Ferrates as a New Approach in Drinking Water Treatment

Petra Najmanova¹, Veronika Simonova¹, Jan Slunsky², Jan Filip³

¹DEKONTA, a.s., Prague, Czech Republic ²NANO IRON, s.r.o., Rajhrad, Czech Republic 3 Palacky University Olomouc, Olomouc, Czech Republic *Corresponding author's E-mail: <u>najmanova@dekonta.cz</u>*

Abstract

Chlorination is the most used disinfection technology for drinking water treatment. Based on last research it is obvious that chlorine disinfectants are releasing harmful substances that can cause serious problems in human health. Since the discovery of harmful by products the new oxidants/disinfectants have been investigated to replace chlorination. Ferrates are a powerful oxidising agent with the strongest redox potential among all of used oxidants. These high-valent states (VI, V, IV) iron compounds can be used as green oxidants in synthetic, organic transformations, water oxidation catalysts, and efficient agents for drinking water treatment. In this study we tested commercial product ENVIFER (NANOIRON, CZ) for reduction of E. coli, faecal coliforms and cultivable microorganisms at 22 and 36 °C (European parameters legislatively observed in drinking water). The ferrates efficiency was compared with commonly used chlorination. ENVIFER in amount of 50 mg/L was much more sufficient for E. coli and microorganisms at 22 and 36 °C removal than sodium hypochlorite. Ferrates are also suitable for elimination of heavy metals (arsenic and many others) and many organic compounds. Rapid reaction with contaminants and low reagent consumption is the advantage. It can serve as an efficient alternative to sodium hypochlorite usage.

Keywords: ferrates, disinfectant, drinking water

1. INTRODUCTION

Potassium ferrate, K_2FeO_4 , is a strong and environmental friendly oxidant (Yang et al. 2013; Talaiekhozania et al. 2017). In addition, the product of the ferrate (VI) oxidation reactions is considered to be ferric hydroxide, which is a useful coagulant (Jiang et al. 2007; Homolkova et al. 2016). Potassium ferrate is usually produced through a wet synthesis or using an electro-synthesis where the equipment is exposed to aggressive conditions (Sharma et al. 2005). Both methods use high concentration of hydroxides that are usually present in the final solution together with various salts. Moreover, ferrate solution is unstable due to high reactivity of the compound so it needs to be applied immediately after the synthesis.

The ENVIFER product (potassium ferrate) is produced by unique method and delivered in form of dry powder which can be stored for a long time in absence of moisture. It can be applied directly into contaminated water or a stock solution can be easily prepared. The disinfectant efficiency of ENVIFER was tested in microbiologically contaminated water from the domestic well.

2. MATERIAL AND METHODS

The naturally contaminated drinking water with fecal coliforms from the well was used for the experiment. The two different doses of two oxidants, potassium ferrate (ENVIFER) and sodium hypochlorite in concentrations of 50 and 100 mg/L were tested. All variants were performed in triplicates.

Following analyses were observed within oxidation lab tests: (i) culture-able microorganisms at 22 and 36 °C (EN ISO 6222); (ii) Escherichia coli and coliform bacteria (EN ISO 9308-1:2014); (iii) standard chemical parameters of water - pH and redox potential using multimeter Multi 3320, WTW.

3. RESULTS AND DISCUSSION

In the figure below there are results of different microbial groups (stated in European legislation for drinking water requirements) after oxidants addition. There are shown averages of triplicates determination in the following graphs.







Coliforms - 50 mg/L

0.25

hour

■ Envifer Ø Hypochlorite

E. coli - 50 mg/L

1

24

120,0

100,0

60,0

40,0

20.0

0,0

0

CFU/ 100ml 80,0

Culturable microorganisms at 22 °C - 100 mg/L



Culturable microorganisms at 36 °C - 100 mg/L



Envifer 🖾 Hypochlorite



E. coli - 100 mg/L





The influence of both oxidants on reduction of cultivable microorganisms at 22 °C was comparable. But if we compare the efficiency of potassium ferrate (98% efficiency) and sodium hypochlorite (64% efficiency) in dosage 50 mg/L for removal of cultivable microorganisms at 36 °C after 24 hours it is obvious that ferrate was more efficient than commonly used disinfectant sodium hypochlorite. The lower dosage 50 mg/L was sufficient to reach the limits for drinking water.

