Reduction of Metal Ion Species in Contaminated Water by Utilizing Potassium Ferrate (K$_2$FeO$_4$) Treatment

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Author's contribution

The sole author designed, analyzed, interpreted and prepared the manuscript.

Article Information

Original Research Article

ABSTRACT

Aims: To demonstrate that potassium ferrate will remove potentially toxic metal ions from contaminated water samples.
Study Design: A known amount of metal ions were solubilized in aqueous solution, then exposed to potassium ferrate in known amounts. Extent of removal was monitored by ion chromatography and visible spectroscopy.
Place and Duration of Study: Department of Chemistry, Durham Science Center, 6001 Dodge Street, Omaha Nebraska 68182 USA.
Methodology: Known amounts of iron (II), manganese (II), copper (II), and calcium were solubilized in aqueous solution to known molarity. These mixtures were treated by utilizing potassium ferrate in known amounts. The presence of metal ions was monitored by ion chromatography and/or visible spectroscopy before and after treatment with potassium ferrate. Potassium ferrate was present with metallic ions for 24 hours at 21ºC.
Results: Metal ions were placed in aqueous solution, iron (II) as Fe(NH$_4$)$_2$(SO$_4$)$_2$, copper (II) as CuCl$_2$•2H$_2$O, manganese (II) as MnCl$_2$•4H$_2$O, and magnesium (II) as magnesium chloride, calcium as calcium chloride. Potassium ferrate treatment did not remove chloride (Cl$^-$), ammonium (NH$_4^+$), and sulfate (SO$_4^{2-}$). The cation calcium was decreased by 84.0%, magnesium was decreased by 42.5%, copper (II) was removed by 100%, iron (II) by 48.7%.
Reduction of calcium, magnesium, copper, and iron (II) was monitored by ion chromatography. Reduction of iron (II), manganese, and copper (II) was monitored by visible spectroscopy. Substantial reduction of metallic ions was found in all tests after a 24 hour period at 21ºC.
Conclusion: These metals have been associated with oxidative stress, damage to mental and

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central nervous system function. Potassium ferrate is shown to be efficient in removing many of these potentially harmful ions. Visible spectroscopy and ion chromatography is shown to be effective in monitoring the reduction of metallic ions during investigations or potassium ferrate treatment of contaminated water.

ABBREVIATION

K_2FeO_4; Potassium ferrate anhydrous

1. INTRODUCTION

The compound, potassium ferrate (K_2FeO_4), has various properties that enable this compound to be useful as treatment model for contaminated or waste water. These properties include high stability, strong oxidizing power, substantial selectivity as an oxidizing agent, high aqueous solubility, and a non-toxic by-product in the form of Fe (III) [1,2]. Many types of organic contaminants found in waste water can be removed by the action of K_2FeO_4 in a short period of time, to form non-hazardous products [1]. Potassium ferrate has been shown to function as a disinfectant (inactivating *Escherichia coli* and viruses), clearing agent, and coagulant of non-solubilized particulate matter [1]. The dry solid is stable for long periods of time when kept dry [1,2]. This compound is an oxidant at all pH levels, but the rate of reaction increases as pH decreases [1]. The by-product following oxidation reactions is Fe (III), which is considered to be non-toxic [1]. The iron (VI) cation reduces rapidly to iron (III) and oxygen in aqueous solution [1].

The kinetics and efficiency of organic compound oxidation utilizing K_2FeO_4 has been accomplished in previous studies for: aldehyde compounds [3], aliphatic sulfur compounds [4], and alcohol compounds [5]. Precious investigation has shown K_2FeO_4 to be highly effective in removing metals and non-metals from contaminated water samples [6]. In addition, this compound has been shown to be effective in removing carcinogenic nitrosamine compounds [7].

