

Photocatalytic degradation of ammonia by light expanded clay aggregate (LECA)-coating of TiO₂ nanoparticles

Masoud Zendehzaban*, Shahram Sharifnia**, and Seyed Nezamedin Hosseini***†

*Faculty of Engineering, Islamic Azad University, South Tehran Branch, Tehran, Iran

**Catalyst Research Center Chemical Engineering Department, Razi University, Kermanshah 67149-67246, Iran

***Research and Production Complex, Pasteur Institute of Iran, Tehran, Iran

(Received 9 June 2012 • accepted 6 December 2012)

Abstract—Photocatalytic degradation of ammonia on supported TiO₂ nanoparticles was investigated. The TiO₂ nanoparticles used as photocatalyst were coated on light expanded clay aggregate granules (LECA), which is a porous and light weight support. Photocatalytic reaction activity of prepared catalyst was determined by ammonia degradation from water synthetically polluted with ammonia. Experiment results showed significantly high photocatalytic activity for the immobilized catalysts. The ammonia was removed more than 85% within 300 min of the process with optimum calcinations temperature 550 °C and pH 11. Kinetics of the photocatalytic reaction followed a pseudo-first order model. XRF, XRD and SEM analyses revealed a rather uniform coating of TiO₂ on the support. By using floated TiO₂/LECA as a photocatalyst in aqueous solution of NH₃, the ammonia was photodegraded into N₂ and H₂ gases, while NO₂⁻ and NO₃⁻ were formed at very low concentrations.

Key words: Wastewater, Photocatalyst, Ammonia, TiO₂, LECA

INTRODUCTION

Presence of ammonia pollution in water is a major threat both to the environment and human health [1]. Ammonia is a source of nutrients as one of the important nitrogen-containing pollutants which reduces dissolved oxygen, decreases disinfection efficiency of chlorine, and exhibits acute toxicity to aquatic life in wastewater effluents [2-4]. The main sources of ammonia pollution in wastewaters include fertilizers, dyes, metal platings, herbicides, pesticides, industrial solvents, chemical, industrials and petrochemical [5,6].

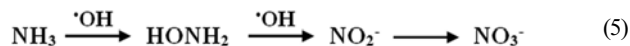
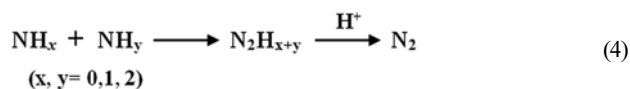
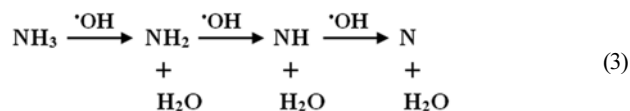
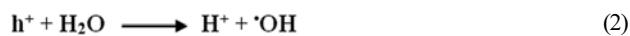
Several methods have been proposed for ammonia removal from wastewater such as biological process [7], stripping [8], ion exchange [9], breakpoint chlorination [10], electrochemical process [11], and photocatalysis [12]. The photocatalytic method for degradation of ammonia is interesting because of its preferences characteristics such as minimal generation of secondary waste, simple operation, remote control, inexpensiveness and high-efficiency [4].

Various structures of nano-TiO₂ have been used for photocatalytic degradation of chemical contaminants [13-17]. Meanwhile, photodegradation of ammonia has also been reported by numerous researchers. TiO₂ supported Pt or Pd catalysts demonstrate that this photochemical reaction treats the ammonia into harmless N₂ and H₂ gases [3,18,19]. The photocatalytic oxidation is activated by ultraviolet (UV) light irradiation (Eq. (1)) [1,5,20-22].



In photocatalytic reactions, the generated positive hole (h⁺) and electron (e⁻) play a major role. Moreover, the hydroxyl produced from the decomposition of water (Eq. (2)) facilitates oxidation of

ammonia into N₂ (Eqs. (3)-(4)) or to NO₃⁻ (Eq. (5)) [20]. It seems that the main difference between the two mechanisms is concealed in their final products.



Glass structures [23-26], stainless steel [27], aluminum [28], activated carbon [29], silica [30], and perlite [31] are examples of substrates which have been used for photocatalytic decomposition by titanium dioxide. In this study, photocatalytic activity of TiO₂ (Degussa P-25) coated on light expanded clay aggregate (LECA) particles (as a new substrate) was investigated in degradation of ammonia. Review of published articles indicates that the LECA just as an adsorbent has been used for removal of some toxic material and metals [32-34]. For example, Haque et al. showed the performance of iron-modified LECA for the removal of arsenic (V) from groundwater [32]. Also, Dordio et al. studied the removal of pharmaceuticals in microcosm constructed wetlands using LECA [33]. However, the use of the LECA has not been reported in photocatalytic processes.

