

Photocatalytic degradation of humic acid in aqueous media using MnFeN-tridoped TiO₂ nanoparticles

Narmin Abdollahi¹, Saeed Dehestaniathar^{2*}, Mahdi Safari³, Maryam Safay⁴, Hiua Daraei⁵

1. M.Sc. Student in Environmental Health, Student Research Committee, Kurdistan University of Medical Sciences, Sanandaj, Iran (abdollahi.narmin@yahoo.com)

2. Assistant Professor, Environmental Health Research Center, Research Institute for Health Development, Kurdistan University of Medical Sciences, Sanandaj, Iran

3. Assistant Professor, Environmental Health Research Center, Research Institute for Health Development, Kurdistan University of Medical Sciences, Sanandaj, Iran (safari.m.eng@gmail.com)

4. B.Sc., Environmental Health Engineering, 5th Tehran Water Treatment Plant, Tehran, Iran (safay_m@yahoo.com)

5. Lecturer, Environmental Health Research Center, Research Institute for Health Development, Kurdistan University of Medical Sciences, Sanandaj, Iran (hiua.daraei@gmail.com)

Received: October 9, 2018

Accepted: May 23, 2018

Extended abstract

Introduction

Humic acid (HA) derived from decomposition of plants and animal's residual and it widely present in surface resources of water. They are found to be the main precursor of carcinogenic disinfection byproducts (DBP_s) such as THM, HAA in the water disinfection process with chlorine. Nowadays, several techniques have been applied for removal of HA but they have their own limitation. Recently Photocatalytic oxidation based on semiconductors has been widely studied. Photocatalytic processes are types of AOPs processes that start with the radiation of photons (equal to or greater than energy bands) on the surface of the semiconductor catalyst and generation of electron/hole (e^-/h^+) in the valence and conduction band respectively. The photons generated holes (h^+) and electrons (e^-) produced hydroxyl (OH^\bullet) and super oxide (O_2^\bullet) by oxidation and reduction of adsorbed H₂O molecules and dissolved oxygen. Therefore, OH^\bullet and O_2^\bullet radical efficiency can removed HA at catalyst surface.

TiO₂ is considered as one of the best catalyst due to its high photocatalytic activity. However, the broad application of TiO₂ has limited because of its large band gap (3.2eV) which requires UV light irradiation for photocatalytic activity. Furthermore, high recombination rate of photogenerated e^-/h^+ pairs is another drawback that reduces the quantum efficiency of TiO₂.

Research has shown that doped TiO₂ with various metal and nonmetal ions is one of the most promising strategies to solve these problems. The ions dopant in TiO₂ can improved the photocatalysis efficiency by decreases the band gap and inhabitation of the e^-/h^+ pair recombination. In this study, TiO₂ doped simultaneously with Fe, Mn and N. MnFeN-tridoped TiO₂ was synthesized by so-gel method and photocatalytic activity of the synthesized pure TiO₂ and tri-doped TiO₂ evaluated by monitoring the degradation of HA as target pollutant.

Material and Methods

MnFeN-tridoped TiO₂ was prepared by a traditional sol-gel method. In a typical procedure, a certain amount of TiCl₄ as procedure of TiO₂ was added dropwise into deionized water under strong magnetic stirring in water bathroom. Then, another solution containing ethanol and certain amount of precursors of nitrogen, iron and manganese was dropwise added to the above solution to form sol. After stirring for 30 minute, drops of ammonium hydroxide were added wisely into above obtained solution to formation of white precipitate and solution was made to settle for twelve hours. Then, precipitate was centrifuged and washed with deionized water. Finally, the precipitate was dried in oven at 200°C for 4 hours and nanoparticles MnFeN-tridopedTiO₂ was obtained. The resulting nanoparticles were calcined at 400°C for 3 hours.

The crystal structure of the samples were characterized by X-ray diffraction, SEM, XRD and EDX analyses. The photocatalytic activity of MnFeN-tridopedTiO₂ particles evaluated by degradation of HA in atmospheric pressure and room temperature. The experiments were conducted in a lab-scale batch photocatalytic reactor with a 3500 ml capacity under the radiation of ultraviolet and visible light (6 lamps with 30 w intensity) sources. The

* Corresponding Author:

E-mail: saeed_dehestani@yahoo.com

nanoparticles were fixed on a glass bed and synthetic solution containing humic acids, flows on the glass bed using a peristaltic pump.

The effects of pH values (3, 5, 7, 9, 11) nanoparticles dose (0.5, 1, 1.5, 2, and 2.5), initial concentration of humic acid (2-50 mg/L) were investigated as critical parameters. HA concentration was monitored using spectrophotometer at wavelength of 254 nm.

