

## THE REMOVAL INVESTIGATION OF NONYLPHENOL ETOXILAT SURFACTANTS IN ACTIVATED SLUDGE SYSTEMS

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Received: 2014.02.21  
Accepted: 2014.06.06  
Published: 2014.07.01

### ABSTRACT

The most significant source of environmental pollution derived from perilous wastes is the circumstantial and intentional emancipation of specific industrial wastes including resistant and/or toxic pollutants to natural environments. Although, biological treatment methods have been commonly found as most effective alternatives in the removal of persistent compounds in industrial wastewaters, they require some increase for obtaining acceptable removal efficiencies, due to the presence of refractory or toxic compounds in the wastewaters. In this study, the use of surfactant of nonylphenol ethoxylates (NPE) in the removal of persistent organic pollutants by biological treatment processes was investigated as an enhancement technique. The application of surfactants can enhance soil and groundwater remediation by increasing contaminant locomotion and solubility to ameliorate the performance of practical conventional remediation technology and by barricading the departure of contaminants to speed the rate of biodegradation of contaminants in environment. The proven effectiveness of surfactants in soil and groundwater remediation has been considered reasonable to expect that surfactants can also enhance the removal of persistent organic pollutants in wastewaters. Different concentrations of nonylphenol ethoxylates (NPE) (1000, 1500, 2000 ppm) were tested to optimize biosurfactant-enhanced degradation of persistent pollutants in wastewaters. The results of this study demonstrate that the biodegradation of persistent organic pollutants in wastewaters is elevated by the use of biosurfactants. The principal mechanism that raises the biodegradation is the augment solvability of poorly soluble compounds in the wastewater. According to the results of this study, it can be anticipated that biosurfactant-enhanced degradation would result in faster and more complete degradation.

**Keywords:** nonylphenol ethoxylates, surfactants, treatability, activated sludge systems, COD.

### INTRODUCTION

APEs have been significant surfactants for more than 50 years. The most joint APE in mercantile use today is the group of nonylphenol ethoxylates (NPEs), comprising about 80 percent of the market, while octylphenol ethoxylates (OPEs) contain most of the remaining 20 percent of the market. NPEs are used primarily for industrial applications, including pulp and paper production, textile structure, and use in the

formulation of crop protection chemicals. They are also used in industrial, institutional, and homemaker cleaners and detergents. While NP is used primarily as a raw material in the generation of NPE, some is also used in the production of plastics, resins and stabilizers. In contrast, OP is made in significantly lower volumes and is used primarily as a chemical intermediate in the generation of phenolic resins [APEREC, 2006]. Derivative of Alkylohenol ethoxylates is given in Table 1.

**Table 1.** Acronyms of Alkylphenol Ethoxylates and their derivatives

Compound or Chemistry	Acronym
Alkylphenol ethoxylates	APE
Alkylphenol	AP
Alkylphenol ether carboxylates	APEC
Carboxylated alkylphenol ether carboxylates	CAPEC
Nonylphenol ethoxylates	NPE
Nonylphenol	NP
Octylphenol	OP
Octylphenol ethoxylates	OPE

### Environmental issues arising from NP

The US Environmental Protection Agency (US EPA) has recently consummated ambient aquatic life water modality criteria for nonylphenol (NP) [US EPA, 2005]. These criteria were expanded under Section 304(a)(1) of the Clean Water Act and indicate the concentration of NP in water at which aquatic life are safe from acute and chronic adverse effects. The US EPA has counsel an acute freshwater touchstone of 28  $\mu\text{g/L}$  and a chronic freshwater criterion of 6.6  $\mu\text{g/L}$  for NP. For saltwater, the proposed sharp and chronic criteria are 7.0  $\mu\text{g/L}$  and 1.7  $\mu\text{g/L}$ .

### Environmental Fate of APEs and NPE

Biodegradation is the overcoming removal process for APEs and NPE in water, settlement and soil. The biodegradation of APEs and NPE has been palmate studied for the past 50 years in a diversity of laboratory studies that have searched both primary and final degradation. Accurate screening tests that measure the ready biodegradability of different APEs and NPE, laboratory modeling tests of potential degradation in specific environmental compartments, and field confirmation studies show that NPE and APEs are extensively biodegraded in surface waters, alluvium, and soil. Collectively, the data from these tests indicate that NPE and APEs, and their degradation moderator are not forestalled to be persistent in the environment. Removal yield for laboratory scale semi-continuous or batch activated sludge and continuous flow activated sludge systems are generally over 90 percent.

