

Electrochemical pilot-scale plant for oil field produced wastewater by M/C/Fe electrodes for injection

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Abstract

Oil field produced water by separated with crude oil were treated by an electrochemical process in laboratory pilot-scale plant, using double anodes with active metal (M) and graphite (C) and iron as cathode and a noble metal content catalyst with big surface. Due to the strong oxidizing potential of the chemicals produced (Cl_2 , O_2 , OCl^- , HO^\bullet and so on), when the wastewater pass through the laboratory pilot-scale plant the organic pollutants including bacteria were oxidized and coagulated by produced M^{n+} ion. It can be concluded that the catalytic electrochemical treatment of oil field produced wastewater is effective. Both chemical oxygen demand (COD) and biochemical oxygen demand (BOD) were reduced by over 90% in 6 min, suspense solids (SS) by 99%, Ca^{2+} content by 22%, corrosion rate by 98% and bacteria (sulphate reducing bacteria (SRB), saprophytic bacteria (TGB) and iron bacteria) by 99% in 3 min under 15 V/120 A. These results indicate that this catalytic electrochemical method could be used for effective oil field wastewater treatment for injection purpose.

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1. Introduction

Produced water is a by-product of production from oil wells. This water is in contact with oil in situ and is generally separated from the crude oil above ground in an oil/water separator. Following separation, a fraction of the produced water is recycled and reused for additional oil production [1–3]. The remaining produced water must be treated and either disposed or reused. Options for reuse include: (1) augmentation of surface waters; (2) recharge to groundwater supplies; (3) irrigation of food crops or grasses (e.g., golf courses). Often the decision for reuse depends on the quality of the produced water following treatment. Depending on factors such as geographic location, method of extraction, treatment chemicals, and contact time with the oil in the formation, the physiochemical composition of produced water can vary greatly in terms of characteristics such as salinity, percent solids, the amount of organic and inorganic constituents including minerals, pH, dissolved oxygen and conductivity. In

produced water containing elevated levels of salt (i.e., saline or brackish-produced waters) as well as other inorganics and organics, the ability to decrease the salinity or conductivity of the produced water may influence the potential for reuse of the water for inject purposes [4–8].

Now with the time go by more water is produced by separated from the mixture of oil and water mixture system (oil to water in the ratio of 10 to 90), for example: collect 10 kg oil and 90 kg wastewater must be produced, and so the treatment of wastewater in china is the second program and more than 90% produced water were injected.

Currently, two general processes predominate in water treatment of produced water: (1) chemical treating processes including flocculation, disinfection and filtration [7,8]; (2) physical method as pressure-driven processes such as reverse membrane separation and nano-filtration [9]. Reverse membrane separation and nano-filtration, which comprises little than 5% of the oil produced water treatment capacity, is a physiochemical separation where the process is reversed by application of pressure to a concentrated solution in contact with a semi-permeable membrane [10,11]. If the applied pressure is in excess of the solution's inherent osmotic pressure, the solvent will flow through

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the membrane to form a dilute solution on the opposite side of the membrane and a more concentrated solution on the side where the pressure is applied [10]. Membrane separation and nano-filtration can be effectively used for removal of solid from produced water and for decreasing the concentrations of many of the associated organics and inorganics [12–16]. However, without a pretreatment step such as flocculation, many organics and inorganics with low molecular weight are not effectively removed by physical method and additional treatment of the produced water may be necessary to meet a designated reuse [17–19].

Produced water from an arid region of the oil field provided the opportunity to evaluate the performance of a pilot-scale method followed by a specifically designed constructed new treatment system (i.e., electrochemical pilot-scale plant for oil field produced wastewater system) for achieving desired treatment goals [20]. The overall objective of this research was to evaluate the water quality achieved by the electrochemical pilot-scale plant for oil field produced wastewater for recharge or discharge to surface water. Specifically, the characteristics of treated produced water in terms of SS, bacteria (SRB, TGB and iron bacteria) and ion content (especially of Ca^{2+} , Mg^{2+} , $\text{Fe}^{2+/3+}$, S^{2-}) following the electrochemical pilot-scale plant treatment system were examined.

This study deals with the treatment of oil field produced water by catalytic electrochemical method using M/C/Fe electrodes under catalytic system for deeply oxidizing the organic compound, some inorganic ions as S^{2-} and bacteria and decreasing or removing some of the ions content such as Ca^{2+} , Mg^{2+} , $\text{Fe}^{2+/3+}$, S^{2-} and some causing factors aims to prove the injection.

