Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.20266

65 (2017) 387–393
February

Removal of inorganic nickel and organic compounds from source water by enhanced coagulation

Jian Yuan[a,b,*], Boyu Wang[a,b], Tao Sun[a,b]

[a]*School of Environmental and Municipal Engineering, Tianjin Chengjian University, Tianjin, China, Tel. +86 22-23085117; Fax: +86 22-23085555; emails: yuanjian63@126.com (J. Yuan), wangboyu2016@126.com (B. Wang), 1052507902@qq.com (T. Sun)*
[b]*Tianjin Key Laboratory of Aquatic Science and Technology, Tianjin 300384, China*

Received 25 April 2016; Accepted 16 October 2016

ABSTRACT

Based on the present technology in the water plant, the removal of humic acid and nickel have been enhanced by adding coagulant aid polyaluminium chloride (PAC) or potassium ferrate (K_2FeO_4). The results show that its pH and the dosage of coagulant aid are the two main factors that have effect on the removal of nickel and humic acid (expressed as total organic carbon, TOC). Charge neutralization was the dominant mechanism by PAC, thus incorporating the humic acid and nickel into flocs more efficiently, producing settleable flocs of greater density, size and strength. When the dose of PAC was 40 mg/L at optimum pH 10, the removal efficiency of nickel and TOC reached 95% and 58.7%, respectively. The removal mechanism of complexes by K_2FeO_4 can be explained by both oxidation and coagulation. Percentage removals of 90 and 61 for nickel and TOC, respectively, were achieved by the addition of 20 mg/L K_2FeO_4 at optimum pH 8. It is concluded that the enhanced coagulation through the addition of PAC and K_2FeO_4, as coagulant and oxygenant, is more effective and efficient than traditional coagulation for economic treatment of micro-polluted humic acid and nickel containing surface water.

Keywords: Enhanced coagulation; Nickel; Humic acids; PAC; K_2FeO_4

1. Introduction

Water pollution by heavy metals and natural organic matters (NOM) have become a public concern in light of the development of high-technology industries around the world [1,2]. The storm water carries a large number of organic and inorganic pollutants in colloidal and dissolved forms such as suspended solids, NOM and heavy metals. Among the different heavy metals, nickel is one of the common and most toxic pollutants released into the natural waters from various industrial activities such as electroplating, battery manufacturing, mineral processing, steam-electric power plants, paint formulation, porcelain enameling and so on [3]. All these activities discharge significant amounts of nickel in various forms into the environment. Nickel is essential to human life and health but, like all heavy metals, is potentially toxic as well. The long-term intake of drinking water containing even low concentrations of heavy metals may cause fatal diseases by the accumulation of heavy metals in the internal organs of human body [4,5]. The removal of NOM has become increasingly important due to the potential for mutagenic and carcinogenic disinfection-by-products (DBP) to form if organic carbon is insufficiently removed [6–9]. A considerable increase in the content of NOM in surface waters has been observed to occur during the past 20 years in several areas [10,11].

Coagulation/flocculation process has been found to be cost-effective, easy to operate and energy-saving treatment alternatives [12,13]. Metal salt coagulants of polyaluminium chloride (PAC) and potassium ferrate (K_2FeO_4) are commonly used in this process. PAC are a group of highly effective coagulants in water treatment that have replaced a large part of traditional aluminous coagulants in recent years

---

* Corresponding author.

because of low dosage, high efficiency, low cost and convenient usage. PAC coagulant has been used in water treatment as an effective removal method for certain contaminants, TOC, turbidity and color, since 1980s throughout the world [14–16]. In addition, K_2FeO_4 as a multifunctional new type of high-efficiency water treatment chemical can remove organic pollutants and heavy metal ions, which is a kind of inorganic strong oxidant with multiple action, such as removing algae and oxidizing organic pollutants in water, strengthening coagulation and so on. Specially, the decomposition product of K_2FeO_4 will have remarkable effect in water purification not without harmful metal ions or other derivatives. In the last decade, people pay more attention to the K_2FeO_4, which were being called green oxidant [6,17]. Aslani et al. [18] concluded that ferrate (VI) can be effectively used in colloidal substances removal. Lan et al. [19] demonstrated that using potassium ferrate is a viable water treatment technology to remediate arsenic and antimony combined pollution.

As the main part of the conventional water treatment process, the removal of suspended solids and colloids in water can be achieved by strengthening the coagulation process, so that the organic material and metal can be effectively removed, then can be attained double effect on decreasing the treatment process and cost. However, there have been a few reports about the simultaneous removal of heavy metals and NOM [20,21]. NOM often reduces the removal of target substances through its adsorption onto adsorbents and the formation of a complex with the target substances [22]. Precipitation is hindered by complexation of heavy metal ions with organic matters. The removal efficiency of compound pollutants are badly just by conventional coagulation process, but adjusting the pH and the dosage of coagulant aid can increase the removal rate of compound pollutants effectively. Hence, it is essential to appropriately remove heavy metals and NOM through various water treatment processes for satisfying the water quality standard.