### Investigations accomplished in this Topic

A collation of the definitive biodegradability (transformation of organic carbon to  $\text{CO}_2$ ) of AE

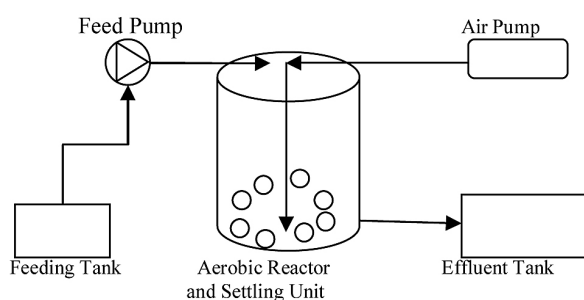
and NPE was manufactured in an improved Sturm test [Sturm, 1973]. Habituate activated sludge cultures from the AE and NPE units were incubated with 50 mg/l surfactant and the rate of  $\text{CO}_2$  formation measured over 14 days at 25 °C. AE was quickly and extensively oxidized to 70–75% of the theoretical  $\text{CO}_2$  yield. Organic carbon from the NPE ethoxylate, however, was metabolized to 25–30% of the theoretical  $\text{CO}_2$  yield during the same period headings should not be indented).

Studies by Yoshimura [1986], and Stephanou and Giger [1982] have also shown that waste water sewage from act NPE-type surfactants are extremely toxic (e.g.,  $\text{LC}_{50}$  – 48 hours) to fish and *Daphnia* in the presence of residual ethoxylate (5–10 mg/l), nonylphenol ethoxyacetate metabolites (9–10 mg/l) and nonylphenol (0.15–0.3 mg/l).

## MATERIALS AND METHODS

### Experimental system

A schematic diagram of the experimental set-up is showed in Figure 1. A continuously stirred tank reactor (CSTR) was used in the experimental study. Volume of the aerobic reactor was 4 liter. The influent wastewater was continuously fed through the top of the reactor by a feed pump and the reactor was aerated by an air pump. The effluent from the precipitation tank was collected in an effluent tank.



**Figure 1.** A schematic diagram of the activated sludge bioreactor used in experimental studies

### Preparation of activated sludge

A mixed culture was used in the aerobic reactors. The activated sludge culture was received from the wastewater treatment plant of Oil National Company in Tehran, Iran. The aerobic reactor was inoculated with this culture. The constituents of wastewater used throughout the studies are given in Table 2. Whilst the main substrate requirement is for carbon, the growth also de-

depends on the intake of nitrogen and phosphorus. The optimum ratio of C:N:P in the mixed liquor is generally thought to be 100:5:1. The ratio of these nutrients in settled domestic sewage is variously reported as 100:17:5 or as 100:19:6. This indicates that nitrogen and phosphorus will not be limiting for growth. Trace ingredients, which include S, Na, Ca, Mg, K, and Fe are also required, and are available in plenty in domestic sewage. By contrast, wastewater from brewing, pulp and paper, and food-processing industries can be deficient in nitrogen and phosphorus. Nutrients therefore need to be added to the mixed liquor to receive maximum bacterial growth and to optimise carbonaceous treatment. From an operational point of view, lack or insufficiency of a critical nutrient may result in incomplete treatment, because the bacteria are unable to grow optimally.

Phosphor, Nitrogen, Carbon and Oxygen are required that were added every day. In the starting test, first and second day the sludge settling time was two hours then collected the dead cells. On the third day sludge feeding began. The amount of feed was equal to glucose 7.5 g/day, Ammonium phosphate 0.34 g/day and Ammonium nitrate 0.93 g/day. The feeding was done for a week. So the culture was ready for testing.

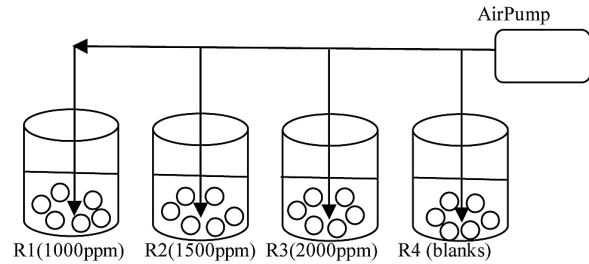
**Table 2.** Inorganic constituents of microorganismos

Chemical Compounds	Percent
MgO	8
K <sub>2</sub> O	6
Fe <sub>2</sub> O <sub>3</sub>	1
P <sub>2</sub> O <sub>5</sub>	50
SO <sub>2</sub>	15
Na <sub>2</sub> O	11
CaO	9

**Experimental procedure**

Four reactors with the same structure and volume, as explained above, were used in parallel tests. Experiments were start up batchwise. Activated sludge from wastewater treatment plant was added to the reactors as seed. The similar value of sludge was inoculated in four parallel reactors. The test reactors (R1, R2 and R3) contained biosurfactant. The NPE biosurfactant concentration were added to R1, R2 and R3 respectively: 1000, 1500, 2000 ppm. In the control reactor (R4), the feed water did not contain any surfactant in or-

der to specify the effect of surfactant. Each of the test series dissolve in distilled water and make up 1 litter. All of the reactor was aerated by an air pump. These conditions were Fixed for the entire duration of the experiment. The temperature and pressure were 25 °C and 625 mmHg and pH adjusted to 7. A schematic diagram of the experimental setup is showed in Figure 2.



