Inactivation of Bacteria in Oil Field Injected Water by a Pulsed Plasma Discharge Process*

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Abstract  Pulsed plasma discharge was employed to inactivate bacteria in the injection water for an oil field. The effects of water conductivity and initial concentration of bacteria on elimination efficiency were investigated in the batch and continuous flow modes. It was demonstrated that Fe2+ contained in injection water could enhance the elimination efficiency greatly. The addition of reducing agent glutathione (GSH) indicated that active radicals generated by pulsed plasma discharges played an important role in the inactivation of bacteria. Moreover, it was found that the microbial inactivation process for both batch and continuous flow mode well fitted the model based on the Weibull’s survival function.

Keywords: high-voltage pulsed discharge, water injection, bacteria inactivation, oil industry

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(Some figures may appear in colour only in the online journal)

1 Introduction

The injected water for maintaining the strata pressure in the oil industry usually contains algae and micro-organisms. There are two ways that have consequence on equipment corrosion [1,2]. On one hand, some primary substances including H2S are produced. On the other hand, secondary conditions in favor of electrochemical corrosion are created. It is reported that up to 80% of all corrosion damages in some oil field systems are attributed to the bio-corrosion [3]. Biocides are usually used to control the microorganism pollution, including bacteria, algae and fungi in injected water [3,4]. However, the common biocides are often persistent in the environment and the inhibition of bacteria biocide has been reported widely [5,6]. The high toxicity would cause long-term damage to human and aquatic life. Therefore, it is of significance to develop novel technologies for the inactivation of microorganisms in the injected water.

Recently, the pulsed plasma discharge (PPD) process has been attracted great attention for the development of degradation of toxic organic substance [7–10] as well as micro-organisms [11]. When high voltage pulsed discharges occur, a non-thermal plasma channel is formed and various active chemical radicals are produced along with the formation of pulsed electric field, ultraviolet radiation, and shock waves [12–14]. The PPD method for the inactivation of bacteria in solution is short in the treatment time, minimal in the sample damage, and uses less chemicals. The PPD method was first developed by Mizuno et al [15]. However, little research progress has been obtained [16,17], especially for the inactivation of bacteria in the oil industry.

Conductivity is an important parameter that affects the inactivation efficiency of the discharge process [18]. The injected water is characterized as high content of inorganic salts, including Fe2+. It is well known that the critical reaction in Fenton’s chemistry is the catalysis on the basis of the generation of hydroxyl radicals from reaction of H2O2 and Fe2+. Herein, Grymonpre et al. adopted Fe2+ into plasma discharge to enhance phenol degradation via the Fenton’s reactions [19]. In the present study, PPD process was applied to eliminate the representative bacteria in the injected water from oil field, and the role of ferrous ions as well as inactivation mechanism was also examined.

The solution conductivity and the initial concentration of bacteria were studied. The Weibull function was occupied to fit the inactivation process for both batch and continuous flow mode.

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2 Materials and methods

2.1 Materials

The simulated bacteria solution was used in the study. Micro-organisms were isolated from sludge in Hangzhou municipal sewerage treatment plant. Conductivity was adjusted by KCl to 0.03 mS/cm, 0.2 mS/cm, 0.5 mS/cm, 2 mS/cm, and 5 mS/cm. The initial concentrations were set at $1.0 \times 10^3$, $1.0 \times 10^4$, $1.0 \times 10^5$, $1.8 \times 10^6$ and $2.7 \times 10^7$ colony forming unit/mL (CFU/mL). FeSO$_4$·7H$_2$O (analytical grade) was used for the preparation of 0.1 mM Fe$^{2+}$, which is similar to actual oil injection water. The pH of the prepared solution was 6.5 ± 0.4. A conductivity meter (DDS-11A, INESA, China) and a pH meter (pHS-25, INESA, China) were used to measure the conductivity and pH of the solution, respectively. Before treatment, the discharge reactor was sterilized with 75% alcohol, and then rinsed by sterile deionized water for three times.