In this study, we have used PAC and K_2FeO_4, respectively, to simultaneously remove inorganic nickel and NOM from surface water. Experiments on the removal of compound pollutants were carried out under various conditions such as PAC dose, K_2FeO_4 dose, and pH. Most of the harmful substances can be quickly removed by PAC or K_2FeO_4, with much lower investment cost than the biochemical and other links. Therefore, it is of theoretical significance and practical value to study on the removal of inorganic nickel and organic compounds in the process of water treatment.

2. Materials and methods

2.1. Test sample

Model water treatment experiments were performed with raw water spiked with premade nickel sulfate, humic acid and kaolin reserves. Raw water was obtained through the water purification plant of Tianjin, China. Important characteristics of the model water used are shown in Table 1.

Dissolve 4.5468 g of nickel sulfate ($NiSO_4 \cdot 6H_2O$) in ultrapure water, then transfer this solution to a 1,000-mL volumetric flask, dilute with water to volume, and mix. Thus, the final concentration of nickel ion was 1 g/L. Dissolve 1 g of humic acid in sodium hydroxide solution, and reserves was obtained by the processed 0.45 μm cellulose acetate membrane filtration technique, meanwhile calibrate the TOC value. Dissolve 1 g of kaolin in ultrapure water to make 1,000 mL, stirring at the speed of 300 rpm for 1 h; finally, the turbidity of kaolin reserves was determined by the turbidity meter.

Table 1
Water quality index

Water quality	Source water	Water sample
pH	7.7–8.05	6–12
Zeta potential (mV)	–5.46 to –6.65	–15 to –18
TOC (mg/L)	0.85–1.15	10
Turbidity (NTU)	1.55–4.75	15–20
Ni^{2+} (mg/L)	–	–

2.2. Reagents

PAC was purchased from Sinopharm Chemical Reagent Co., Ltd., Beijing. Stock solution of PAC (polyaluminium chloride with containing 29% Al_2O_3, stock solution with 1,200 mg/L Al_2O_3) was prepared in ultrapure water.

Potassium ferrate (K_2FeO_4) was prepared by hypochlorite oxidation of ferric nitrate according to the method of Delaude and Laszlo [23] and Schreyer et al. [24]. It had purity higher than 96% checked by the chromite titration method and was stored in a desiccator until needed.

2.3. Apparatus

The TOC analyzer of the samples (Shimadzu TOC-VCPH, Japan) was used for determining the TOC content. The concentration of Ni^{2+} analysis was performed on an atomic absorption spectrophotometer (AANALYST, PerkinElmer company, USA). pH values were measured using a PHS-3C meter (Shanghai Precise Science Instrument, China). Turbidity was measured in a 2100N Turbidimeter (HACH company, USA). The zeta potential measurements in this study utilized a zeta meter (Zetasizer Nano ZS90, Malvern Instruments, UK), which measures the zeta potential using a combination of the measurement techniques: electrophoresis and laser Doppler velocimetry. The flocculation index (FI) was detected with the intelligent particle dispersion analyzer (iPDA; Econovel Company Ltd., Korea), and observation of the forming process of the floc by using the online coagulation analyzer, which is a detection methodology of high sensitivity. The ratio of the root mean square (RMS) of the fluctuating intensity to the average transmitted light intensity (DC) is a measure termed the FI. The variation of FI is a function of the number and size of floc that reflect the formation of the flocculation, so the FI value is proportional to floc size [25]. Coagulation experiments were carried out on a program controlled jar-test apparatus with 1 L beakers (ZR4-6, Zhongrun Water Industry Technology Development Co. Ltd., China).

2.4. Procedure

The experiments were performed through static beaker experiment, using a six-paddle stirrer, and the volume of each reactor was 1 L. Each sample was rapidly mixed for 30 s at 300 rpm, then primary flocculation for 3 min at 150 rpm, followed by a secondary flocculation for 15 min at 50 rpm, and at last a quiet settling of 30 min. PAC and K_2FeO_4 were added firstly at the start of rapid mixing phase. At the end of the settling period, the supernatant was taken from about 2 cm below the water surface for subsequent measurements. Collected samples were prefiltered through a 0.45-µm fiber membrane before testing for TOC and the concentration of Ni^{2+}, while the zeta′ potential was measured without filtration. In addition, test water was withdrawn immediately at the end of slow stirring phase for zeta potential measurement; thus, coagulation mechanism could be analyzed. To estimate the settling ability of flocs, samples were collected to measure turbidity after sedimentation. Therefore, higher removal efficiency of turbidity value means faster sedimentation rate and better settling ability. The forming process of the floc was observed by iPDA during the flocculation process, where the circulating pump flow rate was 20 ml/min. The computer analysis was conducted to study the effect of different experimental conditions on the complex pollutants in water.

3. Results and discussion

3.1. Removal of compound pollutants by PAC

3.1.1. Effect of pH

One of the most important factors that affect coagulation is pH. The influence of pH was tested using 40 mg/L PAC with 1 mg/L Ni^{2+} and 10 mg/L TOC in the range of pH 6–11 (Figs. 1 and 2).

As indicated in Fig. 1, Ni^{2+} and NOM removal showed an up-and-down trend with increasing coagulation pH value, the PAC produced maximum reduction at pH 10, with close to 95% and 58.7% removal of Ni^{2+} and NOM, respectively. When the pH value was 6~9, the removal rate increased slowly, while the removal rate increased rapidly between 9 and 10, then decreased with increasing the pH.

