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THE EVALUATION OF THE APPLICATION EFFICIENCY OF POTASSIUM FERRATE FOR ADVANCED TREATMENT OF MUNICIPAL WASTEWATER

Anoshiravan Mohseni Bandpei [1], Yadollah Fakhri [2], Rouhollah Khodadadi[3], Hamed Mohammadi [4], Nezam Mirzaei[5,6], AbdolAzim Alinejad[2]*, Zohreh Bahmani[7]

[1]Environmental and Occupational Hazards Control Research Center, Shahid Beheshti University of Medical Sciences, Tehran, Iran.

[2,3]Social Determinants in Health Promotion Research Center, Hormozgan University of Medical Sciences, Bandar Abbas, Iran.

[4]Department of Epidemiology and Biostatistics, Health Faculty, Isfahan University of Medical Sciences, Isfahan, Iran.

[5]Environmental Health Research Center, Kurdistan University of Medical Sciences, Sanandaj, Iran.

[6]Department of Environmental Health Engineering, School of Public Health, Tehran University of Medical Sciences, Tehran, Iran.

[7]Environmental Health Engineering, Faculty Member of Health School, Iran University of Medical Sciences, Tehran, Iran.

Email: azimalinejad@gmail.com

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Abstract

Iron (VI) and iron (V), known as ferrates, are powerful oxidants and their reactions with pollutants are typically fast with the formation of non-toxic by-products. The use of potassium ferrate (VI) as an alternative wastewater remediation chemical has been studied and is reported in this paper. Ferrate ion as a strong oxidant has the highest oxidation potential among all oxidants and disinfectants in water and wastewater treatment. Ferrate (VI) Ions are reduced to Fe (III) ions or hydroxide ferric in water, which can simultaneously serve as a coagulant and oxidant or a disinfectant in a versatile process. The aim of this study was to determine the effectiveness of potassium ferrate use for advanced treatment of sewage.

This quasi-experimental study was conducted in laboratory scale. An advanced Wastewater treatment was studied by potassium ferrate on effluent wastewater through determining the effect of pH and concentration on the removal of turbidity, the chemical oxygen Demand (COD) and phosphorus. In order to determine the efficiency of disinfection of ferrate, the effect of three variables, contact times, ferrate concentrations, and pH on disinfection Processes was determined by the most probably number (MPN) index. The results showed that the best condition for COD removal

efficiency and the removal of turbidity was 65% and 90% using potassium ferrate with pH=5 and optimum concentration of 10 mg/L. pH and concentration of potassium ferrate for optimum performance of phosphorus removal was 5 and 12 mg/L, which caused phosphorus removal 72%. The optimum condition for potassium ferrate applied as disinfectant was in 4 mg/l concentration, Contact time of 25minute, and pH=6 Potassium ferrate can be used as an effective oxidant, disinfectant and coagulant Chemical for treating a variety of municipal and industrial wastewaters. It will allow access to multiple targets in a process.

Key Words: Potassium ferrate, Municipal wastewater effluents, advanced wastewater Treatment, Potential-oxidant.

Introduction

Population growth, contamination of surface and groundwater water, non-uniform distribution of water resources and frequent droughts are of the reasons which are led to seek new sources of water supply[1] . The use of highly treated effluents that are released from municipal water treatment plant into environment can be considered as a relatively reliable water resource. The quality of secondary effluents is not often sufficient to meet the standards effluent discharge or reuse; so that further treatment should performed in these cases to improve the quality of secondary wastewater treatment systems or another alternative method should be utilized to sewage disposal [2]. In advanced treatment, which is often utilized to remove the nitrogen and phosphorus compounds, it may be to apply various methods for elimination of suspended solids, dissolved organic compounds and inorganic salts. The standards of drinking water and effluent discharge should be improved to high confidence level due to increasing of water pollution and water scarcity over time in most regions of the world which it is need to applied innovative technology and chemical with lesser by-products [3]. The wide range of coagulants, oxidants and disinfectants are used for water and wastewater treatment. The most of used coagulant are included ferric sulfate, aluminum sulfate, ferrous sulfate and ferric chloride [1, 4]. The aluminum salts produce the aluminum solute in water and they can create health problem [5]. Also, these salts can generate a large amount of sludge which its treatment is associated with high cost [6]. Some problems associated with the coagulant salts are including high oxygen level demand for ferrous sulfate, high alkali level demand for ferric sulfate and ferric chloride and the low efficiency (at high organic concentration and color). The high dose of Iron and alumina salts is required in coagulation processes which it is considered as another major problem [7]. Oxidation and disinfection are of main unit process of water and wastewater treatment and a number of oxidants and disinfectant are used in these processes.

