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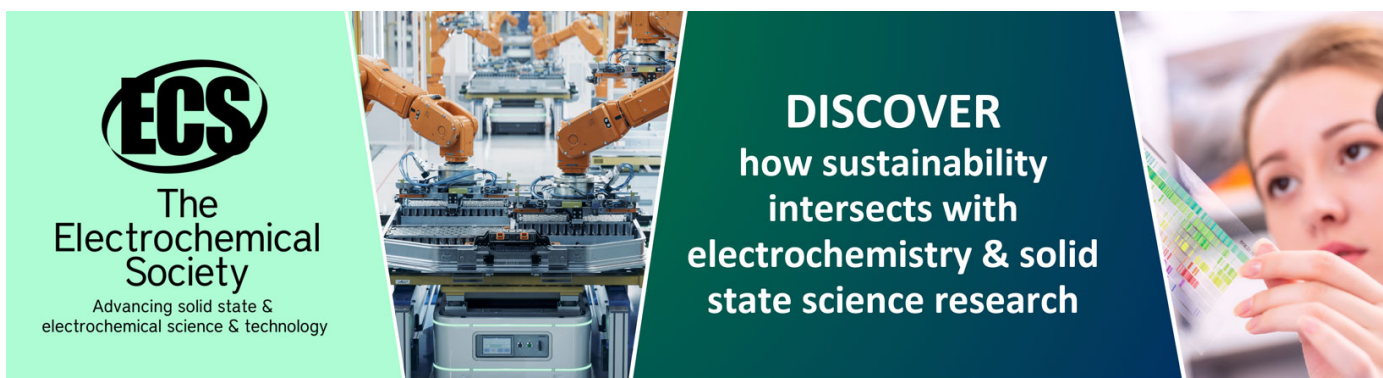
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## Study of Ferrate(VI) oxidation for COD removal from wastewater

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**Abstract.** Produced water (PW) is the abundant by-product of oil and gas industries. It contains several organic pollutants and needs proper treatment before its discharge. This study investigated the effectiveness of Ferrate (VI) ( $\text{Fe}^{6+}$ ) oxidation for remediation of the organic compounds produced water. A series of batch experiments were performed by ferrate oxidation method. A glass beaker of 1000 ml as reactor covered with aluminum foil was used to protect from sunlight. Produced water sample of 300 ml and a pre-decided amount of  $\text{Fe}^{6+}$  was added to initiate the oxidation process. All experiments were performed at constant magnetic stirrer speed of 200 rpm at room temperature. The  $\text{Fe}^{6+}$  dosage of 1-25 mg/l, pH 1-7, and contact time 5-90 minutes were used to determine the effectiveness of  $\text{Fe}^{6+}$  for organic compounds degradation. The COD removal was increased with the increase in  $\text{Fe}^{6+}$  dosage and contact time. The maximum COD removal was achieved with  $\text{Fe}^{6+}$  dosage up to 15 mg/l; further any increase in  $\text{Fe}^{6+}$  dosage decreased the COD removal. The same trend was observed for pH, COD removal was increased until pH 5 beyond that COD removal was decreased. Maximum 55% of COD removal was attained under optimum conditions such as pH,  $\text{Fe}^{6+}$  dosage, and contact time were 5, 15mg/l and 50mins respectively. The results indicate that Ferrate (VI) oxidation is a promising method for the degradation of organic compounds in produced water.

**Keywords:** Ferrate (VI), COD removal, Produced water, Oxidation process

### 1. Introduction

In the past few years, developing disturbance about water quality management has been thoroughly studied. The volume of fresh water is reduced, and its quality has suffered a lot of problems due to the developing of micro-pollutants in wastewater [1]. Therefore, to avoid severe consequences of carcinogenic compounds and infectious agents involved in wastewater, it is a vital need for the prolongation and proper management of water resources[2, 3].

Persistent organic pollutants (POPs) are continuous and very harmful organic compounds that are irrupting into our environment by either naturally or phylogenetic sources. Foregoing wildland fire and volcanic eruption. Nevertheless, but the huge fraction is developed by the end, specifically by automobile exhausts, petrochemical processing, tobacco smoke and by partial combustion of fossil fuels [4, 5]. Even at very low concentration of these compounds can cause a very drastic effect on the ecological system. Some of them show carcinogenic, mutagenic and tumorigenic effect along with endocrine disruption [6]. Furthermore, a class of polycyclic aromatic hydrocarbons (PAHs) with three or more rings have adverse effects on our metabolic systems due to their carcinogenic and mutagenic effects [7].



