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Study on pretreatment of landfill leachate by potassium ferrate

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ABSTRACT

Landfill leachate is nonbiodegradable because it contains many kinds of pernicious and toxic components. Potassium ferrate is used as a pretreatment agent in the experiments for it is a kind of oxidant that can be used to oxidize and disintegrate lots of organics. However, with respect to the treatment effect of landfill leachate, several important parameters should be studied. Such parameters included (a) the dosage of potassium ferrate, (b) the pH value, (c) the reaction time, (d) the concentration of landfill leachate, and (e) the dosage of stabilizing agent. Finally, the optimum conditions for the treatment of landfill leachate were confirmed. The conditions included (a) the dosage of potassium ferrate was 6 g/L, (b) pH value was 10, (c) the reaction time was 30 min, and (d) the dosage of stabilizing agent—sodium silicate was 4 g/L. After treated under those conditions, the COD_{Cr} removal efficiency was 36% and UV-254 value decreased from 10 to 6.64 cm^{-1}.

Keywords: Landfill leachate; Potassium ferrate; Oxidizing treatment; COD_{Cr} removal efficiency; UV-254

1. Introduction

Landfill leachate, a kind of organic effluent with high concentration, is formed based on (a) anaerobic fermentation, (b) disintegrated organics, and (c) rinsed by rain water [1]. Landfill leachate flowing into external environment will result in secondary pollution and endanger human body health and ecological environment. Therefore, the treatment of landfill leachate is extremely urgent.

The components of landfill leachate are complex and variational. The components of landfill leachate can differ if the time of dumped is different. Organics that can be treated by biochemical methods are the major components of the early leachate. Refractory

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organic pollutants, the major components of the late leachate are always toxic and harmful, so there are plenty of attracting attentions to treat the pollutants in the late leachate [2,3].

Fenton oxidation method is an efficient and useful method for the pretreatment of refractory organic pollutants, but it also has several disadvantages including (a) it has strict requirement on pH, (b) it is a high consumption reagent, and (c) the sludge formed by flocculation is too much to deal with [4]. Potassium ferrate oxidation method developed recently is efficient to refractory organics in a wide range of pH [5], and it has a better ability of oxidation than Fenton reagent, so it needs less dosage, less reaction time, smaller space, and less investment of capital construction [6–9].

In the study of Xu et al., the degradation experiments of reactive brilliant red X-3B with Fe(VI) were carried out. When pH was 8.4, the addition of K_2FeO_4 was 25 mg/L, the reaction time was 20 min, the X-3B and COD removal efficiency reached 99 and 42%, respectively [10]. The same good results were obtained by Li et al. in the experiment of the treatment of five endocrine disruptors including bisphenol A, estrriol, etc., with potassium ferrate when pH was 8–12 [11]. Zhu et al. found the BOD_5/COD_{Cr} ratio of alachlor increased from 0.35 to 0.87 treated with potassium ferrate when the reaction time was 10 min [12]. Jiang et al. compared the effect between potassium ferrate and the combination of NaOCl and aluminum sulfate in the advanced treatment of drinking water, the results indicated that compared with the combination of NaOCl and aluminum sulfate, 30% higher COD removal efficiency achieved by potassium ferrate even with less dosage. The above studies demonstrated that both chain hydrocarbon and aromatic compounds obtained the good treated effect with potassium ferrate in the condition of less dosage and short reaction time [13].

The studies of oxidation kinetics of potassium ferrate further indicated it was a fast and efficient method. Read et al. [14–18] proceeded a series of studies on the oxidation kinetics of potassium ferrate. The oxidized objects were including sulfhydryl compounds, thiols and inorganic oxysulfur compounds, the results showed that the substances above degraded completely within 5 min.

Potassium ferrate oxidation for the pretreatment of refractory organics in landfill leachate was studied in this paper. The study put emphasis on the parameters that would influence the stability and oxidation capacity of potassium ferrate, and the influence regulations were found to determine the optimum conditions for the treatment of landfill leachate by potassium ferrate oxidation method.

2. Materials and methods

2.1. Materials

The quality of wastewater taken from a landfill was shown in Table 1. The analytical pure potassium ferrate (made by Xian Yiling Spirit Industry & Trade Co. Ltd, China) was purchased. The wastewater should be treated by flocculation method first because plenty of colloids in wastewater would negatively influence potassium ferrate. 30 mL PAC of 2% and 0.5 mL PAM of 1% were added to 1 L landfill leachate. After the flocculation, the effluent COD_{Cr} concentration was about 3,500 mg/L. In the flowing experiments, the effluent was as the stock solution.

