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Chemical oxidation for removal of hydrocarbons from gas-field produced water

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Abstract

Chemical oxidation of produced water separated from gas stream of a gas refinery in Iran, has been attempted by use of hydrogen peroxide, ozone and calcium hypochlorite. All the experiments were carried out at 30 ºC. The aim of the current work was improving the quality of produced water via degradation of soluble organic materials in order to be re-used as fire-fighting water supply source in the refinery. Produced water separated from natural gas at different stages of gas production process was collected and de-oiled in an API separator. The water effluent of API separator contained chemical oxygen demand (COD) and total dissolved solids (TDS) of 270 and 3450 mgL^{-1}, respectively. The stoichiometry amount of hydrogen peroxide for complete COD removal of produced water (600 mgL^{-1}) of hydrogen peroxide at pH of 7.2 decreased its COD to the level of 228 mgL^{-1} which corresponds to 15% degradation of organic materials. Ozonation of produced water for 1 hour at pH of 7.2 ended to COD value of 203 mgL^{-1} (i.e. 12% COD removal). Increasing pH of the water to 10, improved treated water quality (to COD of 192 mgL^{-1}), which indicated higher ozonation efficiency of the produced water at higher pH values. Maximum COD removal was achieved for calcium hypochlorite oxidant. Employing concentrations of 300, 500, 1000 and 7100 mgL^{-1} of calcium hypochlorite showed COD removal in the range of 36-70%. The final COD values were obtained as 80-173 mgL^{-1}. Kinetic studies of calcium hypochlorite oxidation of produced water revealed that the reaction was completed within 30 minutes at concentrations higher than 500 mgL^{-1}. The results indicated that calcium hypochlorite was the most efficient oxidation agent among the three oxidants employed in this study. The drawback of using calcium hypochlorite is the high concentrations of residual active chlorine in the treated water which should be eliminated before using as fire-fighting water source.

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1. Introduction

Gas well production fluid normally consists of natural gas and gas condensates which are separated from water by physical techniques. The separated water stream is referred to as "produced water". Produced water contains dispersed and soluble organic hydrocarbons. The dispersed hydrocarbons can be found as fine droplets contained in water in the form of emulsion.

The volume of produced water from gas field is less than in oilfields. In gas fields, the produced waters are mixture of well formation water and condensed water [1]. Their chloride content varies from almost those of fresh water to salty formation water with chloride concentration about 14 times that of seawater which is a major contributor of toxicity [2]. A wide range of gas treatment chemicals is used in gas fields including ethylene glycol, and triethylene glycol which are mostly discharged in produced water. Volatile components concentrations in produced water from gas fields are higher than those in produced water from oilfields. Environmental effect of produced water can occur in all regions where oil and gas have been produced [3]. Dispersed oil and droplets rise to the surface of water and increase the biochemical oxygen demand (BOD) of the affected water [4]. Volatile and/or toxic compounds evaporate. These materials are consistently toxic [5]. Also, due to the large volumes of water produced in the oil and gas fields, possible re-use of the treated water has been taken into consideration during recent years.

Wastewater treatment processes are being developed to reduce the amount of hydrocarbons in the produced water to acceptable levels. Conventional phase separation techniques will not remove the water soluble organics from the aqueous phase. Thus, various biological [6, 7] and chemical [8] oxidation methods have been used to treat the produced water of oil and gas industries.

In this research, chemical oxidation of hydrocarbons in produced water separated from gas stream of Parsian Gas Refinery, located in southern part of Iran, has been carried out. Among available oxidants (Table 1), three oxidation agents with different oxidation power (ozone, hydrogen peroxide, and calcium hypochlorite) has been used to decrease the chemical oxygen demand (COD) of the produced water.

2. Materials and methods

All the experiments were carried out on produced water samples taken from effluent of API oil separator of Parsian Gas Refinery located in south of Iran.