2. Materials and methods

The primary operation goal of the pilot-scale catalytic electrochemical system was to decrease the SS, bacteria and toxicity associated with brackish-produced water to levels acceptable for injection and discharge into receiving water systems. The pilot-scale catalytic electrochemical systems were constructed by the

Table 1
Specifications for the pilot-scale catalytic electrochemical unit

Parameter	Specification
Electrodes	10 m ²
Filter material	SiO ₂
Size	Ø 0.95, 1.35, 150 mm
Maximum operating pressure	500 kPa
pH range	5–12
Maximum temperature	90 °C
Maximum flow	0.3 L/s
Voltage	3–30 V
Electric current	10–200 A

Institute of Energy Chemistry of Shaanxi Normal University. A 25 L barrels for produced water were shipped by truck from oil fields to Shaanxi Normal University in March 2005. The shipment spent approximately 2 days. The following section contains a description of the pilot-scale catalytic electrochemical process and the parameters used to measure treatment performance such as toxicity and selected water quality parameters.

2.1. Pilot-scale catalytic electrochemical system

Ions content, bacteria and organic compounds were removed from produced water using a pilot-scale catalytic electrochemical system schematically depicted in Fig. 1. The system was constructed of stainless-steel components to the greatest extent possible.

The characteristics of the pilot-scale catalytic electrochemical system are summarized in Table 1. The pump provided the necessary flow (about 0.5 L/s) and pressure (up to 150 kPa) for efficient filter operation. Filtrated water was collected every 30 min in 1 L polyethylene barrels, and saved for further test. The operating pressure for this catalytic electrochemical oxidation system was maintained at 120 kPa. The feed flow to the catalytic electrochemical oxidation system ranged from 0.12 to 0.25 L/s, while the permeate flow was from 0.1 to 0.3 L/s. The range of flow rates is a function of the degree of pressure of the filters. When flow rate decreased to below 0.1 L/s, the filter

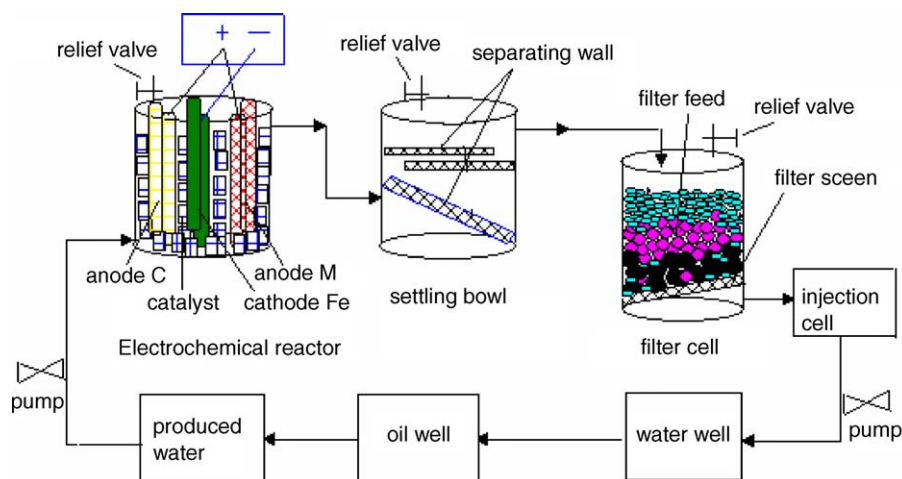


Fig. 1. Flow diagram of electrochemical pilot-scale plant.

Table 2
The quality of produced water prior to and following treatment under 15 V/120 A