2.2. Methods for analysis

2.2.1. Determination of COD_{Cr}

COD_{Cr} was determined by a portable water quality analyzer DR2700 from HACH Company in America.

2.2.2. Determination of UV-254

UV-254 that indirectly reflects the aromatic compound content of the wastewater is defined to be the absorbance of ultraviolet rays at the wave length of 254 nm, and it is determined by G752 type UV–Vis spectrophotometer from Shanghai Yuan chromatography instrument Co. Ltd.

3. Results

3.1. Effect of the dosage of potassium ferrate on the leachate treatment

Potassium ferrate was added by 2, 4, 6, 8, and 10 g/L, respectively, to five beakers, each of which contained 50 ml landfill leachate with pH = 10 and was stirred for 30 min in six association stirrers. The COD_{Cr} removal efficiency and UV-254 values were determined, as shown in Figs. 1 and 2.

As shown in Figs. 1 and 2, the removal efficiency of COD_{Cr} increased first but then decreased with the

Table 1
Quality of wastewater

COD (mg/L)	5,300
pH	8.26
Total suspended solids (mg/L)	250
$N–NH_3$ (mg/L)	1,300
TP (mg/L)	25

increase of potassium ferrate dosage, and the maximum value 35.22% was attained when the dosage of potassium ferrate was 6 g/L. UV-254 decreased until the dosage of potassium ferrate was 6 g/L. Ferrate ion can oxidate organics and be decomposed into Fe^{3+} with the ability of flocculation, the values of COD_{Cr} and UV-254 decreased because organics in the landfill leachate were oxidated by ferrate ion and flocculated by Fe^{3+}, produced from ferrate ion. The effluent COD_{Cr} value increased when the dosage of potassium ferrate was excessive which was caused by the impurity of potassium ferrate. According to our experiments, the COD_{Cr} caused by potassium ferrate was 196.13 mg/L when the concentration of potassium ferrate was 6 g/L. UV-254 refers to the absorption of ultraviolet light at 254 nm, and organics that the molecular weights of which are greater than 3,000 are the major part that absorb ultraviolet light at 254 nm, and other organics, such as lower fatty acid and amino acid do not absorb ultraviolet light, but they contribute to the value of COD_{Cr}. So when the dosage of potassium ferrate was excessive, the COD_{Cr} removal efficiency was influenced obviously by the impurity of potassium ferrate though some organics could be disintegrated by the excessive potassium ferrate. Finally, we confirmed that the optimum dosage of potassium ferrate was 6 g/L.

3.2. *Effect of pH on leachate treatment*

The pH values in beakers with 50 mL landfill leachate were controlled to be 2, 3, 4, 5, 6, 7, 8, 9, 10, and 11, respectively, and the landfill leachate was stirring for 30 min after 6 g/L potassium ferrate was added. The COD_{Cr} and UV-254 values were determined and shown in Figs. 3 and 4.

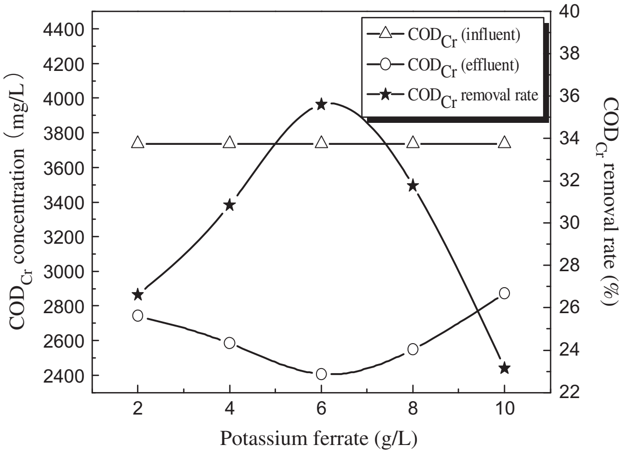

Fig. 1. Effect of potassium ferrate dosage on COD_{Cr} removal efficiency.

