Removal of nonyl phenol ethoxylates in water by catalytic ozonation in presence of silica supported - cobalt nanoparticles

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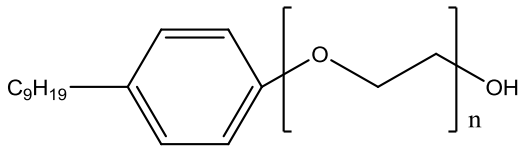
ABSTRACT

The catalytic ozonation of nonionic surfactant nonylphenolethoxylate (NPE) as pollutant in wastewater and its degradation in the presence of silica-supported Cobalt oxide nanoparticles was studied. Characterization of silica supported- cobalt oxide was made using XRD patterns and SEM profiles. The influence of pH, initial NPE concentration, ozonation time and catalyst contents in ozonation process was also investigated. Results show that NPE removals by using silica supported-cobalt oxide catalytic systems are higher than that of using single ozonation. About 99% NPE were removed within 10 min at 30^oC. Furthermore, in this condition more than 50% of total carbon of NPE was mineralized.

Keywords: *nonyl phenol ethoxylate, catalyst, ozonation, Co_3O_4, mineralisation*

1. INTRODUCTION

Nonyl phenol Ethoxylates (NPEs) are nonionic surfactants belongs to alkyl phenol ethoxylates family having structure as following:



Commercial NPEs has n value being from 2 to 16. They are widely used in industrial production such as agriculture, leather, metal, petroleum, pulp and paper, paints, adhesives, coatings, cleaners…NPEs decomposes in strong bases, strong acids or strong oxidizing agents. The shorter length of ethoxylate chain, the more toxic NPEs are. The decomposition of NPE could produce hydrophobic NP, NP1EO, NP2EO having smaller biodegradation rate [1-2] and the carboxylic acid nonylphenols (NP2EC or NP1EC), NPEO having toxicity higher NPE.

Among the methods for treating NPE and other pollutants, ozonation and other advanced oxidation processes (AOPs) are paid more attention since they are "environmental friendly". Based on hydroxyl-free radicals (*OH)

which are immediately generated during the reaction they can decompose the compounds into reaction products with less toxicological effect rather than simply separating them from the flow (such as adsorption or membrane processes). Ozonation is often applied in oxidation processes thanks to its advantages among other common oxidation agents. The oxidizing agent creates the hydroxyl radicals (*OHs) such as H_2O_2, O_3… which will continue take part in intermediate chain reactions.

Additionally, some results have suggested that the surface reactive oxygen species in heterogeneous catalysts might also play an important role in catalytic ozonation of ibuprofen, sodium dodecyl sulfonate...[3,4,5,6]. Many metallic oxides as catalysts could afford this property such as Fe_2O_3, Al_2O_3, MnO_2, Ru/CeO_2, TiO_2, Fe^{2+}, Fe^{3+}, Mn^{2+},.... Some porous materials like silica, activated carbon have been used as adsorbents or catalyst supports. They are effective for the ozonation process in increasing the production of free *OH radicals in aqueous solution and adsorbing organic substances.

Cobalt exhibits several possible oxidation states (Co^{2+}, Co^{3+}, and Co^{4+}), including several types of coordinations (tetrahedral, pyramidal and octahedral). Co_3O_4 nanoparticles exhibit weak ferromagnetic behavior. CoO nanocrystals display superparamagnetism or weak ferromagnetism, whereas bulk CoO is antiferromagnetic.

Co_3O_4 is a magnetic *p*-type semiconductor. Co_3O_4 has a cubic spinel crystal structure in which the Co^{2+} ions occupy the tetrahedral sites and the Co^{3+} ions the octahedral sites. The Co^{3+} ions at the octahedral sites are diamagnetic in the octahedral crystal field. The Co^{2+} ions at the tetrahedral sites form an antiferromagnetic sublattice with a diamond structure. Consequently, cobalt oxides present a broad field for the creation of many frameworks in view of their stoichiometric and non-stoichiometric oxides, and mixed electronic valency of cobalt, and the presence of oxygen vacancies. This multi-electronic valence and rich coordinationis proper to cobalt oxides in comparison to other 3d metal oxides. This provides cobalt the ability to be present in various spin states in its oxide forms: low, high, as well as intermediate spin. The cobalt spinel compounds can act as efficient catalysts in a lot of heterogeneous chemical processes. Among different synthesis techniques for cobalt oxide, the liquid-phase syntheses offer a good way and control for tailoring the structures, the compositions, and the morphological features of nanomaterials. The liquid-phase routes include the coprecipitation, the hydrolytic as well as the nonhydrolytic sol–gel processes, the hydrothermal or solvothermal methods, the template synthesis and microemulsion-based processes. Cobalt oxide nanoparticles with different morphologies such as spheres, rods, wires, cubes and porous structure have been reported. Sol-gel method has been widely used for the synthesis of Co_3O_4 nanoparticles where controlled fabrication of particles could be achieved by varying synthetic parameters such as reaction temperature, time and concentration of reagent [7,8].

