the parameters assessed is presented below. For all parameters, comparison between the water treated by the two oxidizing agents and between the two contact times was based on a t-test at 95% confidence interval.

Total solids removal

Total solids (TS) results for treatment with chlorine dioxide (ClO_2) and calcium hypochlorite ($Ca(CIO)_2$) are as shown in Figure 6. The mean TS for raw water was 441 mg/L and for settled TS at 5 and 15 minutes' contact time for chlorine dioxide was 399 ± 40.8 mg/L and 342 ± 20.9 mg/L, respectively, whilst for $Ca(CIO)_2$ it was 427 ± 39.9 mg/L and 381 ± 14.4 mg/L, respectively. Percentage reduction in TS concentration at 5- and 15-minutes contact time for ClO_2 was 18.2% and 22.3% whilst for $Ca(CIO)_2$ it was 13.4% and 16.7% for 5- and 15-minutes' contact time respectively. The difference in TS concentration between raw water and settled TS for samples treated with both oxidants at 5- and 15-minutes' contact time was statistically significant ($p < 0.05$) based on a paired sample t-test at 95% confidence interval.
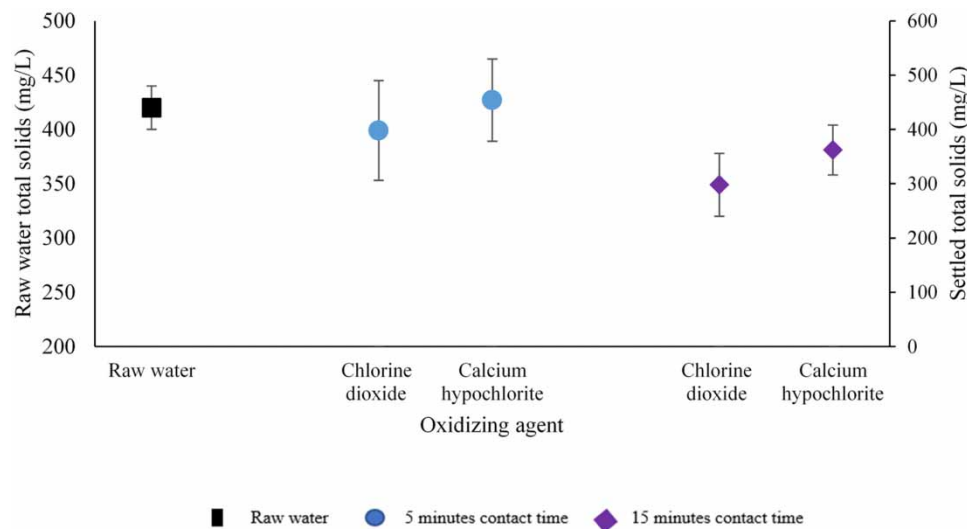

Figure 6 | Comparison between ClO_2 and $Ca(CIO)_2$ at 5- and 15-minutes' contact time in terms of total solids for Jan-March 2020.

Samples treated with chlorine dioxide had a lower TS concentration than those treated with $Ca(CIO)_2$ for both 5 and 15 minutes' contact time. ClO_2 is a more effective biocide than chorine (SUEZ 2020b). Thus, ClO_2 is more effective in removal of algae and biofilm material, which contribute to solids concentration. Based on an independent sample t-test at 95% confidence interval, the difference in settled TS between samples treated with ClO_2 and those treated with $Ca(CIO)_2$ for 5 minutes' contact time was statistically insignificant ($p > 0.05$). However, for 15 minutes' contact time, the difference was statistically significant ($p < 0.05$). Increasing the contact time from 5 to 15 minutes resulted in increased reduction in TS. The respective increase in reduction in TS as a result of increasing the contact time for ClO_2 and $Ca(CIO)_2$ were 4.1% and 3.3% respectively. The increase in reduction in TS as a result of increasing the contact time was statistically insignificant ($p > 0.05$) based on a t-test at 95% confidence interval for both oxidants.

