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THE REMOVAL OF OXYTETRACYCLINE (OTC) BY POTASSIUM FERRATE (VI) IN AQUATIC ENVIRONMENT

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ABSTRACT

The treatment of oxytetracycline (OTC) in test solutions by ferrate (VI) was investigated aiming to propose the effects of pH, concentration of co-existing ions and humic acid on the OTC removal. Ferrate (VI) can remove 97% OTC (from 1000 $\mu g \cdot l^{-1}$) in 30 minutes under the optimal conditions with solution pH of 7 and ferrate (VI) dosage of 20:1 as a molar ratio of ferrate (VI)/OTC. The effects of co-existing ions (0.005 $mol \cdot l^{-1}$ and 0.02 $mol \cdot l^{-1}$) and humic acid (0.1~50 $mg \cdot l^{-1}$) on the OTC removal were investigated for the optimal operating conditions. The results showed that Ca^{2+}, CO_3^{2-}, PO_4^{3-}could inhibit the OTC degradation and its removal rate decreased from 79, 29, 29% to 70, 19, 19%, for the ion concentration increased from 0.005 $mol \cdot l^{-1}$ to 0.02 $mol \cdot l^{-1}$. Mg^{2+} and HCO_3^- could restrain the reaction carried out at 0.02 $mol \cdot l^{-1}$ and the removal rate was only 59%, 62%. Al^{3+}could increase the removal rate which reach to 100%. Humic acid with concentrations of greater than 10 $mg \cdot l^{-1}$ could notably inhibit the OTC removal. Regression analysis indicated good fit of the experimental date to the developed model with coefficient of determination (R^2) value of 0.9991 and the adjusted R^2 value of 0.9978.

Keywords: ferrate (VI); oxytetracycline; humic acid; co-existing; Box–Behnken design;

1. Introduction

Oxytetracycline (OTC) is a common broad-spectrum antibiotic tetracycline. It is widely used in swine, cattle, poultry and fish husbandry as feed additives and veterinary drugs for prophylactic, and therapeutic purposes throughout the world, because of its low cost and effective antimicrobial (Lu *et al.,* 2015). However, the widespread use of it has led to much environmental issues and human health problems (Marx *et al.,* 2015; Li *et al.,* 2015; Burkina *et al.,* 2015; Auerbach *et al.,* 2007; Luis Martinez, 2009), such as the presence of OTC residues in animal foods and environmental pollution (Kim *et al.,* 2014; Fritz *et al.,* 2007; Sun *et al.,* 2014). Most of OTC leaves human and animal body unmetabolized via feces and urine (Liu *et al.,* 2015; Kemper, 2008).Therefore OTC is extensively distributed in soil, groundwater, surface water, sea water, and sediment worldwide (Shibata *et al.,* 2014; Chen *et al.,* 2015; Kuemmerer, 2009). Moreover, the nature of OTC is stable and difficult to be degraded; therefore it can exist in the natural environment for a long time. Its occurrence in natural environment may have harmful impact on human health and ecosystem through the development of drug resistance among pathogens and bacteria. Therefore it is important to remove the pollutant from

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wastewater before discharging into the environment. Several studies have shown that OTC is hardly degraded by conventional water treatment process (Watkinson *et al.,* 2007; Rahmah *et al.,* 2015).

Ferrate (VI) is a strong oxidant in aqueous media with a reduction potential of 2.20 V and 0.70 V in acidic and alkaline, respectively; under acidic conditions, the redox potential of ferrate (VI) ion is strongest among all oxidants/disinfectants used for water and wastewater treatment (Jiang, 2014). It is also an environment-friendly chemical for coagulation, disinfection, and oxidation for multipurpose treatment of water and wastewater; during the oxidation/disinfection process, ferrate (VI) ions are reduced to Fe (III) or ferric hydroxide, and this simultaneously generates a coagulant in a single dosing and mixing unit process (Jiang *et al.,* 2012). Furthermore, the application of ferrate (VI) can improve the removal of nature organic matter or disinfection byproducts (DBPs) precursors (Sharma *et al.,* 2006). There are many processes have been investigated on the degradation of OTC, such as ozone process, Fenton process, UV photolysis, simulated sunlight irradiation (Uslu *et al.,* 2009; Yuan *et al.,* 2011; Chen *et al.,* 2008; Li *et al.,* 2008). However, no study has been reported on the removal of OTC using ferrate (VI).