Fig. 2 presented the floc formation process that enters into a gentle development stage after fast growth got maximum after 150 s. The granular sizes added 2 times under alkaline environment. Meanwhile, highest turbidity removal efficiency was obtained at optimum pH 6. The mechanisms to express pollutants removal in water include condensing the double layer, precipitation, charge neutralization, bridge-aggregation, adsorption and sweep-flocculation [26]. Different mechanisms or their combination may be dominant at different conditions. Effect of initial pH on complexes removal was correlated with the hydrolyzates of PAC [27,28], where the polymerization degrees and alkalinity be reduced under acidic environment due to the disaggregation behavior, while be increased under alkaline environment [29,30]. Hydrolysis of metal ions occurred immediately after adding to water, and PAC could rapidly form dissolved Al species or Al-hydroxide precipitates shown in Table 3 [29,31]. As shown in Fig. 1, compound pollutants removed insignificantly under conditions of pH < 9, because the positively charged $Al_{13}(OH)_{34}^{5+}$, multicore aggregate and sol-$Al(OH)^3$, which are a series of intermediates mainly produced by the hydrolysis of PAC [32]. However, the negatively charged flocs of $Al(OH)_4^-$ and $Al_8(OH)_{26}^{2-}$ formed more than the intermediates with low polymerization degree and high charge under conditions of pH > 9 [33]. Adjusting the quantity of acid and alkali to change pH values, which forms compressing the electrical double layer, will cause potentials decreased, colloidal particles closed together, then coagulated quickly; thus, the removal rate increased rapidly. In addition, when initial pH

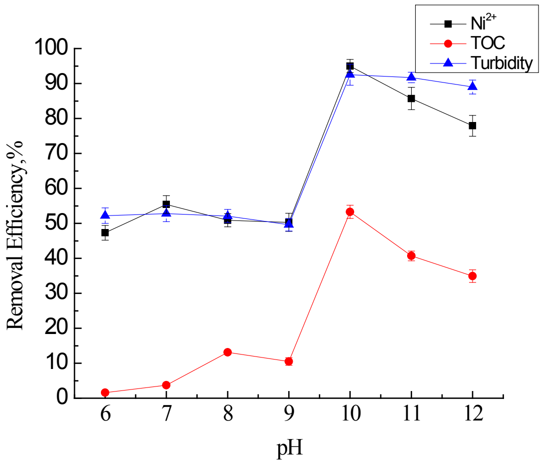

Fig. 1. Ni^{2+}, TOC and turbidity removal efficiency of PAC coagulant at different initial pH.

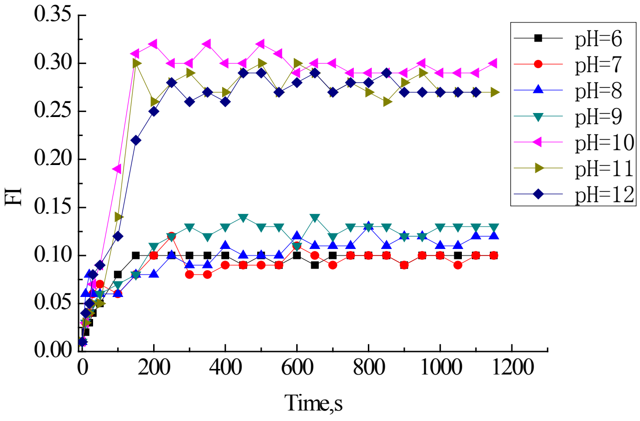

Fig. 2. The FI of flocs formed by PAC at different initial pH in surface water during coagulation treatment.

Table 2
The effect of zeta potential under different initial pH by PAC coagulation

pH	Zeta (mV)	Zeta′ (mV)
6	33.9	35.2
7	34	35.3
8	31	32.5
9	28.1	29.6
10	5.8	8.93
11	–30.5	–31.4
12	–36.6	–38.0

Table 3
The mainly hydrolysis product of PAC under different initial pH [29,31]

pH	Mainly hydrolysis product
pH < 4	$Al(H_2O)_n^{3+}$
4 < pH < 6	$Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{4+}$, $Al_{13}(OH)_{34}^{5+}$
6 < pH < 8	$Al_{13}(OH)_{34}^{5+}$, $Al(OH)_3$ flocs
pH > 8	$Al(OH)_4^-$, $Al_8(OH)_{26}^{2-}$

was 10 or higher, $Ni(OH)_2$ formation had great influence on the removal of nickel, therefore, making Ni^{2+} more easy to be precipitation.

Results in Table 2 can reflect that flocs moved from the positive change into the negative charge with the increase of pH value. Accordingly, we can observe that the electric potential of the colloid changed rapidly with its absolute value decreased obviously after adding PAC, and it achieved the isoelectric point at pH 10. At acidic range, complexes removal was due to charge neutralization effect, which was favorable for Al-hydroxide precipitates formation. In higher pH range, the sol-$Al(OH)_3$ or negatively charges flocs of $Al(OH)_4^-$ formed. Increase of pH favored the hydrolysis of PAC and decreased the formation of positively charged ions. Thereby, pH ascending decreased the ability of PAC to neutralize the negative charge and compressing the electrical double layer, adsorption and precipitation was considered to play a more effective role in complexes removal at higher pH range when treating this specific surface water.

