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Remediation of TCE-contaminated water by enhanced chemical oxidation using $Na_2S_2O_8/H_2O_2$/red mud

Yi Qian*, Qianqian Wang, Feifei Yue

College of Environment and Safety Engineering, Qingdao University of Science and Technology, Shandong Province, Qingdao 266042, P.R. China, Tel. +86 532 84022016; Fax: +86 532 84022617; email: qianyi1962@126.com (Y. Qian)

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ABSTRACT

In this study, the feasibility of degrading trichloroethylene (TCE)-contaminated water (initial TCE concentration of approximately 45 mg/L) was evaluated via persulfate oxidation activated by red mud. The study indicates that red mud is able to activate the persulfate oxidation mechanism producing sulfate radicals ($SO_4^{-}\cdot$) to oxidize TCE. There is a higher TCE removal (92%) with the addition of 2 g/L red mud after 5 h of oxidation reaction vs. non red mud system (42% TCE removal). A maximum TCE removal efficiency is obtained at neutrality condition. The TCE degradation rate reached 95% at lower temperature with the oxidation of hydrogen peroxide and sodium persulfate, respectively. This result reveals that the ability of activated persulfate ($S_2O_8^{2-}$) to generate sulfate radicals ($SO_4^{-}\cdot$) is limited by thermal. In addition, a favorable TCE degradation rate is acquired for Fenton-like oxidation reaction with hydrogen peroxide and sodium persulfate as oxidant.

Keywords: TCE; Oxidation; Red mud; H_2O_2; $Na_2S_2O_8$

1. Introduction

Trichloroethylene (TCE) is a halogenated volatile organic compound (VOC), which is a common industrial solvent and has been mainly used as a degreaser. Due to its prevalent use, it has found its way into groundwater and soil through spills and improper releases [1]. TCE is carcinogenic and may pose a threat to the public health [2]. It is listed as a primary pollutant with 5 μg/L maximum contamination level allowed in drinking water [3].

Among various remediation technologies [4–8], *in situ* chemical oxidation (ISCO) has been known as one of the most powerful tools for the treatment of wastewater and contaminated groundwater. Ozone [4], potassium permanganate [5], persulfate [6], and Fenton reagents [7,8] have been extensively studied. For the degradation of chlorinated organic compounds in ISCO processes, Fenton-like reaction has attracted an attention among the chemical oxidation processes due to its strong oxidative capacity for the degradation of organic contaminants [2,9]. Fenton's reaction utilizes soluble Fe(II) as the catalyst [10]. For Fenton-like reaction, Fe(III) or iron oxides (e.g. goethite (a-FeOOH), hematite (a-Fe_2O_3), iron chelates) are used as catalysts for strong oxidizing radical (·OH) generation [11,12]. Another alternative oxidant for ISCO is persulfate, and sodium persulfate ($Na_2S_2O_8$) is the most suitable one for *in situ* application [13]. Recently, advanced oxidation processes have emerged for organic pollutants degradation, such as activated persulfate oxidation [14]. Currently, it is the latest

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*Corresponding author.

method involved in ISCO to degrade contaminants into less harmful chemical species [15]. Persulfate usually requires higher activation energy than other chemical oxidants such as permanganate. Upon thermal, photochemical, or metal ions [16–20], the activated decomposition of persulfate anion ($S_2O_8^{2-}$) occurred and induced the production of a powerful oxidant known as the sulfate free radical ($SO_4^{-}\cdot$).

Red mud is the solid waste from Bayer process of refining of bauxite to produce alumina [21]. In recent years, the management of red mud has been a major issue in environmental engineering due to the enormous quantities and the associated disposal costs. There are some differences between the residues from China and other countries due to the difference in the ore type in its production processes [21]. Although heavy metals or toxic inorganic with higher concern (e.g. Ti, Cu) are not the major components of red mud, the amounts of released chemicals from the red mud should be monitored. During the practical application, the amounts of red mud existed in the river or subsurface should be managed to prevent the released chemicals from entering into water. In this study, we use red mud in Fenton-like oxidation process, which is a promising field, because it can improve the removal efficiency of TCE and reduce the pollution of red mud in water. Red mud is highly alkaline, and includes some main oxides such as Fe_2O_3, FeO, CaO, SiO_2, Al_2O_3, and NaOH. In addition, FeO and Fe_2O_3 can be dissociated to produce Fe(II) and Fe(III) in aqueous solution. The application of the Fenton-like oxidation for the degradation of chlorinated solvents has attracted wide attention due to its satisfactory removal efficiency [22]. However, few studies of this method have been reported.