The high content of porosity (73-88%) and low density (330-430 kg/m³) allow the LECA to stay afloat on the surface of water, get wetted with the contaminated solution and simultaneously be exposed to the UV light when coated with the photocatalyst. Fur-

†To whom correspondence should be addressed.

E-mail: seyednezam@yahoo.com

Table 1. Chemical composition of LECA granules

Compounds	Composition (wt%)
SiO ₂	64.83
Al ₂ O ₃	15.05
Fe ₂ O ₃	7.45
K ₂ O	2.55
CaO	2.98
MgO	3.67
TiO ₂	0.63
Na ₂ O	1.10
P ₂ O ₅	0.13
MnO ₂	0.13
Loss on ignition	1.37
(SiO ₂ /Al ₂ O ₃)	4.31

thermore, natural abundance, non-toxicity, lifetime utility, and low price increase the possibility of using LECA at industrial scales [34, 35]. The SEM, XRD and XRF characterizations techniques have been applied for studying the morphology and chemical composition of the LECA and its fabricated photocatalysts.

EXPERIMENTAL

1. Materials

For the experiments, TiO₂ (P-25) photocatalyst was purchased from Degussa Co. Ltd., Germany (anatase 75 wt%, rutile 25 wt%, BET specific surface area 48 m²/g, mean particle size 25 nm). LECA is a special type of clay that has been pelleted and fired in a rotary kiln at very high temperatures (with grains size of 4-10 mm). The chemical composition of the LECA granules is shown in Table 1.

2. Preparation of Coating Samples

A simple method was used by Hosseini et al. [31] for immobilization of TiO₂ nano particles on perlite granules, which seems ideal for industrialization. The same technique was applied. In this study with minor changes for preparing coatings of TiO₂ on LECA particles, titanium dioxide powder (P-25) was added to ethanol as the base medium of slurry in which the titania powder could be properly dispersed. A quantitative dilute nitric acid (pH=3.5) was added to facilitate dispersion of titania powder in ethanol and to yield a uniform slurry. The slurry was sonicated for 30 min to separate the flocculated titania powders and obtain a more uniform slurry. Having prepared the slurry, 30 g of LECA granules (which were previously washed for a few minutes in deionized water assisted by air bubbling to remove dust and crushed LECA granules) was added to it. In the final stage of process, the LECA granules which had been adsorbed enough titania slurry were filtered from the slurry and dried at 120 °C, for 12 h, then calcinated at 550 °C for 30 min.

3. Structural Characterization

For characterization of physicochemical properties of the LECA and prepared catalysts, SEM and XRD techniques were applied. SEM analysis was implemented using a Leo 440i scanning electron microscope (SEM), while the crystallographic phases of catalysts were examined by a Philips PW-1800 X-ray diffractometer with a CuK α radiation. Furthermore, the concentration of the major and trace elements in the resultant ash samples was determined using

a wavelength X-ray fluorescence spectrometer (XRF) at Kansaran-e-Binalood Co. (Iran).

4. Analytical Methods

Concentrations of ammonia in the aqueous phase were assessed during the reaction by using Nessler reagent. In this method, ammonia reacts with Nessler reagent to form a complex whose color varies from yellow to deep amber. The intensity of color is proportional to the ammonia content and is expressed in parts per million of nitrogen. The absorbance of ammonia (at 440 nm) UV spectra was measured with a Perkin-Elmer lambda UV/vis spectrometer. Since the Nessler reagent has a pale color, the photometer should be reset with a blank reagent [36]. Concentrations of NO₃-N and NO₂-N in the aqueous phase were also determined by a sample injection analysis consisting of a UV spectrometer (HACH Industry, DR 2800 instrument). In this device, to measure the amount of nitrogen from nitrate, the method of cadmium regeneration (Cadmium reduction method) is used (method 8039). This method makes it possible to measure the NO₃-N, in the range of 0 to 30.0 mg/L. Cadmium metal reduces nitrates in the sample to nitrite. The nitrite ion reacts in an acidic medium with sulfanilic acid to form an intermediate diazonium salt. The salt couples with gentisic acid to form an amber colored solution. Test results are measured at 500 nm. Also, in the case of nitrogen of nitrite, diazotization method, which allows measurement of NO₂-N in the range of 0.003 to 0.5 mg/L, is used (method 10019). The nitrite in the sample reacts with sulfanilic acid to form an intermediate diazonium salt. This couples with chromotropic acid to produce a pink complex directly proportional to the amount of nitrite present. Test results are measured at 507 nm.