3.1.2. Effect of PAC dosage

Compound pollutants removal with increasing dose (10–60 mg/L) of PAC at pH 10 was investigated (Figs. 3 and 4).

The results demonstrated that PAC can achieve about 60.2% Ni^{2+} reduction at a PAC dose of 10 mg/L with the effluent concentration decreased from 1 to 0.398 mg/L. For the enhanced PAC dosage, greater Ni^{2+} reduction was achieved, more than 96% Ni^{2+} can be removed for doses greater than 40 mg/L. When PAC dose of more than 40 mg/L was used, the improvement in Ni^{2+} removal was hardly observed. The removal effect of TOC was significantly lower than that of Ni^{2+}. Maximal TOC removal of the coagulation system was achieved using 40 mg/L PAC, then the TOC removal rate decreased slightly with increasing coagulant dosage. Therefore, the optimum dosage for complexes removal was achieved using 40 mg/L PAC.

As indicated in Fig. 4, the size of flocs increased with increasing PAC dosage. However, when PAC dose of larger than 40 mg/L was used, the improvement in turbidity removal was hardly observed. When the dosage of PAC was 40 mg/L, the flocs had good sedimentation property, formed rapidly and compact, while the flocs were loose, and have poor settling performance when the dosage of PAC was more than 40 mg/L. One of the most important factors that affect settlement is suspended impurity with negative charge [29]. Therefore, the suspended impurity with thicker diffusion layer easy to produce static electricity to disperse materials and avoid precipitating. Adjusting the properties of particle to change surface charge, which means adding coagulant with positive charge electrolyte into the colloidal solution, will affect the nature of colloidal charged, compressing the electrical double layer, thus affects the zeta potential [34]. Table 4 shows the relationship of zeta potential with the dosage of PAC; the zeta potential increased from about –16.8 mV to about –13.5 mV. This indicated that charge neutralization was the dominant mechanism by PAC [35,36]. Since the model water was alkaline, significant precipitation of amorphous

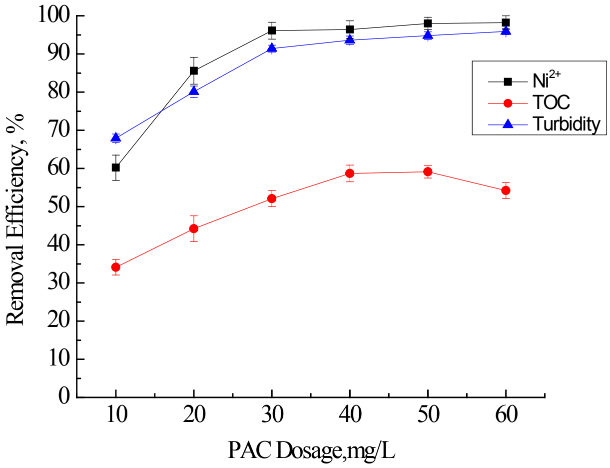

Fig. 3. Ni^{2+}, TOC and turbidity removal efficiency of PAC coagulant at different PAC dosage.

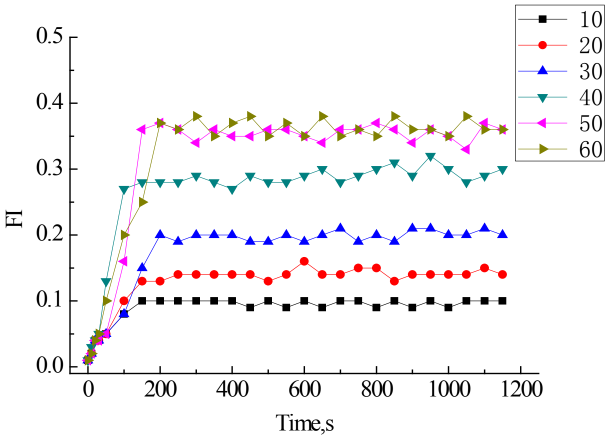

Fig. 4. The FI of flocs formed by PAC at different PAC dosage in water during coagulation treatment.

Table 4
The effect of zeta potential under different dosage by PAC coagulation

PAC dosage (mg/L)	Zeta (mV)	Zeta' (mV)
10	–16.8	–14.6
20	–15.8	–13.7
30	–14.5	–12.8
40	–13.8	–12.3
50	–13.6	–12.1
60	–13.5	–12.2

hydroxide could occur. Therefore, the charge neutralization was more likely to be achieved by adsorbed precipitate [37]. In this case, coagulation behavior was mainly affected by precipitate, but not charge effects. This also explained why efficient turbidity removal still occurred at low dosages, even though the zeta potentials were somewhat below zero.

3.2. Removal of compound pollutants by K_2FeO_4

3.2.1. Effect of pH

The influence of pH was tested using 40 mg/L K_2FeO_4 with 1 mg/L Ni^{2+} and 10 mg/L TOC in the range of pH 6–9 (Figs. 5 and 6).

