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Research Article

Keywords: Advanced oxidation process, In-situ Na_2FeO_4 (VI), CWTP, Manganese (II)

Posted Date: August 9th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-789960/v1>

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Exploring the effectiveness of *in-situ* sodium ferrate (VI) during the bench-scale of manganese removal from raw water collected from a South African WTP

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Abstract

Manganese (Mn) is an essential element for human body and several enzymes rely on its redox properties. Its elevated concentrations in water can be toxic to humans, stain porcelains and can generate an undesirable taste in beverages. Several methods including adsorption, biologically active filtration oxidation and precipitation have been used to reduce it from water. Unfortunately, most of these methods have disadvantages of generating harmful by-products. Ferrate (VI) has been considered as a supplant to common oxidants during the treatment of drinking water. It has main advantages such as production of ferric ion, high oxidation potential, which may support coagulation, and the lack of significant halogenated by-product generation. However, this study aimed at exploring the effectiveness of *in-situ* liquid sodium ferrate (Na_2FeO_4) during the removal of Mn from raw water collected from Cullinan water treatment plant (CWTP) at the bench-scale. Na_2FeO_4 was produced using a wet oxidation method. The treatment of raw water collected from CWTP presented the removal percentage of Mn ranging between 82.70 and 99.20%. The pH of the drinking water samples raised from 7.25 to 10.97 after treatment. The treatability index (TI) was also studied. Only the TI of pH value was less than one. The TI results indicated high value of EC and authors would like to replace sodium by calcium in the ferrate product to reduce EC of the treated water and recommend the application of FeO_4^{2-} ions for the treatment of raw water in a full-scale as it showed to be a promising a green oxidant.

Keywords: Advanced oxidation process; *In-situ* Na_2FeO_4 (VI); CWTP; Manganese (II)

1. Introduction

Manganese is known as an essential nutrient for human life and several enzymes use the redox properties of this element (Li et al., 2020; Mou et al., 2011). However, its high levels in water supply and soil can be toxic to humans, cause an undesirable taste in beverages and stain

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porcelain (Myers et al., 2009; Ehrlich, Newman, & Kappler, 2015; Gerke, Little, & Maynard, 2016; Hao et al., 2015; Tobiason et al., 2016; Li et al., 2020). Evolving health research has revealed that its half-life in bones is about 8 to 9 years once it is absorbed by human cells (O'Neal et al., 2014; Li et al., 2020). Intellectual impairment and hyperactive behaviours in school-age kids exposed to manganese from drinking water has been documented (Li et al., 2020; Bouchard et al., 2011). Even worse, manganese can be transported directly to the brain, leading to nerve toxicity, resulting in dementia, anxiety, mask-like face, and ataxia (Wirth et al., 2007; Selikhova et al., 2016; Li et al., 2020). A disease called manganese poisoning is considered endemic in some South African manganese mines. Due to the adverse effects of manganese on human health, its release to natural freshwater from anthropogenic activities is a foremost environmental concern. Several countries have already set limits for manganese concentration in water courses. For instance, the European Commission set manganese level in drinking water at 0.05 mg/L (Council, 1998). The United States Environmental Protection Agency (USEPA) has not set a regulatory limit on manganese in drinking water but has also published a recommended secondary maximum contaminant limit (SMCL) of 0.05 mg/L (USEPA, 2013). In China, the maximum level of in the surface water is 0.1 mg/L (MEEPRC, 2002), and 5.0 mg/L in wastewater (Li et al., 2019) while in South African drinking water is $\leq 100 \mu\text{g/L}$ (SANS 241:2015). Most environmentally significant Mn contamination is directly related to the mining industry, where drainage effluents have typically high concentrations of dissolved manganese (Silva et al., 2012; Outram, Couperthwaite, & Millar, 2018; Li et al., 2019) and manganese waste residues that can persistently release Mn into terrestrial and aquatic ecosystems (Biswas et al., 2016; Li et al., 2020). South Africa, Russia, Australia, and China are the main host of Mn ore resources in the world (Kuleshov, 2017). Manganese removal is challenging because of the complex chemistry of the element, and the characteristics of manganese mine drainage (Li et al., 2020; Munyengabe et al., 2021a). However, much research has been conducted on the development of effective methods to remove manganese from water and wastewater. For acidic manganese mine drainage, increasing the solution pH and alkalinity are widely used techniques in manganese removal (Munyengabe et al., 2021a/2021b). Manganese can be removed from water through several methods, including adsorption and surface catalysed oxidation by manganese oxide-coated media (Knocke et al., 2010; Islam et al., 2010; Tobiason et al., 2008), biologically active filtration (Burger et al., 2008) and advanced oxidation processes (AOPs) (Munyengabe et al., 2021a/2021b). Another known treatment technique is the use of oxidants (ozone, chlorine dioxide and permanganate) to oxidize soluble manganese (II) to insoluble manganese (III) and (IV) and then separate particles