Metal contamination of anthropogenic origin is generally more concentrated in highly industrialized urban areas, but lower in rural or remote areas [8]. Sources of metal contamination in the atmosphere include [8]: 1) Industrial sites having combustion of fossil fuels (coal, oil, natural gas); 2) Metal manufacturing facilities; 3)

Smelters or mines; 4) Refuse incinerators; and 5) Cement production. Combustion of oil or coal can result in the emission of bismuth, arsenic, cadmium, chromium lead, copper, manganese, nickel, mercury, zinc, and selenium [8]. Because heavy metals tend to bio-accumulate, they can become dangerous [9]. These heavy metals can enter into consumable water supply by industrial or urban waste disposal routes, with potential consequences of reduced or damaged central nervous functions, lower energy levels, and damage to lungs, kidneys, liver, or blood composition [9]. Long-term exposure to heavy metals can result in slow progressing physical, muscular, and neurological degenerative processes that are similar to Alzheimer's disease, Parkinson's disease, and muscular dystrophy; with added risks for cancer, allergies, and multiple sclerosis [9].

Transition metal ions have been implicated as important factors for catalysis in free-radical generation that leads to neurodegenerative processes [10]. Heavy metal contamination has been shown to be an issue for human health in Pakistan [11], in agroecosystems [12], Nigeria [13], India [14], rivers of India [15], lakes of China [16], river estuaries of China [17], river sedimentations [18], tributary sediments of China [19], irrigation run off [20], Ethiopian soils irrigated with wastewater [21], and paddy soils irrigated with acid mine drainage [22]. Removal of heavy metals from contaminated soils through "soil washing techniques" utilizing chelating agents ethylenediaminetetraacetic acid (EDTA), citric acid, and nitrilotriacetic acid all have been shown to be useful [23]. Heavy metal pollution has been shown to be among the most serious of all environmental issues [24].

The ferrate anion (FeO_4^{2-}) is a stronger oxidizing agent than permanganate [25], this and the negative charge of the species induces interaction contributing to flocculent formation leading to coagulation of pollutants [26], and disruption of materials such as sludge [27]. The ferrate ions are quickly reduced by water to form oxygen and ferric complexes considered to be important in actions of coagulation and flocculation [28]. Previous studies have shown

that the ability of ferrate ion to initiate coagulation is vital for the removal of particulate matter and heavy metals [29,6]. This study shows the potential of K_2FeO_4 to be an effective agent for reducing heavy metals associated with anthropogenic origin and a potential cause of human health problems.

2. METHODOLOGY

2.1 Reagents

All reagents used were analytical grade and supplied by Sigma-Aldrich, PO Box 14508, St Louis Missouri 63178 USA. Highly purified potassium ferrate (> 99%) was supplied by the Department of Chemistry, Hamilton Hall, University of Nebraska at Lincoln, Lincoln Nebraska.

2.2 Ion Chromatography

For ion chromatography a 792 Basic IC instrument was utilized for cation and anion ion identification. Mobile solvent utilized for cation ion chromatography are 70% ethanol in distilled water and with Metrosep column 1-2 (spherical silica gel with polybutadiene maleic acid groups). Mobile solvent utilized for anion ion chromatography are 0.10 molar sulfuric acid, 1.8 millimolar sodium carbonate, 1.7 millimolar sodium bicarbonate in distilled water, with IC SEP AN1 column (poly(styrene-divinylbenzene) alkyl dimethyl ethanol ammonium functional group). The 792 Basic IC instrument utilizes a thermostatic conductivity detector. The thermostatic detector maintains a highly stable temperature with minimal variation from the operating temperature. Actual cell volume of detector is 1.5 microliter. Calibration for concentration and peak elution for both cation and anion chromatography was accomplished by used of standards having known concentrations of ions of interest. Samples were injected directly followed by monitoring of ion peaks for both cations and anions.

