Nature Environment and Pollution Technology
An International Quarterly Scientific Journal

ISSN: 0972-6268 | Vol. 14 | No. 1 | pp. 161-163 | 2015

General Research Paper

Review on Shale Gas Produced Water Chemical Characteristics and Treatment Techniques

Tao Yuan*, Ping Lu†, Qiyan Feng** and Jing Li****
*Jiangsu Jianzhu Institute, Xuzhou, 221116, China
**Department of Environmental Science and Spatial Informatics, China University of Mining and Technology, Xuzhou, 221116, China
†Corresponding Author, Ping Lu

Nat. Env. & Poll. Tech.
Website: www.neptjournal.com
Received: 20-3-2014
Accepted: 22-5-2014

Key Words:
Shale gas produced water
membrane filtration
Advanced oxidation process
Electrochemical treatment

ABSTRACT

Water treatment techniques can be applied in shale gas produced water have been discussed, including membrane filtration, advanced oxidation process, and electrochemical techniques. Membrane filtration was effective to decrease TDS, organic matter, etc. Fouling was still a major challenge during the membrane recovery. Advanced oxidation process was suitable for organic matter removal, and electrochemical techniques could be applied for TDS, heavy metals, and organic matters. No documented case of the use of these technologies in shale gas field applications was found. Thus, practice of treatment of produced water needed to be evaluated. Recommendation was given that water treatment technique should be selected and applied based on the produced water characteristics and joint technique might be required according to the complex of produced water.

INTRODUCTION

Shale gas is a clean and efficient natural gas. China National Petroleum Corporation and Shell has signed the first shale gas production sharing contract in the Sichuan Basin in March 2012. Shale gas exploitation will help to meet a significant part of China's fast-growing fuel needs during the years in the 12th Five Year Plan. The vast reserves of shale gas makes it scaled development. However, environmental effect arises with energy exploitation and production, such as large amount of water use accelerate water resources crisis and hazardous chemicals in fracturing liquid contaminating groundwater aquifer. This paper will briefly summarize the produced water characteristics and discuss the water treatment techniques which can be applied in shale gas produced water treatment.

SHALE GAS PRODUCED WATER TREATMENT OPTIONS

Disposal through injection in deep underground wells, storage in large steel tanks, and treatment at a local facility are conventional water management methods. It is difficult to reuse the produced water in the same type of fracturing process without treatment.

Membrane filtration has received considerable attention in the removal and concentration of dissolved solids, since it is capable of removing suspended solids, heavy metals, and even organic compounds according to different pore size. An ultrafiltration (UF) filter has a pore size around 0.01 μm to separate heavy metals, macromolecules and suspended solids. It reduced the amount of heavy metals ranging from 20% to 99.7%, colour and COD removal ranging from 22% to 94% and 58% to >99.9 % respectively depending on water characteristics. Combination of the fine adsorbents with membranes was applied to remove organic matters (such as phenol). The optimum adsorbent amount to achieve 90% removals was obtained.

A nanofiltration (NF) filter has a pore size around 0.001 μm. Contaminated chemicals and biological substances can be removed by NF. NF separation mechanism involves steric (sieving) and electrical (Donnan) effects. A Donnan potential is created between the charged anions in the NF membrane and the co-ions in the effluent to reject the latter. The significance of NF membrane relies on pore size and membrane surface charge, which allows charged solutes smaller than the membrane pores to be rejected along with the bigger neutral solutes and salts. Ion exchange (IE) is used in low-TDS waters and for the removal of sodium in high bicarbonate/carbonate water. For TDS concentrations of up to 20,000 mg/L, reverse osmosis (RO) has been the preferred method, which is used to remove dissolved salts (typically chlorides) with a pore size around 0.0001 μm. Water can pass through the membrane under high pressure in RO. In general, compared to UF and NF, RO is more effective for heavy metal removal from inorganic solution, as indicated by the rejection percentage of over 97% with a metal concentration ranging from 21 mg/L to 200 mg/L, depending on the characteristics of the membrane (i.e., the porosity, material, hydrophilicity, thickness, roughness, and charge of the membrane).

