



Low-temperature Synthesis of α -Fe₂O₃/MWCNTs as Photocatalyst for Degradation of Organic Pollutants

NUHA ABDUL JALEEL OMRAN¹, ZAID HAMID MAHMOUD^{2*},
NOOR KADHUM AHMED and FARAH KEFAH ALI³

^{1,2,3}Department of Chemistry, College of Science, Diyala University, Iraq.

*corresponding author E-mail: zaidhameed_91@yahoo.com

<http://dx.doi.org/10.13005/ojc/350140>

(Received: November 19, 2018; Accepted: January 03, 2018)

ABSTRACT

The nanoparticles of α -Fe₂O₃/multi wall carbon nanotubes (MWCNTs) were successfully fabricated using photolysis and sonication method as a heterogeneous catalyst for photodegradation of 4-chlorophenol. The XRD and SEM were confirmed the supporting and distribution of the MWCNTs between the surface of α -Fe₂O₃ while, preparing nanoparticles proved also using XRD and SEM. The photocatalytic activity of prepared nanoparticles was investigated using 4-CP. The results appeared converting nearly 98% from 4-chlorophenol to 1,4- benzoquinone with optimum conditions of pH 3, 20 ppm of pollutant and 0.3 g of heterogeneous catalyst.

Keywords: Heterogeneous, Catalyst, Photolysis, Nanoparticles, α -Fe₂O₃.

INTRODUCTION

4-chlorophenol is a hazardous and toxic organic pollutants so that the maximum concentration allowed in the water is in the range 1-20 ppb¹⁻⁴. To eliminate the negative impact, the advanced oxidation processes (AOPs) were suggested rather than a traditional biological treatment process because of high efficiency for degradation the dyes and organic pollutants by forming free radicals in the solution under effect UV irradiation^{5,6}. Under UV irradiation, heterogeneous catalysts work on excitation the electrons from the valence band (VB) to the conduction band (CB) leaving positive holes

(h⁺) then, it initiates a series of oxidation-reduction reaction (redox) to product hydroxide and peroxy free radicals as a strong oxidants to degrade the organic pollutants⁷⁻¹². However, use one catalyst in the process cause incomplete mineralization so it was modified by another material to increase the efficiency. This paper reported the new method¹³⁻¹⁶ to prepare heterogeneous catalysts. In this method, building of the nanoparticles takes bottom to top type. This means the UV radiation main role to build the particles from the solution by forming very small particles called seed then, the seed grows to form nanoparticles.



MATERIALS AND METHOD

Materials

4-chlorophenol, hydrochloric acid, sodium hydroxide, ferric chloride hexahydrate and Multiwall carbon nanotubes were supplied from Fluka company and used without purification.

Synthesis of α -Fe₂O₃ NPs

Firstly, in 250 ml beaker, 1 g (0.003 mol) of FeCl₃·6H₂O dissolved in 100 ml distilled water. Then, it transferred to the reactor of irradiation system as shown in Fig. 1. The solution of salt was irradiate until brown precipitate appears. After that, the precipitate separated, collected and washed using acetone and distilled water for 3 times. Finally, the precipitate dried and burned for 2 hours.

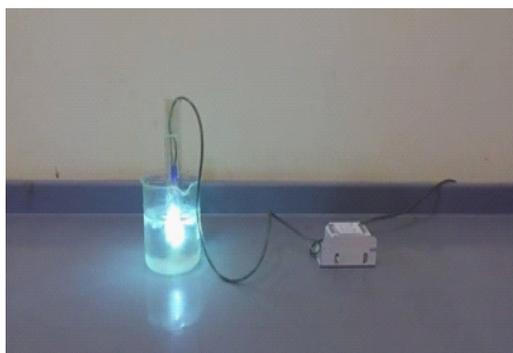


Fig. 1. Irradiation system

Synthesis of α -Fe₂O₃/MWCNTs heterogeneous catalyst

In a typical procedure, 2 g (0.012 mol) of nanorods were dispersed in 250 ml of H₂O₂ containing 0.6 g (0.05 mol) of multi wall carbon nanotube (MWCNTs). Subsequently, the mixture was dispersed and ultrasonically for 30 min until black-brown precipitate appears.