Therefore, the objectives of this study were to find the best reaction time, ferrate (VI) dose and the pH value of reaction solution on the removal of OTC; to assess the influence of the type and strength of coexisting ions on the removal of OTC; to evaluate the effect of humic acid on the removal of OTC and finally to identify the optimal operating conditions to degraded the OTC by ferrate (VI).

2. Experimental section

2.1 Chemicals and reagents

The OTC was purchased from Aladdin (Shanghai, China); acetonitrile (HPLC grade) was purchased from Tianjin Shiyou Chemical Reagent Factory (Tianjin, China) and potassium hydroxide (AR) was purchased from Hangzhou Xiaoshan Chemical Reagent Factory (Hangzhou, China). Humic acid was obtained from Nanjing Chemical Reagent Factory (Nanjing, China). Ferrate (VI) solution of high concentration was synthesized by the electro-chemical method (Wang *et al.,* 2015), and the solid potassium ferrate (VI) was obtained after various purification steps (Li *et al.,* 2005).The ferrate (VI) strength of the resulting dry product was measured by chromite method and direct spectrophotometric method using a wavelength of 505 nm and an absorbance coefficient of 1100 $M^{-1}\cdot cm^{-1}$(Jiang *et al.,* 2006).The purity of ferrate (VI) was continuously monitored on the daily basis. The other reagents (AR) were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Experimental water was generated by ultra pure water supplier (UPHW1-90T, Sichuan europtronic ultra pure Technology Co. Ltd., China). Stock solutions of OTC were prepared in pure water at 100 $mg\cdot l^{-1}$ for the use of jar test experiments.

2.2 Jar test experiment

The oxidation of OTC by ferrate (VI) was studied using a magnetic stirrer (HJ-6, Jintan Jiangnan instrument Factory), with a mixing speed of 500 rpm. Transfer liquid gun (Shanghai Kangmin inspection equipment Co. Ltd, China) was used for sampling at given reaction time intervals and sodium thiosulfate (0.1 $mol\cdot l^{-1}$) was used as a quencher.

The influence of operating conditions were investigated using 100 mL test solutions with initial OTC concentrations of 1000 $\mu g\cdot l^{-1}$ and by adjusting the ferrate (VI) dosages, pH value and humic acid concentrations. Ferrate (VI) was dosed into the test solution as dried powder and the dosage applied was in the molar ratio of ferrate (VI)/OTC from 5:1 to 50:1. The pH value of test solutions was adjusted by 0.01 $mol\cdot l^{-1}$ sulfuric acid and 0.01 $mol\cdot l^{-1}$ potassium hydroxide to pH 5~10. The humic acid concentration in testing solutions was 0.1~50 $mg\cdot l^{-1}$. The OTC concentration and removal percentage of each sample were detected by liquid chromatography (LC) (see sub-section 2.3).

100 ml test solutions with OTC initial concentration of 1000 μg·l^{-1} were used to study the impact of the presence of 0.005 mol·l^{-1} and 0.2 mol·l^{-1} co-existing ions (Na^+, Mg^{2+}, Ca^{2+}, Al^{3+}, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}, Cl^-, NO_3^-, HCO_3^-) on the OTC degradation performance by ferrate (VI). The OTC solutions were mixed with given amount of NaCl, KCl, KNO_3, $Mg(NO_3)_2$, $CaCl_2$, $Al_2(SO_4)_3$, Na_2CO_3, Na_2SO_4, $NaHCO_3$ and Na_3PO_4, respectively, to achieve the required ion concentrations. The ferrate (VI) with dosage of 20:1 as ferrate (VI)/OTC in the molar ratio was mixed with the test solution and the sampling time was 30 minutes. All samples in experiments were filtered by 0.45 μm glass membrane filters (Shanghai Xingya purifying material factory, China) before analyzing the residual OTC concentrations. The OTC concentration and removal rate of each sample were detected by high performance liquid chromatography (HPLC) (Agilent 1200 series, USA) (see sub-section 2.3).

2.3 Detection Method

The quantification of OTC was measured by an Agilent 1200 Series HPLC system equipped with a UV detector. A C18 Eclipse XDB (Supelco) column (150 mm× 4.6 mm, 5 μm particle size) was used as a stationary phase. The mobile phase for OTC was 0.1% oxalic acid water solution /acetonitrile (82/18, v/v %) at a flow rate of 0.5 ml·min^{-1}. The detection wavelength was set at 360 nm, the sample injection volume was 10 μl and the column temperature was kept at 30 °C. The pH value was measured using a portable pH meter (SensION, HACA, USA).