According to EPA (2011) chlorine dioxide (ClO_2) has a stronger oxidizing ability than calcium hypochlorite ($Ca(CIO)_2$). Thus, the lower solids concentration in samples treated with ClO_2 can be attributed to its high oxidizing power compared to $Ca(CIO)_2$. Thus, ClO_2 performed better than $Ca(CIO)_2$ for solids removal . Increase in contact time resulted in increase in reduction in total solids.

Turbidity removal

Results for raw water turbidity and settled turbidity for jar tests at 5 and 15 minutes' contact times for both chlorine dioxide (CLO_2) and calcium hypochlorite ($Ca(CIO)_2$) followed by alum dosage are shown in Figure 7. The mean turbidity for raw water was 7.3 NTU while for settled turbidity for jars treated with chlorine dioxide were 0.8 ± 0.13 NTU (5 minutes) and 0.7 ± 0.07 NTU (15 minutes). The corresponding settled turbidity for treatment with $Ca(CIO)_2$ were 0.99 ± 0.14 NTU and 0.7 ± 0.06 NTU at 5 and 15 minutes' contact time for pre-oxidation respectively. Reduction in turbidity at 5 and 15 minutes' contact times for chlorine dioxide were
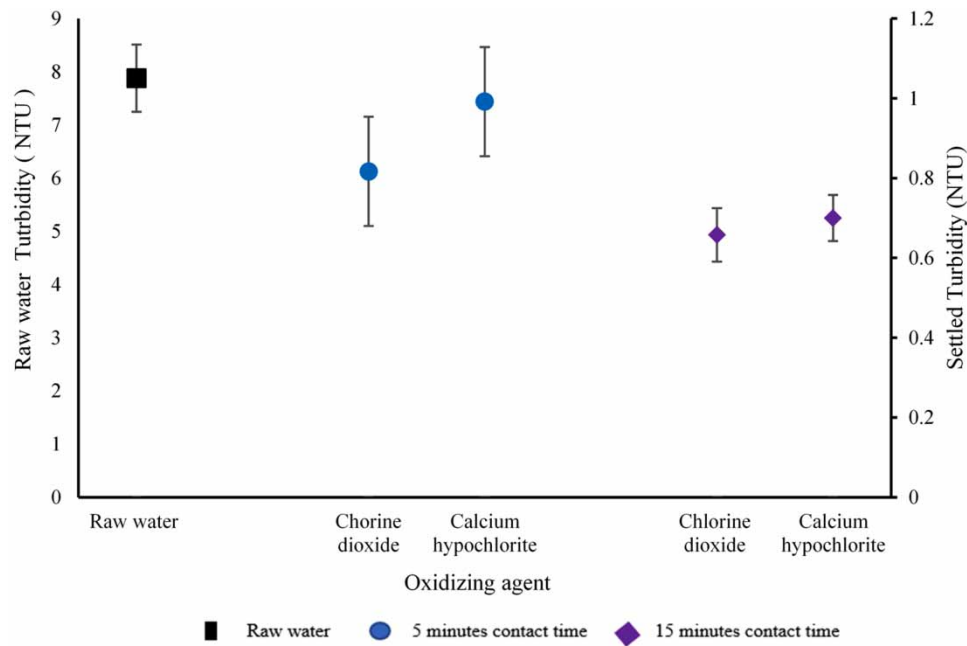
Figure 7 | Comparison between ClO_2 and $Ca(ClO)_2$ at 5 and 15 minutes' contact time in terms of settled turbidity for Jan-March 2020.

88.5% 91.0%, respectively, while for $Ca(ClO)_2$ it was 86.0% and 90.2% respectively. The difference in turbidity between raw water and settled turbidity for samples treated with both oxidants at 5 and 15 minutes' contact time was statistically significant ($p < 0.05$) based on a paired sample t-test at 95% confidence interval.