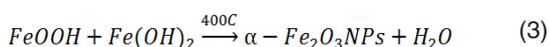
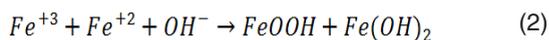
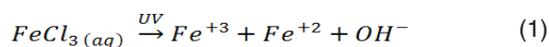
Degradation of 4-chlorophenol experiments

The photoactivity of heterogeneous catalyst prepared was investigated by degradation of 4-chlorophenol under ultraviolet irradiation (UV) with power 125 W. All experiments were carried out using beaker with volume 250 ml as a reactor at room temperature (2^oC). The catalyst dispersed in pollutant solution in the dark for 15 minutes. Many conditions such as concentration of catalyst and pollutant, time of irradiation and different pH values was studying to get best result.

RESULT AND DISCUSSION

Reaction Kinetic

α -Fe₂O₃ nanoparticles prepared using photolysis method. During this method, the irradiation of UV play as a reduce reagent where it works on reduction of ferric to ferrous ions and with the presence of the hydroxide ions in the solution, the remains ions of ferric combine with hydroxide to produce FeOOH while, the ferrous ions combine with hydroxide ions to get Fe(OH)₂. Then, the FeOOH and Fe(OH)₂ were burned to product brown nanoparticles of α -Fe₂O₃ as shown in below mechanism.



In the mechanism, hydrogen peroxide acted on fuctionalization of MWCNTs and these functional groups work as a site to adsorb the nanoparticles results of Vander wall forces or chemical interaction.

Analysis of XRD

XRD technique was used to investigate the structure of α -Fe₂O₃ and α -Fe₂O₃/MWCNTs and the size of particles prepared. The XRD spectrum of α -Fe₂O₃ and α -Fe₂O₃/MWCNTs was shown in Fig. 2. The characteristic peak of carbon MWNTs with small intensity appeared a clearly at 26.24 in spectrum of MWNTs and α -Fe₂O₃/MWCNTs and the results is in agreement with (JCPDS no. 41-1487). When comparing the spectrum of MWCNTs and α -Fe₂O₃/MWCNTs, any change wasn't shown in the position of peaks just the peak of MWCNTs and this indicate incorporated the MWCNTs molecules in the lattice of nanocomposite.

Analysis of SEM

The morphology of samples prepared was studied and showed using scanning electron microscope (SEM). The morphology of α -Fe₂O₃ and α -Fe₂O₃/MWCNTs was shown in Fig. 2 (A) and 2 (B). The Fig. 2 (A) obtained prepare nano ferric oxide in rod shape with random distribution and it can be noted the particles fabricated are cylindrical shape while, the Fig. 2 (B) shows the presence of MWCNTs around or between the rod particle prepared and this indicate the conform of the preparation of α -Fe₂O₃/MWCNTs nanocomposite. The ratio of

nanocomposite elements was investigated by the EDS spectrum and it shows the high purity of the product as shown in Figure 2 (C).

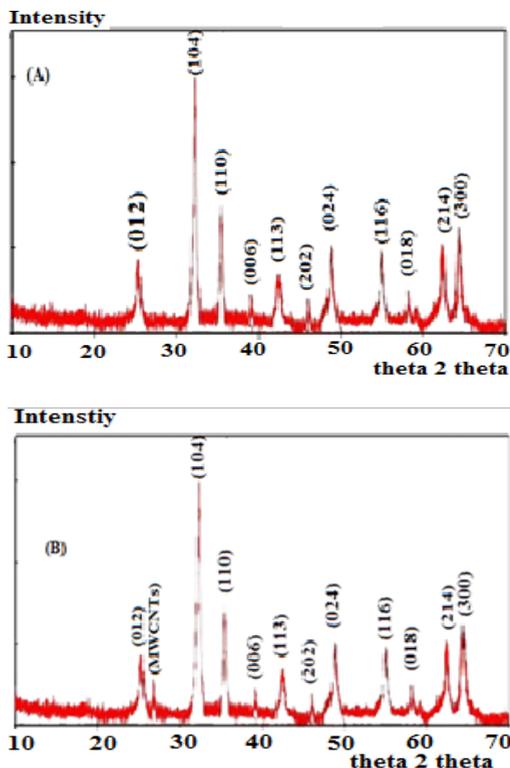


Fig. 2. XRD of (A) $\alpha\text{-Fe}_2\text{O}_3$ and (B) $\alpha\text{-Fe}_2\text{O}_3$ with MWCNTs