2.2 Experimental setup

![Fig.1 Schematic diagram of experimental apparatus in batch (a) and continuous flow (b) modes](image)

1 Pulsed power supply, 2 Ground electrode, 3 High voltage electrode, 4 Gas flowmeter, 5 Air pump

Fig.1 Schematic diagram of experimental apparatus in batch (a) and continuous flow (b) modes

The setup consisted of pulsed high-voltage power (ETL Company, ZH-2006, China) and treatment chamber, as shown in Fig. 1. The two components were connected with a high voltage co-axial cable. The peak input voltage and frequency were set at 3 kV and 5 Hz, respectively. A needle-cylinder electrode was adopted. The high voltage electrical wire was used as the needle electrode, and the length of discharge tip was about 2 mm. The cylinder electrode was made of titanium, and the inner diameter and length were 40 mm and 120 mm, respectively. 150 mL injected water was treated in batch mode. An air pump was used to aeration. A typical waveform was detected by an oscillograph (Rigol, DS1022C, China), as seen in Fig. 2.

![Fig.2 The typical waveform in the discharge](image)

2.3 Analytical methods

The same enumeration of saprophytic bacteria, iron bacteria and sulfate reducing bacteria was used in our previous work [20]. Every treatment was repeated for three times and the average was reported. The relative standard deviations of the data were less than 10%. The concentration of dissolved O$_3$ in solution was followed by the indigo method [21]. The concentration of H$_2$O$_2$ was measured by colorimetry on the basis of analysis of the maximum absorbance of the yellow peroxotitanium (IV) complex at wavelength $\lambda$=410 nm [22]. The concentration of nitrates was measured by ion chromatograph (IC-1000, Techcomp, China).

3 Results and discussion

3.1 Effect of conductivity on inactivation

The initial concentration of saprophytic bacteria is set at $4 \times 10^4$ CFU/mL. The variations of inactivation efficiency versus the treatment time for different conductivities are shown in Fig. 3. It is observed that high final inactivation efficiencies were achieved in several hundred seconds’ treatment, and the inactivation efficiency increased with the increasing of conductivity. However, it did not further increase when the conductivity increased to 5 mS/cm. A discharge is hard to form in distilled water due to its low conductivity of 0.03 mS/cm, and the added mineral salts can promote the formation of discharge. High conductivity can obtain the high power density in the channel which led to increase of plasma density
and temperature. The generated ultraviolet (UV) radiation and acoustic waves would be high. A turbulent flow with high pressure around the needle electrode was observed in the discharge process with high conductivity, which could enhance the mass transfer on the electrode surface area. Therefore, high inactivation efficiencies are obtained. However, the increased conductivity means that there are more ions in the solution. Zhang et al. addressed that the charged ions finally cause the hard establishment of strong electric field of the plasma channel. Moreover, the solution conductivity is related to the radical emission intensity and discharge characteristics. Sun et al. have reported that the emission intensity became weak when the conductivity continuously increased. Therefore, this reveals that the initial conductivity is critical to the bacteria inactivation.

![Figure 3](image)

**Fig.3** The effect of conductivity on inactivation of saprophytic bacteria (a) and the inactivation efficiency at varied conductivity after 150 s discharge

### 3.2 The effect of initial bacteria concentration on inactivation

Fig. 4 shows effects of the initial concentration on the sterilization of saprophytic bacteria. It is observed that higher efficiency was obtained for lower initial concentration. In particular, the efficiency is not significantly affected by the initial concentration of bacteria in the range from $10^4$ CFU/mL to $10^6$ CFU/mL. Saprophytic bacteria concentration in actual injection water is about $10^5$–$10^6$ CFU/mL, which indicates that plasma discharge treatment could be applied to inactivate bacteria in oil field injected water.

![Figure 4](image)

**Fig.4** The effect of initial concentration of bacteria on saprophytic bacteria inactivation

### 3.3 The role of ferrous ions on the inactivation process

Fig. 5 shows the effect of ferrous ions on inactivation of different bacteria using pulse discharge plasma with or without air bubbling. This indicates that the addition of ferrous ions could improve the efficiency of plasma discharge under both conditions with or without air bubbling. For sulfate reducing bacteria, as shown in Fig. 5(a), the inactivation efficiency increases to 2.26 log reduction after 90 s discharge combined with the assistance of air bubbling and the addition of Fe$^{2+}$. The inactivation efficiency of iron bacteria is also improved for the sulfate reducing bacteria. Wang et al. have reported that the addition of ferrous sulfate enhanced the inactivation efficiency of E. coli in a three-phase discharge plasma reactor. However, the enhancement is not significant due to the low production of H$_2$O$_2$ by underwater discharge.