from solution (Goodwill et al., 2016; Brandhuber et al., 2013). Most of these strong oxidants have several disadvantages of generating harmful by-products. Ferrate (VI) as an emerging advanced oxidation process, has been chosen for pre-oxidation in drinking water treatment as a substitute to other strong oxidants (Sharma et al., 2015; Ma and Liu, 2002; Goodwill et al., 2016). The main advantages for ferrate salts in drinking water treatment include the production of ferric ion, which may support coagulation process (Ma and Liu, 2002; Graham et al., 2010; Goodwill et al., 2015), a strong oxidation potential (Wood, 1958) and the lack of significant halogenated by-product generation (DeLuca et al., 1983; Sharma et al., 2015; Jiang et al., 2016). However, despite these advantages, there is a scarcity of research experience that examines the implications of using *in-situ* ferrate for treating drinking water sources for potable water production. In natural water, ferrate (VI) addition could produce significantly more nanoparticles than ferric addition. As a strong oxidant, ferrate (VI) can supplant ozone or different chlorine-based oxidants. Its by-products containing ferric ions can be reused as an adsorbent (Munyengabe et al., 2020) and coagulant due to their high surface area and lead to the removal of contaminants such as arsenic and organic matter through particle removal processes, thus decreasing the need for an additional coagulant. In December 2019, the Tshwane metro located in Gauteng province, South Africa has experienced heavy floods, which loaded different metals in raw water especially manganese to the CWTP supply (Ntwaagae, 2019) as shown in Figure 1.

Figure 1: Flood observed in Mamelodi, Tshwane (Alex Mitchley, News24, 2019)

It is in that way the management of CWTP sought a new active water treatment method to reduce manganese level in the treated water. Sodium ferrate (VI) (Na_2FeO_4) came up in the first place as it is a cost-effective and emerging green chemical oxidant in the entire pH range. This chemical could raise the pH of the water to ≥ 9.5 and this can assist in the removal of heavy metals such as zinc and manganese (Patil, Chavan, & Oubagaranadin, 2016), which are hardly removed from water at $\text{pH} < 9$ by different treatment methods. However, this study aimed at exploring the effectiveness of *in-situ* Na_2FeO_4 during the removal of manganese from raw water collected from CWTP.

2. Experimental methods

2.1. Study area and physical parameters of raw water samples

The CWTP is located in the City of Tshwane Metropolitan Municipality, Pretoria, Northern Gauteng Province, South Africa with geographical coordinates of 25° 40'30.81" S and 28° 31' 45.78" E. The CWTP presented in Figure 1 receives raw water from the Bronkhorspruit Dam-Wilge River system. The design capacity of the plant is 16 ML/d and it supplies Cullinan Diamond Mine, Zonderwater Correctional services, City of Tshwane as well as individual small consumers (MWAR, 2015).

Figure 2: Aerial view of Magalies Water-CWTP (Source:

<http://www.magalieswater.co.za/wp-content/uploads/2016/01/AnnualReport-2011-2012.pdf>)

Raw water samples were collected from CWTP and immediately analysed on-site. Table 1 shows some physical parameters of the raw water samples recorded during the study. These include temperature, pH, turbidity, colour and electrical conductivity (EC).

Table 1: Physical parameters

2.2. Preparation of liquid sodium ferrate (VI)

Liquid sodium ferrate (VI) was synthesized using liquid sodium ferric chloride (43%), sodium hydroxide (43%) and hypochlorite (15%) in the ratio of 1:5:10 v/v through a wet chemical method (Munyengabe, & Zvinowanda, 2019). Equation 1 of its synthesis which was firstly proposed by Thompson et al. (1951) was considered in this study.

The working calibration curve (0 to 50 mg/L) was elaborated using potassium ferrate (VI) as a standard. The concentration of liquid Na_2FeO_4 was determined using Ultraviolet-Visible spectrophotometer, Cary 60 ($\lambda_{\text{max}} = 510 \text{ nm}$ for FeO_4^{2-}) (Munyengabe, & Zvinowanda, 2019).

3. Results and discussions

3.1. Analysis of Manganese (II) using inductively coupled plasma-optical emission spectroscopy (ICP-OES)

The initial and final concentrations of Mn (II) in water were determined using an ICP-OES and the results are illustrated in Table 2.