In addition, the sample gas was bubbled through boric acid solution in which ammonia and NO had been adsorbed. The residual gas was collected in a syringe through a needle valve and was analyzed by using a commercial gas chromatograph GC-CGCA-1 apparatus equipped with a thermal conductivity detector (TCD). These analyses were done isothermally at 50 °C in a parallel setup with two packed columns of Molecular Sieve 5A and Porapak Q (for N₂ and O₂). For the analysis of gas products of photocatalytic ammonia decomposition, air flow enters the reactor and after that the gas sampling system. For nitrogen balance, the amount of nitrogen in air flow (before reaction and the status lamp is off), as an internal calibration (internal standard) was used. Any change in the amount of nitrogen during the reaction (after the lamp is switched on) shows the decomposition of ammonia to nitrogen. The calculation of the N₂ in the beginning and end of the experiment shows that the percentage error was less than %5.

5. Photocatalytic Experiments

Photocatalytic efficiency of the prepared catalysts was investigated during degradation of ammonia under UV irradiation. The catalyst was directly poured on the surface of contaminated solution surface in the reactor vessel (made of Pyrex glass 18×18×8 cm). 750 mL of the ammonia solution (0.01, 0.05 M) was processed in the experiments. The UV source, medium-pressure mercury lamp (Osram) having a power of 80 W (wave length of 254 nm), was located 12 cm above the solution level. Then the outside of the Pyrex glass was covered with a cooling system of circulating water to keep the temperature constant at 10 °C. All experiments were repeated to ensure the accuracy of the results. The experimental setup is schematically depicted in Fig. 1.

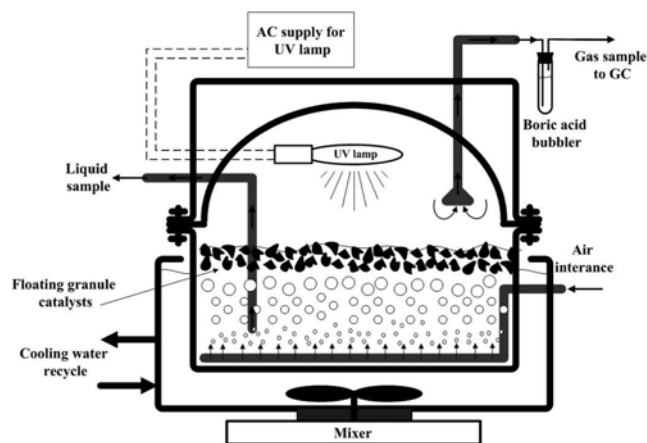


Fig. 1. Simplified schematic diagram of experimental setup.

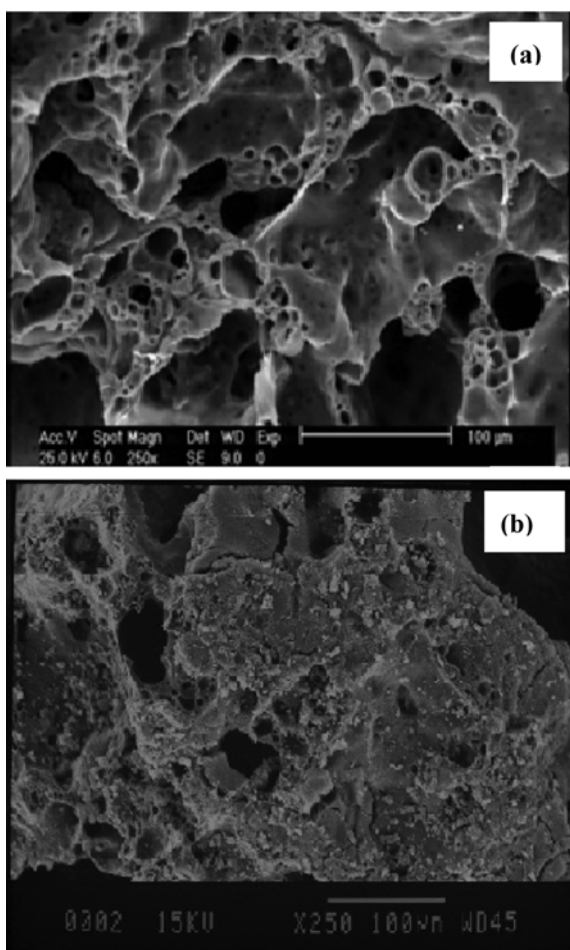


Fig. 2. The SEM images: (a) LECA, (b) plain of TiO_2/LECA .