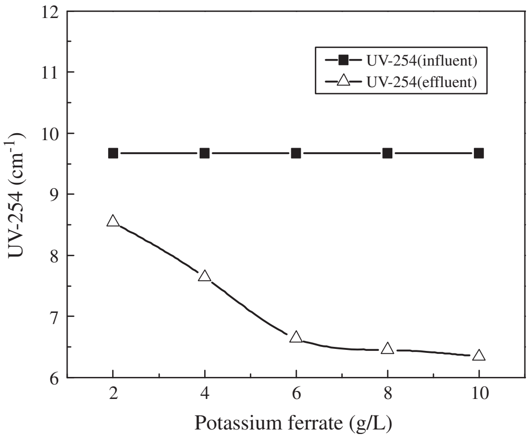

Fig. 2. Effect of potassium ferrate dosage on UV-254.

As shown in Figs. 3 and 4, the influence of pH on treatment effect of landfill leachate treated by potassium ferrate is complex. The removal efficiency of COD_{Cr} changed undulately in the whole pH range. And the values of UV-254 decreased to a constant with the pH values increasing under acid conditions. Under alkali conditions, the values of UV-254 increased first but then decreased with the pH values increasing. Two elements were influenced by the pH values, one was the oxidation potential of ferrate ion and the other was the stability of potassium ferrate. When the pH values were low, potassium ferrate was unstable and easy to be disintegrated with water though the oxidation potential was high. When the pH values were high, the potassium ferrate was stable while the oxidation reduction potential was low, but the potential of potassium ferrate kept a relatively high value when pH was 10. So the dual influences of the stable and potential of potassium ferrate by pH

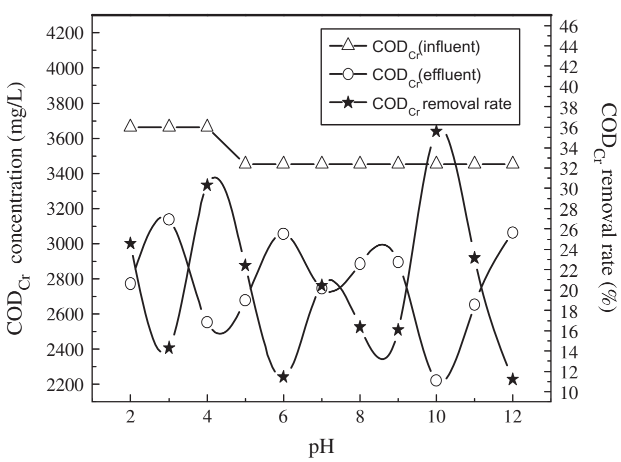

Fig. 3. Effect of pH on COD_{Cr} removal efficiency.

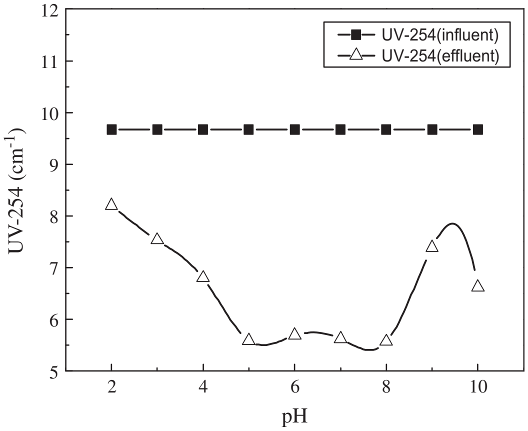

Fig. 4. Effect of the pH on UV-254.

resulted in the maximum COD$_{Cr}$ removal efficiency of at pH of 10, as shown in Fig. 3. But the UV-254 value was minimum when the pH value was 5–8, as shown in Fig. 4. The UV-254 value represented the aromatic organics concentration in the landfill leachate. The aromatic rings broking needed higher oxidation reduction potential. When the pH values were lower than 8, the potential of potassium ferrate was high enough to break the aromatic rings. When the pH was higher than 8, the stability increased and the potential was enough for the oxidative degradation of the chain hydrocarbon compounds, but weaker for the degradation of the aromatic compounds, so the UV-254 value increased slightly at pH of 10. When pH was lower than 5, though the potential was high, but most potassium ferrate decomposed by the reaction with water, so was the poor effect for the aromatic compounds degradation. According to the removal efficiency of CODcr and UV-254, the optimum pH value was determined to be 10.