2.3 Visible Spectroscopy

The Vernier SpectroVis Plus spectrophotometer with LabQuest 2 (Vernier, 13979 SW Millikan Way, Beaverton, OR 97005 USA) was utilized for monitoring metal ion content before and after treatment with potassium ferrate. The SpectroVis instrument employs an LED and tungsten bulb to transmit light through a solution containing the sample. The transmitted light then passes through a high-quality diffraction grating and the diffracted light is sorted and collected by a linear CCD array detector. For operation the SpectroVis is interfaced directly to LabQuest or a computer USB port. SpectroVis Plus is a portable visible light spectrophotometer with fluorescence capabilities. Measure wavelengths from 380 nm to 950 nm and analyze results in full color. Samples were placed in 1 cm cells for monitoring of appropriate cation peak from 370 nm to 870 nm. Analysis was accomplished before and after treatment of aqueous mixtures with potassium ferrate lasting 24 hours and at 21ºC.

3. RESULTS AND DISCUSSION

With increasingly stringent regulations, heavy metals are determined to by environmental priority pollutants and are environmental problems [24]. Removal of toxic heavy metals include methods such as chemical precipitation, ion-exchange, adsorption, membrane filtration, electrochemical treatment technologies, chelation, etc [24]. The approach in this study is chemical precipitation by use of potassium ferrate. The ferrate anion species FeO_4^{2-} forms a self-clearing Fe (III) species that precipitates organic compounds [3,4,5] and certain metallic ions as a colloidal-like mat [6].

If the oxidizing action of FeO_4^{2-} does not act upon a contaminant directly, the contaminant can still be removed by co-precipitation with the by-product Fe (III) in a red gelatinous form of $Fe_2O_3 \bullet H_2O$ [2,6]. The reaction of potassium ferrate with the solvent water has been shown to produce [2]: oxygen gas, KOH (assuming K_2FeO_4), and ferric (III) oxide (Fe_2O_3). The reddish gelatinous formation was observed in all test samples in this study, following treatment with K_2FeO_4.

3.1 Measurement of Clarification by Potassium Ferrate Utilizing Spectroscopy

To evaluate the clarification of a non-organic complex salt compound in a water sample, a mixture of ferrous diammonium sulfate $(Fe(NH_4)_2(SO_4)_2 \bullet 6H_2O)$ was dissolved to a concentration of 0.007561 molar. An absorbance spectra was obtained from 370 nm to 870 nm was accomplished prior to treatment (see Fig. 1). Following treatment with potassium ferrate (2.727×10^{-5} moles or 2.7272×10^{-3} molar) and treatment at room temperature (21ºC) for 24 hours, substantial clarification was accomplished (see Fig. 1).
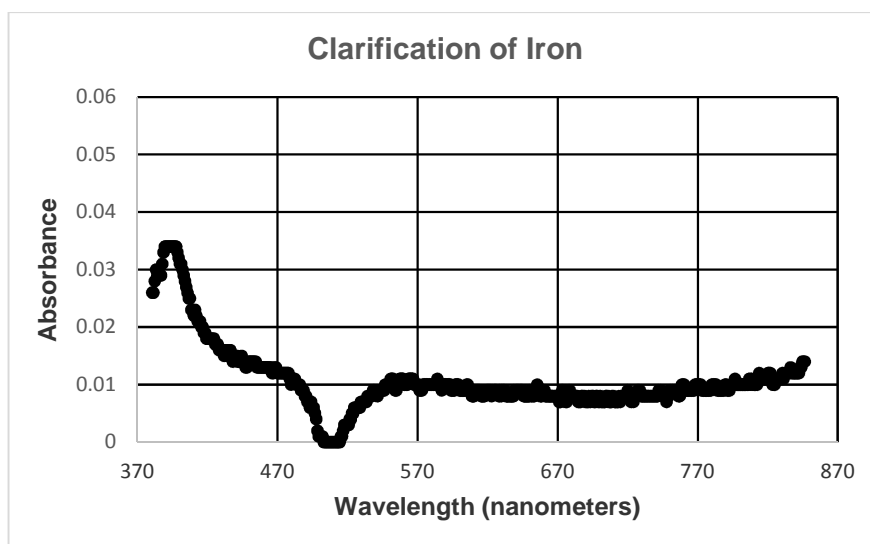
Fig. 1. Clarification of iron from solution accomplished by potassium ferrate. Spectra of ferrous diammonium disulfate hexahydrate at 0.593 grams/200 milliliters or 0.007561 molar (top plot). After addition of potassium ferrate (2.727 x 10^{-5} moles or 2.7272 x 10^{-3} molar) (bottom plot) and subjecting test sample solution at room temperature (21ºC) for 24 hours