Commonly used oxidants and disinfectants include chlorine, hypochlorite, chlorine dioxide and ozone that their use has some limitations such as the formation of dangerous byproducts. An ideal and efficient chemical disinfectant should be able to inactivate microorganisms and a partially decomposed and oxidation of organic and inorganic pollutants, suspended solids and heavy metals and colloids. Ferrate salt (VI), K2FeO4, is a chemical with high Redox potential which has all these criteria. Ferrate ion (VI), as a very potent oxidant, has the highest Redox potential among all of oxidants and disinfectants which is used for the water and wastewater treatment. The Redox potential of potassium ferrate is 2.2 V in acidic condition whereas this potential for ozone and chlorine is 20.4 and 1.4 V, respectively. The Redox potential of ferrate potassium in acidic and alkali condition has presented in reactions 1 and 2. Also, the reaction 3 shows that ferrate ion (VI) can reduce to Fe (III) or ferric hydroxide during the oxidation and disinfection process and can be used in a multipurpose process or as coagulant (1).

$$Feo_4^{2-} + 8H^+ + 3e^- \rightarrow Fe^{3+} + 4H_2o \qquad (E^0 = +2.2V) \qquad (1)$$

$$Feo_4^{2-} + 4H_2o + 3e^- \rightarrow Fe(oH)_3 + 5oH^- \qquad (E^0 = 0.72V) \qquad (2)$$

$$4K_2Feo^4 + 10H_2o \rightarrow 4Fe(oH)_3 + 3o_2 + 8KoH \qquad (3)$$

K_2FeO_4 is a strong oxidant that can oxidize organic compounds efficiently[8]. Potassium ferrate is quite stable solid, but it decomposed by contact with oxygen or dissolving in water. Potassium ferrate solution is unstable in acidic condition and stable in alkali condition. Some applications of potassium ferrate includes water disinfection, decomposition of synthetic organic contaminants, oxidation of inorganic pollutants, removal of humic materials, treatment and disinfection of water, wastewater and sludge [5, 9]. Such unique properties make the ferrate(VI) to be an environmental friendly and dual function chemical reagent and could combine the pre-disinfection/oxidation with coagulation into one unit [10]. Ferrate (VI) salt is a promising dual-functional chemical for water and wastewater treatment and can achieve the reduction of a wide range of organic and inorganic pollutants in waste-water [11]. It can be expected that potassium ferrate oxidation disintegrate biomass particulates and transform them into soluble compositions, destruct bacterial cell membranes [12]. Many studies have been conducted on application of water and wastewater treatment processes. Jiang et al has been surveyed and compared the potassium ferrate performance with sodium hypochlorite, ferric sulfate and aluminum sulfate in inactivation of E.coli and COD removal. The results of their study indicated that the COD removal efficiency by