3.3. 3Effect of reaction time on the leachate treatment

The reaction time was 10, 20, 30, 40, 60 min, respectively. And the concentration of potassium ferrate in 50 mL landfill leachate was 6 g/L, pH value was 10. COD$_{Cr}$ values and UV-254 values were determined and shown in Figs. 5 and 6.

As shown in Figs. 5 and 6, the removal efficiency of COD$_{Cr}$ increased and the UV-254 values decreased with the reaction time lengthened. The removal efficiency of COD$_{Cr}$ and the UV-254 value were constants until the reaction time was 30 min. The reaction between potassium ferrate and landfill leachate was not complete if the reaction time was shorter than 30 min, and the COD$_{Cr}$ values and UV-254 values

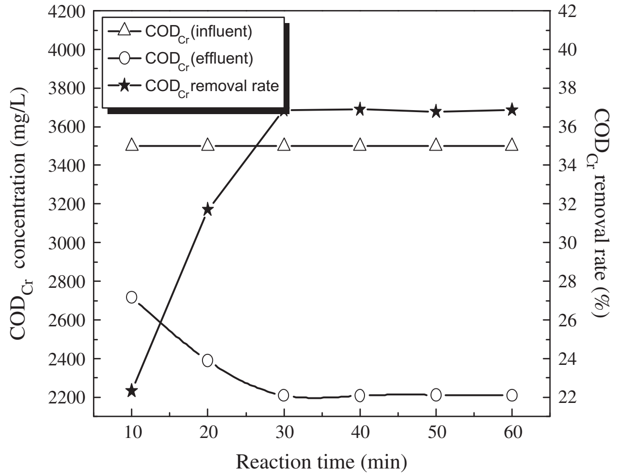

Fig. 5. Effect of the reaction time on COD$_{Cr}$ removal efficiency.

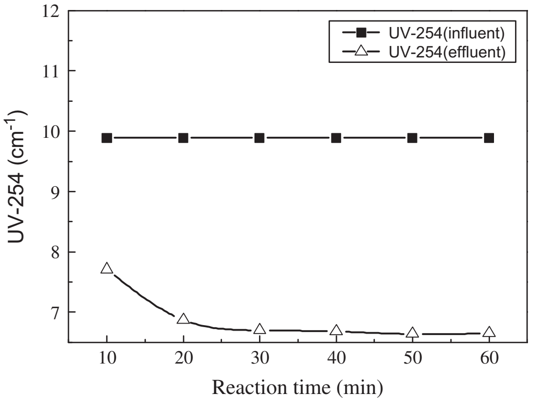

Fig. 6. Effect of the reaction time on UV-254.

were constant when the reaction time was longer than 30 min. So the optimum reaction time was 30 min.

3.4. Effect of the concentration of landfill leachate

The concentrations of landfill leachate were always different, so the influence of the concentration of landfill leachate on treatment effect was studied. Three different concentrations of landfill leachate were used in our experiments, they were raw landfill leachate, two times diluted landfill leachate, and three times diluted landfill leachate and they were treated under the same conditions, and the results are shown in Figs. 7 and 8.

As shown in Figs. 7 and 8, the removal efficiency of COD$_{Cr}$ decreased with the concentration of landfill leachate decreasing. The differences of concentrations of landfill leachate reflected that the components of landfill leachate were different which caused the treatment effects being different, which corresponded to the study of Wu et al. [19]. In short, potassium ferrate should not be used to treat landfill leachate with low concentrations.

3.5. Influence of stabilizing agent on treatment effect

Stabilizing agents can be used to enhance the stability of potassium ferrate, such as Na_2SiO_3, Na_3PO_4, Na_2MoO_4, the types and dosages of different stabilizing agents were studied, and the removal efficiency of COD_{Cr} and UV-254 was determined to reflect the influence of stabilizing agents on treatment effect.

3.5.1. Influence of the dosage of sodium silicate

The dosages of sodium silicate were 0, 2, 4, 6, 8, 10 g/L, respectively. The volume of landfill leachate was 50 mL, pH value of landfill leachate was 10, the dosage of potassium ferrate was 6 g/L, and reaction time was 30 min. Influences of dosages of sodium silicate on the removal efficiency of COD_{Cr} and UV-254 are shown in Figs. 9 and 10.