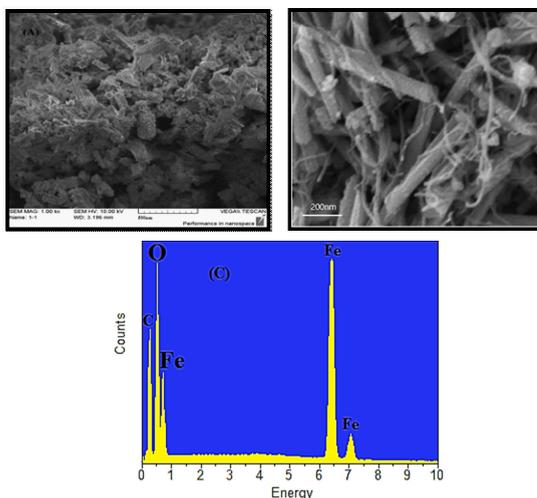
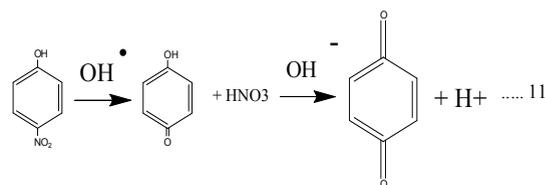
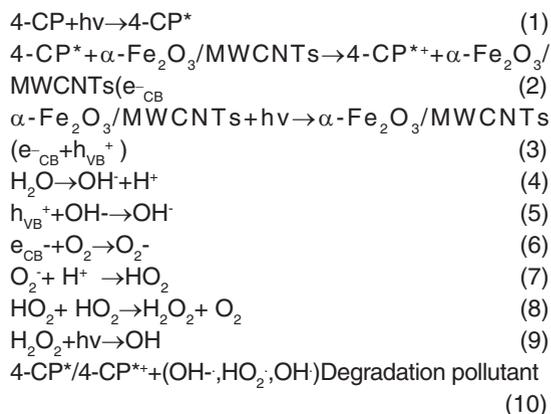


Fig. 3. SEM of (A) pure $\alpha\text{-Fe}_2\text{O}_3$, (B) $\alpha\text{-Fe}_2\text{O}_3$ -MWCNTs and (C) EDS of $\alpha\text{-Fe}_2\text{O}_3$ -MWCNTs

Photodegradation of 4-chlorophenol by $\alpha\text{-Fe}_2\text{O}_3$ /MWCNTs

To investigate the photocatalytic activity of

heterogeneous catalyst prepared, degradation of 4-nitrophenol solution in presence catalyst fabricated under UV irradiation was observed. In general, the results showed high efficiency for photocatalytic degradation of 4-chlorophenol. The degradation of pollutant followed the following mechanism.¹⁷⁻¹⁹



The degradation mechanism proposes breaking the bond between C-Cl and the product which in turn react with oxygen to form 1,4-benzoquinone as shown in (Eq.11) and the results from GC-mass prove it as shown in Fig. 4. After irradiation, the spectra of GC-mass shows peak equal to 108 g/mol assigned to 1,4-benzoquinone.

Effect of pH

pH considered one of important factors that can be effected on degradation of pollutant due its effect on the rate of generating hydroxide free radicals and the charge of catalyst surface. To investigate the effect of it, the range from 3-10 of pH was studied. The results show that the best efficiency of degradation at 3 as shown in Fig. 5. At basic value, the repulsion force between catalyst and phenolate ions play the main role in decrease the efficiency while, in acidic medium the catalyst has a positive charge and it's become a favorite for an adsorption of ions on the surface^{20, 21}.

on the other side, the ferric ions in oxide were reduced to ferrous ions in acidic medium and

adsorbed on (001) surface of $\alpha\text{-Fe}_2\text{O}_3$ and this cause the Fenton system. The charge of catalyst

and the Fenton system can increase the efficiency of degradation²².