An independent sample t-test at 95.0% confidence level revealed insignificant differences ($p > 0.05$) in settled turbidity between samples treated with chlorine dioxide and those treated with $Ca(ClO)_2$ at both and 5 and 15 minutes' contact time. Increasing contact time from 5 to 15 minutes enhanced the reduction in turbidity by 2.5% (CLO_2). and 4.2% ($Ca(ClO)_2$). Chlorine dioxide is more effective in the removal of turbidity-causing substances such as algae (Jia *et al.* 2019). Increasing contact time had an insignificant ($p > 0.05$) effect on the decrease in turbidity for both oxidants.

Chemical oxygen demand removal

The results for chemical oxygen demand (COD) for pre-oxidation with chlorine dioxide (ClO_2) and calcium hypochlorite ($Ca(ClO)_2$) at 5 and 15 minutes' contact time are presented in Figure 8. Prior to oxidation with either ClO_2 or $Ca(ClO)_2$ the raw water had a mean COD of 84 mg/L. The mean settled COD for ClO_2 at 5 and 15 minutes' contact times were 13.3 ± 2.6 mg/L and 10.83 ± 3.7 mg/L, respectively, while for $Ca(ClO)_2$ it was 15.83 ± 3.8 mg/L and 14.17 ± 3.6 mg/L. ClO_2 achieved an 84.3% and 87.3% reduction in COD whilst $Ca(ClO)_2$ reduced the COD by 81.4% and 83.0% at 5 and 15 minutes' contact time respectively. The difference in COD concentration between raw water and settled COD for samples treated with both oxidants at 5 and 15 minutes' contact time was statistically significant ($p < 0.05$) based on a paired sample t-test at 95% confidence interval. However, ClO_2 can oxidise more organic material to carbon dioxide and water than both chlorine gas and $Ca(ClO)_2$ since it is a stronger oxidising agent (EPA 2011). This consequently results in lower chemical oxygen demand for water samples treated with ClO_2. Although samples treated with chlorine dioxide had relatively lower mean COD than $Ca(ClO)_2$ treated samples, the difference in settled COD was statistically insignificant ($p > 0.05$) at 95% confidence interval at both 5 and 15 minutes' contact. The mean settled COD for each of the two oxidants was lower at a contact time of 15 minutes compared to that at 5 minutes. The difference in COD levels at the two contact times for each of the oxidizing agents was statistically insignificant based on independent sample t-test at 95% confidence level. When the contact time was increased from 5 to 15 minutes, the COD removal efficiency for ClO_2 and $Ca(ClO)_2$ increased by 12.51% and 27.27% respectively. The increase in removal efficiency as a result of changing the contact time from 5 to 15 minutes was statistically significant ($p < 0.05$) for both chlorine dioxide and calcium hypochlorite.
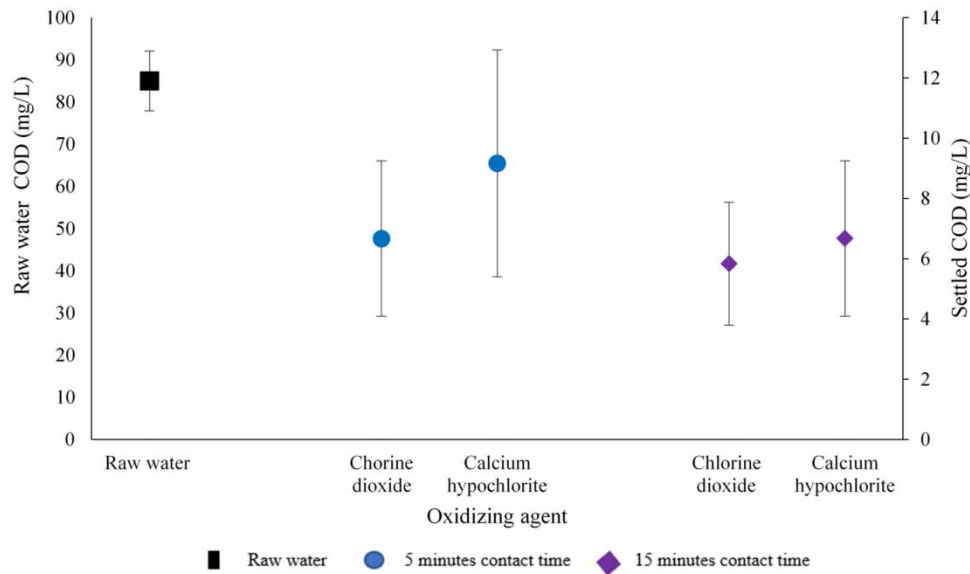
Figure 8 | Comparison between ClO$_2$ & Ca(ClO)$_2$ at 5 and 15 minutes' contact time in terms of COD for Jan–March 2020.