As shown in Figs. 9 and 10, the removal efficiency of COD_{Cr} and UV-254 value increased first but then decreased with the dosages of sodium silicate increasing. The removal efficiency of COD_{Cr} attained the maximum and UV-254 value attained the minimum value when the dosage of sodium silicate was 4 g/L, and they were 52.25% and 6.68 cm^{-1}, respectively. When the dosage of sodium silicate was lower than 4 g/L, the decomposition rate of potassium ferrate was high, so the treatment effect was weakened. When the dosage of sodium silicate was higher than 4 g/L, the reaction between potassium ferrate and landfill leachate was influenced, so the optimum dosage of sodium silicate should be 4 g/L. Compared

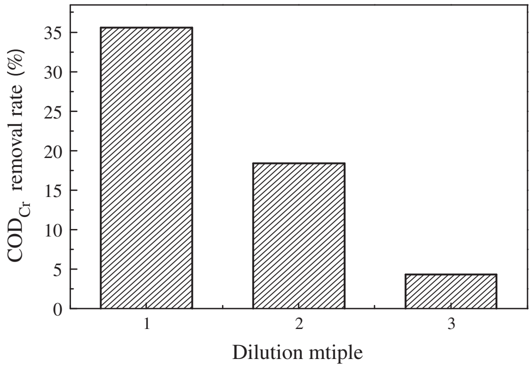

Fig. 7. Effect of the concentration of landfill leachate on COD_{Cr} removal efficiency.

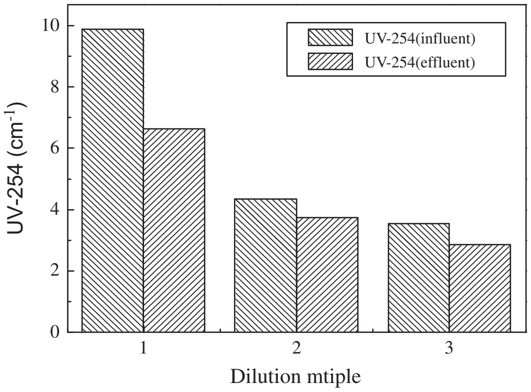

Fig. 8. Effect of the concentration of landfill leachate on UV-254.

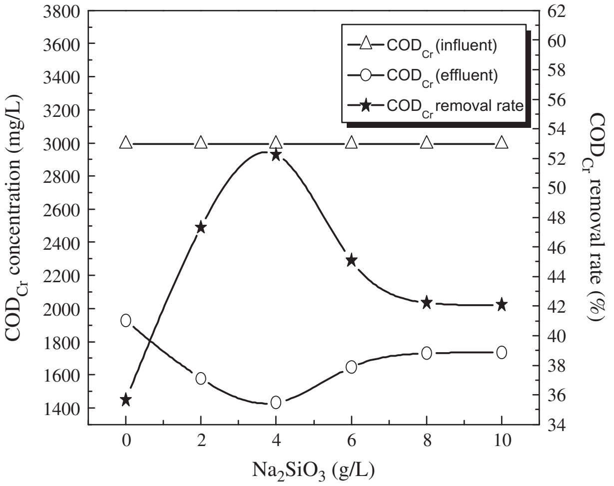

Fig. 9. Effect of Na_2SiO_3 dosage on COD $_{Cr}$ removal efficiency.

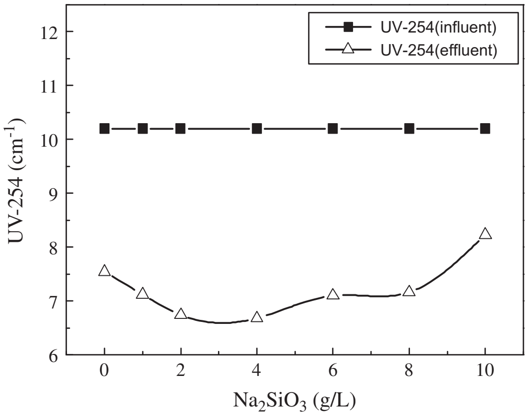

Fig. 10. Effect of Na_2SiO_3 dosage on UV-254.

with the reaction without sodium silicate, sodium silicate (4 g/L) caused the removal rate of COD_{Cr} increasing from 35.67 to 52.25%, and the UV-254 value decreasing from 7.54 to 6.68 cm^{-1}.

