Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.980978

56 (2015) 3247–3251
December

Membrane and AOP processes—their application and comparison in treatment of wastewater with high organics content

Nataliya Savchuk*, Petra Krizova

MemBrain s.r.o., Pod Vinici 87, 471 27 Straz pod Ralskem, Czech Republic, Tel. +420 601 572 457; email: nataliya.savchuk@membrain.cz (N. Savchuk), Tel. +420 724 956 329; email: petra.krizova@membrain.cz (P. Krizova)

Received 28 July 2014; Accepted 7 October 2014

ABSTRACT

Many studies have investigated the effectiveness of a variety of technologies for treatment of industrial wastewaters with increased concentration of dangerous organic matter. Nowadays, there are many ways to solve these kind of problems: biological and enzymatic processes, membrane and electromembrane technology, oxidation and advanced oxidation processes (AOP), evaporation and many others. All of the methods have their advantages, but also economical and technical limits of their usability. In our case, we dealt with a problem of landfill leachate treatment. We used reverse osmosis, ozonation and Fenton's reaction in various combinations to reduce the organic matter content in the wastewater from the landfill. The AOP processes we used did not achieve complete destruction of the organic compounds, but only degraded to simpler organic compounds. The best result was achieved by combination of ozonation and reverse osmosis.

Keywords: Landfill leachate; Membrane processes; Reverse osmosis; AOP; Ozonation

1. Introduction

1.1. AOP processes

Chemical oxidation is a widely studied method for the treatment of the wastewater with high concentration of organic compounds. Nowadays, there is a growing interest that has been focused on advanced oxidation processes (AOP). Most of them, except simple ozonation (O_3), use a combination of strong oxidants, e.g. O_3 and H_2O_2, ultraviolet and ultrasound irradiation, and catalytic reaction of metal ions or photocatalyst. Typical AOP processes are [1]:

(1) Homogeneous system

  (a) With irradiation:

    (i) O_3/ultraviolet
    (ii) H_2O_2/ultraviolet
    (iii) Electron beam
    (iv) Ultrasound
    (v) H_2O_2/ultrasound
    (vi) Ultraviolet/ultrasound
    (vii) H_2O_2/Fe^{2+}/Ultraviolet (photo-Fenton's reaction)

---

*Corresponding author.

Presented at the MELPRO 2014 Conference Membrane and Electromembrane Processes, 18–21 May 2014, Prague, Czech Republic

  - (b) Without irradiation:
    - (i) O_3/H_2O_2
    - (ii) O_3/OH^-
    - (iii) H_2O_2/F^{2+} (Fenton's reaction)
- (2) Heterogeneous system
  - (a) With irradiation
    - (i) $TiO_2/O_2/UV$
    - (ii) $TiO_2/H_2O_2/UV$
  - (b) Without irradiation
  - (c) Electro-Fenton's reaction

Nowadays, most of AOP processes that have commercial applications are actually a combination of two or more processes, and usually ozonation is one of them. Ozone forms a variety of free radicals species through a sequential decay cycle in water. Ozone also forms hydroxyl radicals when it reacts with high molecular organic compounds. At high pH values, free radicals scavengers such as carbonate ions compete for these radicals with organic compounds; thus, the effectiveness of ozonation processes diminishes at high pH [2].

However, many other factors besides the pH influence the extent of removal of organic compounds by AOP. The most important is the concentration and character of organic and inorganic compounds in the feed water; but the oxidant dose, temperature and other general water-quality characteristics can influence the result of oxidation. Another factor in the use of oxidation for the macromolecular organic compounds removal is that the chemical reactions between oxidants and organics might produce undesirable products [1,3]. So the ozonation does not cause the complete destruction of organic molecule, but "tear" it to other simpler organic compounds. Hence we use other technologies, like bioreactor or reverse osmosis, to remove the organic wastes from the wastewater.

1.2. Reverse osmosis

The reverse osmosis is one of the pressure membrane processes. This process is generally known and frequently used for water demineralization in many industrial branches. A semi-permeable membrane is used for separating substances dissociated in water [4]. This process is based on the ability of the semi-permeable membrane to pass water and to retain micro-organisms, colloids, ions of dissociated salts as well as molecules of organic substances. The liquid is able to pass the membrane in case if the hydrostatic pressure gradient is higher then osmoic pressure.

Literature has shown the reverse osmosis is very effective in removing organic compounds to a high degree [1,4].

However, there is some major drawbacks for the implementation of pressure-driven membrane processes, and particularly RO, to the treatment of wastewater with high organic content: membrane fouling (which requires extensive pretreatment or chemical cleaning of the membranes, results in a short lifetime of the membranes and decreases process productivity) and the generation of large volume of concentrate (which is unusable and has to be discharged or further treated) [5].