ClO$_2$ had a higher removal efficiency for COD compared to Ca(ClO)$_2$. However, there were no significant differences in the COD removal efficiencies between ClO$_2$ and Ca(ClO)$_2$ for both contact times.

Total algae removal

Total algae results comparing the effectiveness of chlorine dioxide (ClO$_2$) and calcium hypochlorite (Ca(ClO)$_2$) at 5 and 15 minutes' contact times for pre-oxidation of MJWTW raw water are as shown in Figure 9. The mean total algae count for raw water was 28.5×10^6 count/mL. The settled total algae count for chlorine dioxide treated water at 5 and 15 minutes was $(0.83 \pm 0.58) \times 10^6$ count/mL and $(0.75 \pm 1,3) \times 10^6$ count/mL, respectively, whilst for Ca(ClO)$_2$ treated water it was $(5.41 \pm 1.24) \times 10^6$ count/mL and $(3.58 \pm 1.46) \times 10^6$ count/mL. Reduction in total algae count using chlorine dioxide at 5 and 15 minutes' contact time was 97.0% and 97.3% respectively while for Ca(ClO)$_2$ it was 80.6% and 87.2% at 5 and 15 minutes respectively. The difference in total algae count concentration between raw water and settled total algae count for samples treated with both
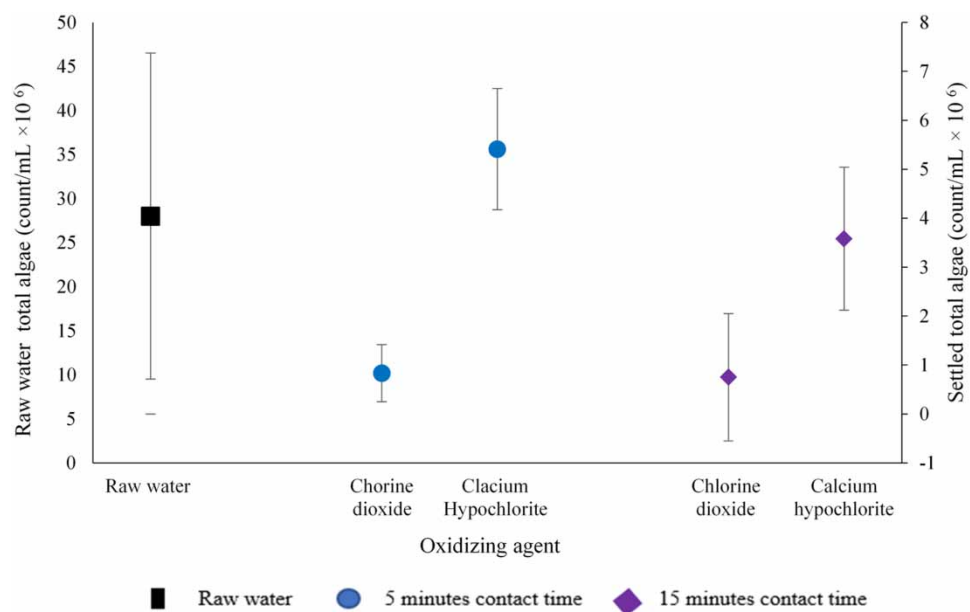