RESULTS AND DISCUSSION

1. Photocatalyst Characterization

Fig. 2 shows the SEM images of the LECA (having porosity greater than 73–88%), before and after TiO_2 immobilization. The images taken from LECA surface confirm the high porosity of LECA particles as a good support for TiO_2 (Fig. 2(a)), and even after being covered with TiO_2 particles (Fig. 2(b)). Moreover, it uncovers an excep-

tional property of this material which can float on the surface of water because of its low density. It means that when TiO_2 coated pieces of LECA are used as photocatalysts floating on top of the contaminated water solution, they will be placed in direct contact with the contaminated solution and the UV light source, at the same time. However, the resulting XRD analysis demonstrates that the amorphous part of TiO_2/LECA sample can be attributed to LECA and P-25; without creating considerable changes due to the covering process of TiO_2 (Fig. 3).

2. Photoreactor Tests

Fig. 4 summarizes the percentage of ammonia removal at different times of the reaction. Due to the photocatalytic degradation, more than 85% of the ammonia was removed after 300 min. Meanwhile, a set of experiments were conducted at different conditions to measure the percentage of degradation or adsorption of ammonia on support and catalysts (TiO_2 in dark, LECA in dark, TiO_2/LECA in dark, LECA+UV, TiO_2 +UV, and $\text{TiO}_2/(\text{LECA}+\text{UV})$) (Fig. 5). In each experiment, 750 mL of ammonia solution at initial concentration

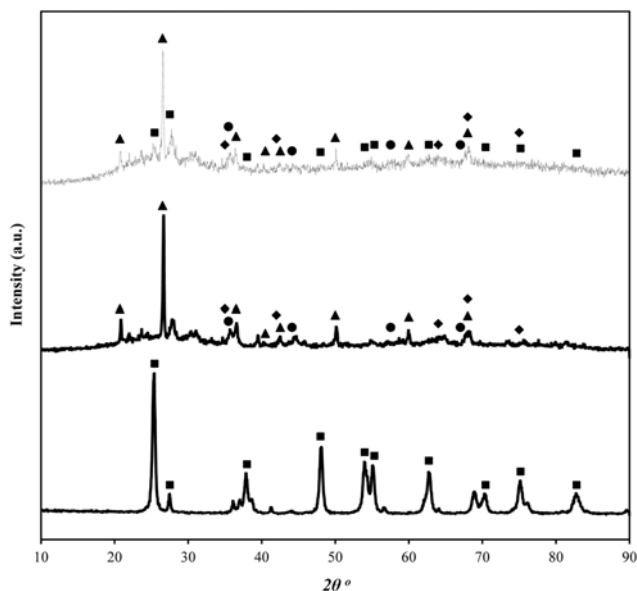


Fig. 3. XRD patterns of TiO_2 (P-25), LECA and TiO_2/LECA (TiO_2 (■), SiO_2 (▲), Al_2O_3 (●) and Fe_2O_3 (◆)).

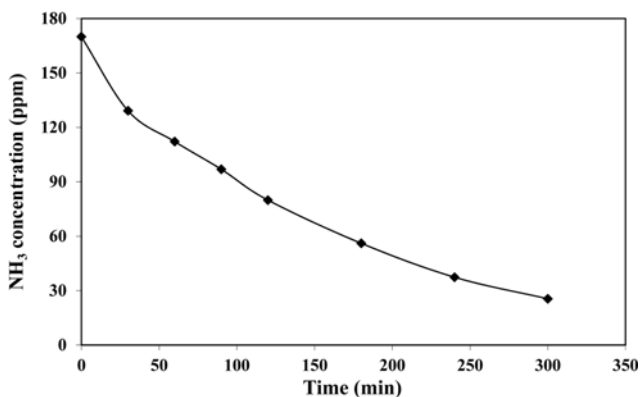


Fig. 4. The photocatalytic degradation of ammonia under UV irradiation (750 mL of ammonia solution, initial concentration of 0.01 M and with 30 g of TiO_2/LECA photocatalyst).