UF and RO were used to treat oily wastewaters generated by ships, the rejection of COD was 98.5% and total dissolved solids (TDS) was 95.7% (Karakulski et al. 1995). However, fouling is still a major challenge during the water recovery due to higher contaminant loadings of membranes. Four fouling types present in RO, bio-fouling, inorganic/scaling, organic and particulate fouling.

Despite the bio-fouling, less understood but dominant, other fouling mechanisms have been overcome by well-developed pre-treatments. Moreover, as there is no documented case of the use of this technology in shale gas field applications, the practice of membrane removal of high concentration of TDS needs to be evaluated. The most powerful oxidants are fluorine, hydroxyl radicals (·OH), ozone, and chlorine with oxidation potentials of 2.85, 2.70, 2.07 and 1.49 electron volts, respectively.

AOPs refer to a set of chemical treatment procedures designed to remove organic (or inorganic) materials in water and wastewater by oxidation through reactions with hydroxyl radicals (·OH), by employing ozone (O_3), hydrogen peroxide (H_2O_2), UV light (UV), TiO_2 catalysis, and Fenton's reaction, etc. All of these processes can produce hydroxyl radicals, which can react rapidly and nonselectively with nearly all electron-rich organic compounds. These oxidation processes can be applied separately or combined together. Study demonstrated that the H_2O_2, O_3 and UV treatment processes alone showed less impact on TOC reduction compared to the combined oxidizing agents (H_2O_2/O_3, UV/O_3, and H_2O_2/UV).

When oxidants are simultaneously applied to the water, they react to form ·OH, which could oxidize most of the dissolvable organic matter. While an investigation on the degradation of polycyclic musk HHCB by three processes (O_3 alone, UV radiation alone, and UV/O_3) indicated degradation efficiency of HHCB follow the trend of $O_3 > UV/O_3 > UV$.

Applying H_2O_2/O_3 together might lead to disinfection by-products (DBPs) formation and require to treatment of excess H_2O_2 to potential for microbial growth. H_2O_2/O_3 was applied to reduce the concentration of the active components involved (i.e., methylisothiazolone, chloromethyl isothiazolone and dichloromethylisothiazo-lone). Results indicated using an O_3 flow rate of 1g/L h, at a pH value of 10 and with the addition of 5 mL of H_2O_2 (0.3 M) proved to be the most effective treatment (Poberžnik et al. 2011). UV/O_3 is more effective to generate ·OH than H_2O_2/UV for equal oxidant concentration, while might lead to bromate formation. Turbidity may interfere with UV light and H_2O_2/UV application and DBPs formation might be increased during the process.

UV/H_2O_2 has no potential for bromated formation, while the disadvantages of this process are that turbidity may interfere with UV light and combined UV/H_2O_2 might increase DBPs formation. Additionally, H_2O_2 has poor UV adsorption characteristics and might lead to waste of UV light. Moreover, special reactors designed for UV illumination are required. Initial contaminants concentration, amount of H_2O_2, water pH and bicarbonate concentration are major affecting factors. Thus, initial wastewater dilution should be done. COD removal from oil recovery industry wastewater showed that almost 90% of the COD could be removed. Increase of initial COD concentration resulted to a decrease of the process performance.