2.4 Box-Behnken experimental design

Response surface methodology is an empirical modeling technique used to evaluate the relationship between a set of controllable experimental factors and observed results (Mourabet *et al.,* 2012). In this study, the Box-Behnken (BBD) was used to design the experiment. The most important factors, which affect the efficiency of OTC removal extremely, are contact time, ferrate (VI) dose and pH. Therefore the three parameters are the contact time (min), ferrate (VI) dose (Fe(VI)/OTC in molar ration) and pH, represented as X_1, X_2, X_3, separately. A three-factor, three-level second-order model was developed. The OTC removal (Y) was considered the response. Experimental range and the levels of the independent variables are showed in Table 1. This design was applied using Design-Expert 8.0.6.1 to the study. The following equation represents a second-order model (Equation 1):

$$Y=\beta_0+ \beta_i+ x_i+ \Sigma\beta_{ii}+ x_{ii}^2+ \Sigma\beta_{ijxixj}+ \varepsilon \qquad (1)$$

Where, Y is the predicted response surface function, β_0 is the model constant, β_i is the slope or linear effect of the input factor x_i, β_{ij} is the quadratic effect of input factor x_i and β_{ij} is the linear by linear interaction effect between the input factor x_i and factor x_j (Mourabet *et al.,* 2012).

Table 1. Experimental range and levels of independent variables

Independent Variables		**Range and level**		
		-1	**0**	**+1**
X_1	contact time(min)	10	20	30
X_2	Ferrate(VI) dose	15:1	20:1	25:1
X_3	pH	6	7	8

3. Results and Discussion

3.1 Effect of reaction time and ferrate (VI) dosage

The ferrate (VI) dosage ranged from 5:1 to 25:1 as molar ratio of [ferrate (VI)/OTC] and the reaction time was 60 minutes. Fig. 1 shows that most OTC was degraded in 5 minutes. Along with the time, the concentration of OTC decreased slowly and at the time of 30 minutes, the reaction finished. From 30 minutes to 60 minutes, the OTC concentration did not change. Therefore the optimum reaction time is 30 minutes.

In order to obtain the best dosage of ferrate (VI), dosage was increased from 5:1 to 50:1 as [ferrate (VI)/OTC] in molar ratio. Fig.2 shows that the average removal efficiency of OTC in the model wastewater was 88%~97%. It’s obviously that with the increase of the ferrate (VI) dosage, the removal rate gradually increased, however the removal rate increased slowly when the dosage range from 15:1 to 50:1 as [ferrate (VI)]/[OTC]. Moreover, the removal rate slightly decreased if the dosage reaches to 50:1.This indicates that the OTC unit degradation performance at high ferrate (VI) dose was not as high as that at low ferrate (VI) dose. It could be that the ferrate (VI) decomposed and the ferrate (VI) decomposition speed increased when the dosage of ferrate (VI) increased (Sharma *et al.,* 2006). The best ferrate (VI) dosage ranged from 10:1 to 25:1 as [ferrate (VI)]/[OTC] and thus for the subsequent experiments, a dose of 20:1 as [Ferrate (VI)]/[OTC] in molar ratio was chosen.