potassium ferrate is 30% greater than ferric sulfate and aluminum sulfate. In addition, the ferrate was successfully able to reduce the E.coli (up to 3 log) rather than other coagulants [13]. Another study of Jiang et al has verified the proper ability of potassium ferrate in pollutant removal [14]. Sharma et al were applied the potassium ferrate to evaluated its ability for oxidation of organosulfur compound. Ciabatti et al has been conducted a study to evaluate the potassium ferrate ability for colorful textile wastewater treatment. In their study, the potassium ferrate represented high efficiency for simultaneous removal of dye, turbidity, TSS and organic material at the optimum dosage of 70 mg/l. The use of potassium ferrate for water and wastewater treatment do not produce the mutagens and carcinogen by-products. Ferric oxide generated from the decomposition of potassium ferrate produces a potent coagulant which it removes many metals, non-metallic and humic acid [15]. In addition, it can inactivate a wide range of microorganisms at lower dosage and contact time. Due to the relatively high efficiency of potassium ferrate in removing of various pollutants, the main objective of this study was to evaluate the efficiency of this compound in advanced treatment of wastewater and to survey the effect of different variables on the process.

Material and methods

This quasi-experimental study was conducted in laboratory scale using the batch system on secondary wastewater effluent. This effluent was not chlorinated. The samples were collected from the wastewater treatment plant of Shahid Beheshti University of Medical Science. The sampling method was composite sampling and was performed at 24 hours. The collected samples were transferred to the water and wastewater laboratory of the university and were maintained in the in a refrigerator. The primary properties of the wastewater including pH, organic compound, turbidity, phosphorous and MPN/ 100 ml were measured. The potassium ferrate (purity of 90%) was purchased from Sigma Aldrich CO. The experiments were performed in step, e.g. microbial and chemical, to investigate the potassium ferrate efficiency and the effect of studied parameter. The jar test device (Phipps & Bird Stirred) equipped with 6 stirrer and 1000 cc container. To determine the optimum pH for coagulation, pH was adjusted at 4, 5, 6, 7, 8, and 9 and ferrate dosage was regulated at 4, 6, 8, 10, 12 and 14. At the first, the ph values were used for a constant dosage to determine the optimum pH. After that, the optimum pH was kept constant and the dosages were varied to find the optimum dosage of ferrate.

Initially, the samples were mixed rapidly at 140 rpm (rapidly) for 1 min and then the coagulation was performed slowly at 35 rpm for 20 min and the sample were settled for 60 min. After settling, 100 ml of supernatant water was used to

measure the COD, turbidity and phosphorus. The reduced amount of these parameters was determined by comparison of the inlet and output concentration. All the experiments were carried out according to edition 22th of standard method [16]. The ferrate potassium efficiency as a disinfectant was studied in a batch reactor in lab scale. The disinfection efficiency was determined with MPN/ 100ml and at ferrate dosage of 4, 6, 8 and 10 mg/l and pH values of 5, 6, 7 and 8 at contact times of 10, 15, 20, 25, 30 min. pH and phosphorus was measured by pH meter (janway 3035 model) and by stannous chloride method using spectrophotometer (DR 5000 Hach), respectively. The COD was determined by methods of 5220 B of standard methods. The turbidity was measured using the turbidity meter (2100 AN model).

Results

The chemical and physical characteristics of initial wastewater including COD, turbidity and phosphorous was 270 mg/l, 37.5 NTU, 8 mg/l, respectively **(Figure. 1 and Figure. 2)**. Also, at the pH=7 the number of coliforms was obtained 16×10^7/100 ml. The results of the studied parameter in this study indicated that the efficiency of COD and turbidity removal using the potassium ferrate was found to be 65% and 90% at the dosage of 10mg/l and pH=5, respectively. Also, the maximum phosphorous removal efficiency was observed to be 725 in pH=5 and optimum dosage of 12 mg/l. The potassium ferrate has presented best performance as a disinfection at optimum condition including ferrate dosage of 4mg/l, contact time of 25 min and pH=5 **(Figure. 3-6)**.