As initial pH increased from 6.0 to 9.0, the removal rate of compound pollutants in water increased gradually when initial pH was lower than 8.0, while lower removal rate was obtained with a further increase in initial pH (pH > 8.0). It achieved the maximum reduction at pH 8.0, with close to 91% and 61% Ni^{2+} and TOC removal, respectively, in the filtered water. This trend was also evident in data depicted in Fig. 5.

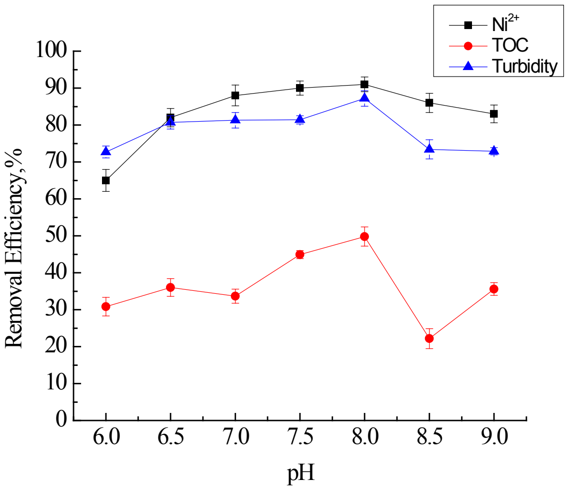

Fig. 5. Ni^{2+}, TOC and turbidity removal efficiency of K_2FeO_4 coagulant at different initial pH.

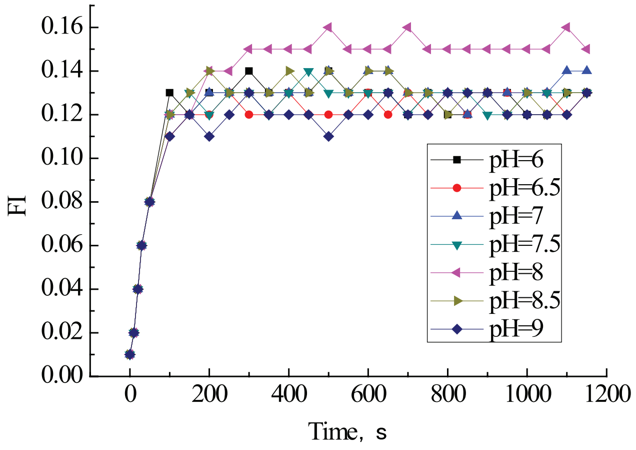

Fig. 6. The FI of flocs formed by K_2FeO_4 at different K_2FeO_4 dosage in surface water during coagulation treatment.

This could be ascribed to the unique properties of K_2FeO_4 with powerful oxidization, under the acidic, alkaline condition, the oxidation-reduction potential of K_2FeO_4 were 2.20 and 0.72 V, respectively, and there is a stronger oxidation in acidic conditions in theory [38]. However, oxidation flocculation efficiency is low under acidic condition; this may be as a result of instability of K_2FeO_4 and badly for the growth of $Fe(OH)_3$ floe at this condition. K_2FeO_4 presents in the form of any species of $H_3FeO_4^+$, H_2FeO_4, $HFeO_4^-$ and FeO_4^{2-} depending on the pH of the solution [6,39]. The FeO_4^{2-} will be restored momently and have shorter contact time with compound pollutants, thus strong oxidizing property was difficult to be played at pH < 7. As shown in Table 5, when initial pH was between 7.0 and 8.0, the zeta potentials were about −14.8 V, which caused the zeta potential to increase to a higher absolute value, which will affect the stability of colloidal material. The colloids were easily promoted adsorption bridging action and co-precipitated by formed high polymeric of inorganic polymer colloidal of $Fe(OH)_3$. In particular, K_2FeO_4 exists as the species of $HFeO^{4-}$ in the neutral solution [40]. Under this experimental condition, heavy metals, which exist as divalent cations (Ni^{2+}), can precipitate by the ionic bonding with $HFeO^{4-}$, an anion species of K_2FeO_4. On the other hand, intermediate products of K_2FeO_4 were Fe(IV), Fe(V) and so on, which get a better network and higher polymeric positive hydrolyzate than aluminium or ferric salts, due primarily to charge neutralization. These intermediate and end products are easy to further destabilize colloids by adsorption coagulation, then remove complexes. Hence, highest removal efficiency was obtained at optimum pH range (7.0~8.0) for K_2FeO_4 coagulation. In contrast, for pH 9~10, K_2FeO_4 is stable and reflects the decreasing oxidation potential of ferrate with pH in this range. Complexes could be removed by the adsorption onto $Fe(OH)_3$ produced in the neutral or alkaline solution [40,41]. Thereby, the suspension system was difficult to be destabilized and the removal efficiencies of compound pollutants were lower than those at optimum pH range.

3.2.2. Effect of K_2FeO_4 dosage

Compound pollutants removal with increasing dose (5–50 mg/L) of K_2FeO_4 at pH 8 was investigated (Figs. 7 and 8).