Herein, the affectivity of red mud to activate Fenton-like oxidation processes to remediate TCE-contaminated water was investigated. In addition, the influence of temperature and pH on chemical oxidation processes was evaluated. This study will be useful in the development of a practical system for application.

2. Materials and methods

2.1. Materials

The chemicals used were purchased from the following sources: TCE (99.5%, Tianjin Kemiou Chemical Reagent Co.), hydrogen peroxide (30% Sinopharm Chemical Reagent Co., Ltd), sodium persulfate (99%, Sigma), sodium hydroxide (96%, Sinopharm Chemical Reagent Co., Ltd), sulfuric acid (99.8%, Sinopharm Chemical Reagent Co., Ltd), and *n*-hexane (99.9%, Merck). Red mud was kindly supplied by Aluminum Corporation of China Shandong Branch as a sponsored material. It contains O (41.87%), Na (6.72%), Al (10.46%), Si (7.43%), Ca (1.32%), Ti (1.51%), Fe (28.55%), and Cu (2.14%) (The result is examined by an INCA Energy X-ray energy spectrometer (EDS, Oxford) after roasted at a temperature of 650℃ for 4 h). Red mud was sieved with a No. 100 mesh (1 mm) sieve to remove large slag and was washed with distilled water, dried at 120℃ in an oven, and cooled down in a desiccator. Red mud was analyzed to determine the iron components (e.g. Fe(II), total iron (Fet), and Fe(III)). Concentration of Fe(II) and Fet was measured by o-phenanthroline spectrophotography at 510 nm. The Fe(II) and Fet contents were determined by a HACH DR 2400 spectrophotometer. Table 1 shows the major compositions of the red mud applied in this study.

2.2. Experimental procedures

Each experiment was performed in a continuous stir batch reactor system (close system), composed of a 500 mL brown bottle and a Water-bathing Constant Temperature Vibrator. The initial TCE concentration was approximately 45 mg/L (after equilibration). Experiments were conducted to investigate the effect of temperature, red mud, initial pH, and types of oxidants (H_2O_2 and $S_2O_8^{2-}$) on the degradation TCE in the Fenton-like system. The effect of pH was investigated at different initial pH condition (2, 4.6, 7, and 10.2), pH was adjusted by 1 M H_2SO_4 and 1 M NaOH. No buffer was added to maintain pH constant. All samples and controls for the experiments were prepared according to the above-experimental procedure. The effect of temperatures was measured at three different temperatures (15, 30, and 45℃, Table 2). Water-bathing Constant Temperature Vibrator was used to

Table 1
The major compositions of red mud

Compositions	Value (%)
O	41.87
Na	6.72
Al	10.46
Si	7.43
Ca	1.32
Ti	1.51
Fe	28.55
Cu	2.14
Total	100.00

set temperature. Samples were collected under different reaction time to analysis the concentration of TCE and chloride ion. The first-order decay constant (k_{obs}, h^{-1}) of TCE was calculated to evaluate the effect of temperature on TCE oxidation rate. We designed single-factor experiment and orthogonal experiment to evaluate the effect of oxidant, such as H_2O_2 and $Na_2S_2O_8$.