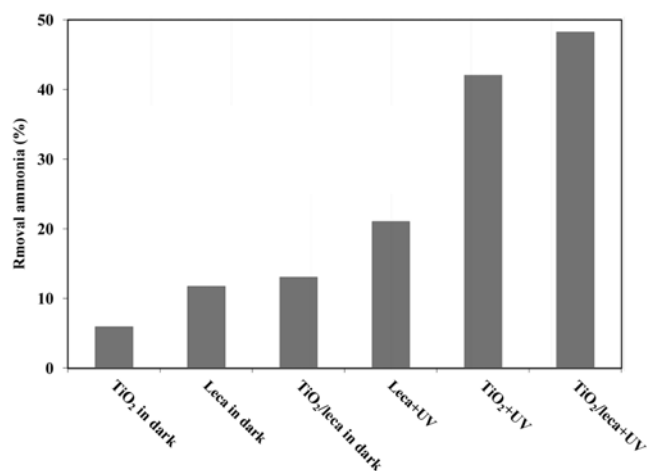


Fig. 5. Comparison of adsorption and degradation of ammonia on pure and coated LECA.

of 0.01 M was introduced and ammonia concentration was measured after 120 min. The adsorption amount of ammonia reaches about 13%, and the performance of TiO₂/(LECA+UV) increases to nearly 50%. The LECA play a major role in increasing the creation and consolidation of the TiO₂ on the surface. Due to the unique characteristics of LECA (high porosity, low density and floating on the surface of water), photocatalytic reaction is increased. Also, comparing the performance of TiO₂ and TiO₂/(LECA+UV) photocatalysts shows enhancement in the performance of TiO₂/(LECA+UV) photocatalyst up to 15%. Moreover, no need of using a separation system to separate TiO₂ is one of the advantageous of coated TiO₂. With immobilization of TiO₂ on the LECA, the photocatalytic performance of TiO₂ will inevitably decrease for interaction of photocatalyst with LECA surface. For this case, it was expected that the overall performance of the two LECA+UV and TiO₂+UV systems is less than of the TiO₂/(LECA+UV) system.

Our preliminary investigation showed that by using suspended

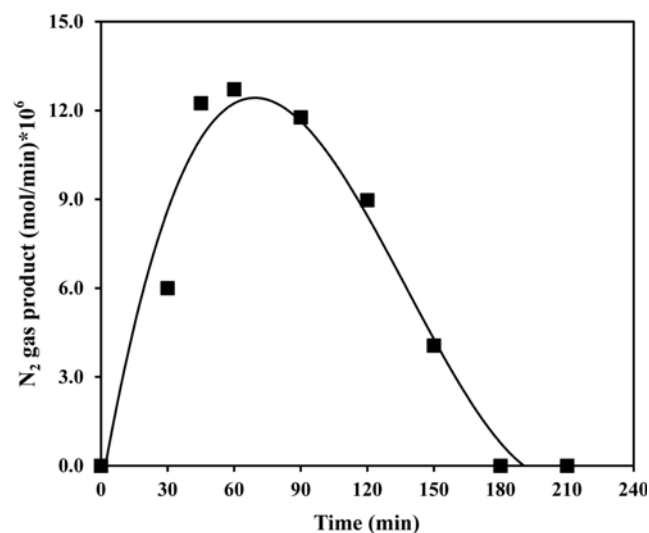


Fig. 6. Time-course of the N₂ gas product (mole/min) in the photocatalytic degradation of NH₃ solution (0.05 M, pH=11, 750 ml), under air, and 30 g TiO₂/LECA.

Table 2. Performance of the TiO₂/LECA photocatalyst for selective oxidation of NH₃ to NO₂-N and NO₃-N products

Time (min)	Removal ammonia (%)	NO ₂ (ppm)	NO ₃ (ppm)
60	30	0.17	0.65
120	50	0.55	0.98
180	75	0.64	1.02

(TiO₂/LECA), a NH₃ aqueous solution can be decomposed photochemically into N₂ gas if reacted at pH levels over 11. Having entered the TiO₂/LECA (30 g) as a photocatalyst in the NH₃ aqueous solution (0.05 M, 750 ml), the reaction was directed for some 210 min of irradiation in an air atmosphere. With photocatalytic decomposition reaction of ammonia, the output of gas products containing hydrogen and nitrogen was studied (Fig. 6). As it was predicted, the amount of nitrogen increases and reaches its value to maximum point in the interval 30-60 min of starting the reaction. These results are consistent with the highest rate of decomposition of ammonia during the reaction (Fig. 4).