To clarify the role of Co_3O_4 catalyst in catalytic ozonation of nonylphenol ethoxylate, the Co_3O_4-SiO_2 material was prepared and tested for the ozonation decomposition of NPE. Methods of X-ray diffraction(XRD), Brunauer-Emmett-Teller (BET) surface area measurement,

SEM images were used to characterise the catalyst.

2. EXPERIMENTAL

Reagents

All chemicals were analytical grade and used without further purification. Nonylphenol Ethoxylate (NPE), silica were purchased from Sigma-Aldrich. Cobalt (II) nitrate hexahydrate, urea, acetonitrile, ammonium acetate, ammonium chloride were from Merck.

Synthesis of Co_3O_4- SiO_2

The material containing cobalt oxide supported on silica used as catalyst was prepare using sol-gel method [9]. In a typical experiment, 1g of silica was dispersed in 500mL of 10mM cobal tnitrate hexahydrate solution and sonicated for 3 min. After that, 10g of urea was added. The mixture was heated at 85^{o}C and stirred for 6 h. During the reaction, the color of the mixture changed from pink to violet indicating the formation of α-cobalt hydroxide. The mixture was then cooled to room temperature, filtered using Munktell® paper, washed with Millipore® water several times and dried overnight in the oven. The obtained product was calcined in a muffle furnace (Lenton thermal®) under air at 500^{o}C for 3 hours at heating rate of 2^o/min. The as-prepared product would be Co_3O_4-SiO_2.

Characterization of catalyst

Structural analysis of the synthesized samples was carried out using powder X-ray diffraction on a Brucker AXS D8 diffractometer over the 2θ range of 10-90^o and the scan rate was of 1^o/min. Copper was used as the target (Cu-Kα; λ = 1.5406 Å).

Morphological studies of the samples were carried out using Hitachi S-4800 II Field Emission Scanning Electron Microscope (SEM) with light element analysis using energy dispersive spectroscopy (EDS) operating at 10 kV. Nitrogen adsorption-desorption measurement was also made at 77K using BET method for specific surface area of the catalyst.

Ozonation of NPE9 with Co_3O_4-SiO_2

Ozone was produced from dry air by use of Vina Ozone Generator model VN3 using Cold Plasma Technology. Ozone flow was measured by a ball flow rate meter. The concentration of ozone in aqueous solution was determined by UV-Vis spectrometer model T70+ manufactured by PG Instrument Ltd. at 258 nm. Molar extinction coefficient is of 2950 $cm^{-1}M^{-1}$.

The flask containing NPE placed on a magnetic stirrer at 80rpm was used as ozonation reactor. The superflous ozone was adsorbed by activated carbon in aqueous absorption flask. The pH of the solution was adjusted by HCl or NaOH. The Ozone flowrate was controlled by needle valves.

After ozonation, in order to avoid the influence of organic compounds in the mixture, residual ozone concentration was determined by indirect method in place of UV method: Ozone reacts with KI in solution to produce I_2 which rapidly forms complex with p-phenylenediamine for a UV-VIS absorption at λ = 540 nm and using Beer-Lambert equation A = ε.l.C where A is the absorbance measured (unitless), ε is the molar absorption coefficient (ε = 3300 $mol^{-1}cm^{-1}$), l is the cuvette length (cm), C is the concentration of ozone (mole/L) [9].