Constituent (Units)	Desired levels for injection	Produced water (prior to treatment)	Coagulate-sedimentation	Produced water (following treatment)
Total dissolved solids (mg L ⁻¹)	–	34030	34576	32403
SS (mg L ⁻¹)	5	210	10	3
pH (mg L ⁻¹)	6.9	6.5	8.5	8.5
Fe ^{2+/3+} (mg L ⁻¹)	≤0.05	7.6	3.5	0
Mg ²⁺ (mg L ⁻¹)	–	230	220	150
Ca ²⁺ (mg L ⁻¹)	–	2250	2300	1720
Cl ⁻ (mg L ⁻¹)	–	15400	15600	14800
Na ⁺ (mg L ⁻¹)	–	11800	11920	11680
K ⁺ (mg L ⁻¹)	–	3800	3790	3780
S ²⁻ (mg L ⁻¹)	0.5	20	3.5	0
CO ₃ ²⁻ /HCO ⁻ (numbers mL ⁻¹)	0	150	145	20
SO ₄ ²⁻ (mg L ⁻¹)	–	450	400	480
Bacteria				
SRB	100	10 ⁴	100	30
TGB	100	10 ⁴	100	0
Iron bacteria	100	10 ³	50	0
COD (mg L ⁻¹)	–	5800	5500	130
BOD (mg L ⁻¹)	–	4590	4500	75
COD/BOD	–	1.26	1.22	1.73
Corrosion rate (mm a ⁻¹)	0.076	2.4	0.1	0.02

should washed with purified water (temperature > 60 °C). It is important to note here that the more untreated feed provided in the first 60 min the more easily to destroy the filter, in order to get the optimized treatment level, the flow rate must be controlled and then a normal rate can be reached.

2.2. Water quality characterization

Produced water was characterized by measuring selected water quality parameters prior to treatment and following treatment with catalytic electrochemical oxidation system (Table 2). The experiment was performed 3 months continuous.

Total dissolved solids were measured using an Orion 142 Conductivity/TDS and Salinity meter. The pH value of produced water was monitored using an Orion 290 pH meter. Na⁺, Cl⁻, K⁺, Ca²⁺, Mg²⁺, Fe^{2+/3+}, S²⁻, CO₃²⁻/HCO⁻ and SO₄²⁻ were measured using Perkin-Elmer Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICPAES) according to Standard Methods [21–23]. Alkalinity was measured by titration according to Standard Methods [23]. Sodium adsorption ratio (SAR) is a ratio of the Na⁺ versus Ca²⁺ and Mg²⁺ in irrigation water. COD were carried out with a Hach-2000 spectrophotometer using dichromate solution as the oxidant in a strong acid media. BOD were performed by means of a Hg-free WTW 2000 Oxytop unit thermo-stated at 20 °C. Bacteria and corrosion rate were tested by standards methods [21,23].

2.3. Theoretical approach [2–8]

Time of electrochemical reaction depends upon the stability and concentration of organic compounds, concentration of dissolved salt (as NaCl, KCl and so on relative to conductivity

compounds), temperature, pH of the solution, size of the anode, current and voltage applied.

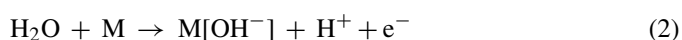
The electrochemical reactions performing during the electrolysis of produced water are complicated. For the time being assumptions can be made, based on the products that can be determined (Cl₂, ClO₂, O₃, •OH, O•, H₂O₂, O₂, H₂, CO₂). Two possible mechanisms of electrolysis are described below based on dissolved salt content, pH value and so on. The electrolytic evolution of hydrogen in acid and alkaline solutions occurs in different ways for low Cl⁻ content water. In acid solutions, the source of hydrogen is hydroxonium ions that are discharged at the cathode to form hydrogen gas and all pH condition as Eqs. (1a) and (1b):



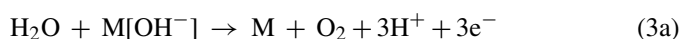
For alkaline solutions it is assumed that electrons are directly added on to water molecules and then decompose to yield hydrogen and hydroxyl ions:



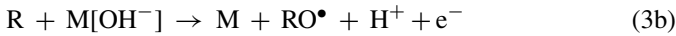
Anodic discharge of the water takes place forming hydroxyl radicals that are absorbed on the active sites of the electrode surface M or active catalyst:



It is believed that reaction (Eq. (2)) may also proceed in acid solutions but at high current densities. Near the anode the main by-reaction during the procedure of electrochemical reaction (Eq. (1b)) is the oxygen formation (Eq. (3a)):



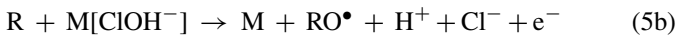
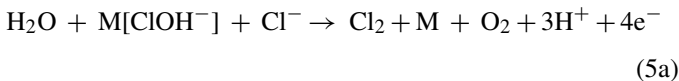
The electrochemical oxidation of aqueous solutions which contain organics, by the use of traditional anodes (Ti/Pt, Ti/IrO₂, ...) proceeds in two steps and also by active catalyst. The first step is the reaction (Eq. (2)). After this, the absorbed hydroxyl radicals oxidize the organics (Eq. (3b)):