2.3. Analytical methods

TCE concentration in aqueous solution with pH being adjusted to eight and was measured within 5 min after sampling by Tekmar Atomx Automated VOC Sample Prep System and Shimadzu QP 2010 Ultra Gas Chromatograph Mass Spectrometer (GC–MS). Atomx Automated VOC Sample Prep System was used to extract TCE. The temperatures of valve oven and transfer line were all 140˚C. The preheat temperature, desorb temperature and bake temperature was 245, 250, and 280˚C, respectively. The time for purge, desorb and bake was 11, 2, and 2 min, respectively. GC–MS was equipped with electron impact and Rxi-5ms column (30 m × 0.25 mm × 0.25 μm). The temperature of injection and interface was 150 and 235˚C, respectively. And ion temperature was 200˚C. Aqueous samples were withdrawn by a syringe at each sampling time and filtered with 0.25 μm membrane filter. Chloride produced from the oxidative degradation of TCE in the Fenton-like reaction was analyzed by ion chromatography and pH was measured by a pH meter.

3. Results and discussion

3.1. TCE oxidation by persulfate with/without red mud

Results from the red mud analyses indicated that the measured extractable iron (e.g. Fe(II), Fe(III)) in red mud is approximately 8.26 g/kg, which could be used to supply iron catalyst to activate the persulfate oxidation process. TCE oxidation by persulfate with/without red mud was conducted to determine the effectiveness of red mud (initial pH 2) on persulfate activation. Because the dissociation rate of iron mineral is affected by the pH of solution. Although Fenton-like reaction can be operated under neutral conditions, lower pH is suggested for practical application to enhance the TCE removal efficiency [23]. Fig. 1 presents the effect of red mud on the efficiency of TCE (initial TCE concentration of approximately 45 mg/L) removal. The concentration of $S_2O_8^{2-}$ was 6 g/L. In the absence of red mud, 42% of TCE was removed after 5 h (TCE concentration dropped from 45 to 26 mg/L). The results show that approximately 92% of TCE was removed with the addition of 2 g /L red mud after 5 h. Activation of persulfate with red mud addition is a potential approach to degrade TCE over a single persulfate addition (without red mud). This study reveals that red mud contains an amount of Fe(II), which could be used to supply iron catalyst to activate the persulfate for the oxidation of TCE. Gupta and Gupta [24] had demonstrated that $S_2O_8^2$ can be activated by transition metal ions, such as Fe (II), to produce a powerful oxidant known as the sulfate free radical ($SO_4^{-}\cdot$) (Eq. (1)). Besides, there would be a reaction among $SO_4^{-}\cdot$, OH^- and H_2O resulting in the generation of $HO^{\cdot}$ (Eq. (2)):

$$S_2O_8^{2-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-} + SO_4^{-}\cdot \quad (1)$$

$$SO_4^{-}\cdot + OH^- \rightarrow SO_4^{2-} + HO^{\cdot} \quad (2)$$

Similar researches [9,22] have pointed out that BOF slag could treat the TCE-contaminated water. Red mud is similar to BOF slag, which contains large amounts of Fe_2O_3 and FeO. It can be used repeatedly for iron supplement. This study has also demonstrated that the addition of red mud is a feasible method to enhance the treatment efficiency of TCE-contaminated water.

3.2. Effects of initial pH value on TCE oxidation

In this experiment, sulfuric acid and sodium hydroxide were added for pH adjustment to evaluate the effects of pH on Fenton-like system oxidation of TCE. Fig. 2 shows the effect of pH on Fenton-like

Table 2
Results of TCE oxidation after 5 h of operation

pH	$Na_2S_2O_8$ (g/L)	Red mud (g/L)	Temperature (˚C)	k_{obs} (h^{-1})	R^2	$T_{1/2}$ (h)
7	6	2	15	0.361	0.983	1.92
			30	0.519	0.982	1.34
			45	1.021	0.974	0.68

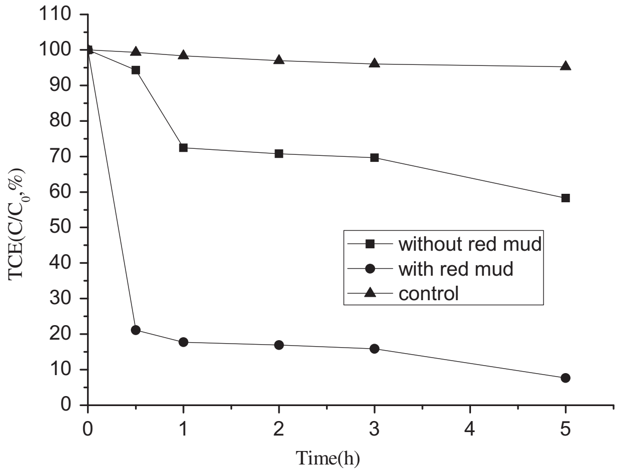

Fig. 1. Effect of red mud addition on the efficiency of TCE removal; conditions: $[TCE]_0 \approx 45$ mg/L, $Na_2S_2O_8 = 6$ g/L, initial pH 2, temperature = 15˚C, and reaction time = 5 h.