3.5.2. *Influence of dosage of sodium molybdate*

The dosages of sodium molybdate were 0, 2, 4, 6, 8, 10 g/L, respectively. The volume of landfill leachate was 50 mL, pH value of landfill leachate was 10, the dosage of potassium ferrate was 6 g/L, and reaction time was 30 min. Influences of dosages of sodium molybdate on the removal efficiency of COD_{Cr} and UV-254 are shown in Figs. 11 and 12.

As shown in Figs. 11 and 12, the removal efficiency of COD_{Cr} increased first but then decreased with the dosage of sodium molybdate increasing, and UV-254 value decreased first but then increased with the dosage of sodium molybdate increasing. The optimum dosage of sodium molybdate was 2 g/L. Compared with the reaction without sodium molybdate, sodium molybdate (2 g/L) caused the removal efficiency of COD_{Cr} increasing from 35.67 to 47.39%, and the UV-254 value decreasing from 7.54 to 6.92 cm^{-1}.

3.5.3. *Influence of dosage of sodium phosphate*

The dosages of sodium phosphate were 0, 2, 4, 6, 8, 10 g/L, respectively. The volume of landfill leachate was 50 mL, pH value was 10, the dosage of potassium ferrate was 6 g/L, and reaction time was 30 min. Influences of dosages of sodium phosphate on the removal rate of COD_{Cr} and UV-254 are shown in Figs. 13 and 14.

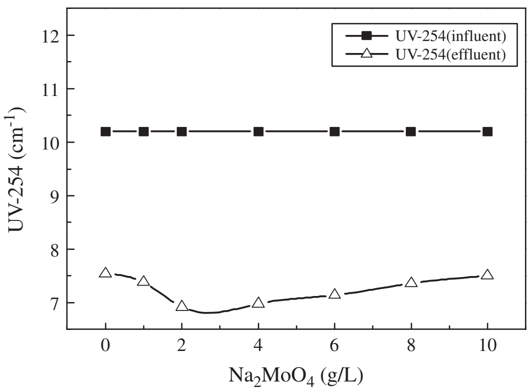

Fig. 12. Effect of Na_2MoO_4 dosage on UV-254.

As shown in Figs. 13 and 14, the removal efficiency of COD_{Cr} increased first but then decreased with the dosages of sodium phosphate increasing, and UV-254 values decreased first but then increased with the dosages of sodium phosphate increasing. When the dosage of sodium phosphate was 2 g/L, the removal efficiency of COD_{Cr} attained the maximum value and UV-254 attained the minimum value, and they were 41.96% and 7.17 cm^{-1}, respectively.

Collectively, sodium silicate and sodium molybdate were all good choice as stabilizing agents. Because sodium silicate is much cheaper than sodium molybdate, so sodium silicate was the optimum choice as stabilizing agent.

4. Discussion

The iron ion was generally +2 valence or +3 valence, but in the potassium ferrate, it was +6

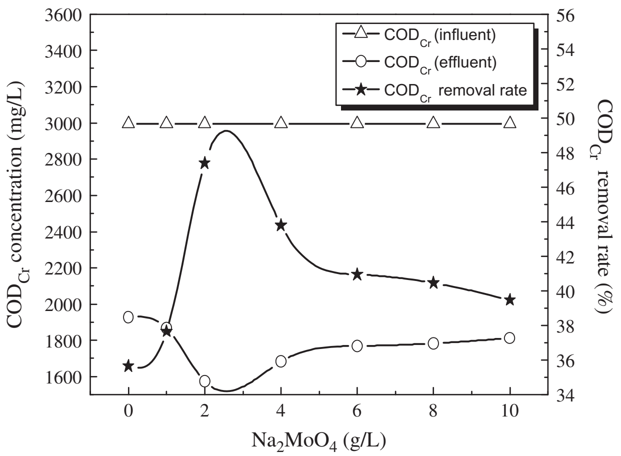

Fig. 11. Effect of Na_2MoO_4 dosage on COD_{Cr} removal efficiency.