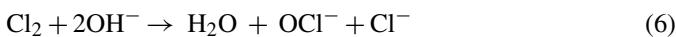
RO[•] representing the oxidized organics can be produced from the hydroxyl radicals that are formed continuously, since the anodic discharge of the water goes on. While for high Cl⁻ content conditions, the anodic discharge of chlorides take place simultaneously, forming possible chlorine hydroxyl radicals, which are absorbed on the active sites of the anode surface M (Eq. (4)):



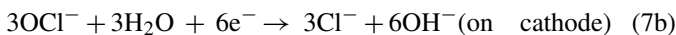
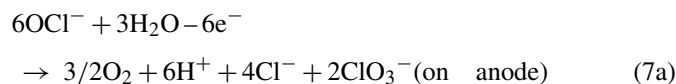
Under a pathway similar to Eqs. (3a) and (3b) the free chlorine and chlorides, as well as oxidized organics, are formed according to Eqs. (5a) and (5b) reactions:



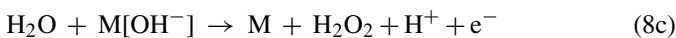
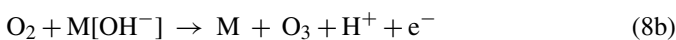
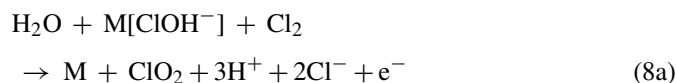
The free chlorine produced is in equilibrium with OCl⁻ ion:



So the products from the primary electrochemical reactions are Cl₂, O₂, OCl⁻ and RO[•]. As concentrations of the above oxidants increased in the electrolyzed solution, several other secondary electrochemical reactions take place. At high OCl⁻ concentrations, elevated temperature and turbulent flow conditions, the mass transport reactions that are created (Eq. (7a) and (7b)):



At the same time, ozone, hydrogen peroxide and chlorine dioxide are found among the oxidants produced from the C/Fe electrolysis of brine solutions. These oxidants are produced on the anode according to the following hypothetically electro-reactions (Eqs. (8a)–(8c)):



The radicals have a very short life due to their high oxidation potential, and either they decompose to other oxidants (Cl₂, O₂, ClO₂, O₃ and H₂O₂) or oxidize organic compounds (direct oxidation). The primary (Cl₂, O₂) and secondary (ClO₂, O₃ and

H₂O₂) oxidants that are produced from the destruction of radicals have quite a long life and are diffused into the area away from the electrodes continuing the oxidation process (indirect oxidation or by catalytic).

But for active metal, the anode electrochemical reaction follows as Eq. (9):

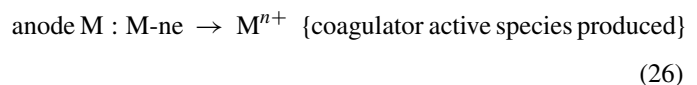


Mⁿ⁺ species formed from the above reaction combine with [OH⁻] or Cl⁻ and new compound as M[OH]_n or M[ClOH] formed that possess large surface and play an function as coagulator to purify wastewater.

The direct electro-oxidation rate of organic pollutants is dependent on the catalytic activity of the anode, the diffusion rate of organic compounds in the active points of the anode and the applied current density. The indirect electro-oxidation rate is dependent on the diffusion rates of secondary oxidants into the solution, the temperature, property of catalyst and pH. An effective pollutant degradation is based on a direct electrochemical process because the secondary oxidants are not able to completely convert all organics into water and carbon dioxide. Therefore, it is concluded that in acid solutions, oxygen, free chlorine and maybe some amounts of ozone and chlorine oxides are the main secondary oxidants as by-products of the direct oxidation process. In moderate alkaline solutions a cycle of chloride-chlorine-hypochlorite-chloride takes place, which produces OCl⁻, oxygen and some amounts of hydrogen peroxide and maybe, ozone. In strong alkaline solutions the cycle of chloride-chlorine-chloride is reduced due to production of ClO₃⁻ that is a stable anion. So, in low pH solution chlorides are removed during the electrolysis process producing free chlorine, while in high pH chlorides are removed producing chlorates. Only in moderate alkaline to neutral conditions does the initial concentration of chlorides remain stable, producing free hydroxyl radicals continuously. But the catalyst introduced can consolidate the secondary oxidants to remove the pollutant in wastewater. Table 3 shows the possible electrochemical and chemical reactions that can take place in a mixture of produced water and wastewater in an electrolysis cell with M/C/Fe electrodes.