Table 2: Concentrations of Na_2FeO_4 and volume of raw water

The initial concentration of Mn in raw water collected from Cullinan WTP was greater than the SANS 241:2015, which is $\leq 100 \mu\text{g/L}$ Mn for risk-defined health-aesthetic and less than the SANS 241:2015, which is $\leq 400 \mu\text{g/L}$ Mn for risk-defined health-chronic purposes and the WHO guidelines for drinking water ($500 \mu\text{g/L}$) while after treatment all residual concentrations from 4 batches were below the standard limits for drinking water. Table 2 and Figure 2 clearly show that as the oxidation rate of manganese (II) increases as the concentration of ferrate increases. An exception to this statement was found when the concentration of ferrate was 20.0 mg/L , which could be attributed to the overdosing (mole ratio) of the oxidant and this can lead to the formation of soluble manganese (VII) (Goodwill et al., 2016). As a recommendation, drinking water treatment plants utilizing ferrate salts for manganese (II) oxidation would need to limit overdosing beyond the stoichiometric requirement to prevent the formation of this manganese (VII).

Figure 2: Residual concentration of manganese (II) in drinking water treated by

3.2. Treatability index

Table 2 clearly indicates the values of different physical parameters of the raw and treated water as well as their treatability index.

Table 3: Treatability index of drinking water treated by sodium ferrate (VI)

This table also shows that some parameters such as EC, pH and temperature of the treated water increased due to the input of sodium ions in water from sodium ferrate salt while turbidity and colour decreased considerably indicating a good settling and flocculation of suspended solids (Munyengabe et al., 2020; Munyengabe et al., 2021a). The average data was benchmarked against the specified limits as stipulated in SANS 241:2015 limits. To effectively communicate the raw water quality, a robust treatability assessment tool was applied. This tool is well-known as treatability index (TI) (Nihalani, 2015; Masindi, 2020). It is defined as the ratio of the aliquot's concentration and the maximum allowed limit as shown in Equation 2.

$$\text{Treatability index (TI)} = \frac{\text{Concentration of the aqueous parameter } (\mu\text{g/L, mg/L, etc.)}}{\text{Maximum allowed limit}} \quad (2)$$

Where, the concentration of the parameter is the level of the contaminants in aqueous solution or the analysed samples and the maximum allowed limit is the specified limit from different

water quality guidelines, standards and specifications such as SANS 241:2015, World Health Organization (WHO) and Environmental Protection Agency (EPA). On that note, Equation 2 suggests that when the treatability index is less than 1 the water will require zero treatment to comply to the required limit (Masindi, 2020). When the treatability index is greater than 1 the water will require treatment to comply to the required limits. When the treatability index is equal to 1 the water will require limited to no treated to comply to the required limit. The TIs of all parameters of the treated water were greater than 1 except the one of pH which was 0.93. This means that the treated water requires some post-treatment processes to comply to the required limits. The results show that the final EC was greater than the initial EC. This might be caused by the input of sodium ions in raw water from the sodium ferrate product. However, its replacement by a metal of group II in the product is highly recommended to reduce this EC in the treated water.

4. Conclusion and recommendation

The oxidation potential of ferrate salts is known to be pH-dependent and ranges from 0.70 V in basic conditions to 2.20 V in acidic conditions. The principal hypothesis of this work was to evaluate the effectiveness of manganese (II) oxidation by ferrate (VI) and inform its potential use in drinking water treatment. Manganese (II) is barely removed from water at low pH values. However, findings indicated that ferrate is a viable substitute to other strong oxidants used for manganese (II) oxidation in drinking water treatment. The treatment of raw water collected from CWTP presented the removal percentage of Mn ranging between 82.70 and 99.20%. Using ferrate for manganese treatment process would likely not cause concerns over-regulated halogenated byproducts, including bromate. The pH of the drinking water samples raised from 7.25 to 10.97 after treatment with sodium ferrate which was favorable for manganese removal. The TI results indicated high value of EC and authors would like to replace sodium by calcium in the ferrate product to reduce EC of the treated water.

Acknowledgements

Authors would like to thank the entire team of Magalies water-CWTP, especially Dr Masindi Vhahangwele for the assistance with ICP-OES.

Conflict of interests

The authors declare that they have no personal relationships or known competing financial interests that could have appeared to influence the work reported in this manuscript.

Contributions of all authors

AM prepared the sodium ferrate (VI), AM and CZ took and treated water samples, and MV analyzed the raw and treated water samples using ICP-OES.

Data availability statement

All data are presented in this manuscript.

Ethical statement

There was no ethical issue required during this work. The work does not concern to humans or animals.

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Figures

Figure 1

Flood observed in Mamelodi, Tshwane (Alex Mitchley, News24, 2019)

Figure 2

Aerial view of Magalies Water-CWTP (Source: <http://www.magalieswater.co.za/wp-content/uploads/2016/01/AnnualReport-2011-2012.pdf>)

Figure 3

Residual concentration of manganese (II) in drinking water treated by