system oxidation of TCE between 2 and 10.2 at 30˚C. According to Fig. 3, the solution pH has changed little with the extent of reaction time. From this, it can be concluded that it is possible to maintaining the pH at about 7.

In Fig. 2(a), the TCE removal efficiency was in the order of pH 7 (95.8%) > pH 2 (92.3%) > pH 4.6 (90.9%) > pH 10.2 (87.4%). Based on the results, from our previous studies for an INCA Energy X-ray energy spectrometer analysis, the Fe content is 28.55% in the red mud. Lower pH can release more iron ion. Fenton-like oxidation should use red mud for an iron supplement. Thus, the pH becomes one of the most important control factors in this process. This indicated that pH plays an important role in the enhancement of oxidation rates. Lower pH can significantly induce increase in TCE removal rates. However, the maximum TCE degradation rate occurred at pH seven. As previously demonstrated and discussed by Liang [25], more $HO^{\bullet}$ would be generated and scavenged by SO_4^{2-} in alkaline solution than at neutral pH in the thermal persulfate activation system, resulting in a decrease in the TCE degradation rate under alkaline condition and a relatively improved performance at pH 7. The extent of degradation of TCE can also be monitored by the formation of chloride. Sulfate free radical oxidation of TCE can be described as follows [25]:

$$6SO_4^{-\bullet} + C_2HCl_3 + 4H_2O \rightarrow 2CO_2 + 9H^+ + 3Cl^- + 6SO_4^{2-} \qquad (3)$$

Stoichiometry of Eq. (3) indicates that the complete mineralization of 1 mol of TCE would release 3 mol of

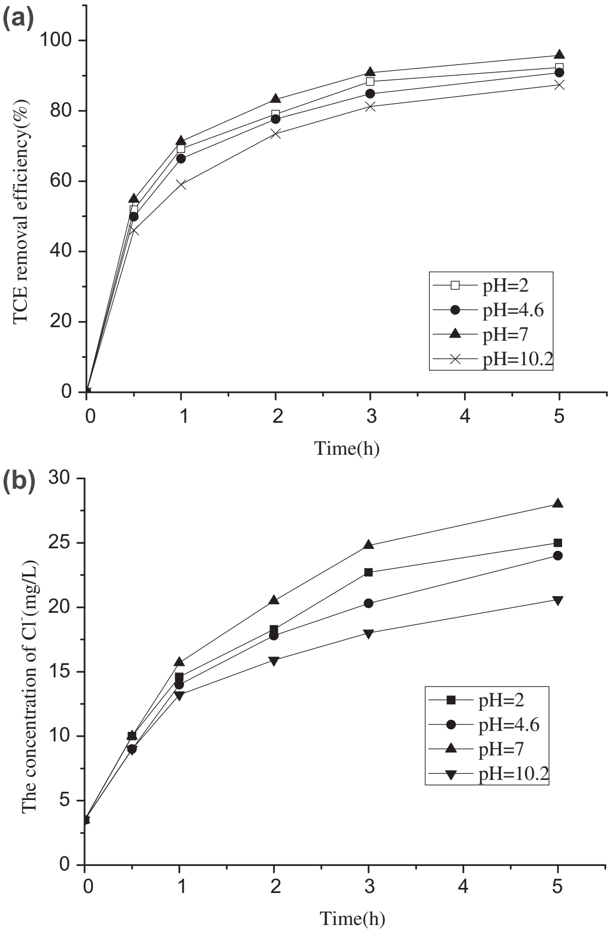

Fig. 2. (a) Effects of initial pH value on TCE oxidation; (b) Effects of initial pH value on concentration of Cl; experimental conditions: $[TCE]_0 \approx 45$ mg/L, $[Na_2S_2O_8]_0 =$ 6,000 mg/L, red mud concentration = 2 g/L, temperature = 30˚C, and reaction time = 5 h.