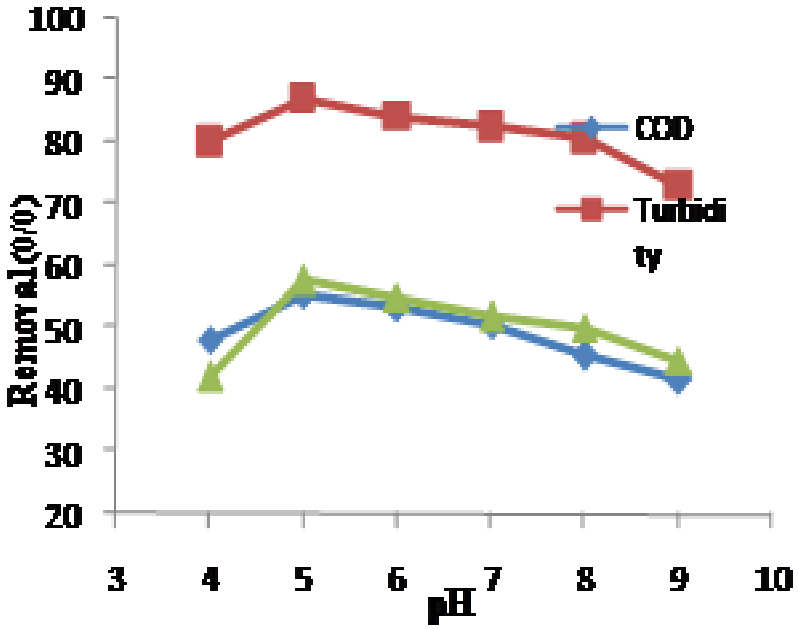

Figure.1. Determination of optimum pH for potassium ferrate in COD, turbidity and phosphorus removal.

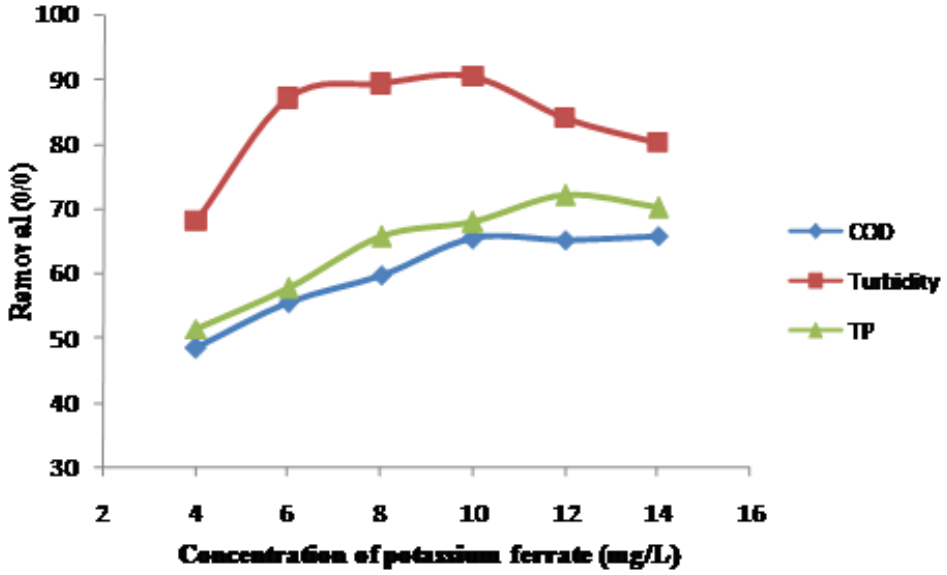

Figure.2. Determination optimum potassium ferrate dosage for COD, turbidity and phosphorus removal.