2.1. Sampling

Composite samples were taken from wastewater effluent of API oil separator of Parsian Gas Refinery every 4 hours for two days. Average values of the samples have been reported.

2.2. Materials

Laboratory-grade hydrogen peroxide at concentration of 341.7 gL^{-1} and calcium hypochlorite of 70% purity (Merck Co.) was used for oxidation process. All other chemicals were analytical grade and obtained from commercial sources.

Table 1. Oxidation power of some oxidation reagents [9]

Oxidation species	Oxidation power
Hydroxyl radical	2.80
Ozone	2.07
Hydrogen peroxide	1.77
Permanganate	1.67
Chlorine dioxide	1.50
Hypoiodous acid	1.45
Chlorine	1.36

2.3. Analysis

COD analysis was conducted by reactor digestion HACH method 8000, which was approved by USEPA as per Federal Register, April 21, 1980, 45 (78) 26811-26812, using high range vial (0-1500 mg/L). HACH methods are described in detail in the HACH' Odyssey DR/2400 spectrophotometer manual.

Concentration of oxidants were analyzed by iodometric titration [10].

2.4. Experiments

Oxidation by hydrogen peroxide and calcium hypochlorite was carried out in 250 mL agitated reactor contained 200 mL solution at 30 ºC. Ozone was produced from a 1VTTL-Ozomax ozone generator with maximum capacity of 10 gr h^{-1} utilizing pure oxygen gas feed. Ozonation of samples was carried out using a glass reactor with a working volume of 1800 mL equipped with a teflon diffuser. 1.3 liters of sample was added into the glass reactor agitated at 100 rpm and 30 ºC. Ozone gas was supplied at concentration of 6 Gh^{-1} by flowing of 0.09 Nm^3H^{-1} oxygen. The performance of chemical oxidation was evaluated based on chemical oxygen demand (COD) removal.

3. Results and discussion

The focus on waste minimization and water conservation in recent years has resulted in the production of concentrated or toxic residues. Due to the increasing presence of molecules, refractory to the microorganisms in the wastewater streams, the conventional biological methods may not be used for complete treatment of the effluent in some cases and hence, using chemical oxidation to degrade these refractory molecules into smaller molecules, has become imperative. The produced small molecules can be further oxidized by biological methods.

Table 2 represents the characteristics of the composite sample of produced water after oil separation in API unit. All experiments were carried out using this sample. Three oxidants, hydrogen peroxide, ozone and calcium hypochlorite, which present different oxidation power, were selected for oxidation of dissolved and dispersed hydrocarbons.

Hydrogen peroxide is a strong oxidant readily applied to wastewater treatment in the past. Hydrogen peroxide has been found to be effective in degradation of compounds or treatment of real wastewaters requiring less stringent oxidation conditions [11] but applications to complex mixture of effluents like dyes, textile industry effluent, heteroaromatics and the present produced water need to be explored. The stoichiometry amount of hydrogen peroxide for

complete COD removal of produced water was calculated as 570 mgL^{-1}. Oxidation of produced water by 600 mgL^{-1} of hydrogen peroxide after 4 hours reaction decreased its COD to the level of 228 mgL^{-1} which corresponds to 15% degradation of organic materials (Table 3).

Table 2. Properties of the composite wastewater sample

Property	Quantity
Total dissolved solids (mgL^{-1})	3450
Chloride (mgL^{-1})	1400
COD (mgL^{-1})	270
Total Iron (mgL^{-1})	13
pH	7.2

Table 3. Chemical oxidation of produced water by hydrogen peroxide after four hours

H_2O_2 Concentration (mgL^{-1})	COD (mgL^{-1})
0	270
600	228

The results show low degradation rate of organic materials in the produced water. A major problem encountered with the application of hydrogen peroxide alone for wastewater treatment applications are very low rates for applications involving complex materials. Moreover, stability of H_2O_2 remains a question, as the catalytic decomposition agents present in effluents compete with the pollutants [11].