1.3. Fenton's reaction

It is not a selective but an efficient method of removing organic pollutants. The destruction of the organics molecule is caused by hydroxyl radical, which appears in reaction of hydrogen peroxide under the catalytic action of iron. This reaction, discovered in the late nineteenth century, shows the first stage of Fenton's process—reaction between hydrogen peroxide and divalent iron in the low pH range [6]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^{\cdot}$$

The Fe^{3+} ions can react with H_2O_2 and hydroperoxide radicals to regenerate back to Fe^{2+}:

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + OOH^{\cdot}$$

$$Fe^{3+} + {}^{\cdot}OOH \rightarrow Fe^{2+} + O_2 + H^+$$

In oxidation of organic molecule, the initiation reaction can take place by two ways:

(1) Dehydrogenation (alkanes and alcohols):

$$CH_3OH^{\cdot} + OH \rightarrow CH_2OH + H_2O$$

(2) Addition (unsaturated hydrocarbons and aromates):

$$OH^{\cdot} + C_6H_6 \rightarrow C_6H_6(OH)$$

2. Experiments and results

2.1. Fenton's reaction

The wastewater we used was the real water from the landfill, and it has been pretreated by coagulation and filtration before the laboratory experiments. Because in the Fenton's reaction the ions of iron are needed as catalyst for the decomposition of organic substances, we decided to include this process to the technological line of landfill leachate treatment after the clarification—we used $FeCl_3$ as the coagulant in pretreatment stage and lots of iron ions has been remains in the water. Subsequently, to use this iron as a catalyst, it would be necessary only to change the pH and add the hydrogen peroxide [7,8].

It was decided to provide the experiment with trivalent iron salt, with the same dose of ferric chloride, which was calculated in the coagulation tests—1.2 g/l. Despite the fact that in this case it could have lower efficiency in removing organic substances by Fenton's reaction—experimentally, it was found that in this case there was a much lower concentration of iron ions in treated water. The amount of hydrogen peroxide was adjusted to a dose of iron, so that the molar ratio of ferric ion to hydrogen peroxide was 1:10, which represents about 2.5 g of hydrogen peroxide [1,9].

To Erlenmeyer flask, which was placed on a magnetic stirrer, was measured 0.5 l of the sampling water. This water was the sample of a real clarified landfill leachate. The pH was adjusted to 2.3 by dosing of sulphuric acid. Ferric chloride was added as a 40% solution, and then while stirring, one portion of hydrogen peroxide was added. The experiment was performed at laboratory temperature.

Every 10 min, the samples were withdrawn from the flask for analysis. Experiment duration was 1 h.

The kinetic of the COD removal during the experiment is shown in Fig. 1.

As we can see from the results, the efficiency of removing the organic compounds by Fenton's reactions under these conditions was not higher than 42%. Furthermore, it was found that the consumption of acid for pH regulation for the correct course of Fenton's reaction is very high and as a result of this, the water had much higher salinity.

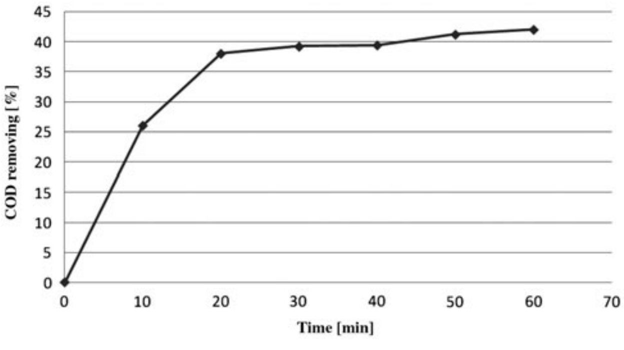

Fig. 1. The process of removal of COD during the Fenton's reaction.

2.2. O_3/H_2O_2

For the ozonation tests, we used the laboratory generator of ozone LIFEPOOL 1.0/OXCW by LifeTech. The source of oxygen for generating the ozone was obtained by the oxygen pressure bottle which supplies oxygen with purity of 99.5%. Ozonation of water samples was performed in a glass column of internal diameter 5.5 cm and a height 80 cm. Glass column was filled with 1 l sample. The lower part of the column is fitted with a frit, which ensures an uniform distribution of ozone in the whole volume of the sample and provides a relatively small gas bubbles. Just above the frit and the top of the column are valves for sampling.

With this laboratory unit, the regulation of ozone generation and oxygen flow can be achieved by the production of ozone in the range 0.2–7 g/h.

In case of using a combination O_3/H_2O_2, the hydrogen peroxide (30% solution) was added all at once in the start of the experiment directly into the column.

All experiments were performed at laboratory temperature of 21–24°C.

Experiments were carried out at two pH values: the original (6.7) and in the high alkaline range (initial pH value was adjusted to 12). For alkalization process, concentrated NaOH solution of 5 ml was added to 1 l of water to adjust the pH to 12 was needed 5 ml to 1 l of water.