Table 2 summarizes the yields values for NO₂-N, and NO₃-N products in the photodegradation of ammonia by having 30 g of TiO₂/LECA catalyst at different reaction times. The NO₂ and NO₃ concentrations after 3 h were 0.67 and 1.02 ppm, respectively, while %75 of ammonia was removed from the wastewater. The lower limits of the detection for NO₂ and NO₃ imply that the hydroxyl radicals serve as the primary reactive species facilitating oxidation of ammonia to nitrogen gas (Eqs. (3)-(4)) [20].

TiO₂ on LECA was calcined for 30 min at 350, 450, 550, and 650 °C. Fig. 7 presents the results obtained during photodegradation of NH₃ for different calcination temperatures. The highest effectiveness of ammonia decomposition was achieved in case of calcination at 550 °C.

3. Effect of pH

Fig. 8 represents the effect of pH on photocatalytic degradation of 0.01 M solution with TiO₂/LECA catalyst after 120 min. The experiments were implemented to study the effect of pH on NH₃ reduction in different starting solutions at various pH values (i.e., 3, 7, 10.3, 11 and 12.5) during 120 min of irradiation time. The maximum observed degradation of ammonia was almost 54% in the re-

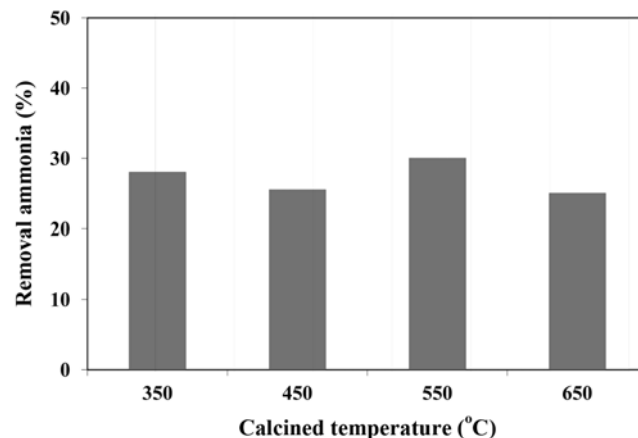


Fig. 7. The calcination temperature effect on the efficiency of ammonia removal for 120 min.

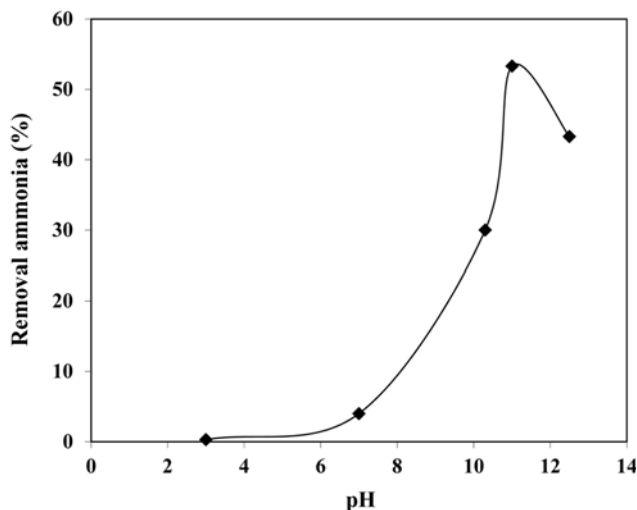


Fig. 8. Dependence of photocatalytic degradation on pH from 0.01 M NH_3 solution.

gion of pH 11. Moreover, a lower value of pH incurred a considerable decline in the performance of photocatalytic degradation performance. The evolution of NH_3 increased steeply at the pH content of 9 to 10, showing that the dissociation of NH_4^+ to free NH_3 is important for the photodecomposition process ($\text{p}K_a$ of $\text{NH}_4^+/\text{NH}_3$ is 9.24). On the other hand, the degradation rate of NH_3 decreased over $\text{pH}=11$. As mentioned in the mechanism of NH_3 photodegradation (Eq. (1)), the charge separation produced some electrons (e^-) and holes (h^+). Therefore, the hole can split an adsorbed molecule of water to reproduce a hydroxyl radical (OH^\cdot) during oxidation of NH_3 followed by the reduction of the proton on TiO_2 [3], suggesting that the oxidation of ammonia at high pH can be attributed to changes in proton concentration and increasing the possibility of recombination reaction between holes and electrons.