Results & Discussion

Characterization of nanoparticles

The results obtained from the XRD analysis of pure TiO_2 and doped TiO_2 with N, Fe and Mn nanoparticles indicated that all samples consist of anatase phase as the dominant crystalline phase nanoparticles. The size of the nanoparticles was calculated with Scherer's equation. It is observed that the size of nanoparticles decreased with increasing ions dopant into the TiO_2 lattice as follows $\text{TiO}_2 > \text{NTiO}_2 > \text{FeNTiO}_2 > \text{FeMnNTiO}_2$. It might be due to this fact that the dopant ions can restricts the crystal growth. Furthermore decreasing peaks intensity and increasing the width of the peaks confirmed the substitution dopants into TiO_2 lattice. The surface morphology of pure and doped TiO_2 with N, Fe, N Mn, Fe, N nanoparticles are revealed by SEM micrographs. SEM micrographs of doped and un-doped nanoparticles exhibit particles size in the range of 20–60 nm, which is in agreement with the results obtained from the XRD analyses. These results confirmed the impurity added to the TiO_2 structure by preventing the expansion of the Ti-O-Ti bond decrease the growth of the crystalline particles. Also, EDX analysis indicated the corresponding signals to Fe, N and Mn in the synthesized samples that confirmed all dopants incorporated into the TiO_2 crystal structure. Fourier transform infrared (FTIR) analyze of synthesis nanoparticles performed in the wavenumber range of $400\text{--}4000\text{ cm}^{-1}$. The absorption peaks at about 3440-3420 and 1630-1620 are related to stretching vibration of O-H and the bending vibration absorbed water molecules. The bands in the range of $400\text{--}800\text{ cm}^{-1}$ were attributed to the symmetric and asymmetric stretching vibrations of Ti-O-Ti and Ti-O bands.

Effect of operating parameters on the degradation of humic Acid

The effect of different values of pH (3, 5, 7, 9, 11) on photocatalytic degradation of HA was evaluated in a solution with the same initial concentration of humic acid (10 mg/L), dose of stabilized nanoparticle on the surface of glass bed (1.5 g MnFeN-tridoped TiO_2) under ultraviolet radiation for 120 minutes. The results showed that the maximum degradation of HA was obtained at pH=3 (86.72%) and the degradation percentage decreased with increasing pH to 11. At acidic pH, the surface of the titanium dioxide due to existence of h^+ , has positive charge. Therefore, removal efficiency of HA increased by electrostatic attraction of the negatively charged HA molecules and positively charged TiO_2 surface.

In order to evaluate the effect of catalytic dosage on photocatalytic degradation HA, different amounts of nanoparticles were investigated. This study showed that the increase of dosage of nanoparticles and the increase of removal efficiency. The increase in degradation efficiency with increasing dosage of nanoparticles can be attributed to increasing the available surface area, number of active sites at the catalyst surface and UV trapping that leads to the more electron/ hole pairs release and production more oxidizing radicals such as OH^\bullet and O_2^\bullet to degradation of HA.

Effect of initial concentration of HA on the efficiency process was tested by various concentrations (10, 20, 30, 40, 60, and 100 mg/L) in the same reaction conditions (1.5g MnFeN-tridoped TiO_2 fixed on the glass, pH =3) under ultraviolet radiation for 120 minutes. In this study, with increasing initial concentrations of HA, from 2 to 50 mg/L, the photocatalytic degradation efficiency of MnFeN-tridoped TiO_2 nanoparticles decreased from 92% to 30%, respectively. In the photocatalytic process with the constant reaction condition such as pH, catalyst dosage, intensity light and contact time leads to production the same number of electron/ holes and also hydroxyl radicals. Therefore, by the same number of available oxidizing species, the solution with a lower concentration of HA will have a higher decomposition rate than a solution with higher concentration solution. Also, at higher concentrations, more HA molecules were absorbed on the surface of the catalyst, which prevents from reaching photons on catalyst surface that leads to reduce the formation of hydroxyl radicals and efficiency of photocatalyst.

In order to evaluate the photocatalytic efficacy of various samples of doped TiO_2 nanoparticles (N-doped TiO_2 , Fe-N-codoped TiO_2 and MnFeN-tridoped TiO_2) and pure TiO_2 , photocatalytic degradation of HA took place in the same conditions (10 mg/ l humic acid, pH= 3, and 1.5 g catalyst dose) under radiation of ultraviolet radiation. Results showed that the photocatalytic activity of nanoparticles follows the $\text{UV}/\text{TiO}_2 < \text{UV}/\text{N-dopedTiO}_2 < \text{UV}/\text{FeN-codopedTiO}_2 < \text{UV}/\text{MnFeN-tridopedTiO}_2$. Increasing photocatalytic efficacy with substitution of impurity elements (N, Fe, Mn) into the structure of TiO_2 relative to pure TiO_2 can be attributed to the reducing crystalline nanoparticle size, anatase dominant phase, efficient separation of electrons/ holes and reducing their recombination rates in the charge transfer path.

The effect of all synthesized nanoparticles with visible radiation on the degradation of HA in optimal conditions (10 mg/L HA, pH= 3, and 1.5 g catalyst dose) was investigated. It was observed that photocatalytic activity against visible light has improved with the substitution of N, Mn, Fe into the structure of TiO₂. N, Mn and Fe doped with titanium dioxide reduce the energy gap by creating sub-levels between the capacity and conduction bands. Thus, by reducing the energy gap, the light absorption spectrum changes to the visible light region and photocatalytic efficiency of TiO₂ increases against visible light.

Conclusion

According to the results obtained from this study, it can be concluded that simultaneous doping is an effective way to improve the efficiency of photocatalytic activity of TiO₂ in the removal of environmental pollutants such as humic acid in aqueous media. Also, by doping of TiO₂ and enhancement of visible light response, the sunlight can be used as a natural source of energy in the photocatalytic process.

Keywords: doped titanium dioxide, humic acid, hydroxyl radical, photocatalyst process.

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