Determination of NPEs concentration

Determination of NPEs concentration was done by LC-MS of Agilent 1200 series with Quadrupole LC/MS 6120 detector, scan positive 100–1000 with fragmentor 70V, acetonitrile and 5mM Ammonium acetate (80:20, v/v) buffered. Millipore water was used as mobile phase solvent. The flowrate of the solvent was kept at 0.5 mL/min and a XDB-C18 column of Agilent (4.6x150 mm, 5µm) was used.

LC-MS confirmation and quantification of the concentration of NPEs were based on sum of each NPE with the number of ethoxylate group from 2 to 16. The chromatogram of NPEs was presented in Fig.1. and its mass spectrometry in Fig.2.

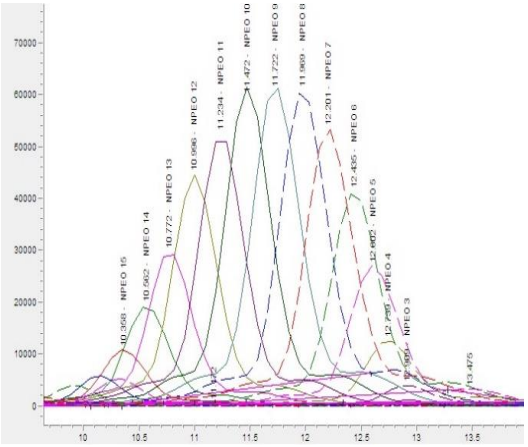


Figure 1. Chromatogram of NPEs

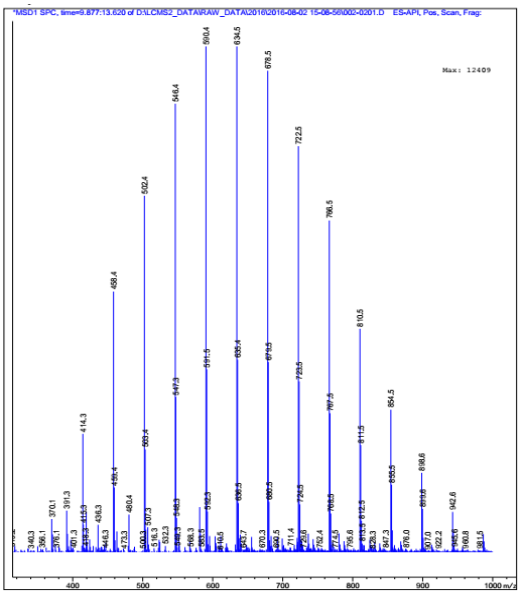


Figure 2. Mass spectrometry of NPEs

NPEs conversion yield (X%) calculated by following equation:

$$X\% = \frac{C_o - C}{C_o} \times 100\%$$

where Co, C are subsequently NPES concentrations before and after treatment.

Mineralization of ozonation was investigated by measuring the mass of the CO_2 gas in absorption of a 0.5M $Ba(OH)_2$ solution. The barium carbonate precipitate was dried at 110^oC for an hour until constant weight. All the experiments were performed under ambient conditions in an environmentally controlled laboratory where the room temperature was 30 ± 1 ^oC. Noncatalytic ozonation (without Co_3O_4-SiO_2) experiments were carried out in addition to catalytic ozonation (with Co_3O_4-SiO_2) experiments for comparison.

3. RESULTS AND DISCUSSION

Characterization of Co_3O_4-SiO_2

Cobalt oxide were obtained by calcination of cobalt hydroxide at 350°C with presence of SiO_2 as support. The XRD diffractogram showed characteristic peak of SiO_2 at 2θ = 15.7°, 25.3°. The diffraction peaks at 19.0°, 31.3°, 36.9°, 55.7°, and 65.2° can be indexed to (111), (220), (311), (422), and (440) planes of Co_3O_4 crystal given by the standard data file (JCPDS file No. 42-1467), space group: Fd-3m (227); lattice constants: a = 8.083 A°). Such sharp diffraction peaks indicate the well crystallization of Co_3O_4 (Fig.3). The particle size calculated from the line broadening of XRD peaks using Sherrer's formula (d = 0.9λ/cosβ) is of 50nm. Specific surface area of the catalyst measured by BET method is about 300 m^2/g.

