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Removal of humic acid from aqueous solution using UV/ZnO nano-photocatalysis and adsorption

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ABSTRACT

Humic acid is a natural organic material produced as a result of biological and geochemical reactions and it is one of the main precursor materials of disinfection by-products. The rapid removal and fast adsorption of humic acid using zinc oxide nanoparticle irradiated by the ultraviolet light (ZnO/UV) were well elucidated and investigated. The impact of various influential factors such as ZnO dosage, initial humic acid concentration, reaction time and pH on the adsorption capacity and removal of humic acid was well studied and optimized. The optimization study confirms that an increase in the initial concentration of humic acid and the pH of the environment decreased the removal efficiency while increase in the time of irradiation increased the removal efficiency. The maximum removal efficiency of humic acid for the single-stage process was found to be 0.2 g/l ZnO and for that of two-stage process was found to be 0.5 g/l ZnO. The obtained results reveal that the two-stage photocatalysis was the most preferable method for the humic acid removal and it results in more than 98.95% of humic acid within only 30 min of photocatalysis.

1. Introduction

Natural organic matter (NOM) is an organic compound originating from the biological and synthetic sources that are one of the major impurities which are present in all the nearby aqueous sources. These compounds are different in their chemical reactivity, structure and color [1,2]. The major components of NOM include carbohydrates, protein, and lignin; a significant percentage of their molecular weight comprised of decomposed oxygen-containing functional groups. Hydrophilic NOM has a higher potential for formation of halo acetic acid in comparison to that of the hydrophobic NOM [3]. The presence of NOM affects the water quality and is a major problematic issue for municipal wastewater treatment plants. In the past, the existence of humic acid in potable water was undesirable primarily for its lack of esthetic appeal (color). It is now known to be undesirable for its disinfection by-products, such as THMs, which are often carcinogenic. Although NOM is harmless by itself, it produces adverse reactions with chlorine and forms disinfection by-products [4].

Evaluation of NOM in untreated wastewater consists of the potential carcinogenic trihalomethane (THM) compounds which have severe detrimental effect on the human health. The decline in potable water resources and rise of noxious impurities in water require a tremendous effort of the research groups for purification and strict disinfection laws for the control of THM and haloacetic acids, which occur in amounts of about 80 μg/l and 60 μg/l, respectively, in water. It illustrates the need for new technologies for water treatment. One new method for the removal of disinfection by-product (DBP) precursors is advanced oxidation [4,5]. The major advantage of this method is organic carbon mineralization [6]. This process is based on the formation of highly reactive species of hydroxyl radicals that can remove a wide range of contamination [7]. Photocatalysis has been successfully used for the oxidation of many organic pollutants by advanced oxidation. Heterogeneous photocatalysis disrupts the mineralization of most organic compounds [8–17]. Heterogeneous metal oxides such as ZnO have the potential to remove organic substances from aquatic environments in

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the presence of ultraviolet light. The main advantage of ZnO is that it absorbs a range of electromagnetic waves and shows high performance as a decomposition photocatalyst of organic compounds in aqueous solutions [18–49].

The present study evaluated the performance of a nano-photocatalytic reactor (UV/ZnO) for removal of humic acid from aqueous solutions. ZnO nanoparticles were used as catalysts for the removal of humic acid. The effects of pH, concentration of humic acid, concentration of nanoparticles, processing time, and absorption were examined and synthetic studies were carried out.

2. Materials and methods

The experimental study was carried out using a batch system and the natural organic material humic acid was obtained from Acros Organics. Further materials used were obtained from Merck (Germany).