Based above discussions three electrodes M/C/Fe, double anodes as active metal M and C, Fe as cathode, have been designed and an oxidation catalyst introduced then a reaction pilot gram for produced water treatment reaction maybe pilot summarized as follows:

Double anodes (M/C):



or

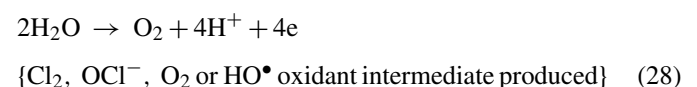


Table 3
Possible electrochemical and chemical reactions

Anode (noble metal M, M=Pt, Ru, Rh, ...)	
Primary electrochemical reactions:	
$\text{H}_2\text{O} + \text{M} + \text{Cl}^- \rightarrow \text{M}[\text{ClOH}^-] + \text{H}^+ + 2\text{e}^-$	(10)
$\text{H}_2\text{O} + \text{M} \rightarrow \text{M}[\text{OH}^-] + \text{H}^+ + \text{e}^-$	(11)
$\text{M-ne} \rightarrow \text{M}^{n+}$ (active metal as Fe, Cu, Zn, ...)	(12)
Secondary electrochemical reaction:	
$6\text{OCl}^- + 3\text{H}_2\text{O} - 6\text{e}^- \rightarrow 3/2\text{O}_2 + 6\text{H}^+ + 4\text{Cl}^- + 2\text{ClO}_3^-$	(13)
Cathode (noble metal M, M=Pt, Ru, Rh... or C)	
Primary electrochemical reactions:	
$2\text{H}_3\text{O}^+ + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{H}_2\text{O}$	(14)
$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$	(15)
Secondary electrochemical reaction:	
$\text{OCl}^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Cl}^- + 2\text{OH}^-$	(16)
Oxidation reactions (or under catalytic and noble metal M, M=Pt, Ru, Rh, ... used)	
In a closed anode are:	
$\text{R} + \text{M}[\text{OH}^-] \rightarrow \text{M} + \text{RO}^\bullet + \text{H}^+ + \text{e}^-$	(17)
$\text{R} + \text{M}[\text{ClOH}^-] \rightarrow \text{M} + \text{RO}^\bullet + \text{H}^+ + \text{Cl}^- + \text{e}^-$	(18)
$\text{H}_2\text{O} + \text{M}[\text{OH}^-] \rightarrow \text{M} + \text{O}_2 + 3\text{H}^+ + 3\text{e}^-$	(19)
$\text{H}_2\text{O} + \text{M}[\text{ClOH}^-] + \text{Cl}^- \rightarrow \text{Cl}_2 + \text{M} + \text{O}_2 + 3\text{H}^+ + 4\text{e}^-$	(20)
Away from electrodes:	
$\text{R} + \text{O}_2 + 2\text{H}^+ \rightarrow \text{RO}^\bullet + \text{H}_2\text{O} - 2\text{e}^-$	(21)
$\text{R} + \text{Cl}_2 \rightarrow \text{RCl} + \text{Cl}^- - \text{e}^-$	(22)
$\text{R} + \text{OH}^- \rightarrow \text{RO}^\bullet + \text{H}^+ + 2\text{e}^-$	(23)
$\text{RCl} + \text{OH}^- \rightarrow \text{RO}^\bullet + \text{Cl}^- + \text{H}^+ + \text{e}^-$	(24)
Equilibrium reactions:	
$\text{Cl}_2 + 2\text{OH}^- \rightarrow \text{H}_2\text{O} + \text{OCl}^- + \text{Cl}^-$	(25)
Cathode Fe:	
$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ {pH value have been adjusted}	(29)
Catalytic oxidation reactions:	
Catalyst + oxidant + organics, bacteria, SS, Fe^{2+} ...	
$+ \text{OH}^- \rightarrow$ environment friendly product + sediment.	(30)

3. Results and discussions

The results for produced water characteristics prior to treatment and following treatment with catalytic electrochemical system are presented in Table 2. Because one objective of this study was to evaluate the reuse of the treated produced water for injection purposes, the concentrations of Ca^{2+} , pH, bacteria and SS were compared to injection standards. Water treated by the catalytic electrochemical system can meet the injection guidelines by decreasing Ca^{2+} , bacteria and SS content and elevating pH value, and the treated water quality is improved and overmatch to standards and also gain advantage of coagulate-sedimentation method. In addition, a decreasing of COD and BOD value was observed and met the irrigation requirement. Some of detailed results are given below.