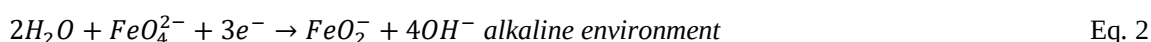
Like many other production activities, oil and gas exploration also has been responsible for producing a huge amount of liquid waste which referred as Produced water (PW). Produced water is the water that is trapped beneath the earth surface and brought up during the extraction of oil and gas. PW contains many toxic organic compounds, inorganic and dissolved hydrocarbons such as monocyclic and polycyclic aromatic hydrocarbon, endocrine disrupting compounds and high molecular weight alkyl phenols [2, 8]. Nowadays, to meet the WHO (world health organization) regulations, it is necessary to treat the PW very efficiently and remove toxic organic compounds through advanced options before disposal of PW into nearby water bodies.

Several physical, chemical and biological methods can be practiced for the remediation or transformation of various potential pollutants in the wastewater. The physical process that typically involves membrane filtration, volatilization, and adsorption techniques to reduce the suspended solids and visible impurities in the wastewater, but they aren't enough capable of to degrade contaminants in wastewater [9]. Conventional phase separation methods are unable to remove dissolved solid compounds in wastewater [10]. As a result, several biological methods and chemical oxidation have been employed for the treatment of produced water (PW). Undoubtedly, the biological treatment method one of the most cost-effective technique. Nevertheless, biological methods show limited removal of aromatic hydrocarbon from PW because of high chemical toxicity and fused benzene rings [11]. At last, organic matters are quite resistant to biological oxidation [12] and chemical oxidation treatment. Several studies confirmed that advanced oxidation processes (AOPs) are alternative techniques for the remediation of micro-pollutant and can be used for the treatment of PW. The hydroxyl radicals are generated in AOPs which degrade the organic pollutants [2]. Among the AOPs, the Fe(VI) one of the most suitable methods to treat PW due to environmentally friendly, cost-effective, high performance and technological simplicity [13, 14]. It may act as multipurpose chemicals like oxidation, flocculation/coagulation, and disinfection of water [15].

### 1.1. Ferrate chemistry

Iron ores exist in  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  states but when the strong oxidizing environment is provided it transform into higher oxidation state such as  $\text{Fe}^{6+}$ . Fe (VI) is a strong inorganic oxidant; it has a redox potential of 2.2V and 0.72 V in acidic and basic environment respectively. Fe (VI) has the ability to oxidize over a wide pH range however; it more active in acidic condition and decomposes faster [16]. Mechanism of Fe(VI) decomposition in acidic, basic and neutral conditions are shown in Equations 1-3 [13].

When wastewater is treated using Fe (VI), it oxidizes the organic compounds present in it and then reduces into Fe (III) ions which cause physical removal of an organic compound by precipitating in the form of ferric oxide or hydroxide [17]. pH of the reaction affects organic removal in two ways. Firstly, as Fe (VI) decomposes faster under acidic conditions than under alkaline conditions. Secondly, if the compound has more affinity for the solid phase in an acidic environment then it can aid the increase in physical removal in acidic conditions. There is also a chance of second precipitation with iron oxides depending upon the pH being adjusted to 7 after oxidation, this mechanism depends upon the differences in ion solubility among reaction and neutral pH. Such as, humic substances have greater tendency for solid phase and hence less soluble in acidic conditions [18, 19], therefore, such substances will produce more precipitates at low pH.



acid, neutral and alkaline environment

In other words, Fe(VI) is suitable for the treatment of wastewater because it can degrade the organic and inorganic pollutants and may be able to remove non-degradable impurities. Moreover, the Eq. 1 shows Fe(VI) generate  $\text{Fe}^{3+}$  which is a best coagulant and flocculant and later may be removed non-degradable pollutants by coagulation and flocculation.

The main aim of the present study is to focus on the feasibility of COD removal from PW using Fe(VI) at room temperature. The influence of three factors (i.e. Fe(VI) dosage, pH, and contact time) on COD removal will be determined.