The experimental results can be summarized as follows:

- During the experiment of the treatment of the real clarified landfill leachate by ozonation, it was impossible to reduce the concentration of COD under the limits of detection. The best result we achieved was by removing 65% of COD.
- Ozonation at the original, neutral pH reached a higher efficiency of COD removing than ozonation at pH 12.
- The kinetic of the COD removal during the experiment with neutral pH range is shown in Table 1.
- Addition of hydrogen peroxide brings the positive result in efficiency of COD removal, only at ozonation, at neutral pH, but at the cost of higher consumption of ozone. The lower efficiency of ozonation in the alkaline pH range can probably be caused by specific content of inorganic solids in the water—high concentrations of chloride or bicarbonate ions.

Table 1
Some parameters of ozonation experiment with neutral pH and dosing the hydrogen peroxide

Time, min	0	20	60
pH	6.7	8.3	8.4
COD, mg O_2/l	460	350	160
E, %		24	65

The parameters of best achieved result:

Sample volume: 1 l, Gas flow rate: 1 l/min, Total O_3 dose: 3.7 g, Relate O_3: 2.4 g, H_2O_2 dose: 1 g.

2.3. Reverse osmosis

The experiment of reverse osmosis was like the pilot-scale testing of the real landfill leachate. The clarification and the sand filtration were chosen for the pretreatment of this technology. Pilot testing took place in the summer for about 50 d. All the technological components were placed in the storage container of appropriate size, which was situated in the landfill and installed in the immediate vicinity of the landfill leachate collection pit. Waste streams have been discharged back into the pit (Table 2).

How can we see, the treated water has very low mineralization, and the efficient of COD removal is nearly 100% (organic compound are under the limits of quantification).

Table 2
Some parameters of the wastewater before and after reverse osmosis

Parameter	Feed water	Treated water
pH	7.6	6.8
TDS, mg/l	4,950	119
TSS, mg/l	172	
COD, mg O_2/l	894	<5.0
Cl^-, mg/l	1,090	36.8
Mn, mg/l	1.13	0.00450
Al, mg/l	1.99	<0.010
As, mg/l	0.250	<0.0050
B, mg/l	6.86	4.64
Ca, mg/l	126	0.194
Cr, mg/l	0.176	<0.0010
Fe, mg/l	14.5	0.0028
K, mg/l	756	26.4
Mg, mg/l	104	0.133
Mn, mg/l	1.13	0.00450
Na, mg/l	937	32.6
P, mg/l	4.94	<0.010
Pb, mg/l	0.022	<0.0050

3. Conclusion

Based on the laboratory and pilot testing, we designed the technological line for the landfill leachate treatment. This line includes the pretreatment stage: clarification and sand filtration, O_2/H_2O_2 process to reduce the concentration of organic compounds and reverse osmosis.

The role of pretreatment stage:

- reducing the TSS in the feed water to protect the membranes and decrease the consumption of ozone;
- reducing the oils, which can cause problems for both following technology stages.

The role of O_2/H_2O_2 process stage:

- reducing the concentration of organic compound to solve the problem with fouling of the reverse osmosis membranes;
- reducing the concentration of ammonium;
- reducing the concentration of iron.

The role of reverse osmosis process stage:

- removing organic and inorganic compounds from the water.

Even the combination of these processes will not be able to solve the problem with large volume of concentrate (nearly 25% of feed water). To reduce the volume of concentrate, the next technology stage is needed—it could be e.g. vaporizer or electrodialysis process.

References

[1] S. Renou, J.G. Givaudan, S. Poulain, F. Dirassouyan, P. Moulin, Landfill leachate treatment: Review and opportunity, J. Hazard. Mater. 150 (2007) 468–493.

[2] C.A. Lee, K.J. Howe, B.M. Thomson, Ozone and Biofiltration as an Alternative to Reverse Osmosis for Removing PPCPs and EDCs from Wastewater, The University of New Mexico, New Mexico, 2010.

[3] J. Chudoba, M. Dohanyos, J. Wanner, Biologicke cisteni odpadnich vod (Biological treatment of the wastewaters), SNTL, Prague, 1991.

[4] Z. Honzajková, M. Kubal, M. Podhola, Membranove technologie a jejich pouziti pri cisteni podzemnich vod a skladkovych vyluhu (Membrane technology and their using for the treatment of groundwater and landfill leachate), Chem. Listy 105 (2011) 245–250.

[5] J. Lozier, A. Fernandez, Using a membrane bioreactor/reverse osmosis system for indirect potable reuse, Water Sci. Technol.: Water Supply 1 (2001) 303–313.

[6] P. Pitter, Hydrochemie (Hydrochemistry), ICT Prague, Prague, 2009.

[7] P. Dolejs, N. Kalouskova, M. Macek, Prirucka pro cisteni a upravu vody (Guide for water treatment and purification), KEMIFLOC, a.s., Přerov, 1996.

[8] M. Horakova, Analytika vody (Water analysis), ICT Prague, Prague, 2010.

[9] J. Zábranská, Laboratorni metody v technologii vody (Laboratory methods in water technology), ICT Prague, Prague, 2007.