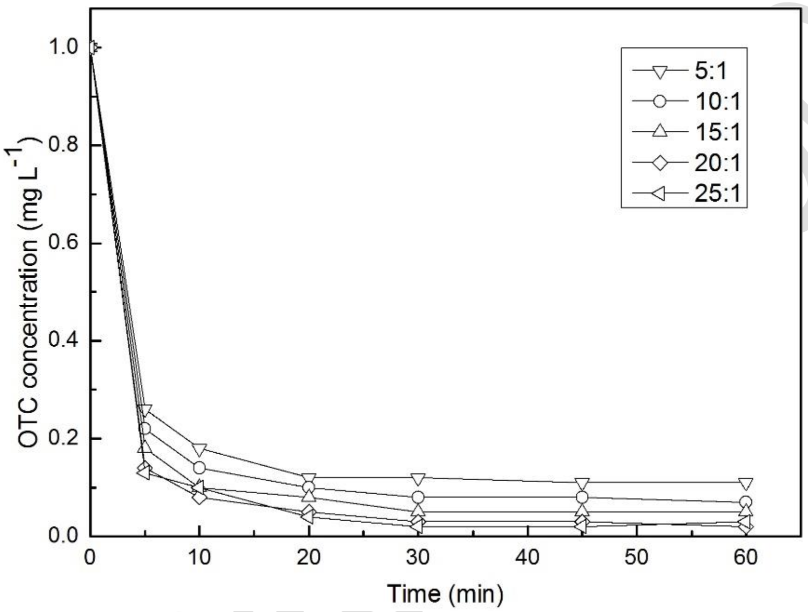

Figure 1. Effect of reaction time on the oxidation of OTC with ferrate (VI)

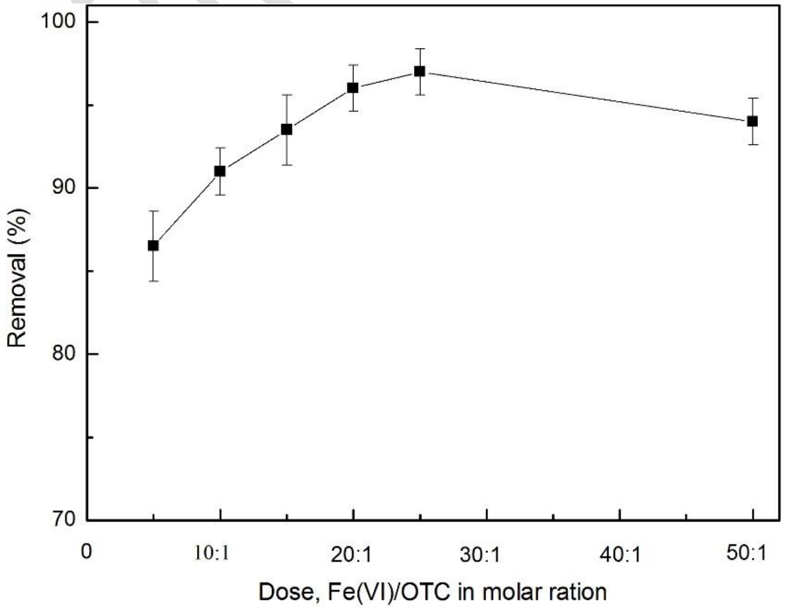

Figure 2. Effect of different dosage of ferrate (VI) on the oxidation of OTC

3.2 Influence of pH

The initial concentration of OTC was 1000 $\mu g \cdot l^{-1}$, and the pH was adjusted to between 5 and 10; the reaction time was 30 minutes, and the dosage of [ferrate (VI)]/[OTC] was 20:1 in molar ratio. Fig.3 shows that the pH of the solution has a great influence on the removal of OTC. Under neutral and faintly acid conditions, the removal efficiency of OTC is significantly higher than in alkaline conditions. When the pH value of solution was 7, the OTC removal was 97%.This is mainly because the pH of the reaction solution will affect the stability and oxidation ability of ferrate (VI); Moreover, with the increase of the pH, the redox potential of ferrate (VI) becomes more and more weak, so the reaction rate and removal efficiency of OTC become lower and lower. On the other hand, with the decrease of the pH, the ferrate (VI) solution becomes more and more unstable. When the pH value of the reaction solution changes from 5 to 7, ferrate (VI) mainly exits in the form of $HFeO_4^-$ and H_2FeO_4 (Eq. (2)-(4)). Ferrate (VI) is unstable and prone to self decomposition and then the removal efficiency of OTC becomes low. Moreover, OTC has three ionization equilibriums (Jiao *et al.,* 2008; Figueroa *et al.,* 2004). When pH is neutral or weak acid, the dissociation degree of OTC is higher. Studies have shown that the organic matter of dissociation state is more likely to be oxidized (Li *et al.,* 2005); therefore the OTC can be oxidized by ferrate (VI) easily.