3.1. The changes of pH value

The changes of pH value in the procedure are given in Fig. 2. The starting pH value is 6.5, with time longer the pH elevated and the end pH value after 10 min is about 12. This can be explained from the fact that H_2 produced and resulting in a shift of pH to the alkaline region, which is consistent with the theoretical approach [5].

3.2. Suspended solids

With time longer more metal turn to M^{n+} ion due to the electrolysis and pH elevated that lead to more coagulator produced, the suspended solids improved, some of macromolecular aggregation formed and the smaller particle become bigger and deposited [24]. The solids separated out and filtrated (Fig. 3) and reduced by 99%.

3.3. Effect of catalytic electrolysis time on the number of bacteria

The bacteria decreasing with time longer are shown in Fig. 4. SRB is difficult to remove related to TGB and ion bacteria [25], but with the time longer the number of SRB sharply decrease to 30 numbers mL^{-1} and in 3 min more than 99% have been

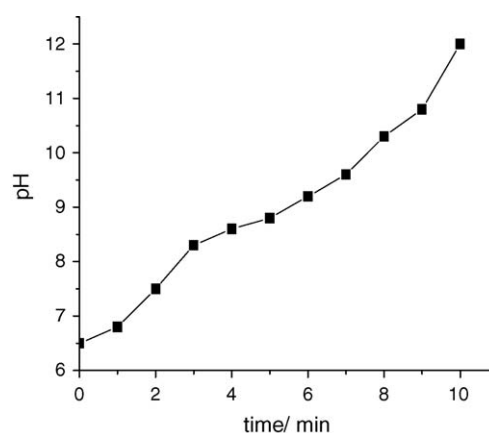


Fig. 2. The changing of pH value with time.

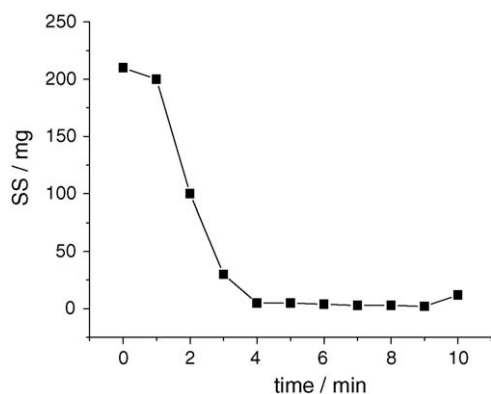


Fig. 3. Suspended solids at the different time.

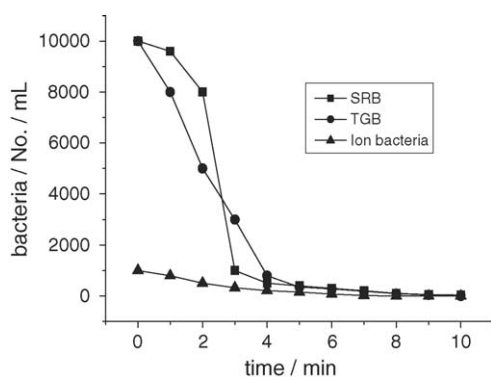


Fig. 4. Bacteria number at different time.

removed, while ensuring to meet the criterion or guideline the electrolysis time must be over 4 min.

3.4. Effect of time on the COD and BOD value

The effect of time on the convert ratio of COD and BOD decreasing are shown in Fig. 5. Both values decreasing with electrolysis prolong and to satisfy the demand the list time must be over 10 min. For shorten the electrolysis time noble metal content catalyst with bigger surface added superfluity and repeated the experimental, it is found that the COD and BOD removing rate both up to 90%. The ratio COD/BOD of the produced water prior to treatment is 1.26, while after treating with the electro-

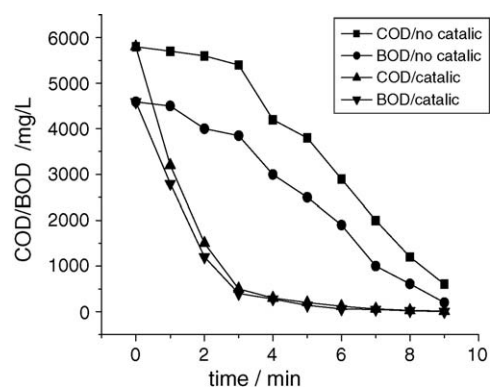


Fig. 5. COD and BOD value at different time.