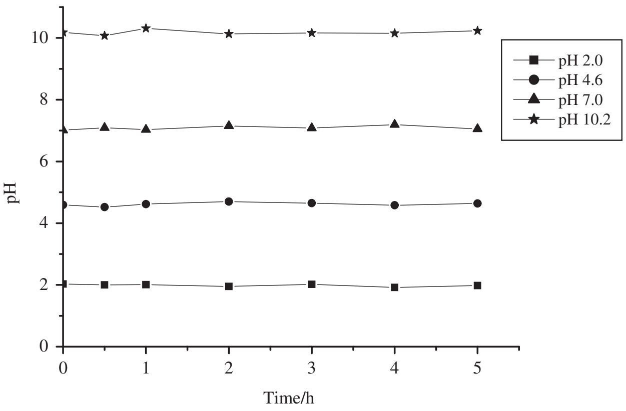

Fig. 3. Effects of reaction time on solution pH; experimental conditions: $[TCE]_0 \approx 45$ mg/L, $[Na_2S_2O_8]_0 = 6$ g/L, red mud concentration = 2 g/L, room temperature.

chloride ions. Fig. 2(b) shows the results of concentration of chloride ion. A maximum concentration of chloride ion was 28 mg/L at pH 7, while theoretical value of concentration of chloride ion was 35 mg/L. This indicates that TCE has not been completely destroyed. The rate of destroying TCE was 80%, while the TCE degradation rate was 95.8%. It is obvious that all initial TCE was not eventually transformed into the chloride form. It may produce some intermediates. The samples at the end of reaction were collected and analyzed by GC–MS. The results demonstrated that there are no obvious VOCs except for the residual target TCE contaminant. The possible reason is that the intermediates are not enough for the limit of detection of the GC–MS. The analysis of intermediates would be the major subject in the future, and the oxidation of any potential byproducts or degradation pathways of contaminant will be discussed.

3.3. Effects of temperature on TCE oxidation

Fig. 4 shows the results of the temperature on Fenton-like oxidation of TCE over a range of 15–45℃. In this experiment, a Water-bathing Constant Temperature Vibrator was used to control the temperature. In Fig. 4, the TCE removal efficiency was in the order of 45℃ (99.6%) > 30℃ (95.8%) > 15℃ (88.5%), while the first-order decay constants were 1.021, 0.519, and 0.361 h^{-1}, and half life constants were 0.679, 1.335 and, 1.920 h for the initial temperature of 45, 30, and 15℃, respectively, after 5 h of reaction (Table 2). Results also show that the temperature value is linear correlation with the k_{obs} of TCE in the tested temperature range, while the correlation coefficient, $R^2 = 0.993$, 0.993, 0.991 for the initial temperature of 15, 30, and 45℃, respectively (data not shown). Compared with the results obtained, the result also reveals that the TCE removal efficiency increased and the k_{obs} of TCE degradation increase with increased temperatures. Thus, higher temperature is an attractive method to activate persulfate to produce sulfate free radical $SO_4^{-}\cdot$, which is a powerful oxidant and can degrade the TCE effectively. The formation of $SO_4^{-}\cdot$ by the thermal decomposition (as known "thermal activation") of the persulfate anion in an aqueous phase is shown in Eq. (4):

$$S_2O_8^{2-} + \text{heat} \rightarrow 2SO_4^{-}\cdot \tag{4}$$

As we know, the reaction rate of $S_2O_8^{2-}$ with organic matter at ambient temperatures (e.g. 20℃) is very slow. Liang et al. [25] has demonstrated that the persulfate anion itself results in only a limited amount of TCE destruction at ambient temperatures. As can be seen in Fig. 4, the TCE removal efficiency was 88.5% at 15℃ after 5 h.