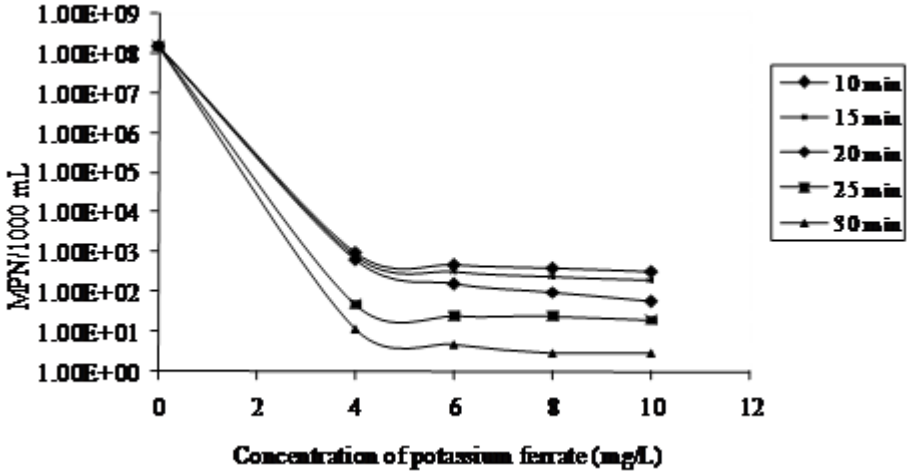

Figure.3. MPN /100 ml at the various dosage and contact time in pH of 5.

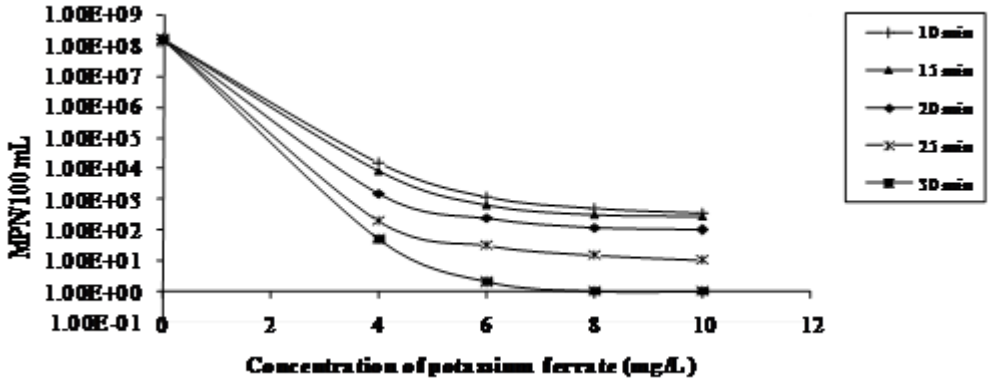

Figure.4. MPN /100 ml at the various dosage and contact time in pH of 6.