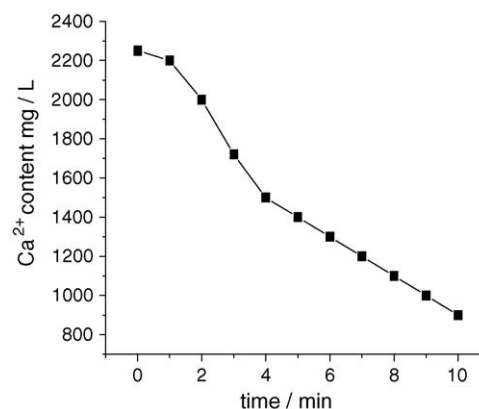
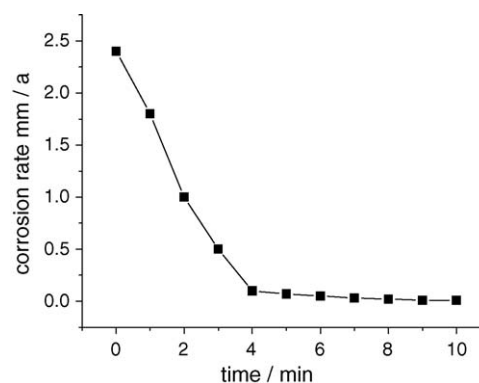
Fig. 6. Ca²⁺ content at the different time.

Fig. 7. Corrosion rate at the different time.

chemical system that rise to 1.73, higher than that of treating with chemical method (1.22), it can be inferred from that the biochemical degradability of the produced water increased and the electrochemical method is effective in the treatment of produced water.

3.5. Effect of catalytic electrolysis time on Ca²⁺ content

Fig. 6 shows the Ca²⁺ content changing during the catalytic electrochemical oxidation reaction. With the electrolysis prolong Ca²⁺ content decreasing continuously, may be due to the pH elevated and more Ca(OH)₂ or Ca complex as M–OH–Cl–Ca²⁺ deposited out.

3.6. Effect of catalytic electrolysis time on corrosion rate

It is definiteness demonstrated that with the electrochemical process go on, the corrosion rate decreased and up to 4 min the corrosion rate is lower than the standards of less than 0.076 mm a⁻¹ and quality of anticorrosion have been improved (Fig. 7).

4. Conclusion

Produced water treatment of oil field is important and some indexes as SS, Ca²⁺, Mg²⁺, bacteria, pH and corrosion rate are the control factor. The treatment, here active producing coag-

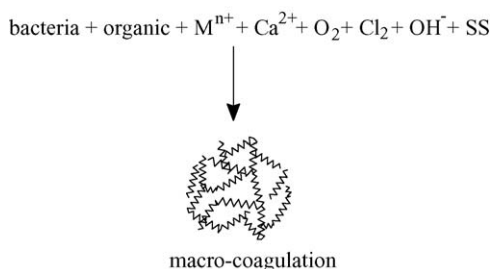


Fig. 8. Catalytic electrochemical diagram for produced water.

ulator active species, C anode producing oxidants as Cl_2 , O_2 and OCl^- or HO^\bullet and Fe cathode adjusting water pH value for H_2 produced and catalyst for catalytic oxidation reactions, aims to decrease the perniciousness maximum and elevate the injection quality, while by tradition method described as coagulate-sedimentate-filtrate, the water quality is low and cost most, and by direct electrochemical method also need longer time to improve the technology, we made try to introduce catalytic system and obtain the satisfied experimental results. A concise diagram of catalytic electrochemical oxidation for produced water as Fig. 8.

In the catalytic electrochemical oxidation system a big surface catalyst introduced so absorption and catalytic reaction have been intensified and an excellent purifying result have been obtained, especially show as COD and BOD remove rate.

For the experimental run in laboratory pilot-scale plant, using double anodes with active metal (M) and graphite and iron as cathode and noble metal content catalyst with big surface, it can be concluded that the catalytic electrochemical method treating oil field produced water is effective.

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