For the enhanced coagulation increasing the dosage of K_2FeO_4, greater metal nickel reduction was achieved; more than 72% nickel can be removed at a K_2FeO_4 dose of 5 mg/L, but the removal rate of TOC was 11% (see Fig. 7). Maximal Ni^{2+} and TOC removal of the coagulation system is achieved at a K_2FeO_4 dose of 20 mg/L, while the K_2FeO_4 dose increase caused the ups and downs in TOC removal, the reduction in nickel removal and the fluctuation upward in turbidity removal.

When the dose of K_2FeO_4 was 5 mg/L, the formation of the floc with small size was only about 0.08, which means the insufficient flocculation and a low removal rate of complexes. When the amount of K_2FeO_4 increased to 20 mg/L, the coagulation reaction was completely with increasing the size of the volume to about 0.13, thus settles easily and achieves the optimal removal effect. As shown in Table 6, with the increase of the amount of K_2FeO_4, the absolute value of zeta potential increased first and then decreased, and it reached

Table 5
The effect of zeta potential under different initial pH by K_2FeO_4 coagulation

pH	Zeta (mV)	Zeta′ (mV)
6	–15.2	–15
6.5	–16	–15.3
7	–15.6	–15.1
7.5	–15.6	–15.3
8	–14.8	–14.5
8.5	–16.4	–16
9	–17	–16.3

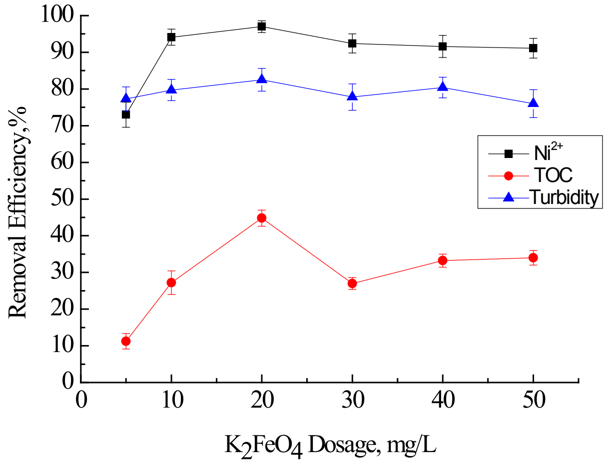

Fig. 7. Ni^{2+}, TOC and turbidity removal efficiency of K_2FeO_4 coagulant at different K_2FeO_4 dosage.

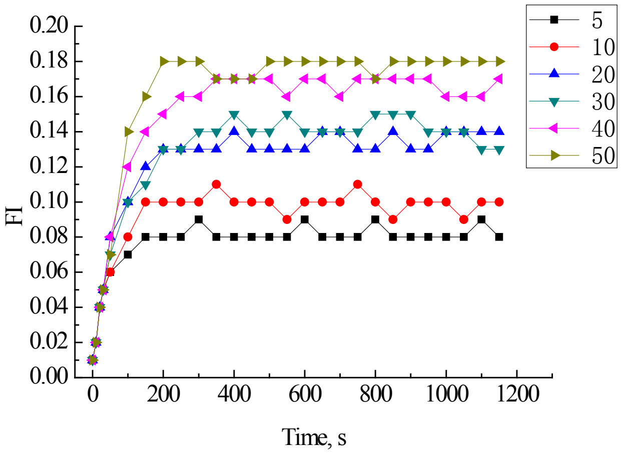

Fig. 8. The FI of flocs formed by K_2FeO_4 at different dosage in water during coagulation treatment.

minimum value at the dose of 20 mg/L. It was found that 20 mg/L K_2FeO_4 was very effective for the treatment of complexes. The removal mechanism of heavy metals by K_2FeO_4 can be explained by both ionic bonding and adsorption [42]. At the doses of more than 20 mg/L, any great change in the removal efficiency of heavy metals and NOM was not shown, meaning that the efficiency becomes saturated [6].

Table 6
The effect of zeta potential under different dosage by K_2FeO_4 coagulation

K_2FeO_4 dosage (mg/L)	Zeta (mV)	Zeta′ (mV)
5	–16	–16.5
10	–15.7	–15.9
20	–15.1	–15.4
30	–16.2	–16.5
40	–16	–16.2
50	–16.2	–16.8

4. Conclusion

The present study has demonstrated that enhanced coagulation adding PAC and K_2FeO_4 possesses the capacity for removal of metal nickel and organic compounds in micro-polluted source water. The following are the conclusions arrived from this study.

Both nickel and NOM (humic acid) spiked in test sample were simultaneously removed efficiently using coagulant (PAC or K_2FeO_4).

Complexes removal showed an up-and-down trend with increasing pH, and the removal efficiencies increased with increasing PAC dosage (<40 mg/L). The main coagulation mechanism of PAC was charge neutralization. At the optimal PAC dosing rate of 40 mg/L with pH 10, the maximum removal efficiency of Ni^{2+}, TOC and turbidity reached 96.4%, 58.7% and 93.6%, respectively.

This study, and others, have shown that K_2FeO_4 is a highly oxidative and unstable chemical in aqueous conditions; pH is an important factor that influences the nature of the reaction between the oxidant and reacting species. The removal mechanism of heavy metals by K_2FeO_4 can be explained by both oxidation and coagulation. Additionally, K_2FeO_4 was proven to be very effective in the removal of complexes at relatively lower dosage. When the dose of K_2FeO_4 was 20 mg/L at optimum pH 8, the maximum removal efficiency of Ni^{2+}, TOC and turbidity reached 97%, 44.8% and 82.5%, respectively.