To evaluate the clarification of a non-organic salt compound in water, a mixture of manganese chloride tetrahydrate ($MnCl_2 \cdot 4H_2O$) was dissolved to a concentration of 0.005811 molar. Again, an absorbance spectra was obtained from 370 nm to 870 nm was accomplished prior to treatment (see Fig. 2).

Following treatment with potassium ferrate at 5.504 x 10^{-3} molar and room temperature (21ºC) for 24 hours, substantial clarification was accomplished (see Fig. 2). Removal of manganese (clarification) was accomplished by application of potassium ferrate. It was observed that the absorbance from 390 nm and higher (up to 550 nm) was substantially reduced or eliminated completely (this at 550 nm and higher).

In a similar manner, it was determined that a salt form of copper (II), as the compound $CuCl_2 \cdot 2H_2O$, could be substantially reduced by treatment with potassium ferrate.

Measureable amounts of copper, as copper chloride in solution, was removed after use of 1.919 x10^{-3} molar potassium ferrate. The diagnostic absorbance at 770 nm to 870 nm (see Fig. 3) was initially at 0.058. However, after treatment for 24 hours at room temperature the absorbance at 770 nm to 870 nm was reduced to 0.040. The amount of reduction is determined to be at least 33% reduction of metal ion (see Fig. 3).

Chemical precipitation as a means of clarification and removal of undesired materials from water is effective and the most widely used method in industry due to simplicity and lesser expense [24]. The formation of precipitates is followed by sedimentation or filtration, with treated water decanted and appropriately discharged [24]. Shown here, is the effective reduction of manganese chloride tetrahydrate, copper chloride dihydrate, and ferrous diammonium disulfate hexahydrate by use of potassium ferrate and monitoring of the course of the reduction by use of visible spectroscopy measurement from 370 nm to 870 nm.