Figure 9 | Comparison between ClO$_2$ and Ca(ClO)$_2$ at 5 and 15 minutes' contact time in terms of total algae Jan–March 2020.

oxidants at 5 and 15 minutes' contact time was statistically significant ($p < 0.05$) based on a paired sample t-test at 95% confidence interval. The greater removal efficiency of chlorine dioxide in algae removal was as expected since chlorine dioxide has a stronger biocidal effect than chlorine (SUEZ 2020c). Increasing the contact time resulted in a corresponding increase in algae removal by 9.96% for chlorine dioxide and 33.82% for $Ca(ClO)_2$. However, based on a t-test at 95% confidence interval, increasing the contact time from 5 to 15 minutes had no significant ($p > 0.05$) effect in the reduction of algae count for treatment with both chlorine dioxide and calcium hypochlorite. Chlorine dioxide had significantly lower algae counts ($p < 0.05$) than calcium hypochlorite based on a t-test between results for the two agents at both 5 and 15 minutes' times.

The use of $Ca(ClO)_2$ for pre-oxidation of algae can lead to formation of undesirable byproducts while chlorine dioxide has less potential for THMs and is more effective than chlorine for algae removal and prevention of algae regrowth in the distribution system (Pearson & Swartz 1992). Thus, replacing calcium hypochlorite with chlorine dioxide will improve the water treatment process and reduce formation of disinfection byproducts. Chlorine dioxide had a better performance in removing algae and has potential to reduce regrowth of algae in the distribution system, which has been cited as a problem in Harare. A significant change was realized by increasing the contact time for chlorine dioxide, while for calcium hypochlorite the change was insignificant.

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

Raw water pH was found to be (6.8–8.3), which is out of the optimum range for use of alum as a coagulant thus necessitating pH adjustment before coagulation. The raw water parameters had low variability except total algae, which had a coefficient of variation of 65%. The alum dosage without pre-oxidation but with pH correction was determined to be 80 mg/L. The optimum chlorine dioxide dosage for pre-oxidation at Morton Jaffray Water Treatment Works during the period of the study was determined to be 0.075 mg/L and this corresponded to an optimum alum dosage of 60 mg/L. It was found that chlorine dioxide was more effective than calcium hypochlorite as water pre-oxidized with chlorine dioxide had relatively lower values for all parameters studied. Samples treated with chlorine dioxide had a significantly ($p < 0.05$) lower total algae count compared to those treated with calcium hypochlorite based on an independent sample t-test at 95% confidence interval. Use of chlorine dioxide may remove the need for pH correction with H_2SO_4 (current practice). Increasing the contact time from 5 to 15 minutes improved the oxidation efficiency of both chlorine dioxide and calcium hypochlorite. Thus, given the implications and potential complications of ensuring a longer retention time, especially related to either space or length of abstraction pipeline from source, 5 minutes' contact time before alum dosing may be suitable at Morton Jaffray Water Treatment Works. Thus, the use of chlorine dioxide will reduce chemical requirements as a relatively lower dose of chlorine dioxide could result in reduced alum demand. In addition to reduction in chemical usage, there are opportunities for improving treated water quality especially with respect to algae when chlorine dioxide is used.

Recommendations

Chlorine dioxide should be considered for pre-treatment of Morton Jaffray raw water. However, further studies should be carried out to assess the potential for both pre-oxidation and post oxidation using chlorine dioxide and impact on algae regrowth and toxins in the distribution system. Assessment of seasonal variation of the performance of chlorine dioxide is also recommended. There is need to further carry out research on the impact of chlorine dioxide on the other chemicals that are used at MJWTW such as powdered activated carbon (PAC), sulphuric acid, white hydrated lime and also anhydrous ammonia, and on the removal of biofilms in the distribution network.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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