During the coagulation period, the largest floc size is formed after 150 s, thus can be appropriate to reduce the time of primary flocculation.

Overall, adjusting coagulant dosage and pH are more effective and feasible than traditional coagulation for treatment of micro-polluted nickel and organic containing surface water.

Acknowledgment

This work was supported by a grant from the Development Program of Ministry of Housing and Urban-Rural Development, China (No. 2012-k7-20) and the Chinese National Foundation of Natural Sciences (No. 51308374).

References

[1] E.L. Sharp, S.A. Parsons, B. Jefferson, Seasonal variations in natural organic matter and its impact on coagulation in water treatment, Sci. Total Environ., 363 (2006) 183–194.

[2] H.A. Aziz, M.N. Adlan, K.S. Ariffin, Heavy metals (Cd, Pb, Zn, Ni, Cu and Cr(III)) removal from water in Malaysia: post treatment by high quality limestone, Bioresour. Technol., 99 (2008) 1578–1583.

[3] Y.K. Henneberry, T.E.C. Kraus, J.A. Fleck, D.P. Krabbenhoft, P.M. Bachand, W.R. Horwath, Removal of inorganic mercury and methylmercury from surface waters following coagulation of dissolved organic matter with metal-based salts, Sci. Total Environ., 409 (2011) 631–637.

[4] A. Malik, Metal bioremediation through growing cells, Environ. Int., 30 (2004) 261–278.

[5] S.S. Ahluwalia, D. Goyal, Microbial and plant derived biomass for removal of heavy metals from wastewater, Bioresour. Technol., 98 (2007) 2243–2257.

[6] M. Lim, M. Kim, Effectiveness of potassium ferrate (K_2FeO_4) for simultaneous removal of heavy metals and natural organic matters from river water, Water Air Soil Pollut., 211 (2010) 313–322.

[7] H. Gallard, U. von Gunten, Chlorination of natural organic matter: kinetics of chlorination and of THM formation, Water Res., 36 (2002) 65–74.

[8] E.R. Blatchley, D. Margetas, R. Duggirala, Copper catalysis in chloroform formation during water chlorination, Water Res., 37 (2003) 4385–4394.

[9] J.J. Shim, J.G. Kim, Copper corrosion in potable water distribution systems: influence of copper products on the corrosion behavior, Mater. Lett., 58 (2004) 2002–2006.

[10] F. Worrall, T.P. Burt, Trends in DOC concentration in Great Britain, J. Hydrol., 346 (2007) 81–92.

[11] F. Worrall, T.P. Burt, Changes in DOC treatability: indications of compositional changes in DOC trends, J. Hydrol., 366 (2009) 1–8.

[12] O.S. Amuda, I.A. Amoo, O.O. Ajayi, Performance optimization of coagulant/flocculant in the treatment of wastewater from a beverage industry, J. Hazard. Mater., 129 (2006) 69–72.

[13] D. Bromley, M. Gamal EI-Din, D.W. Smith, A Low Cost Treatment Process to Reduce phosphorus and Suspended Solids in Liquid Wastes from Animal Farm Operations, Proc. Fourth International Livestock Waste Management Symposium and Technology Expo., Malaysia Society of Animal Production, Penang, Malaysia, 2002, p. 215.

[14] R. Sudoh, M.S. Islam, K. Sazawa, T. Okazaki, N. Hata, S. Taguchi, H. Kuramitz, Removal of dissolved humic acid from water by coagulation method using polyaluminum chloride (PAC) with calcium carbonate as neutralizer and coagulant aid, J. Environ. Chem. Eng., 3 (2015) 770–774.

[15] A.K. Choudhary, S. Kumar, C. Sharma, Removal of chloroorganics and color from pulp and paper mill wastewater by polyaluminium chloride as coagulant, Desal. Wat. Treat., 53 (2015) 697–708.

[16] H. Parka, S. Lima, H. Leeb, D. Wooa, Water blending effects on coagulation-flocculation using aluminum sulfate (alum), polyaluminum chloride (PAC), and ferric chloride ($FeCl_3$) using multiple water sources, Desal. Wat. Treat., 57 (2016) 7511–7521.

[17] H. Su-jiao, Preparation and determination progress of potassium ferrate, Technol. Dev. Chem. Ind., 39 (2010) 39–42.

[18] H. Aslani, R. Nabizadeh, S. Nasseri, A. Mesdaghinia, M. Alimohammadi, A.H. Mahvi, N. Rastkari, S. Nazmara, Application of response surface methodology for modeling and optimization of trichloroacetic acid and turbidity removal using potassium ferrate (VI), Desal. Wat. Treat., 57 (2016) 25317–25328.

[19] B. Lan, Y. Wang, X. Wang, X. Zhou, Y. Kang, L. Li, Aqueous arsenic (As) and antimony (Sb) removal by potassium ferrate, Chem. Eng. J., 292 (2016) 389–397.