$$H_3FeO_4^+ \longleftrightarrow H^+ + H_2FeO_4, pK_a = 1.6 \pm 0.2 \tag{2}$$

$$H_2FeO_4 \longleftrightarrow H^+ + HFeO_4^-,\ pK_a = 3.5 \tag{3}$$

$$HFeO_4^- \longleftrightarrow H^+ + FeO_4^{2-}, pK_a = 7.3 \pm 0.1 \tag{4}$$

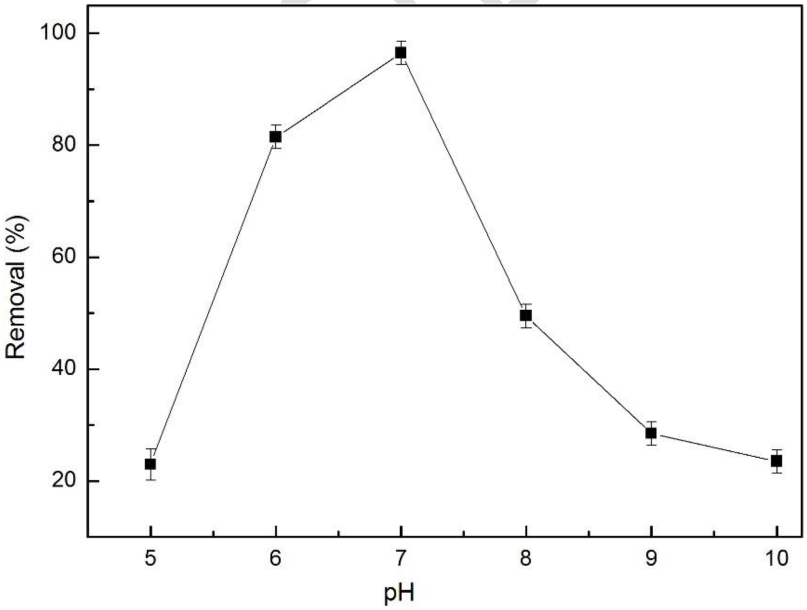

Figure 3. Effect of pH value on the oxidation of OTC with ferrate (VI)

3.3 Influence of the type and strength of coexisting ions

There are numerous types of ions in natural water bodies. Because of their different valence states, alkaline activity and other property, they have different effects on the reaction process. In order to investigate the influence of different types of ions and concentrations on the oxidation of OTC with ferrate (VI), the chloride

(Cl^-), nitrate (NO_3^-), carbonate (CO_3^{2-}), sodium (Na^+) ,bicarbonate (HCO_3^-), aluminum (Al_3^+), sulfate (SO_4^{2-}), magnesium (Mg_2^+), calcium (Ca^{2+}) and phosphate (PO_4^{3-}) were selected for the study. The ion concentration was 0.005 $mol \cdot l^{-1}$ and 0.02 $mol \cdot l^{-1}$respectively. Fig.4 shows that ions of phosphate, calcium, carbonate, magnesium, bicarbonate, aluminum have an effect on the degradation of OTC. Calcium, carbonate, phosphate can inhibit the reaction carried out: when the ions' concentration was 0.005 $mol \cdot l^{-1}$, the removal rate was 79, 29, 29% and decreased to 70, 19, 19% when the ions' concentration reached to 0.02 $mol \cdot l^{-1}$. The inhibition ability of phosphate and carbonate is stronger than calcium ion. Magnesium ion and bicarbonate only can slow down the reaction when its concentration was 0.02 $mol \cdot l^{-1}$ and the removal rate was only 59%, 62%. It is mainly because calcium ion and magnesium ion can form complex with OTC (Paroloa *et al.,* 2012; Cesaretti *et al.,* 2014) and the complex hinder the reaction of oxidation of OTC with ferrate (VI). Carbonate and bicarbonate are known as free radical scavenger; therefore they can reduce the OTC removal rate. It has also reported that bicarbonate can form inner-sphere monodentate complexes with surface functional groups of $Fe(OH)_3$ (Su *et al.,* 1997), therefore bicarbonate ions and OTC will competitively react with $Fe(OH)_3$, which lead to the amount of $Fe(OH)_3$ decreased which could play roles to adsorb OTC. Phosphate can form complex with Fe^{3+}, resulting from the ferrate (VI) decomposition, which inhibit the hydrolysis of Fe^{3+} and then reduce the generation of $Fe(OH)_3$. Aluminum ion can increase the degradation rate of OTC, which reach to 100%. This could attribute to that the particle size of the Fe(III)-Al(III) oxy/hydroxide precipitates is smaller than Fe (III) oxy/hydroxide leading to higher surface area and more adsorption sites available for OTC retention (Jain *et al.,* 2009).