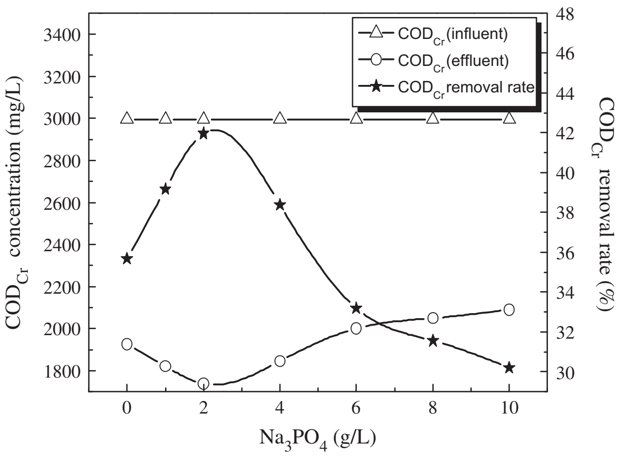

Fig. 13. Effect of the amount of Na_3PO_4 on COD_{Cr} removal rate.

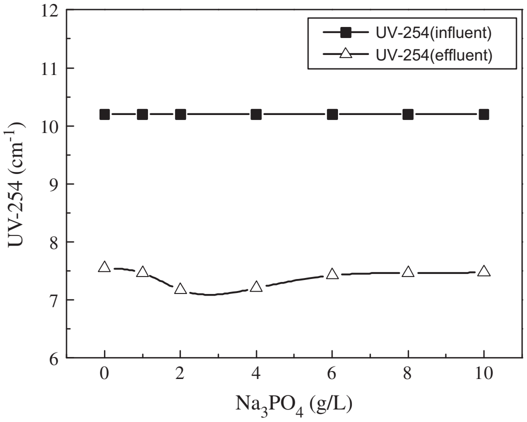

Fig. 14. Effect of the amount of Na_3PO_4 on UV-254.

valence which was the highest state and the strongest oxidizing of iron element. The oxidability of potassium ferrate was fairly strong in the whole pH scope, which was stronger than that of potassium chromate and potassium permanganate. The standard electrode potentials were $E^0FeO_4^{2-}/Fe^{3+} = 2.20\,V$ and $E^0FeO_4^{2-}/Fe(OH)_3 = 0.72\,V$ in the acidic and alkaline conditions, respectively [20]. The product Fe^{3+} formed by the reduction of FeO_4^{2-} was a good flocculant which could absorb the organic compounds and heavy metal in the wastewater by forming to $Fe(OH)_3$. So the pollutant removal in the wastewater by potassium ferrate was the combined results of the oxidation and the flocculation.

It was indicated that the effect of pH on the stability and the oxidability of potassium ferrate were very important [5]. The lower the pH was, the higher the standard electrode potential was, the higher the oxidability was. But the lower pH led to the worse stability of the potassium ferrate solution. In the acidic condition, potassium ferrate could easily react with water to form Fe^{3+}, losing the ability to oxidize the organics in the wastewater. The lower the pH was, the worse the stability was, the more amount of potassium ferrate reacted with water was. In the alkaline condition, the standard electrode potential decreased, but the stability increased, so the probability with water decreased, while the probability with organic compounds improved.

The addition of inorganic salts had important effect to the stability of potassium ferrate. Deininger indicated that the addition of phosphate was in favor of the stability of potassium ferrate [21]. In the study of Zhuang et al., the stability of the alkaline potassium ferrate solution increased with the addition of sodium silicate [22]. The addition of the inorganic salts as the stabilizer resulted in the lower probability of the reaction between potassium ferrate and water, so the invalid decompose of potassium ferrate reduced and the probability of the contact between potassium ferrate and the organics in the wastewater enhanced, the better treatment efficiency of landfill leachate achieved. Moreover, the ion concentration increased with the addition of the inorganic salts, resulting in a higher collision probability among the molecules [23], and the reaction rate of potassium ferrate with water and the organics simultaneously increased, so the organics oxygenolysis in the wastewater was accelerated.

5. Conclusions

(1) The conditions for the treatment of landfill leachate by potassium ferrate were as follows: the dosage of potassium ferrate should be 6 g/L, pH value should be 4, reaction time should be 30 min, and the concentration of landfill leachate should be high. And under those conditions, the removal efficiency of COD_{Cr} attained 36% and UV-254 value decreased from 10 to 6.6 cm^{-1}.
(2) Stabilizing agents could enhance the stability of potassium ferrate and improve the treatment effect. Sodium silicate and sodium molybdate added as stabilizing agent could improve the treatment effect significantly, and sodium silicate was better than sodium molybdate for it was cheaper. The removal efficiency of COD_{Cr} was 52.25% and UV-254 value was 6.6 cm^{-1} when the dosage of sodium silicate was 4 g/L.

Acknowledgments

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