3.2 Ion Reduction by Potassium Ferrate Measured With Ion Chromatography

Ion chromatography is a methodology able to measure concentrations of inorganic anions, in addition to anions fluoride, chloride, nitrate, nitrite, and sulfate. There are various method to assay for cations by spectroscopy, however ion chromatography can easily handle cations such as lithium, sodium, ammonium, potassium, calcium, and magnesium with a detection sensitivity to trace levels [30]. Concentrations of organic acids can also be measured utilizing ion chromatography. Analysis for cations utilizing ion chromatography offers the advantage of providing information on metal speciation [30].
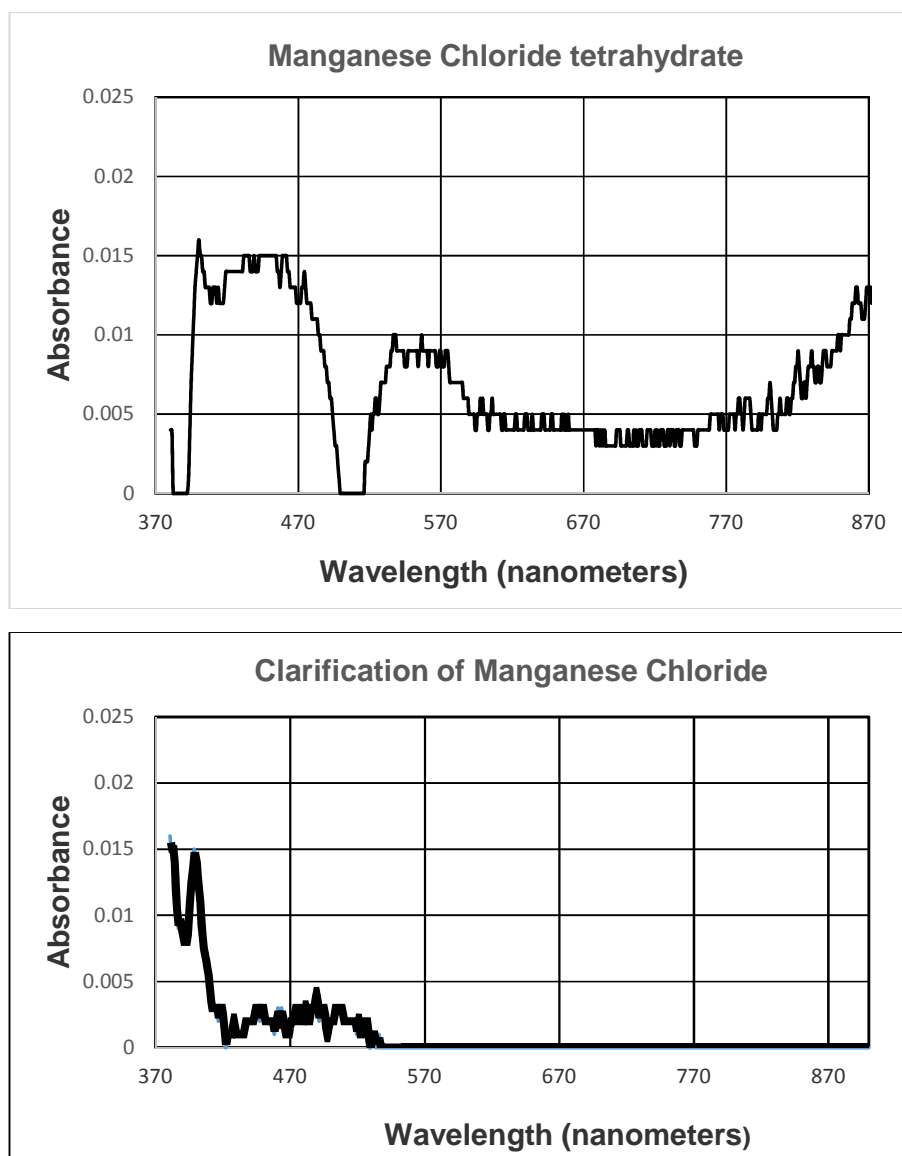
Fig. 2. Clarification of manganese chloride. Top spectra is manganese chloride tetrahydrate in water at 0.236 g/200 ml or 5.811 x 10^{-3} molar. Note absorbance area after 390 nm to 870 nm is descriptive. After treatment with potassium ferrate (5.504 x 10^{-5} moles or 5.504 x 10^{-3} molar) (bottom spectra), for 24 hours at 21⁰C, the overall absorbance from 390 nm and higher is substantially reduced (up to 550 nm) or eliminated completely (550 nm and higher)

The conductivity detector is a very common detector type used in ion chromatography, this is due in part to electrolytic conductivity being a universal property shared by all ions. Elution peaks were readily identifiable and resolved. Ion chromatography is well established as a regulatory method for analysis of inorganic anions in environmental samples, an advantage because there are few alternative methods which can determine multiple anions in a single analysis [30].

Ion chromatography was applied in this study to provide a workable duplex approach for determining the reduction of ionic species by the action of potassium ferrate. The reduction of metal ions is a genuine health concern for developing nations as well as industrial nations [1,9,11,12]. In this study, visible spectroscopy followed the apparent absorbance spectrum of various salt compounds of manganese, copper, and iron (II). The reduction of copper and iron (II) was shown by absorbance measurement from

370 nm to 870 nm. Ion chromatography was applied to show the reduction of calcium and magnesium by the action of potassium ferrate.