Ozonation of produced water for 1 hour at pH of 7.2 ended to COD value of 203 mgL^{-1} (i.e. 12% COD removal). Increasing pH of the water to 10, improved treated water quality (to COD of 192 mgL^{-1}), which indicated higher ozonation efficiency (29%) of the produced water at higher pH values. Higher pH values enhance the formation of hydroxyl radical which is a strong oxidation in the presence of ozone.

Table 4. Chemical oxidation of produced water by ozone at different pH

Time (min)	pH	COD (mgL^{-1})
0	7.2	270
60	7.2	203
60	10.0	192

Thus, it appears that the use of ozone alone is not feasible for the treatment of complex compounds in the produced water and combination with other advanced oxidation techniques seems to be a better alternative.

Maximum COD removal efficiency was achieved for calcium hypochlorite oxidant. Employing concentrations of 300, 500, 1000 and 7100 mgL^{-1} of calcium hypochlorite, showed COD removal in the range of 36-70% (Table 5). The final COD values were obtained as 80-173 mgL^{-1}. In spite of lower oxidation power of chlorine, the results show the higher efficiency of calcium hypochlorite in degradation of organic materials within the sample. This might be due to the structure of the water pollutants. It was found that calcium hypochlorite is cost-effective and easy to use for chemical oxidation of the produced water. The drawback of this process is the residual chlorine in the water which should be eliminated for further use of the water.

Figure 1 indicates the kinetic studies of calcium hypochlorite oxidation at the concentrations of 500 and 7100 mgL⁻1. The results revealed that the reaction was completed within 30 minutes at concentrations higher than 500 mgL^{-1}.

Table 5. Chemical oxidation of produced water by calcium hypochlorite after four hours

$Ca(OCl)_2$ Concentration (mgL^{-1})	COD (mgL^{-1})
0	270
300	173
500	139
1000	107
7100	81

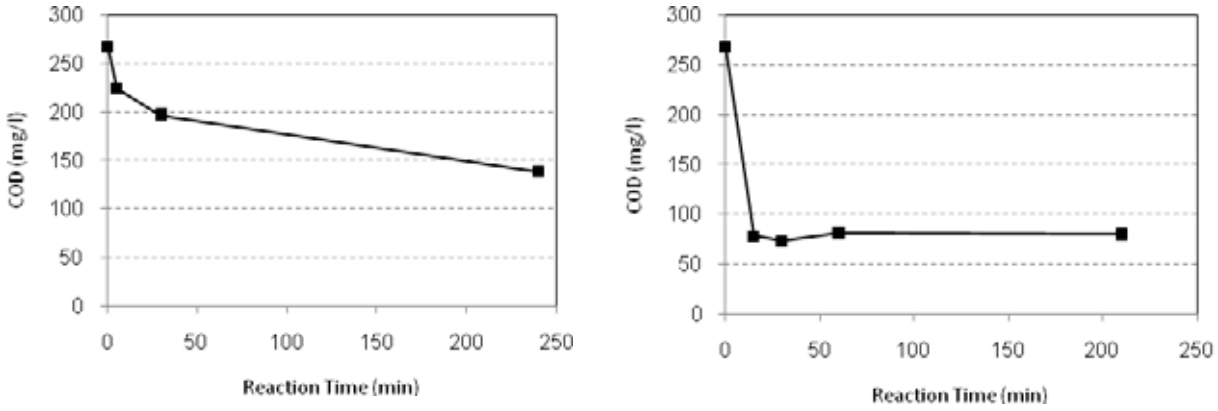

Fig. 1. Kinetic of produced water oxidation by calcium hypochlorite at two concentration; 500 mgL^{-1} (Left); 7100 mgL^{-1} (Right)

In any case, 100% efficiency of the oxidants might not be achieved because the whole amount of oxidant added in wastewater may not be available for the oxidation of organic matter [12]. Some amount of oxidant might have been used for the oxidation of heavy metals (Cr, Cu, Fe, Zn) present in wastewater [13].

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