As described in the following reactions, the ferrous ions can react with hydrogen peroxide, producing a larger amount of OH radicals, which are reactive, non-selective, and responsible for bacteria inactivation:

\[
\text{H}_2\text{O} \rightarrow \cdot\text{OH} + \cdot\text{H} \tag{1}
\]

(highly energized electron’s action)

\[
\cdot\text{OH} + \cdot\text{OH} \rightarrow \text{H}_2\text{O}_2 \tag{2}
\]

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \cdot\text{OH} \tag{3}
\]
more efficient direct production of active chemical species would be produced by the J/pulse discharge [19]. The role of reactive chemical species generated by electrolydraulic discharge may be significant since the power supply used in this work is relatively low.

Reduced glutathione (GSH) was used for the protection of cells from alkylating agents, free radicals and oxidative stress, where the thiol group in GSH can scavenge chemical oxidants. However, bacteria cells would still be directly damaged due to the high applied electric current, or membrane permeabilization [29]. Herein, GSH was added to examine the effect of active chemical species. The variations of inactivation efficiency in saprophytic bacteria with the addition of GSH are shown in Fig. 6. Fig. 7 shows the inactivation of iron bacteria and sulfate reducing bacteria. This indicates that sterilization efficiency by pulsed plasma discharge dramatically decreases owing to the addition of GSH. Hence, it was demonstrated that active chemical oxidation was the major contribution to the inactivation of micro-organisms during the discharge. The inactivation mechanisms of bacteria cells may proceed through the damage to DNA, protein and membrane [30].

Fig.5 Inactivation of saprophytic bacteria (a), iron bacteria (b) and sulfate reducing bacteria (c) with the addition of Fe^{2+}, the centration of Fe^{2+} is 0.1 mM

3.4 The role of active chemical species on inactivation process

During the electrolydraulic discharge process, pores on the bacteria membrane can be formed if the voltage across membrane is allowed to build. Therefore, free radicals generated by discharge would penetrate the cell through these pores and inactivate the bacteria. Grymonpré et al. demonstrated that capacitor discharge in the kJ/pulse range would lead to the intense shock waves and strong UV light, whereas

Fig.6 Inactivation of saprophytic bacteria with the addition of GSH

Fig.7 Inactivation of iron bacteria (IB) and sulfate reducing bacteria (SRB) with the addition of GSH
The main active chemical species generated by electrohydraulic discharge are H$_2$O$_2$, O$_3$ and radicals etc. [31]. The concentrations of H$_2$O$_2$ and O$_3$ were detected in both bacteria suspensions and sterilized water with or without gas bubbling. The highest concentration of H$_2$O$_2$ is 7.4 mg/L, while the concentrations of O$_3$ are less than 1.5 mg/L [20].

The inactivation efficiencies of saprophytic bacteria for treatment by 7.4 mg/L H$_2$O$_2$ and 1.5 mg/L O$_3$ were investigated, respectively. This shows that no inactivation was found by H$_2$O$_2$ and about 0.42 log reduction achieved by O$_3$ after 150 s treatment. Similar results were also obtained by another researcher [32]. This happens because a much longer lethal time is needed for H$_2$O$_2$ treatment, and the contribution of H$_2$O$_2$ itself by plasma discharge treatment can be ignored. Although O$_3$ is an effective disinfectant, the relatively short reaction time (150 s), which was used in this study, would limit its performance. Hence, it concludes that OH radicals are the major contribution to the inactivation of microorganisms during the discharge. Additionally, apart from the active chemical oxidation, the effects on the electric field, electric current, shock wave etc. are also contributed to bacteria inactivation.

### 3.5 The inactivation performance in the continuous flow reactor

Inactivation in the continuous flow mode was further investigated since it was significant for large-scale application. Fig. 8(a)–(c) show the inactivation efficiency of bacteria by electrohydraulic discharge with or without air bubbling. It is observed that the inactivation efficiency increased with the increase of hydraulic retention time (HRT). The microorganisms cells are readily recovered from the stress in short treatment time, thus the efficiency would be low. Moreover, inactivation efficiencies of all bacteria were enhanced greatly by air bubbling. A possible reason for this is that high energy electrons could react with oxygen, producing active chemical species including OH radicals, O radicals, H$_2$O$_2$, and O$_3$ etc. effectively [33,34]. The following reactions would occur [35–37]:

$$\begin{align*}
H_2O & \rightarrow OH + H \\
O_2 & \rightarrow O + O(1D) \\
O(1D) + H_2O & \rightarrow OH + OH \\
OH + OH & \rightarrow H_2O_2 \\
O + O_2(gas) & \rightarrow O_3(gas) \\
O_3(gas) & \rightarrow O_3(aq) \\
N_2 & \rightarrow N + N \\
N + OH & \rightarrow NO + H \\
NO + OH & \rightarrow HNO_2
\end{align*}$$

$$\begin{align*}
HNO_2 + OH & \rightarrow NO_2 + H_2O \\
NO_2 + OH & \rightarrow HNO_3
\end{align*}$$