Results of treatment of aqueous samples having various cation species by use of potassium ferrate and measurement by ion chromatography are shown in Table 1. Again the treatment was for a 24 hour period at 21ºC. The calcium cation was decreased by 84.0%, with the magnesium cation decreased by 42.5%. The copper and iron (II) analysis shown in Table 1, were the identical

mixtures applied for visible spectroscopy detection approach. As measured by ion chromatography, the copper (II) species was completely reduced following treatment of mixture with potassium ferrate for a 24 hour period of time. Treatment of mixture test sample having ferrous diammonium disulfate hexahydrate (the same sample presented in visible spectroscopy measurement) with potassium ferrate for 24 hours resulted in a measurable reduction of iron (II) of 48.7%.
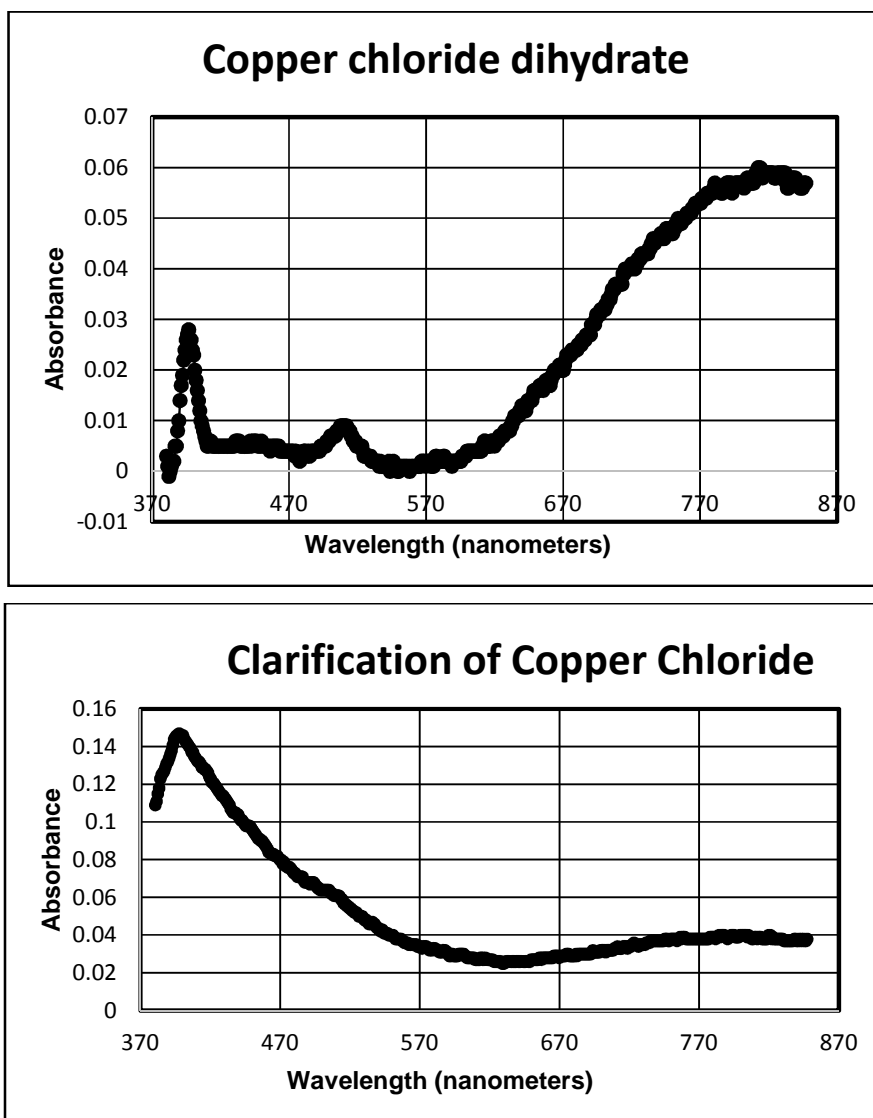