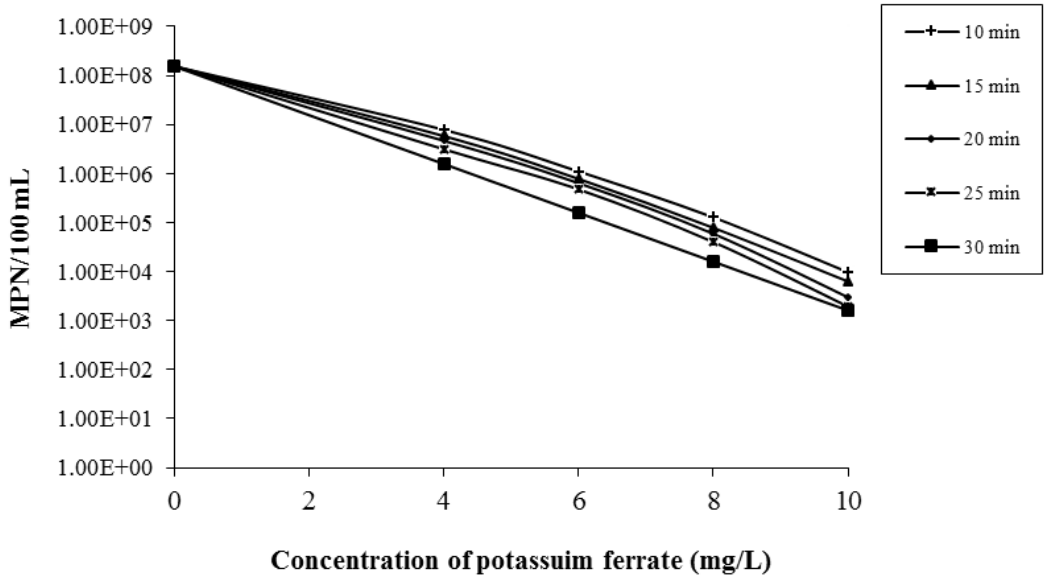

Figure.5. MPN /100 ml at the various dosage and contact time in pH of 7.

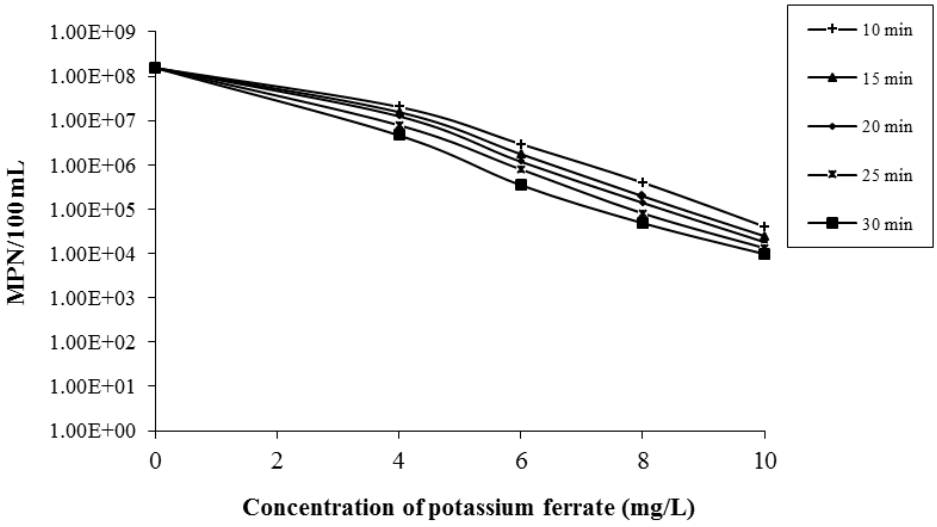

Figure.6. MPN /100 ml at the various dosage and contact time in pH of 8.

Discussion

The effect of pH and concentration on removal of COD, turbidity and phosphorus by potassium ferrate illustrated that the pH=5 and optimum potassium ferrate concentration of 10 mg/l is most appropriate for COD removal. The COD removal efficiency is decreased by an increase in pH which it can be due to the decreasing of oxidation ability of potassium ferrate in alkali condition. The COD removal efficiency was obtained to be 65% whereas a slight increase in COD removal efficiency was observed by increasing of the potassium ferrate concentration above the optimum amount which it could not be satisfied the economic acceptability. The results of present study were comparable to the results of Sharma et al