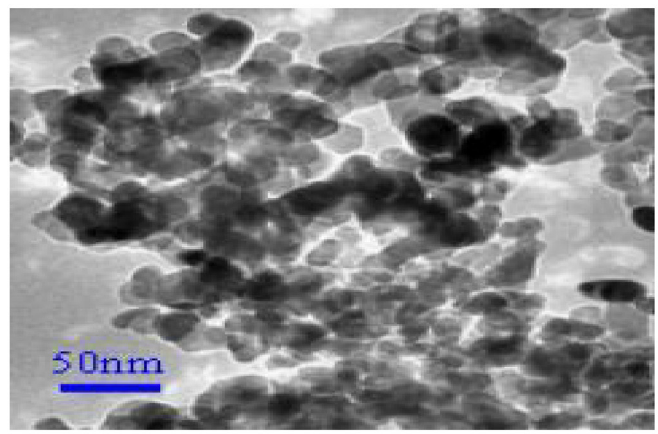
A stock solution of 1 g/l humic acid was prepared using humic acid that contained impurities. It was purified according to the method reported by Zaccone et al. (2007). According to this method, we first measure out 1.82 g of 57% purified humic acid [50], which was further treated with 0.2 M KOH and then 0.3 M KOH solution and stirred for 4–5 h. It was then centrifuged to remove the insoluble substances such as organic litter. The pH of the supernatant was acidified using HCl to pH = 1.5 and the coagulated parts were separated by centrifugation. The purified humic acid was washed with distilled water and HCL (pH = 3), then centrifuged.

The sedimentation volume was increased to 1000 mg/l with distilled water and the solution was added and shaken for 3 h. The final product was a hypotonic solution with a concentration of 1 g/l. The blank stock solution was kept at 4 °C. The concentration of humic acid remaining in the samples was determined by spectroscopically using PerkinElmer Lambda 25 UV/vis; CT, USA with a calibration curve drawn at 254 nm [51].

The reactor consists of a cylinder of volume of 3 l. A magnetic stirrer inside the cylinder thoroughly mixed the samples under UV irradiation. To adjust the light from UV irradiation, a sample was cooled on ice. The temperature was monitored using a thermometer and kept constant. UV radiation was supplied by a medium pressure mercury lamp at 125 W (Arda, France). The lamp was placed inside a transparent quartz cover with a diameter of 3 cm. Nanoparticles of ZnO were obtained from Nanopars Spadana Company. Table 1 lists the properties of the obtained nanoparticles. The surface textural and morphological properties i.e. SEM and TEM microphotograph of ZnO nanoparticle were presented in Fig. 1.

ZnO/UV processing was carried at initial humic acid concentrations of 2, 5, 7 and 10 mg/l at contact times of 1, 3, 5, 10, 20, 30, 45 and 60 min, different pH values (4, 7, 10) and two concentrations of nanoparticles (0.2 and 0.5 g/l). The processing was performed in one and two stages. The single-stage samples were 250 ml with ZnO added at the desired concentrations. The samples were stirred under UV irradiation using a magnetic stirrer. The samples were periodically sampled by extracting out 10 ml, which created a perceptible change in the volume of the synthetic solution.

a. SEM microphotograph of ZnO nanoparticle



b. TEM microphotograph of ZnO nanoparticle

Fig. 1. SEM and TEM microphotograph of ZnO nanoparticle.

Table 1
ZnO nanoparticle specifications.[a].

Product name	ZnO nanoparticle
Chemical formula	ZnO
Purity	99.8%
Grain size	6–12 nm
Specific surface	40–150 m^2/g
Appearance	Light spongy mass
Color	White
Shape particle	Orb (sphere)
Density	105 kg/m^2
Crystal structure	Hexagonal
Phase form	ZnO

[a] Nanoparticles of ZnO were obtained from Nanopars Spadana Company (Isfahan, I.R., Iran).

Because these nanoparticles can spontaneously deposit, the sample was kept motionless for 30 min so that the majority of particles settled to the bottom. The samples were then centrifuged for 10 min (Hettich-Universal) at a speed of 6000 rpm so that the remaining particles were deposited. After centrifuging, turbid samples were filtered through a filter with a pore size of 0.45 μn using a vacuum pump. The concentration of humic acid remaining was then measured by spectrophotometer. The two-stage phases were carried out in a similar manner.

This step determined the optimal conditions for the nanophotocatalytic operating system. It tested the levels and ranges of the variables to get optimum results from the nanophotocatalytic reactor. A synthetic study of the nanophotocatalytic process was also carried out to obtain optimum conditions.

Ethic statement

a. No specific permits were required for the described field studies.
b. No specific permissions were required for these locations/activities.
c. Location is not privately-owned or protected in any way.
d. The field studies did not involve endangered or protected species.

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