4. Kinetics of the Reactions

The Langmuir-Hinshelwood model is recommended for the kinetics of the photocatalytic reactions (Eq. (6)) [31,37-39]:

$$r_R = \frac{-dC_R}{dt} = \frac{k_r K C_R}{1 + K C_R} \quad (6)$$

Where, r_R , C_R and t are degradation rate of ammonia, concen-

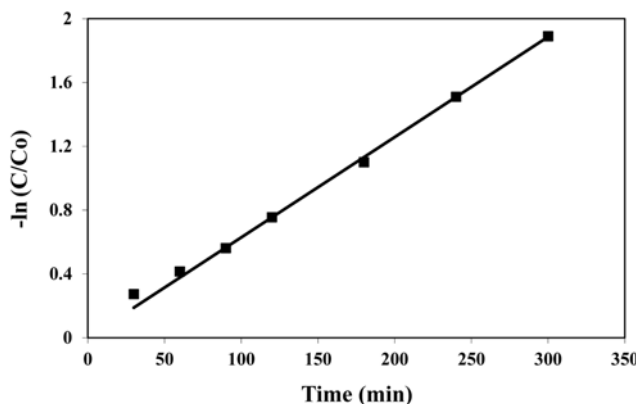


Fig. 9. Pseudo-first order plot for the photocatalytic degradation of ammonia.

tration of, and the time of reaction, respectively. Meanwhile, k_r and K are reaction and adsorption constants were determined from a least-squares fit technique on experimental results of the ammonia concentrations. The apparent rate of reaction will follow a pseudo-first-order model with boundary conditions of $C_R=C_{R0}$ at $t=0$ (Eq. (7)):

$$-\ln(C_R/C_{R0})=K_{app}t \quad (7)$$

Where C_{R0} is the initial concentration of the substrate and k_{app} is apparent first-order rate the reaction. Fig. 9 indicates that the photocatalytic degradation of ammonia has increased linearly with the reaction time with the degradation rates being kept constant during the process, which can be explained by pseudo zero-order kinetics [31].

CONCLUSIONS

The performance of LECA supported by TiO_2 nanoparticles in the photocatalytic oxidation of ammonia was investigated. The results obtained from photocatalytic treatment experiments of water synthetically polluted with ammonia showed a fairly good performance for the immobilized catalysts. The ammonia was removed (more than 85%) within 300 min of the process, and the kinetics of photocatalytic reaction followed a pseudo-first order model. Meanwhile, the maximum degradation of NH_3 in the presence of TiO_2/LECA occurred at $\text{pH}=11$. Results of SEM, XRF and XRD analyses demonstrated an acceptable uniformity of the coating process, while nitrogen analysis indicated that most of the ammonia was converted into nitrogen gas (low amounts of NO_2^- and NO_3^- products).

ACKNOWLEDGEMENTS

The laboratory experimental support provided for this study from Kernmashah Petrochemical Industrial Company (KPIC) is gratefully acknowledged. Also, the authors would like to thank Dr. Maryam Khatami from Pasteur Institute of Iran for her kindness to accept editing the manuscript.

REFERENCES

1. J. Netting, *Nature*, **406**, 928 (2008).
2. H. Yuzawa, T. Mori, H. Itoh and H. Yoshida, *J. Phys. Chem. C*, **116**, 4126 (2012).
3. D. Saha and S. Deng, *J. Chem. Eng. Data*, **55**, 5587 (2010).
4. X. ShuHu, Q. J. Hui, Z. Xu, L. H. Juan and W. D. Jin, *Water Res.*, **43**, 1432 (2009).
5. E.-M. Bensen, S. Schroeter, H. Jacobs and J. A. C. Broekaert, *Chemosphere.*, **35**, 1431 (1997).
6. D. K. Lee, *Environ. Sci. Technol.*, **37**, 5745 (2003).
7. F. N. Ahmed and C. Q. Lan, *Desalination*, **287**, 41 (2012).
8. A. Bonmati and X. Flotats, *Waste Manage.*, **23**, 261 (2003).
9. A. R. Ricardo, G. Carvalho, S. Velizarov, J. G. Crespo and M. A. M. Reis, *Water Res.*, **46**, 4556 (2012).
10. T. A. Pressley, D. F. Bishop and S. G. Roan, *Environ. Sci. Technol.*, **6**, 622 (1972).
11. Y. Wang, J. Qu, R. Wu and P. Lei, *Water Res.*, **40**, 1224 (2006).
12. X. D. Zhu, S. R. Castleberry, M. A. Nanny and E. C. Butler, *Environ. Sci. Technol.*, **39**, 3784 (2005).