## 2. Methods/Materials

### 2.1. PW sampling and reagents

The PW sample was collected in 30L plastic bottles from a oil and gas extraction company working in south east asia region and it was kept in cold storage before being used for experimental work, characteristic of PW are listed in Table 1. APHA standard method was followed for the collection and storage of PW. NaOH (30% w/v) and H<sub>2</sub>SO<sub>4</sub> (95-98%), were bought from R&M chemicals. Potassium ferrate (VI) in granular form was purchased from NANO IRON (Czech Republic).

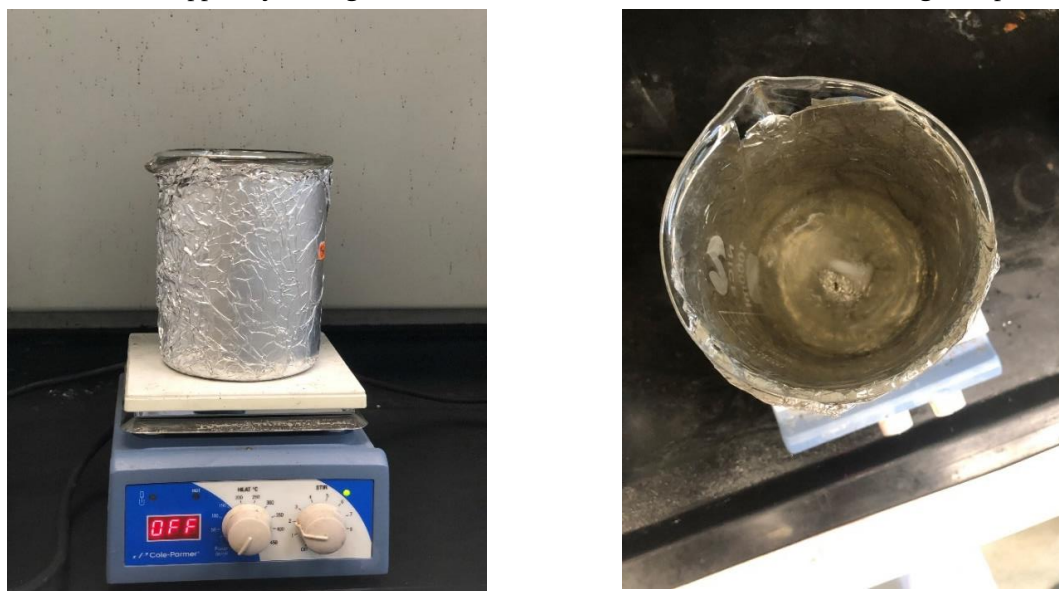
**Table 1.** Characteristics of produced water

| Parameters  | TOC   | COD  | pH   |
|-------------|-------|------|------|
| Unit(mg/l)* | 759.5 | 2213 | 8.03 |

\*All other values except pH are in mg/L

### 2.2. Ferrate oxidation Experiments

Batch experiments were performed in an acidic environment and at room temperature to understand the influence of different operational factors on COD removal. 1L glass beaker was used as a reactor for experiments. The aluminium sheet was utilized to cover the outside of the glass beaker to protect it from sunlight. The magnetic stirrer was used for homogeneous mixing in the reactor. For each experiment, 300 ml of PW was stirred at constant speed (200 rpm) and temperature (see Figure 1). The acidic environment was provided to aqueous solution by adjusting pH (using H<sub>2</sub>SO<sub>4</sub>). To start the oxidation, process a calculated amount of Fe(VI) was added into reactor. After the calculated time (5-120 minutes) the reaction was stopped by adding the desired volume of 1M NaOH solution to change the pH of the



**Figure 1.** Experimental Setup for Ferrate Oxidation

aqueous solution up to 11. The aqueous solution was filtered using Whatman filter paper (Size 45 mm Ø). At last, the sample of treated PW was taken from the glass reactor to analyze COD.

### 2.3. Analytical analysis

High rang COD vials and HACH DR 2800 spectrophotometer was used to determine the concentration of COD in raw and treated PW samples. All required solutions were prepared using distilled water. For pH measurement, Hach pH meter was used. Total organic carbon (TOC) was measured by TOC analyzer (TOC-VCSH-TOC analyzer) and CCAL 20A standard operating procedure was used. All the experimental runs were performed in triplicate to achieve the accuracy of COD. For COD removal percentage, Eq. 4 was used [20].