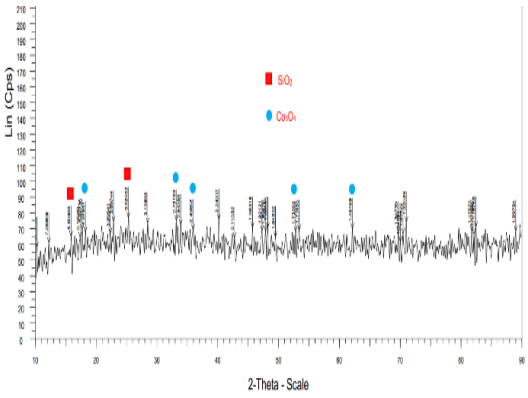


Figure 3. XRD pattern of Co_3O_4-SiO_2

The SEM images of Co_3O_4-SiO_2 in Fig.4 showed the nanorods morphology formed from silica spherical particles. It could be imagined the formation of (silica) – (Co_3O_4) composite after the precipitation of $Co(OH)_3$ on the silica surface. The aggregation of particles is also performed on the images. The shape of cobalt – silica composite oxide looks like rod.

These short nanorods have average length of 200-300nm and diameter of 40-50nm

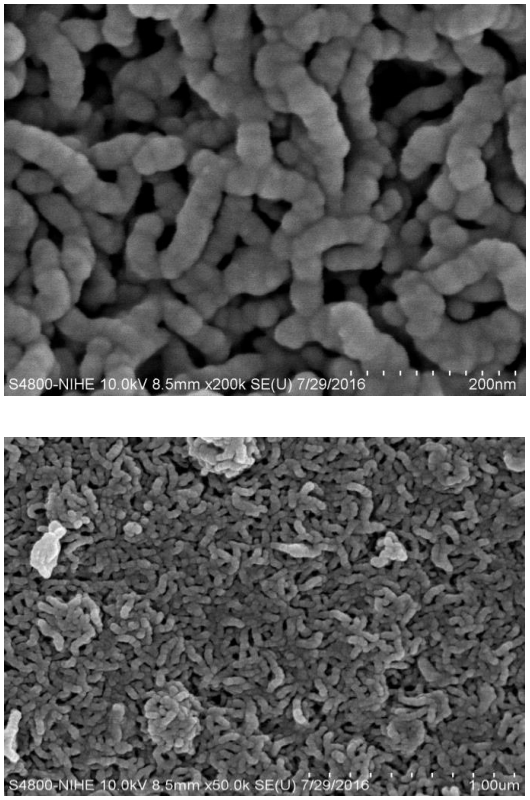


Figure 4. SEM images of Co_3O_4-SiO_2

Effect of initial pH on NPE catalytic ozonation

In the NPE ozonation, the hydroxide ions plays an important role in initiating ozone decomposition which involves a series of reactions as follows [9,10]:

$$O_3 + OH^- \rightarrow O_2 + HO_2^- \; k = 70 M^{-1} s^{-1}$$

$$O_3 + HO_2^- \rightarrow OH + O_2 + O_2^{\bullet -} \; k = 2.8 \times 10^6 M^{-1} S^{-1}$$

$$O_3 + O_2^{\bullet -} \rightarrow O_3^{\bullet -} + O_2 \; k = 1.6 \times 10^9 M^{-1} s^{-1}$$

$$O_3^{\bullet -} + H^+ \leftrightarrow HO_3^{\bullet} \; k = 5 \times 10^{10} M^{-1} s^{-1}$$

$$HO_3^{\bullet} \rightarrow OH^{\bullet} + O_2 \; k = 1.1 - 1.4 \times 10^5 s^{-1}$$

$$OH^{\bullet} + O_3 \rightarrow HO_2^{\bullet} + O_2 k = 1.0 \times 10^8 - 3.0 \times 10^9 M^{-1} s^{-1}$$

During the reaction as an oxidant the ozone molecule has selective electrophility for an interaction with amines, phenols and double bonds in aliphatic compounds. In appropriate medium, the ozone decomposition may also generate active secondary oxidants (mainly $\cdot O^{2-}$ and $\cdot OH$ radicals have higher potential and no selectivity) to oxidize molecules. Ozone is more selective than hydroxyl radical but the latter is stronger in reaction. Thus the reaction paths of ozone and organic compounds determined pH which changed the redox reactions also the amount of $\cdot OH$ radical [7,8].