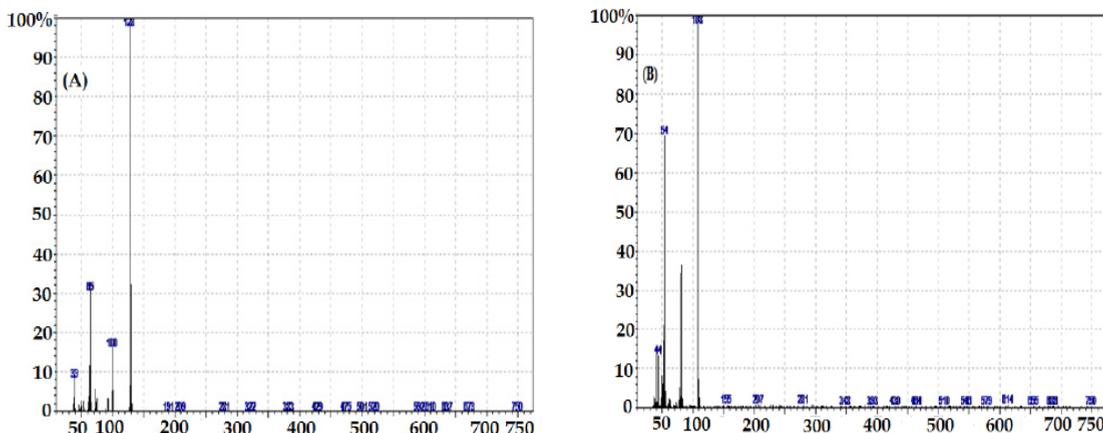


Fig. 4. GC/mass spectrum of 4-CP (A) before irradiation and (B) after irradiation

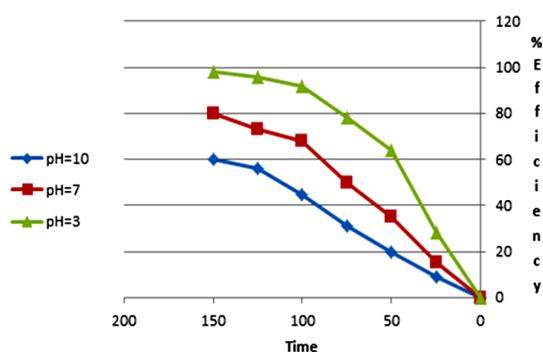


Fig. 5. Effect of pH on efficiency of degradation at room temperature (20C)

Effect of catalyst concentration

The photodegradation efficiency of 4-CP was studied verse the a amount of catalyst used as shown in Fig. 6. The amount of catalyst ranged 0.1–0.5 g/L. The results appear the efficiency increase with the increase concentration and then decrease because with the increase it, the active site 23 is increasing and the generation of hydroxyl free radicals increase that react with pollutants and destroyed it otherwise, the efficiency decreases with increasing the catalyst load due to the agglomeration of nanoparticles and this cause decrease of OH. that react with the pollutant²⁴⁻²⁶.

Effect of initial concentration of pollutant

The effect of initial concentration of 4-CP on photodegradation rate was investigated in the range 20–80 ppm. The results were illustrated in Fig. 7. The photodegradation yield depends on the reaction that occur on the surface of catalyst through reaction

between OH free radicals and 4-CP. The results appeared the photodegradation efficiency decrease with increasing the concentration of 4-CP and this may be back to saturate of active sites of catalyst and cause to decrease the generate of hydroxyl free radicals 27-28 as well as adsorbed the important amount of UV by pollutant instead of the catalyst.

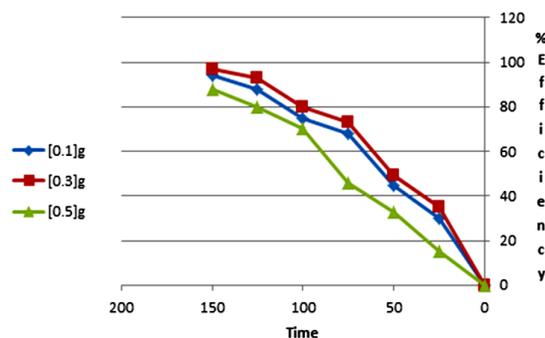


Fig. 6. Effect of catalyst concentration on efficiency of degradation at pH=3 and temp =20C

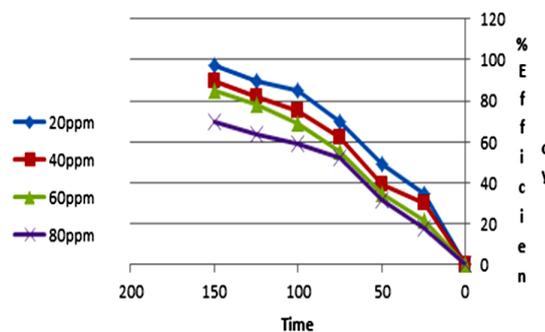


Fig. 7. Effect of initial concentration of 4-CP on efficiency of degradation at pH=3, 0.1g catalyst and temp = 20C

CONCLUSION

Alpha phase iron oxide with nanoparticles can be prepared using the low temperature photolysis method and doping it with MWCNTs utilizing sonication method. UV irradiation plays a main role in the reduction of ferric to ferrous ions and product goethite compound that reacts with ferrous hydroxide to get hematite nanoparticles. The results from XRD

proved don't enter the MWCNTs inside the crystal lattice of α -Fe₂O₃. The attack of hydroxyl free radicals on 4-CP destroyed the C-Cl bond and converted it to 1,4-benzoquinone.