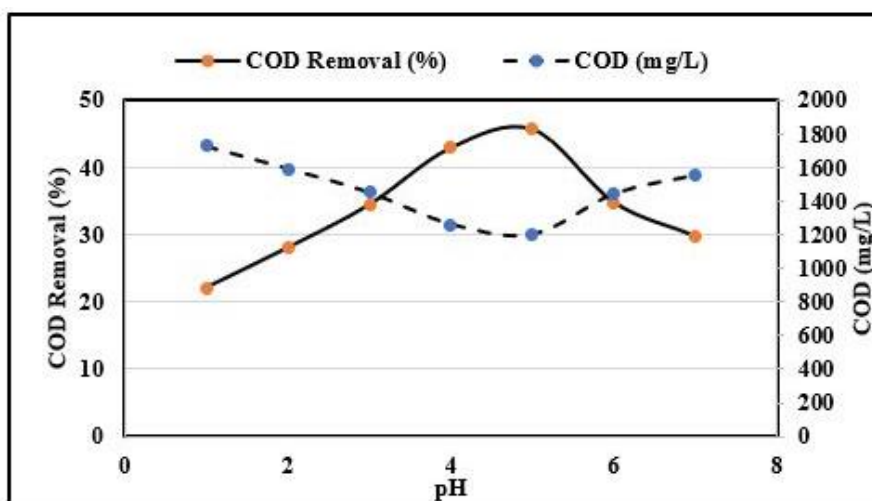
$$\text{COD removal (\%)} = \left( \frac{C_o - C}{C_o} \right) \times 100 \quad \text{Eq. 4}$$

$C_o$  = COD before treatment and  $C$  = COD after treatment

## 3. Result and Discussion

### 3.1. pH effect on COD removal

The reaction of Fe(VI) is highly dependent on the pH of the aqueous solution. Fe(VI) is very reactive in an acidic environment and it can change oxidation state from +6 to +3. Ferrate can oxidize organic pollutants very quickly in an acidic environment [21]. Therefore, for the optimum pH value for maximum COD removal efficiency, various pH values from 1-7 were performed. The dosage of Fe(VI) and contact time during this process kept the same for each experimental run at 10 mg/l and 60 minutes, respectively.

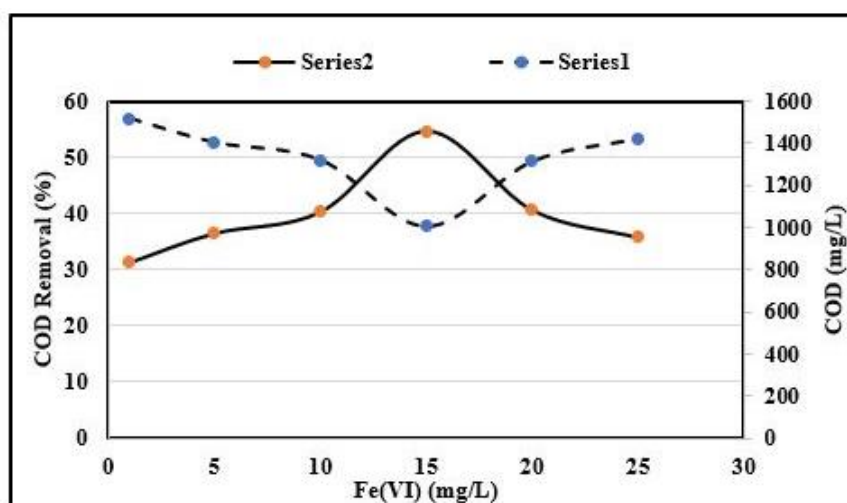


**Figure 2.** COD removal efficiency at different pH

The maximum COD removal 45.7% was obtained at pH 5 and beyond that pH the COD removal was decreased gradually (see Fig. 2). This result correlated with the results presented by Batarseh et al. [22] who increased pH from 3 to 5 and obtained maximum removal at 5 pH. For the basic environment, the Fe(VI) generate  $\text{Fe(OH)}_4^-$  and  $\text{Fe(OH)}_3$  species instead of  $\text{Fe(OH)}_3$  which cause to decrease the coagulation process [23].