13. A. Fujishima and K. Honda, *Nature*, **238**, 37 (1972).
14. K. Kalyanasundaram, M. Graetzel (Eds.), *Photosensitization and photocatalysis using inorganic and organometallic compounds*, Kluwer Academic Publishers, Dordrecht (1993).
15. A. Fujishima, K. Hashimoto and T. Watanabe, *TiO₂ photocatalysis fundamental and applications*, BKC Inc., Tokyo (1999).
16. M. Kaneko, I. Okura (Eds.), *Photocatalysis Science and Technology*, Kodansha/Springer (2002).
17. N. Keshavarz Jafarzadeh, S. Sharifnia, S. N. Hosseini and F. Rahimpour, *Korean J. Chem. Eng.*, **28**, 531 (2011).
18. W. Choi, J. Lee, S. Kim, S. Hwang, M. C. Lee and T. Lee, *J. Ind. Eng. Chem.*, **9**, 96 (2003).
19. J. Taguchi and T. Okuhara, *Appl. Catal. A.*, **194-195**, 89 (2000).
20. J. Lee, H. Park and W. Choi, *Environ. Sci. Technol.*, **36**, 5462 (2002).
21. X. D. Zhu, S. R. Castleberry, M. A. Nanny and E. C. Butler, *Environ. Sci. Technol.*, **39**, 3784 (2005).
22. S. Kim and W. Choi, *Environ. Sci. Technol.*, **36**, 2019 (2002).
23. M. Karches, M. Morstein, P. R. v. Rohr, R. L. Pozzo, J. L. Giombi and M. A. Baltanás, *Catal. Today*, **72**, 267 (2002).
24. J. C. Lee, M. S. Kim and B. W. Kim, *Water Res.*, **36**, 1776 (2002).
25. S. Horikoshi, N. Watanabe, H. Onishi, H. Hidaka and N. Serpone, *Appl. Catal.*, **B 37**, 117 (2002).
26. I. N. Martyanov and K. J. Klabunde, *J. Catal.*, **225**, 408 (2004).
27. J. Shang, W. Li and Y. Zhu, *J. Mol. Catal. A.*, **202**, 187 (2003).
28. H. Chen, S. W. Lee, T. H. Kim and B. Y. Hur, *J. Eur. Ceram. Soc.*, **26**, 2231 (2006).
29. C. H. Ao, S. C. Lee and J. C. Yu, *J. Photochem. Photobiol. A.*, **156**, 171 (2003).
30. M. S. Vohra and K. Tanaka, *Water Res.*, **37**, 3992 (2003).
31. S. N. Hosseini, S. M. Borghei, M. Vossoughi and N. Taghavinia, *Appl. Catal. B.*, **74**, 53 (2007).
32. N. Haque, G. Morrison, I. Cano-Aguilera and J. L. Gardea-Torresdey, *Microchem. J.*, **88**, 7 (2008).
33. A. Dordio, A. J. P. Carvalho, D. M. Teixeira, C. B. Dias and A. P. Pinto, *Bioresour. Technol.*, **101**(3), 886 (2010).
34. H. Amiri, N. Jaafarzadeh, M. Ahmadi and S. Silva Martínez, *Desalination*, **272**, 212 (2011).
35. L. S. Piro and I. L. Piro, *Cement Concrete Compos.*, **26**, 639 (2004).
36. BETZ Laboratories Inc., *BETZ Handbook of Industrial Water Conditioning*, 9th Ed., BETZ Laboratories (1991).
37. I. M. Arabatzis, N. Spyrellis, Z. Loizos and P. Falaras, *J. Mater. Process. Technol.*, **161**, 224 (2005).
38. A. H. C. Chan, J. F. Porter, J. P. Barford and C. K. Chan, *Water Sci. Technol.*, **44**, 187 (2001).
39. D. Vione, C. Minero, V. Maurino, M. E. Carlotti, T. Picatonotto and E. Pelizzetti, *Appl. Catal. B.*, **58**, 79 (2005).