ACKNOWLEDGEMENT

The authors would like to Acknowledge their Department storage for the supply of Chemical Materials.

REFERENCE

- Xu, X.; Liu, Z.; Zhang, X.; Duan, S.; Xu, S.; Zhou, C. *Electrochim. Acta.*, **2011**, *58*, 142–149.
- Wu, J.; Wang, X.; Kang, H.; Zhang, J.; Yang, C. *Int. J. Environ. Stud.*, **2014**, *71*, 534–545.
- Peretz, S.; Cinteza, O. *Eng. Asp.*, **2008**, *319*, 165–172.
- Mishra, K.P.; Gogate, P.R. *Ultrason. Sonochem.*, **2011**, *18*, 739–744.
- Gao, Y.; Wang, Y.; Zhang, H. *Appl. Catal. B: Environ.*, **2015**, *178*, 29–36.
- Huang, Z.; Wu, P.; Lu, Y.; Wang, X.; Zhu, N.; Dang, Z. *J. Hazard. Mater.*, **2013**, *246–247*, 70–78.
- Nezamzadeh-Ejehieh, A.; Amiri, M. *Powder Technol.*, **2013**, *235*, 279–288.
- Phanikrishna Sharma, M.V.; Durga Kumari, V.; Subrahmanyam, M. *Chemosphere.*, **2008**, *73*, 1562–1569.
- Elmolla, E.S.; Chaudhuri, M. *Desalination*. **2010**, *252*, 46–52.
- Ahmed, S.; Rasul, M.G.; Brown, R.; Hashib, M.A. *J. Environ. Manage.*, **2011**, *92*, 311–330.
- Gar Alalm, M.; Tawfik, A.; Ookawara, S. *J. Water Process Eng.*, **2015**, *8*, 55–63.
- Banerjee, S.; Pillai, S.C.; Falaras, P.; O'Shea, K.E.; Byrne, J.A.; Dionysiou, D.D. *J. Phys. Chem. Lett.*, **2014**, *5*, 2543–2554.
- Zaid, H.M.; Nuha, F.A.; Aklas, A.A. *Asian J. Chem.*, **2018**, *30*, 223–225.
- Zaid, H.M. *J. Chem Pharm Res.*, **2017**, *9*, 29–33.
- Zaid H.M. *DJPS.*, **2018**, *14*, 136–146.
- Rawnaq, B. J.; Zaid, H. M.; Farah K. A. *Entomol. Appl. Sci. Lett.*, **2018**, *5*, 91–100.
- Sundaramurthy, J.; Suresh Kumar, P.; Kalaivani, M.; Thavasi, V.; Mhaisalkar, S.G.; Ramakrishna, S. *RSC Adv.*, **2012**, *2*, 8201–8208.
- Shen, Y.; Zhao, Q.; Li, X.; Hou, Y.; Chen, G. *Col. Surf. A: Physicochem. Eng. Asp.*, **2012**, *403*, 35–40.
- Babuponnusami, A.; Muthukumar, K. *J. Environ. Chem. Eng.*, **2014**, *2*, 557–572.
- Carp, O.; Huisman, C.L.; Reller, A. *Prog. Solid State Chem.*, **2004**, *32*, 33–177.
- Pouretedal, H. R.; Motamedi, H.; Amiri, A. *Desalin. Wat. Treat.*, **2012**, *44*, 92–99.
- Huang, X.; Hou, X.; Zhao, J.; Zhang, L. *Appl. Catal. B.*, **2016**, *181*, 127–137.
- Sun, S. P.; Zeng, X.; Li, C.; Lemley, A.T. *Chem. Eng. J.*, **2014**, *244*, 44–49.
- Nezamzadeh-Ejehieh, A.; Shahriari, E. *J. Ind. Eng. Chem.*, **2014**, *20*, 2719–2726.
- Bahrami, M.; Nezamzadeh-Ejehieh, A. *Mater. Sci. Semicond. Process.*, **2014**, *27*, 833–840.
- Amiri, M.; Nezamzadeh-Ejehieh, A. *Mater. Sci. Semicond. Process.*, **2015**, *31*, 501–508.
- Assi, N.; Mohammadi, A.; Manuchehri, Q. S.; Walker, R. B. *Desalin. Wat. Treat.*, **2015**, *54*, 1939–1948.
- San, N.; Hatipog˘lu, A.; Kocturk, G., C., inar Z. *J. Photochem. Photobiol. A: Chem.*, **2002**, *146*, 189–197.