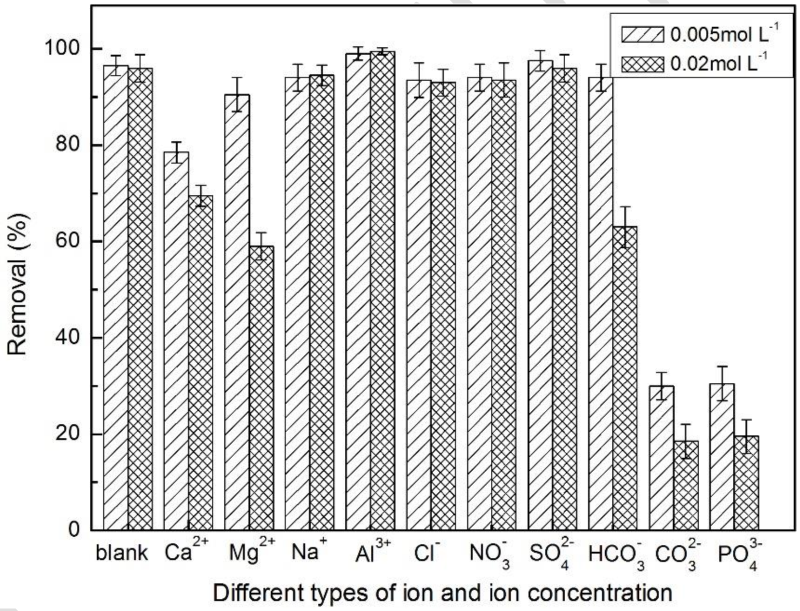

Figure 4. Effect of different types of ion and ion concentration on OTC removal

3.4 Influence of humic acid

Natural organic matters are considered to interfere with the OTC removal by ferrate (VI) oxidation. Humic acid is a natural organic matter which is widely present in natural waters. It has large surface areas, complex structure, and with a variety of functional groups (-COOH,-OH, etc.). The chemical structure of humic acids has complexity and diversity and different chemical structure; which will react with various oxidants and result in different chemical reactions. The OTC removal vs coexisting humic acid concentrations is shown in Fig.5. When the concentration of humic acid is less than 10 $mg \cdot l^{-1}$, the removal efficiency of OTC will not be affected, however with the increase of concentration of humic acid (>10 mg l^{-1}), the removal efficiency of OTC gradually reduced. When the concentration of humic acid reaches to 20 mg·l^{-1}, the removal rate dropped from 97% to 86% and when it reaches 50 mg·L-1, the removal rate is only 60%. At the same time, humic acid which is not completely oxidized and its reduction product can absorb Fe(OH)3, coming from the ferrate decomposition. This will weaken the sorption capacity of Fe(OH)3. The removal rate of OTC obviously reduced because of humic acid competition for Fe (VI) with OTC and the competition reactions between reduction product of humic acid and OTC with Fe(OH)3.

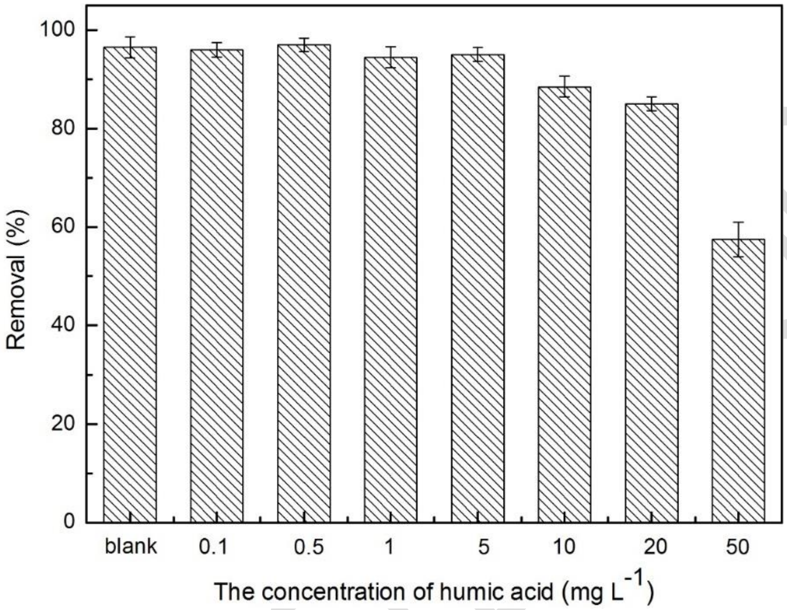

Figure 5. Effect of humic acid on the OTC removal

3.5 Box-Behnken statistical analysis

In order to evaluate the effects of various factors on the OTC removal efficiency, a total of 17 experiments were performed. The observed and predicted results are shown in Table 2.The final equation, as shown in Eq. (5), was got in terms of actual factors.