[20] A. Jain, V.K. Sharma, O.S. Mbuya, Removal of arsenic by Fe(VI), Fe(VI)/Fe(III), and Fe(VI)/Al(III) salts: effect of pH and anions, J. Hazard. Mater., 169 (2009) 339–344.

[21] D.Y. Stupin, M.I. Ozernoi, Removal of Ni(II) with sodium ferrate(VI) from EDTA-containing aqueous solutions, Russ. J. Appl. Chem., 77 (2004) 1312–1315.

[22] Y. Seida, Y. Nakano, Removal of humic substances by layered double hydroxide containing iron, Water Res., 34 (2000) 1487–1494.

[23] L. Delaude, P. Laszlo, A novel oxidizing reagent based on potassium ferrate(VI)^1, J. Org. Chem., 61 (1996) 6360–6370.

[24] J.M. Schreyer, G.W. Thompson, L.T. Ockerman, Oxidation of chromium(lll) with potassium ferrate(VI), Anal. Chem., 22 (1950) 1426–1427.

[25] F. Xiao, J. Ma, P. Yi, J.H. Huang, Effects of low temperature on coagulation of kaolinite suspensions, Water Res., 42 (2008) 2983–2992.

[26] J. Qin, M.H. Oo, K.A. Kekre, F. Knops, P. Miller, Impact of coagulation pH on enhanced removal of natural organic matter in treatment of reservoir water, Sep. Purif. Technol., 49 (2006) 295–298.

[27] S. Mozia, M. Tomaszewska, Treatment of surface water using hybrid processes — adsorption on PAC and ultrafiltration, Desalination, 162 (2004) 23–31.

[28] C. Wu, X. Xu, J. Liang, Q. Wang, Q. Dong, W. Liang, Enhanced coagulation for treating slightly polluted algae-containing surface water combining polyaluminum chloride (PAC) with diatomite, Desalination, 279 (2011) 140–145.

[29] Z. Yang, B. Gao, Y. Wang, Q. Wang, Q. Yue, Aluminum fractions in surface water from reservoirs by coagulation treatment with polyaluminum chloride (PAC): influence of initial pH and OH^-/Al^{3+} ratio, Chem. Eng. J., 170 (2011) 107–113.

[30] Z. Yang, B. Gao, B. Cao, W. Xu, Q. Yue, Effect of OH^-/Al^{3+} ratio on the coagulation behavior and residual aluminum speciation of polyaluminum chloride (PAC) in surface water treatment, Sep. Purif. Technol., 80 (2011) 59–66.

[31] L. Istv'an, On the type of bond developing between the aluminium and iron (III) hydroxides and organic substances, Water Res., 27 (1993) 249–252.

[32] P. Zhang, Z. Wu, G. Zhang, G. Zeng, H. Zhang, J. Li, X. Song, J. Dong, Coagulation characteristics of polyaluminum chlorides PAC-Al_{30} on humic acid removal from water, Sep. Purif. Technol., 63 (2008) 642–647.

[33] S. Kim, B. Moon, H. Lee, Effects of pH and dosage on pollutant removal and floc structure during coagulation, Microchem. J., 68 (2001) 197–203.

[34] M. Yan, D. Wang, J. Ni, J. Qu, C.W.K. Chow, H. Liu, Mechanism of natural organic matter removal by polyaluminum chloride: effect of coagulant particle size and hydrolysis kinetics, Water Res., 42 (2008) 3361–3370.

[35] Y.X. Zhao, B.Y. Gao, Y. Wang, H.K. Shon, X.W. Bo, Q.Y. Yue, Coagulation performance and floc characteristics with polyaluminum chloride using sodium alginate as coagulant aid: a preliminary assessment, Chem. Eng. J., 183 (2012) 387–394.

[36] S. Zhao, B. Gao, Q. Yue, S. Sun, W. Song, R. Jia, Influence of Enteromorpha polysaccharides on variation of coagulation behavior, flocs properties and membrane fouling in coagulation–ultrafiltration process, J. Hazard. Mater., 285 (2015) 294–303.

[37] S.K. Dentel, Application of the precipitation-charge neutralization model of coagulation, Environ. Sci. Technol., 22 (1988) 825–832.

[38] J.D. Rush, J.E. Cyr, Z. Zhao, B.H. Bielski, The oxidation of phenol by ferrate(VI) and ferrate(V). A pulse radiolysis and stopped-flow study, Free Radic. Res., 22 (1995) 349–360.

[39] V.K. Sharma, Potassium ferrate(VI): an environmentally friendly oxidant, Adv. Environ. Res., 6 (2002) 143–156.

[40] N. Graham, C. Jiang, X. Li, J. Jiang, J. Ma, The influence of pH on the degradation of phenol and chlorophenols by potassium ferrate, Chemosphere, 56 (2004) 949–956.

[41] L. Yunho, U. Ik-hwan, Y. Jeyong, Arsenic(III) oxidation by iron(VI) (ferrate) and subsequent removal of arsenic(V) by iron(III) coagulation, Environ. Sci. Technol., 37 (2003) 5750–5756.

[42] M. Lim, M. Kim, Application of ferrate(VI) to the removal of humic acid and heavy metals (Cu, Mn, and Zn), J. Korean Soc. Environ. Eng., 31 (2009) 454–459.