study (2007). The dosages of 6, 10, 18, 22 and 26 mg/l were used in their study. The optimum dose and COD removal efficiency was found to be 22 mg/l and 40%, respectively whereas the optimum dose and removal efficiency was 10mg/l and 65%, respectively. It is clear that the removal efficiency in our study was 25% greater than their study which this phenomenon can be described by higher oxidation potential of potassium ferrate in acidic condition (pH= 5) where as Sharma et al have been conducted their study in natural pH of wastewater [2, 7]. In addition, the optimum ferrate dosage and pH were selected 12 mg/l and 5 for phosphorus removal, respectively. The increasing of pH was led to reduce the phosphorus removal efficiency which this event could be explained by lower oxidation ability of ferrate in alkali condition. The phosphorus removal efficiency was obtained to be 72% at optimum dosage of 12mg/l and there was not appreciably changed in higher dosages. Potassium ferrate was presented good performance in phosphorous removal at lower dosage and was able to eliminate most of these compounds by coagulation, deposition and withdrawal of the solution due to its high oxidation potential and major changes in the surface properties of suspended solids and phosphorus [17]. On the other hand, the ferric ions and ferric hydroxide are the by-products of ferrate decomposition (Reaction 3) which is the main factor for coagulation and can be act as coagulant after decomposition of organic matter and microorganisms. The results of this study and obtained phosphorus efficiency are consistent with the results of Jiang et al [13]. The optimum dosage and pH for turbidity removal was 6 mg/l and 5, respectively and it was found that there are no significant changes in removal efficiency at the higher dosage then 6 mg/l. Moreover, the study of Jiang et al confirms the obtained results of this study for COD, turbidity and phosphorous removal efficiency. The maximum turbidity removal efficiency was found to be 94% at the optimum dosage of 20 mg/l and pH=7, whereas the removal efficiency was 92% at the optimum dosage of 6 mg/l and pH=5 in our study. The maximum removal efficiency of Coliforms (Up to 6 log reduction) was observed at the optimum ferrate dosage of 4 mg/l and pH=5 at the all contact times; however, the increasing of dosage from 4 to 10 mg/l had not significant effect on removal efficiency. Also, the effluent discharge standards for microbial load (less than 100MPN/ 100ml) were provided in the potassium ferrate dosage of 4 and 6 mg/l at the times of 25 and 30 min while the dosage of 10mg/l can reduce to desired standards after 20 min. The fecal coliforms standards of effluent discharged into the surface and receptive water is determined to be 400 MPN/100 ml by EPA. The dosage of 4 mg/l can be considered as optimum economic dosage but the longer disinfection time is required in this dosage. The inactivation of microorganisms is increased by increasing of dosage at pH=6 and the

maximum removal efficiency were observed at the dosage of 4mg/l. The standards of effluent discharged into receptive waters were obtained at the dosage of 4mg/l and at the 30 min. It should be noted that the entire inactivation of Coliforms was obtained at dosages of 6, 8 and 10 mg/l in pH=3 at 30 min. The disinfection performance of potassium ferrate was declined at higher pH; thus, the disinfection goals are not properly provided using this compound in the neutral and alkali condition. The coliforms is slightly decreased at dosages of 4 and 6 mg/l in pH of 7 and 8 which it indicates that pH is effective parameter on potassium ferrate performance at the lower dosage.

The dosages of 8 and 10 mg/l in pH of 5 and 6 can reduce the number of MPN/100 ml up to standards. Since the amount of chemical and contact time are considered as key factors to estimate the economic costs, therefore, the optimum dosage of ferrate can be lowest possible dosage which can provides the disinfection goals and meet the discharge standard levels [18]. It seems that the best economic efficiency can be obtained at the dosage of 4 mg/l, contact time of 25 and 30 min and the pH=6.

The disinfection effect of potassium ferrate on secondary effluent was evaluated by Jiang et al. they used the dosages of 4, 6 and 8 mg/l in pH of 5 and 7 in their study. The results of their study indicated that the potassium ferrate was able to reduce the number of bacteria up to 4 log at the dosage of 4 mg/l and in mentioned pH values [19]. The results of present study, which indicates the potassium ferrate can reduce the bacteria (up to 6 log) at the dosage of 4 mg/l and pH= 6, are comparable with the results of the Jiang et al [20].

Conclusion

Potassium ferrate is an effective chemical which can be utilized as oxidant, disinfectant and coagulant to treat the various municipal and industrial wastewaters and it provides the accessibility to several targets in a process. This compound is suggested as one of the superior options for advanced wastewater treatment due to existing of inexpensive raw material and professional personnel in Iran and the advantages associated with the potassium ferrate.

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Corresponding Author:

AbdolAzim Alinejad*,

Email: *azimalinejad@gmail.com*