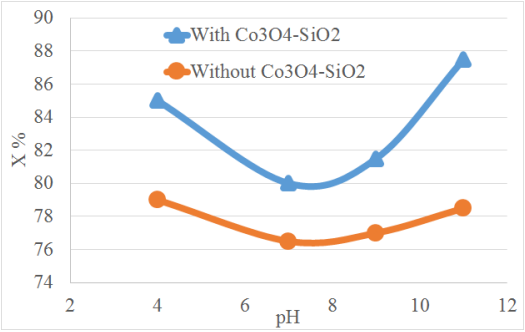


Figure 5. Effect of pH on NPEs ozonation yield (t = 8 min, V_{O3} = 1L/min, $[Co_3O_4\text{-}SiO_2]$ = 0.1 g/L, $[NPEs]_o$ = 20 ppm)

The plots in Fig.5. showed the apparent effect of initial pH on the ozonation efficiency. With Co_3O_4 as catalyst the ozonation efficiency was better than that without catalyst at any pH. After 10 minutes, with catalyst, the NPE ozonation yield reached 88% at pH=11 in comparison to 80% at pH=7 and 85% at pH=4. It is noted above that the mixed valency of cobalt atoms in Co_3O_4 catalyst was important for electron transport. The ability of electrons to transform between various oxidation states of the metallic ions determined the efficiencies of catalysts in redox reactions. This result is similar to our previous work concerning OMS-2 as catalyst in ozonation [3].

For the ozone decomposition on the surface of Co_3O_4 we propose following scheme:

$$O_3 + [Co^{2+}] \rightarrow O_2 + O^-_{ads}[Co^{3+}] \quad (1)$$

$$O_3 + O^-_{ads}[Co^{3+}] \rightarrow O_2 + O_2[Co^{2+}] \quad (2)$$

$$O_2[Co^{2+}] \rightarrow O_2 + [Co^{4+}] \quad (3)$$

The Co^{2+} ions could adsorb ozone so they accelerate ozone to react. In other words, the ozone decomposition could be favored by the presence of redox couple Co^{2+}, Co^{3+}controlled by pH values.

Effect of ozone flowrate

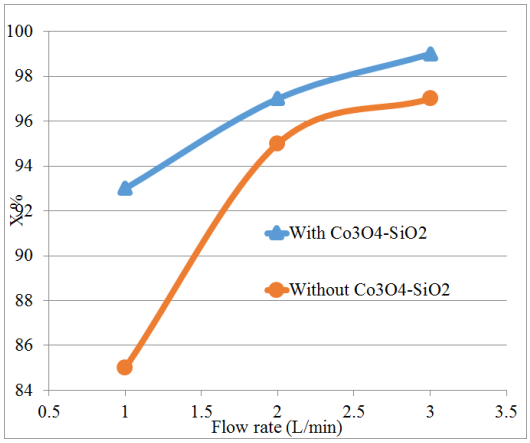


Figure 6. Effect of O_3 flow rate on NPEs ozonation yield (t = 6 min, [NPEs] = 20 ppm, $[Co_3O_4\text{-}SiO_2]$ = 0.1 g/L, pH = 7)

In ozonation the transport of ozone into the solution was very important. An increase of ozone flowrate could conduct a positive reponse to ozone content in solution. This was an acceleration for the reaction and an increase of ozonation efficiency. As shown in Fig.6, after 6 minutes at O_3 flow rate of 3L/min, the decomposition efficiency achieve 99% with catalyst and 97% without catalysts. At small O_3

flow rate of 1L/min, the presence of Co_3O_4-SiO_2 gave a much higher performance.

Effect of initial NPE concentration

The initial NPE concentration in rivers, streams, ponds, lakes, was strongly various in the range of 5-30ppm. It can be seen on Fig.7. that in the same condition, on increasing initial NPE concentration, the decomposition efficiency decreases.

With a small NPE concentration of 5ppm, it took only 2 minutes to decompose almost completely NPE in water. In the same condition, NPE concentration increased fourfold, the ability to treat only reached 65%. It is noted that with an important content of NPE in medium, the rapid formation of foam caused great difficulty to the mass transfer in ozonation process.