$$Y(\%)=94.80+2.50X1+1.50X2-15.75X3+1.25X1X2+0.25X1X3-0.75X2X3-0.28X12-1.77X22-30.78X32 \tag{5}$$

Analysis of variance (ANOVA) was used to test the significance and fitness of the model. The applied ANOVA for the removal of OTC is provided in table 3. The model F-values of 820.16 indicates the model is significant. Values of Prob.>F less than 0.0500 implies mode terms are significant. In this model, A, B, C, AB, B2, C2 is significant. An F-value of 1.43 indicated that the lack of fit is not significant to the pure error and non-significant lack of fit is desired. The values of R2, adjusted R2 and predicted R2 are 0.9991, 0.9978 and 0.9914, respectively. The high values of R2 imply the experimental and predicted results have a strong association.

In order to check the normality of the residuals, data were also analyzed. A normal probability plot or a dot diagram of these residuals is shown in Fig. 6. The data points on this plot lie reasonably close to a straight line. Fig. 7 shows the relationship between the actual and predicted values of Y for the removal of OTC. The result indicates that the residuals for the prediction for most of the responses are less than 10%, and the residuals tend to be close to the diagonal line, so the developed model is adequate. In summary, the model is appropriate for the explanation of the OTC removal process and could be used in future studies.

Table 2. Box-Behnken design matrix with predicted and experimental results

Number	Contact time (min)	Ferrate(VI) dose	pH	The OTC removal, Y (%)	
				observed	predicted
1	0	-1	1	46.00	45.75
2	1	0	-1	82.00	81.75
3	0	0	0	95.00	94.80
4	1	0	1	50.00	50.75
5	-1	1	0	90.00	90.50
6	0	0	0	94.00	94.80
7	1	1	0	98.00	98.00
8	1	-1	0	93.00	92.50
9	0	1	-1	80.00	80.25
10	0	0	0	96.00	94.80
11	0	-1	-1	75.00	75.75
12	0	0	0	94.00	94.80
13	0	0	0	95.00	94.80
14	-1	0	1	45.00	45.25
15	-1	0	-1	78.00	77.25
16	-1	-1	0	90.00	90.00
17	0	1	1	48.00	47.25

Table 3. ANOVA of the proposed model for the OTC removal

Source	Sum of squares	df	Mean square	F value	p-value prob.>F	
Model	6118.08	9	679.56	820.16	<0.0001	significant
A-t	50.00	1	50.00	60.34	0.0001	
B-dose	18.00	1	18.00	21.72	0.0023	
C-pH	1984.50	1	1984.50	2395.09	<0.0001	
AB	6.25	1	6.25	7.54	0.0286	
AC	0.25	1	0.25	0.30	0.5999	
BC	2.25	1	2.25	2.72	0.1434	
A^2	0.32	1	0.32	0.38	0.5549	
B^2	13.27	1	13.27	16.01	0.0052	
C^2	3987.79	1	3987.79	4812.85	<0.0001	
Residual	5.80	7	0.83			
Lack of fit	3.00	3	1.00	1.43	0.3586	not significant
Pure Error	2.80	4	0.70			
Cor Total	6121.88	16				

4. Conclusions

Results demonstrated that ferrate (VI) could effectively remove OTC in water. When the pH value of the test solution was 7 and the ferrate (VI) dose was 20:1 as [ferrate(VI)/OTC] in molar ratio, the removal rate of OTC (1000 µg·l^{-1}) was 97% after 30 minutes. The dosage of ferrate (VI) and the pH value of the reaction solution have a significant impact on the removal rate of OTC. The removal rate increase with the addition of the dosage of ferrate (VI), however, the ability of unit ferrate removal of OTC was decrease, because the decomposition rate of ferrate (VI) increased when the dosage of ferrate increased. The pH of reaction solution had a vital influence on the oxidation ability and the dissociation degree of OTC. Under the conditions of neutral and weak acid, the removal rate of OTC was higher than that under alkaline condition.