Fig. 3. Partial clarification of copper chloride. Top spectra is copper chloride dihydrate at 0.150 g/200 mL water or 4.399 x 10^{-3} molar. Note absorbance at 770 nm to 870 nm at 0.058. After treatment with potassium ferrate (1.919 x 10^{-5} moles or 1.919 x 10^{-3} molar), there is a measureable 33% reduction of metal species indicated at 770 nm to 870 nm (bottom spectra), with absorbance at 0.040

Table 1. Metal ions assayed by ion chromatography and removed by K$_2$FeO$_4$

Species	Initial concentration	*Treatment by potassium ferrate	Remaining in solution after 24 hours treatment
Calcium	2.198×10^{-5} molar	3.585×10^{-5} moles (3.585×10^{-3} molar)	3.518×10^{-6} molar
Magnesium	2.764×10^{-5} molar	3.585×10^{-5} moles (3.585×10^{-3} molar)	1.588×10^{-5} molar
Copper	4.399×10^{-3} molar	4.545×10^{-5} moles (4.545×10^{-3} molar)	0 (Removed all copper)
Iron II	7.561×10^{-3} molar	3.585×10^{-5} moles (3.585×10^{-3} molar)	3.876×10^{-3} molar

Treatment was by amount of K$_2$FeO$_4$ shown in table at 21ºC and for 24 hours

Anion standards were available in the case of anion ion chromatography to help determine if the action of potassium ferrate could be helpful in eliminating simple anion species. The same salt mixtures utilized for visible spectroscopy observation were analyzed prior to and after 24 hour treatment with potassium ferrate. It was found that potassium ferrate treatment of sample water mixtures did not reduce chloride anion, sulfate anion, or ammonium cation as measured by ion chromatography.

The problem of heavy metal contamination of industrial and municipal waste waters is an issue deserving scrutiny and study. The compound potassium ferrate has an iron atom is the Fe (VI), possessing a strong capability for oxidizing a broad range of environmental problematic compounds. This study has shown that potassium ferrate reduces substantially a number of ion species that are of serious consideration as potentially health threatening contaminants of consumable water. This study has also demonstrated that visible spectroscopy and ion chromatography are very useful tools to measure and evaluate the ability of potassium ferrate to reduce/affect the concentration of these species in aqueous samples. Further study will be beneficial in understanding the potential applications of the environmentally friendly strong oxidant potassium ferrate.

4. CONCLUSION

Metal contamination of anthropogenic origin is generally more concentrated in highly industrialized urban areas. Long-term exposure to heavy metals can result in slow progressing physical, muscular, and neurological degenerative processes. The compound, potassium ferrate or K$_2$FeO$_4$, has various properties that enable this compound to be useful as treatment approach for contaminated or waste water. This study has presented results of monitoring the action of potassium ferrate to reduce ions, by visible spectroscopy absorbance spectra from 370 nm to 870 nm. In addition, this study as shown the beneficial efficacy of monitoring the action of potassium ferrate in reducing cations, by use of ion chromatography. These two instrumental methodologies are a powerful approach of studying the effects of a chemical co-precipitation operation in reducing undesirable ionic species. Visible spectroscopy showed that potassium ferrate substantially reduced copper (II) cations, iron (II) cations, and manganese (II) cations after treatment for 24 hours at 21ºC. Ion chromatography also showed that potassium ferrate substantially reduces calcium (II) cations, magnesium (II) cations, copper (II) cations, and iron (II) cations. Potassium ferrate did not remove chloride anion (Cl$^-$), sulfate anion (SO$_4^{2-}$), and ammonium cation (NH$_4^+$). The further investigation of methodologies to remove toxic heavy metals by means that are efficient is a necessary endeavor to assure safe water resources for human consumption.

CONSENT

It is not applicable.

ETHICAL APPROVAL

It is not applicable.

ACKNOWLEDGEMENTS

COMPETING INTERESTS

Author has declared that no competing interests exist.

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