In case of *E. coli* reduction, we can observe 100% efficiency of 50 mg/L of ferrate and meeting standard European limits (for *E. coli* 0 CFU/100 mL) in comparison with 92% efficiency after hypochlorite addition.

The coliforms were also reduced with both disinfectants. The hypochlorite showed higher oxidative activity (for 100 mg/L dosage the efficiency was 98%) in comparison with 71% ferrates efficiency. Nevertheless 100 mg/L concentration of both oxidants was not sufficient to meet limits for drinking water (undetectable in 100 mL) and additional dose of ferrate/hypochlorite would be necessary for complete reduction of coliforms.

During the test the pH value and concentration of iron were also monitored. The pH increased after Envifer addition from 7.40 to 7.78 (for 50 mg/L), resp. 8.33 (for 100 mg/L) and after 24 hours it started decreased. The hypochlorite addition changed pH less, the maximal pH was 7.62. In every way the neutral pH 6-8 was maintained during treatment.

Due to their coagulation ability ferrates are also suitable for elimination of heavy metals. Two different concentrations (0.6 and 1.4 g/L) of ferrate were used for treatment of highly contaminated groundwater with heavy metals and pesticides. The results are shown in the figures below.



Figure 2: Elimination of heavy metals using ferrates

The concentration of heavy metals such as arsenic, barium, nickel and zinc dropped under detection limit after ferrate application in concentration of 1.4 mg/L. Iron, manganese, magnesium, calcium were also rapidly decreased after ferrate addition. It has no effect on boron, lithium and sodium concentration.

The effect of ferrates was also observed on pesticide contamination. The groundwater contained a huge amount of different pesticides such as ametryn, atraton, atrazine, atrazine-2hydroxy, chloridazon, chloridazon-desphenyl, desmetryn, fenuron, lenacil, prometryn, simazine-2-hydroxy and simetryn. The concentration of ametryn, atrazine, desmetryn, lenacil, prometryn and simetryn dropped under detection limit after ferrates addition in concentration of 1.4 g/L (see Figure 3). It has no effect on atraton, atrazine-2-hydroxy, chloridazon, chloridazon-desphenyl and simazine-2-hydroxy concentration.



Figure 3: Decrease of pesticides after ferrates addition

4. CONCLUSION

The disinfectant efficiency of ferrate was higher than hypochlorite at the same concentration for culturable microorganisms at 22 and 36 °C and for *Escherichia coli*. For coliforms an additional dose of ferrate/hypochlorite would be necessary for complete reduction.

Lower dose 50 mg/L of ferrate, resp. hypochlorite was sufficient for removal of culturable microorganisms at 22 and 36 °C and also for *Escherichia coli*.

Potassium ferrate (ENVIFER) was confirmed as a suitable disinfectant for elimination of microorganisms in drinking water and can replace so far used hypochlorite.

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REFERENCES

Homolkova M, Hrabak P, Kolar M, Cernik M (2016). Degradability of chlorophenols using ferrate(VI) in contaminated groundwater, Environmental Science and Pollution Research, 23, 1408-1413.

Jiang JQ, Wang S, Panagoulopoulos A (2007). The role of potassium ferrate(VI) in the inactivation of *Escherichia coli* and in the reduction of COD for water remediation, Desalination, 210, 266–273.

Sharma VK, Kazama F, Jiangyong H, Ray AK (2005). Ferrates (iron(VI) and iron(V)): Environmentally friendly oxidants and disinfectants, Journal of Water and Health, 03.1, 45-58.

Talaiekhozania A, Talaei MR, Rezania S (2017). An overview on production and application of ferrate (VI) for chemical oxidation, coagulation and disinfection of water and wastewater, Journal of Environmental Chemical Engineering, 5, 1828–1842.

Yang X, Gan W, Zhang X, Huang H, Sharma VK (2015). Effect of pH on the formation of disinfection byproducts in ferrate(VI) pre-oxidation and subsequent chlorination, Separation and Purification Technology, 156, 980-986.

Yang X, Guo W, Zhang X, Chen F, Ye T, Liu W (2013). Formation of disinfection by-products after pre-oxidation with chlorine dioxide or ferrate, Water Research, 47, 5856 – 5864.

EN ISO 6222:1999 Water quality - Enumeration of culture-able micro-organisms - Colony count by inoculation in a nutrient agar culture medium

EN ISO 9308-1:2014 Water quality - Enumeration of *Escherichia coli* and coliform bacteria - Part 1: Membrane filtration method for waters with low bacterial background flora