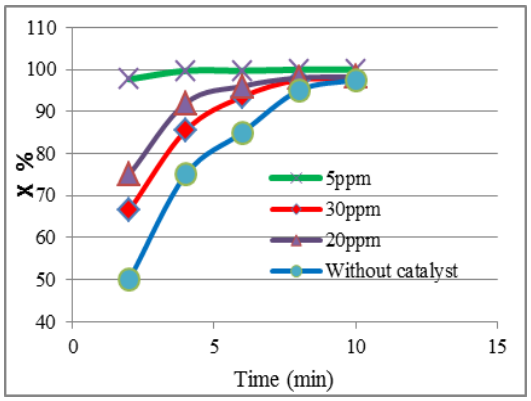


Figure 7. Effect of initial NPE concentration on ozonation yield (V_{O3} = 1 L/min, [Co_3O_4-SiO_2] = 0.1 g/L, pH = 7)

Effect of catalyst content

According to the above proposed possible mechanism of the catlytic ozonation the important role of active surface site (*) were mentioned.

$$O_3 + * \rightarrow O_2 + O* \quad (4)$$

$$O_3 + O* \rightarrow O_2* + O_2 \quad (5)$$

$$O_2* \rightarrow O_2 + * \quad (6)$$

First at all ozone molecules fulfilled a dissociated adsorption on active sites to create active oxygen atoms which then could form active oxidative peroxides or dioxygen radicals. Finally oxygen molecules were liberated along with active sites. In other words, the process involve transfer of electrons from supported metal to ozone molecules with the production of $O_2^{\bullet}$ and $^{\bullet}OH$ generation and further reaction with organic compound [9]. Increasing catalyst amount could give more surface sites for an increase of NPE decomposition yield.

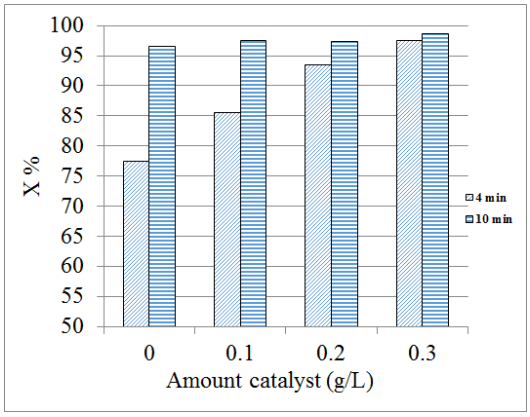


Figure 8. Effect of catalyst content on NPE ozonation yield (V_{O3} = 1 L/min, [NPE] = 20 ppm, pH = 7)

Beside of active sites on Co_3O_4 it is worthy to mention about SiO_2 which could only exchange cations. However SiO_2 alone enhances the ozone decomposition from the collision, adsorption and energy effect.

The examination of the NPE adsorption on surface catalyst without ozonation was done at pH = 7 at various NPE initial concentration.

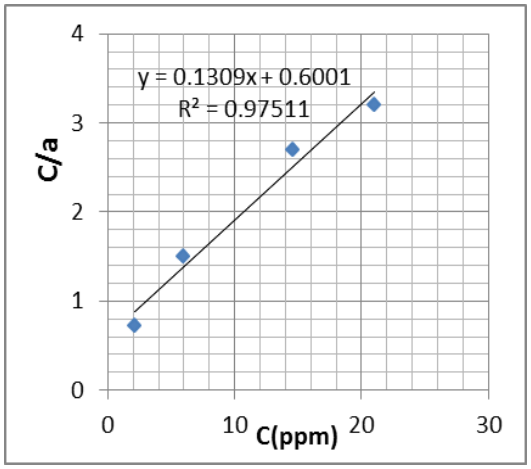


Figure 9. Langmuir adsorption isotherm of NPE on Co_3O_4-SiO_2

The Langmuir adsorption isotherm of NPE on Co_3O_4 –SiO_2 presented on Fig.9 showed the linear relation as equation y = 0,13x + 0,6 (R^2 = 0.975) where C is equilibrium concentration after adsorption and a is adsorption capacity.

Effect of ozonation time

The efficiency of NPEs ozonation gradually increased with the increase of reaction time and showed in Fig. 10.