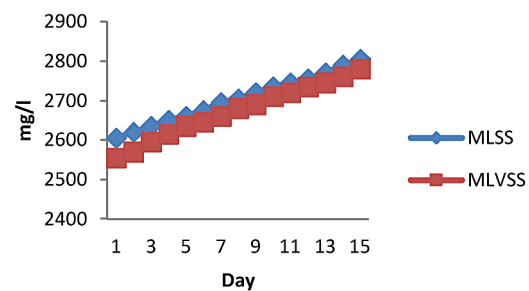
**Figure 2.** Schematic diagram of the experimental setup

**RESULT AND DISCUSSION**

A set of experiments were performed in three different surfactant concentration, for two weeks. The method was based on measurements of American Public Health Association (APHA), 1998.

The rate of MLSS and MLVSS of activated sludge in the experimental period is shown in Figure 3. When sludge age was increased for 14 days, MLSS and MLVSS ratio were increased 2605 to 2805 mg/l and 2555 to 2780 mg/l respectively.

COD removal efficiency with the increase of residence time as shown in Table 3. At the 3 days, COD removal efficiencies was from 5.19% to 48.24 in R1, it was from 7.61% to 48.91 in R2 and 8.14 to 34.89% in R3. Reduction was observed in the first week, equal to 97.49% in R1,90.58% in R2 and 84.69% in R3. Although,in this period at R1 and R2 greater amount from COD were eliminated, in the last, the overall results show that the highest COD decrease was in R3.

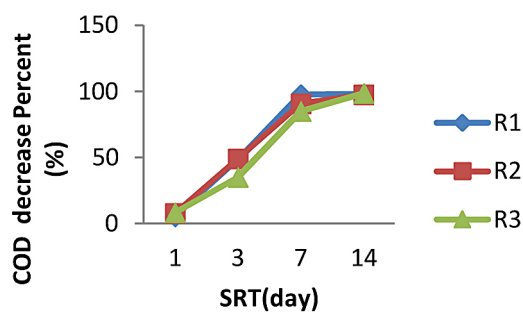


**Figure 3.** The rate of MLSS and MLVSS of activated sludge in during the test

**Table 3.** Comparison of operational parameters of the reactors with different surfactant concentration

Reactor	Run	SRT	COD Removal
		(day)	Efficiency (%)
R1	Run 1	1	5.19
	Run 2	3	48.24
	Run 3	7	97.49
	Run 4	14	97.78
R2	Run 1	1	7.61
	Run 2	3	48.91
	Run 3	7	90.58
	Run 4	14	97.42
R3	Run 1	1	8.14
	Run 2	3	34.89
	Run 3	7	84.69
	Run 4	14	98.34

Figure 4 depicts a shift of COD volumetric removal rates with over time. Sharp slope increase in COD volumetric removal rate with the time in R1, R2 and R3 because of high decreases in COD concentrations occurs in the first 7 days. After that, the removal rate is linearly. The results show, decline slope in the R1 and R2 is more than R3. But at the end of the test, the maximum removal occurs at the highest concentration. At the end of two weeks, more than 98% of COD removal was observed in R3 with concentration Equivalent 2000 ppm NPE

**Figure 4.** The effect of surfactant concentration on COD volumetric removal rates in the test reactors

## CONCLUSIONS

In this paper, the authors investigate the impact of NPE at activated sludge system and COD removal in conventional systems of biological treatment. Increasing the concentration of surfactant would lead to treatment plant efficiency enhance. Also the results showed that increasing the

concentration of solids MLSS makes the removal efficiency increase.

According to the results of this study, it can be completely proven by further investigations that biosurfactant-enhanced degradation would result in prompter (reduced treatment times) and modified water quality, and overall cheaper treatment costs.

The interaction between biosurfactant and the pollutants in wastewater is a very complex phenomenon and is not the subject of this study. But it is possible to say that biosurfactants are very effective in the COD removal as demonstrated in this study. So, the effectiveness of different biosurfactants in the removal of more pollutants should be investigated in the future studies in order to distinguish the best combination.

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