### 3.2. Ferrate (VI) dosage effect on COD removal

In Ferrate oxidation process, the determination of the optimum value of Fe(VI) is an important step due to its direct impact on the removal efficiency and operational cost. Higher dosage of Ferrate (VI) is required for COD concentration. Higher dosage of Fe(VI) leads to higher COD removal efficiency but at the same time, excess dosage causes high slug generation and scavenging effects [24]. Therefore, it is mandatory to determine the optimum dosage of Fe(VI) for higher removal efficiency with lower operational cost.



**Figure 3.** COD removal efficiency at different Fe (VI) dosages

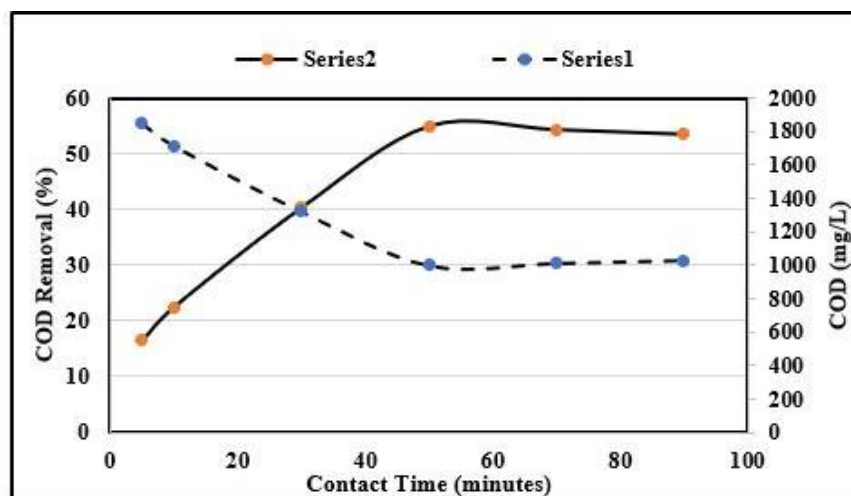
For the optimum value of Fe(VI), a series of experiments were performed keeping the contact time (60 minutes) and pH (5) constant and changing the Fe(VI) dosage from 1 to 25. COD removal efficiency using the different dosage of Fe(VI) is shown in Fig. 3.

The trend can be observed in Figure 3, the COD removal was increased by increasing the dosage of Fe(VI) up to a certain level, beyond that value the COD removal efficiency decreased due to the excess flocculation.  $\text{Fe}^{3+}$  was generated after the decomposition of Fe(VI) which had a mechanism of flocculation. By increasing the dosage of Fe(VI) the flocculation increased and may slow down the reaction between organic pollutants and Fe (VI) [21], which in result may decrease the removal of COD beyond the 15 mg/l dosage of Fe (VI). Maximum COD removal efficiency attained was 54.5 % with a dosage of 15 mg/l.

### 3.3. Contact time effect on COD removal

The contact time is a significant perimeter to obtain a higher removal efficiency therefore to obtain optimum contact time, the experiments were performed at various contacts times i.e., 5, 10, 30, 50, 70 and 90 minutes. The dosage of Fe(VI) and pH during this process kept the same for each experimental run at 15 mg/l and 5, respectively. The maximum COD removal 55 % was obtained at 50 minutes (see Figure 4). It can be observed that an increase in the contact time beyond 50 minutes had no significant effect on the COD removal efficiency. Talaiekhosani et al. [25] reported that Fe(VI) degrades over time, after larger contact time very less amount of Fe(VI) may be available to degrade further organic pollutants. In acidic condition Fe(VI) degrades very fast more than 60-70 % of ferrate degrade in first 30 minutes and remove the maximum portion of organic pollutants [26]. In Figure 4 Fe(VI) was completely degraded after 50 minutes and therefore it was considered optimum





**Figure 4.** COD removal efficiency at different contact time

#### 4. Conclusions

The current study carried out at room temperature for the removal of COD from PW by Fe(VI) in PW. The maximum COD removal 55% was achieved under optimum experimental conditions. The optimum values of ferrate dosage, pH, and contact time were 15 mg/l, 5 and 50 minutes respectively. The COD removal was highly dependent on pH, contact time as well as the Fe (VI) dosage. During the oxidation process, pH played a promising role as increasing the pH the degradation of organic pollutants increased, at high pH the degradation was reduced. With pH 5 up to 54% COD removal was attained while with pH 7 just 30% removal was obtained. For the dosage of Ferrate (IV) the same behaviour was observed. Hence, this is concluded that Fe(VI) oxidation is effective method for the removal of COD from PW.

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