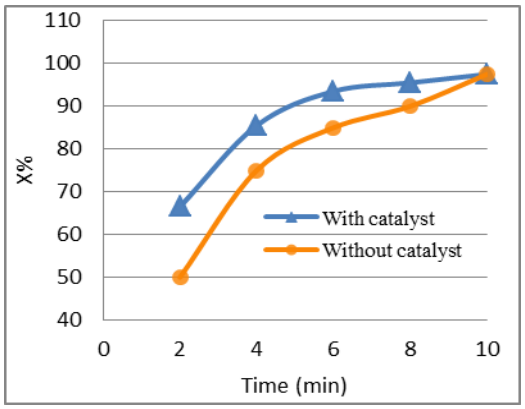


Figure 10. Effect of reaction time on NPEs ozonation yield (V_{O3} = 1L/min, pH = 7, [SiO_2-Co_3O_4] = 0.1 g/L, $[NPE]_o$ = 20 ppm)

Besides, during the NPEs ozonation decomposition, the control of physical properties of the aqueous solution was fulfilled. The conductivity was slightly increased from 2 to 6µS/cm in 10 mins and pH was very slightly changed from 6.88 to 7.06 (Fig.11). It could be thought that the intermediate products of NPE9 ozonation process may a little contribute into the change of H^+ concentration as well as of the conductivity of the solution. The catalytic ozonation using cobalt oxides can increase the yield of ozonation just by creating more hydroxyl radicals on the surface of catalyst, that means the mechanisms of ozonation are nearly the same between catalytic ozonation and basic ozonation. Therefore the products of catalytic ozonation and ozonation would be the same, with a different yield. According to LC-MS analysis, it is interesting that there are no NP in the products. Preliminary investigation showed that more than 50% total carbon in NPE were mineralised after 60 mins of treatment. The study on the distribution of products in degradation ozonation has been continued.

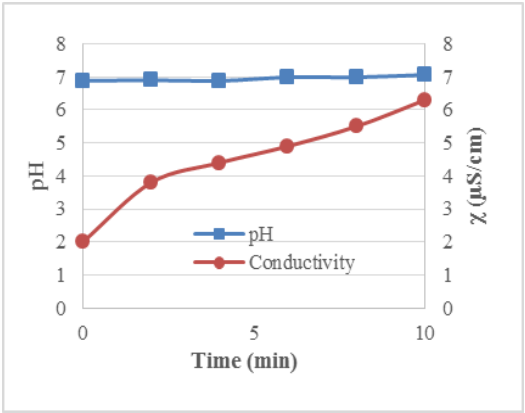


Figure 11. Conductivity and pH change in the NPEs ozonation degradation (V_{O3} = 1L/min, pHo = 7, [SiO_2-Co_3O_4] = 0.1 g/L, $[NPE]_o$ = 20 ppm).

4. CONCLUSION

The degradation ozonation of NPE in the presence of SiO_2-Co_3O_4 as heterogeneous catalyst was investigated. The best ozonation yield of 99% was achieved at temperature of 30^oC, during the reaction time of 10 mins, with an amount of catalyst about 0.1 g/L, at pH of the solution of 11, using inlet ozone flow rate of 3 L/min, along with the initial NPEs concentration of 20 mg/L. In this condition, more than 50% total carbon of NPE were mineralised after 60 mins of treatment. In conclusion, SiO_2-Co_3O_4 catalytic ozonation is a reliable method that can be used as an addition stage in treatment processes to remove NPE from wastewater.

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Xử lý nonyl phenol etoxylat trong nước bằng cách ozon hóa xúc tác với nano oxyt coban - silica

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TÓM TẮT

Quá trình ozon hóa xúc tác và phân hủy chất hoạt động bề mặt không ion NPE (nonylphenolethoxylate) dạng chất bẩn trong nước thải với sự có mặt các hạt nano oxyt coban mang trên silica đã được khảo sát. Các tính chất đặc trưng của oxyt coban mang trên silica được thực hiện bằng nhiễu xạ tia X và chụp ảnh SEM. Ảnh hưởng của pH, nồng độ đầu NPE, thời gian ozon hóa và hàm lượng xúc tác trong quá trình ozon hóa cũng được nghiên cứu. Kết quả cho

thấy NPE xử lý bằng hệ xúc tác oxyt coban mang trên silica nhiều hơn là chỉ dùng ozon đơn thuần. Khoảng 99% NPE được lấy đi trong vòng 10 phút ở 30^oC. Ngoài ra, hơn 50% carbon tổng trong NPE đã bị khoáng hóa trong điều kiện này.

Từ khóa: *nonyl phenol ethoxylate, xúc tác, ozon hóa, Co_3O_4, khoáng hóa*

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