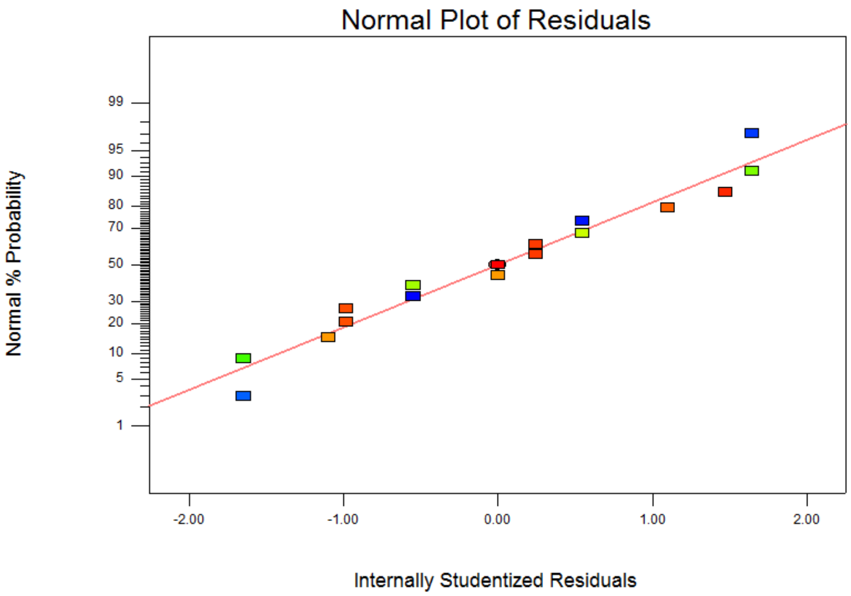

Figure 6. Normal % probability versus residual error

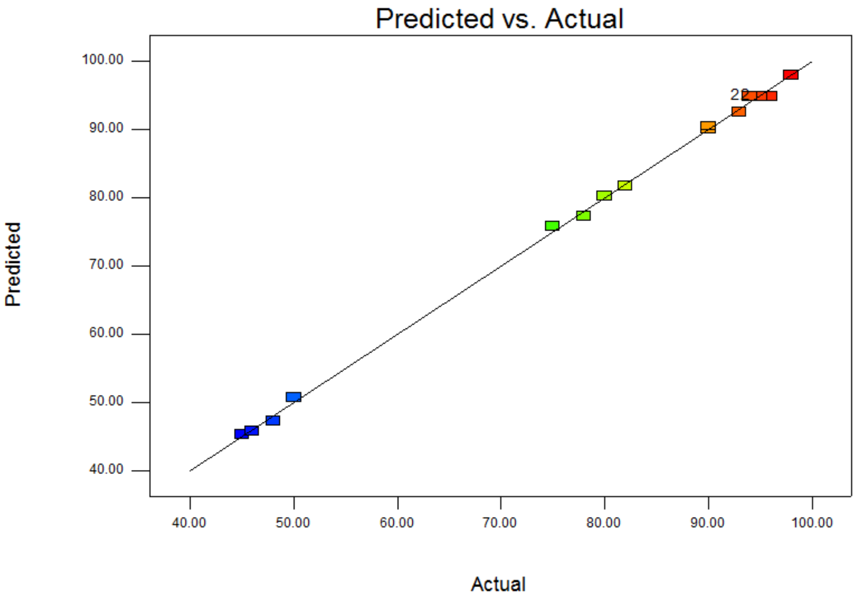

Figure 7. Predicted response versus actual response

The removal rate was highest as the pH value was 7. Different ion species and concentrations had impact on the OTC removal rate. Calcium ion, carbonate and phosphate restrained the reaction carried out at 0.005 mol·l^{-1} and 0.02 mol·l^{-1}. Magnesium ion and bicarbonate inhibited the reaction conducted at 0.02 mol·l^{-1}. Aluminum ion increased the removal rate of OTC. The effect of humic acid on the oxidation of OTC with ferrate was related to its concentration. When the concentration of humic acid was less than

10 mg·l^{-1}, the removal rate will not be affected. However when the concentration of humic acid was greater than 10 mg·l^{-1}, with the increase of the concentration of humic acid, the removal rate of OTC gradually reduced. Response surface methodology by the Box-Behnken model was used to check the three process factors on the OTC removal. The results showed that second-order polynomial regression model could properly interpret the experimental data with coefficient of determination (R^2) value of 0.9991 and an F-value of 820.16.

Acknowledgments

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