3.4. Effects of oxidants on TCE removal

Fig. 5 reveals the variations in TCE concentrations vs. time with the addition of two different oxidants (H_2O_2 and $Na_2S_2O_8$) and sulfuric acid under pH control. Results show that the TCE removal efficiency is in the order of H_2O_2/red mud (initial pH 2) (97%) > $Na_2S_2O_8$/red mud (initial pH 7) (92%) > $Na_2S_2O_8$/red mud (initial pH 2) (87%) > H_2O_2/red mud (initial pH

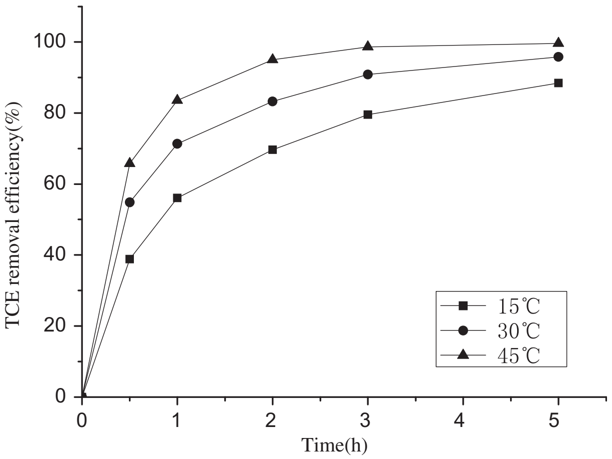

Fig. 4. Effects of temperature on TCE oxidation; experimental conditions: $[TCE]_0 \approx 45$ mg/L, $[Na_2S_2O_8]_0 = 6$ g/L, red mud concentration = 2 g/L, pH 7, reaction time = 5 h.

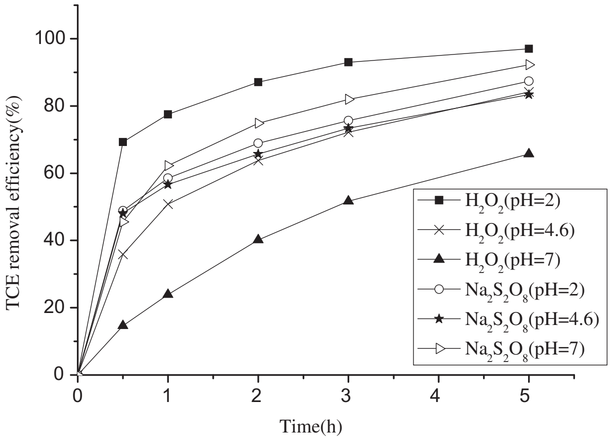

Fig. 5. Effects of oxidants on TCE removal; experimental conditions: $[TCE]_0 \approx 45$ mg/L, $[Na_2S_2O_8]_0 = 6$ g/L, $[H_2O_2] = 3$ g/L, red mud concentration = 2 g/L, room temperature, reaction time = 5 h.

Table 3
The level of factor

Level	Factor A ($Na_2S_2O_8$, g/L)	B (H_2O_2, g/L)	C (pH)
1	4	0.5	2
2	2	0.3	4.6
3	1	0.2	7
4	0.5	0.1	10.2

4.6) (84%) > $Na_2S_2O_8$/red mud (initial pH 4.6) (83%) > H_2O_2/red mud (initial pH 7) (65%) after 5 h reaction time.

As shown in Fig. 5, the results imply that TCE oxidation could be significantly enhanced under low pH conditions (pH < 4.6) in the H_2O_2/red mud reaction system. This indicates that if there was only H_2O_2 in Fenton-like system, pH control plays an important role in the enhancement of oxidation rates. Moreover, the oxidation rate can be significantly enhanced under acidic conditions. Thus, lowering system pH would result in a significant increase in TCE removal rates. But in Fenton-like system with $Na_2S_2O_8$, a maximum TCE degradation rate occurs at pH 7, while under low-pH conditions (pH < 4.6), TCE oxidation rate significantly enhances with the decrease in pH. Two different results were obtained about the effect of pH in the different reaction systems with different oxidants (Fenton-like system with $Na_2S_2O_8$ or H_2O_2).