TiO_2 is proved to be the optimum photocatalysis material with its high catalysis, high stability, low cost, and low toxicity. The photocatalytic mechanism is initiated by the absorption of the photon hv_1 with energy equal to or greater than the band gap of TiO_2 producing an electron hole pair on the surface of TiO_2 nano particle. An electron is promoted to the conduction band while a positive hole is formed in the valence band. Excited state electrons and holes can recombine and dissipate the input energy as heat, get trapped in metastable surface states, or react with electron donors and electron acceptors adsorbed on the semiconductor surface or within the surrounding electrical double layer of the charged particles. After the reaction with water, these holes can produce hydroxyl radicals with high redox oxidizing potential. Depending upon the exact conditions, the holes, OH radicals, H_2O_2 and O_2, play important role in the photocatalytic reaction mechanism. The key advantages of TiO_2/UV process are the operation at ambient conditions, the lack of mass transfer limitations when nanoparticles are used as photocatalysts and the possible use of solar irradiation. Wastewater pH is an affecting factor as reaction rates increase at lower pH for weakly acidic pollutants, and an increase of reaction rate with increase of pH for pollutants which are hydrolysed under alkaline conditions. The presence of ionic species (such as flowback water) could affect the degradation process via adsorption of the pollutants, absorption of UV light and reaction with hydroxyl radicals.

Fenton's reagent, a mixture of ferrous iron (Fe2+) and hydrogen peroxide, has been known as a powerful oxidant for organic contaminants. The major parameters affecting Fenton process are solution's pH, amount of ferrous ions, concentration of oxidizing agent, initial concentration of the pollutant and presence of other ions. The optimum pH for Fenton's reagent processes ranges from 2 to 4, and wastewater pH adjustment is usually needed before treatment with Fenton processes. In addition, increase of Fe2+ and oxidizing agent concentration results to an increase of degradation rate. Photo-Fenton is applied to saline industrial waste-water treatment. The initial Fe2+ concentration and salinity had a significant influence on the degradation process, while the impact of hydrogen peroxide concentration was minor. Laboratory scale photo-Fenton experiments were carried out with aqueous solutions of the PAM polymer (used for fracturing fluid), and results showed that Fe2+ concentration had a significant positive effect for PAM possibly due to the formation of organic complexes; H2O2 concentration had a negative effect. In a recent study investigating COD removal from oil recovery industry wastewater using Fenton process, reported that 86% reduction of COD was achieved for H2O2 to Fe2+ mass ratio equal to 8.7 (Dincer et al. 2008).

Electrochemical treatment has been used to remove TDS and organic matters from water body and soil for many years. Electrocoagulation is a cost effective electrochemical treatment process to remove most contaminants from water (i.e., suspended solids, emulsified hydrocarbons and many dissolved organic compounds, heavy metals, arsenic, bacteria, algae, larvae, etc). The electrocoagulation process is continuous flow and is low in energy consumption. Electrocoagulation cells consist of pairs of parallel plate electrodes separated with a low voltage applied at high current densities. Electrocoagulation was able to produce high quality water both for high and low natural organic matter (NOM) concentration water. The potential applications of water after the treatment could be potable water or industrial freshwater. In addition, physical treatment such as thermal distillation and evaporation is used for waters with TDS concentrations of 40,000-100,000 mg/L. New and cost-effective technologies that treat wastewaters with TDS exceeding 200,000 mg/L are needed.

CONCLUSIONS

Produced water can be managed in a variety of ways. Although there is not so much research on produced water treatment so far, these treatment technologies can be applied for produced water according to water characteristics. For most cases, joint technologies need to be conducted due to the complex produced water characteristics. In addition, treating the wastewater on-site is one of the practical options for the consideration of aquifer protection.

ACKNOWLEDGEMENTS

This project is supported by "the Fundamental Research Funds for the Central Universities" (2013QNB08).

REFERENCES

Dincer, A.R., Karakaya, N., Gunes, E. and Gunes, Y. 2008. Removal of COD from oil recovery industry wastewater by the advanced oxidation processes (AOP) based on H_2O_2. Global NEST Journal, 10: 31-38.

Karakulski, A. and Kozlowski, A.W. 1995. Purification of oily wastewater by ultrafiltration. Separations Technology, 5: 197-205.

Poberžnik, M., Bauman, M., Roš, M. and Lobnik, A. 2011. Reduction of Biocide-polluted wastewater using O_3 and H_2O_2/O_3 oxidation processes, ozone. Science & Engineering: The Journal of the International Ozone Association, 33: 31-36.