### 3.6 Weibull model fitting

The Weibull distribution function has been widely applied to describe bacteria inactivation using the pulsed voltage discharge process [38,39]. The model equation is as follows:

$$\log_{10} \frac{N(t)}{N_0} = -(t/\delta)^p,$$

where the parameter $p$ is the shape parameter, $\delta$ is a time parameter. The shape parameter $p = 1$...
represents a linear survival curve, \( p < 1 \) represents upward concavity, and \( p > 1 \) represents downward concavity \([40]\). Parameter \( \delta \) and \( p \) can be used to calculate \( t_c \) seen in the following equation:

\[
t_c = \delta \Gamma(1 + 1/p).
\]

Where \( t_c \) represents the mean of the distribution and \( \Gamma \) is gamma function. \( t_c \) is a measure for the resistance of microbial to plasma discharge. The higher value of \( t_c \) means that bacteria are more resistant to plasma discharge treatment \([41]\).

The parameters and correlation coefficients for Weibull model are listed in Table 1. It is observed that the Weibull model well fitted experimental data with high value of \( R^2 \). On the basis of analysis of \( t_c \) values, it is found that air bubbling was essential to the bacteria inactivation by plasma discharge and saprophytic bacteria are relatively resistant in comparison with other bacteria.

<table>
<thead>
<tr>
<th>No.</th>
<th>Experimental conditions</th>
<th>( \delta )</th>
<th>( p )</th>
<th>( R^2 )</th>
<th>( t_c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>saprophytic bacteria: batch mode without air bubbling</td>
<td>135.21</td>
<td>1.84</td>
<td>0.97</td>
<td>78.0</td>
</tr>
<tr>
<td>2</td>
<td>saprophytic bacteria: batch mode with air bubbling</td>
<td>75.35</td>
<td>0.84</td>
<td>0.99</td>
<td>37.7</td>
</tr>
<tr>
<td>3</td>
<td>IB: batch mode without air bubbling</td>
<td>63.83</td>
<td>1.15</td>
<td>0.94</td>
<td>32.5</td>
</tr>
<tr>
<td>4</td>
<td>SRB: batch mode without air bubbling</td>
<td>63.05</td>
<td>1.48</td>
<td>0.98</td>
<td>33.9</td>
</tr>
<tr>
<td>5</td>
<td>saprophytic bacteria: continuous flow mode without air bubbling</td>
<td>119.71</td>
<td>0.59</td>
<td>0.97</td>
<td>68.2</td>
</tr>
<tr>
<td>6</td>
<td>saprophytic bacteria: continuous flow mode with air bubbling</td>
<td>83.12</td>
<td>0.77</td>
<td>0.99</td>
<td>42.2</td>
</tr>
<tr>
<td>7</td>
<td>IB: continuous flow mode without air bubbling</td>
<td>43.16</td>
<td>0.69</td>
<td>0.92</td>
<td>22.6</td>
</tr>
<tr>
<td>8</td>
<td>IB: continuous flow mode with air bubbling</td>
<td>18.06</td>
<td>0.68</td>
<td>0.84</td>
<td>9.5</td>
</tr>
<tr>
<td>9</td>
<td>SRB: continuous flow mode without air bubbling</td>
<td>46.70</td>
<td>0.78</td>
<td>0.99</td>
<td>23.6</td>
</tr>
<tr>
<td>10</td>
<td>SRB: continuous flow mode with air bubbling</td>
<td>17.2</td>
<td>0.66</td>
<td>0.92</td>
<td>9.2</td>
</tr>
</tbody>
</table>

4 Conclusion

The pulsed plasma discharge is indicated to be a promising technology for the inactivation of bacteria in oil field injection water. High final inactivation efficiencies were achieved in several hundred seconds’ treatment. The increasing solution conductivity can promote the inactivation. The ferrous ions contained in oil field injection water promote the inactivation process via the Fenton’s reactions. It was demonstrated that OH radicals were the major contribution to the inactivation of micro-organisms during the discharge. Furthermore, The Weibull distribution function can well describe the microbial inactivation process. On the basis of our analysis of the obtained parameters, it is found that air bubbling is essential to the bacteria inactivation by plasma discharge and saprophytic bacteria are relatively resistant in comparison with other bacteria.

References

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