However, the effect of oxidants on TCE removal cannot be clearly obtained. So an orthogonal experiment was designed as shown in Table 3. Tables 4 and 5 reveal the results of $L_{16}(4^3)$ orthogonal design, visual analysis displays that $R_A(6.365) > R_B(2.393) > R_C(1.787)$, so the TCE oxidation rate can be significantly affected by the concentration of $Na_2S_2O_8$. An optimal decision of TCE oxidation can be presented: the concentration of $Na_2S_2O_8$ and H_2O_2 is 0.5 and 0.1 g/L, respectively, and pH is 2. A variance analysis also demonstrates that the TCE oxidation rate is appreciably affected by the concentration of $Na_2S_2O_8$, which plays an important role in Fenton-like system containing $Na_2S_2O_8$, H_2O_2, and red mud.

Table 4 indicates that the system with $Na_2S_2O_8$ and H_2O_2 can reach the same TCE oxidation rate even at lower temperature either $Na_2S_2O_8$/red mud or H_2O_2/red mud reaction. Experimental investigation shows that $Na_2S_2O_8$ was relatively stable at low temperature (<20˚C). It usually requires higher activation energy to produce the sulfate free radical ($SO_4^{-}\cdot$) (e.g. thermal, photochemical, or metal ions) [16–20]. There would be thermal produced by hydrogen peroxide decomposed release hydroxyl radicals, which would be supplied for the activation of $Na_2S_2O_8$. This indicates that the oxidation power of two oxidants is stronger than

Table 4
Results of $L_{16}(4^3)$ orthogonal design

Sequence	A	B	C	D	E	TCE removal efficiency (%)
1	1	1	1	1	1	88.25
2	1	2	2	2	2	89.18
3	1	3	3	3	3	88.65
4	1	4	4	4	4	88.25
5	2	1	2	3	4	89.32
6	2	2	1	4	3	90.70
7	2	3	4	1	2	90.64
8	2	4	3	2	1	92.50
9	3	1	3	4	2	87.87
10	3	2	4	3	1	90.04
11	3	3	1	2	4	94.51
12	3	4	2	1	3	94.53
13	4	1	4	2	3	96.34
14	4	2	3	1	4	93.35
15	4	3	2	4	1	94.03
16	4	4	1	3	2	95.06
*K*1	88.580	90.442	92.38	91.692	91.202	
*K*2	90.787	90.813	91.760	93.130	90.935	
*K*3	91.375	91.958	90.593	91.013	92.555	
*K*4	94.945	92.835	91.315	90.213	91.355	
R	6.365	2.393	1.787	2.917	1.620	

Table 5
Variance analysis of $L_{16}(4^3)$ orthogonal design

Factor	DEVSQ	Degree of freedom	Value of F	$F_{0.05(f1.f2)}$	Significance	Conclusion
A	83.827	3	6.837	4.760	*	Appreciable impact
B	14.328	3	1.169	4.760		
C	6.797	3	0.554	4.760		
Error	24.52	6				

Note: *Significant at 0.05 level.

$Na_2S_2O_8$. Thus, Fenton-like reaction is more appropriate for the remediation of TCE-contaminated water from the remedial efficiency and effectiveness point of view.

4. Conclusions

The factors on the degradation rate of TCE in the Fenton-like system were investigated. The results illuminated that the use of chemical activation of persulfate by red mud is a potential approach for TCE removal. Higher temperature is an attractive method to activate persulfate to produce sulfate free radical $SO_4^{-\cdot}$, which is a powerful oxidant for the degradation of TCE effectively; however, increasing temperature is not a preferred projects because of higher costs. Herein, a new method is presented, that is to introduce $Na_2S_2O_8$ and H_2O_2 as oxidant for Fenton-like oxidation TCE. The study indicated Fenton-like system with red mud, H_2O_2, and $Na_2S_2O_8$ could improve the degradation rate of TCE effectively. Additionally, there's almost no risk of heavy metals leaching from red mud due to its low level. Thus, this method provides a treatment not only to harness the pollution of TCE, but also to reduce the contamination of the red mud in environment.

Acknowledgments

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