



Evaluation of the efficiency of the TiO₂/UV nano-photocatalytic process in the removal of humic and fulvic acids from aqueous solutions

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Abstract

Background: Removing natural organic substances from drinking water sources is necessary to prevent the formation of toxic and carcinogenic disinfection by-products (DBPs). The nano-photocatalytic oxidation process to remove these substances is easier, faster, cheaper, and more efficient than other methods.

Methods: This study investigated the efficiency of the TiO₂/UV nano-photocatalytic process in removing humic acid (HA) and fulvic acid (FA) from aqueous solutions. Batch tests were performed to investigate the effect of various parameters such as contact time (15, 30, 45, 60, and 75 minutes), initial pH (4, 7, and 9), initial HA and FA concentration (0.5, 1, 2, 5, and 7 mg/L⁻¹), TiO₂ dose (5, 10, 15 and 20 mg/L⁻¹), and different UV irradiation (8 W and 16 W) for the removal of HA and FA from aqueous solutions using TiO₂/UV at room temperature (20 ± 3 °C). The equilibrium adsorption data and the standard parameters were evaluated. Data were analyzed using SPSS version 25.

Results: The efficiency of this process in optimal conditions (pH: 4, anatase TiO₂: 10 mg/L⁻¹, irradiation time: 60 min, UV = 16 W) for removing humic and fulvic (initial HA concentration: 2 mg/L⁻¹ and initial FA concentration: 5 mg/L⁻¹) was 89% and 92%, respectively. The analysis of the experimental isotherm data showed that in the adsorption process of HA and FA on TiO₂/UV, the Langmuir isotherm and the first-order reaction had the best fit with the experimental data.

Conclusion: TiO₂/UV nano-photocatalytic process is suitable for the photo-degradation and removal of HA and FA in aqueous solutions.

Keywords: Humic substances, Titanium dioxide, Photocatalysis, Water purification, Water pollutants

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Introduction

Natural organic matters (NOMs), humic acids (HAs) and fulvic acids (FAs), are the most common amphiphilic substances found in surface waters (1). 90% of the organic carbon dissolved in surface waters consists of humic substances, which include the major part of organic substances dissolved in surface waters (2,3). Humic substances are heterogeneous and polydisperse organic molecules that are obtained from the decomposition of natural organic substances in the environment. Humic substances have an overall negative charge at the pH of natural waters, found in the concentration of 1-50 mg/L⁻¹. Humic substances make up 40% to 60% of dissolved carbon in fresh water and are abundantly found in the

environment (4). NOM is a description of a complex matrix of organic compounds that is heterogeneous and includes particles and dissolved parts. NOMs are an important factor for determining the coagulant and disinfectant dose (5) because they react with chlorine disinfectants and produce disinfection by-products (DBPs) such as trihalomethane and halo acetic acid (with carcinogenic potential) (6,7). Providing safe drinking water has become a problem in many parts of the world and there are many concerns about health, quality, and the presence of by-products from disinfection in water, so maintaining the safety and quality of water is always a major public health problem (8,9). The most common amphiphilic (having a polar end and a non-polar end)



in surface water sources is NOM. NOM concentration in drinking water is usually 2 to 10 ppm (10). Various factors including water chemistry, pH, temperature, and various biological processes in the water body influence the occurrence and fate of NOM in aquatic environments. Therefore, the amount and composition of NOM can vary significantly from one location to another as well as within a water body following seasonal changes that affect natural phenomena such as floods, droughts, and rainfall (11,12). Most NOMs are composed of humic substances (FA and HA). Humic substances cause problems such as smell, taste, and color, increased biological growth in distribution networks and water treatment units, increased chlorine required for disinfection, clogging of membranes, and decreased dissolved oxygen in water (13). And most importantly, they produce DBPs. HAs include a skeleton of alkyl and aromatic units with different reactive groups attached to them, such as carboxylic acid, hydroxyl, and quinone groups (14). Common water treatment processes such as coagulation, flocculation, filtration, and activated carbon are effective in removing NOM from water, and in the best case, they bring the amount of dissolved organic carbon (DOC) between 1-2 mg/L⁻¹. In the coagulation process, increasing the dose of coagulant increases the removal of NOM, but this action will increase the production of sludge, and subsequently, increase the costs and operating time. Also, sludge dewatering is difficult due to the presence of metal ions and organic content (15). The removal of NOM using common water purification methods is minimal and about 10% to 50% (16). To remove organic substances different methods such as electro-ultrafiltration (17), biological removal (17), enhanced coagulation (18,19), activated carbon (20,21), advanced oxidation processes (AOPs) (21-24), ion exchange resins (10), reverse osmosis (RO), nanofiltration (NF) membranes (25), and electro-microfiltration (26), are used that each has its disadvantages (27,28). AOPs are processes based on the production of highly oxidizing radical species that react with organic materials and eventually lead to their destruction (29-32). Advanced chemical oxidation such as photocatalysis using nanoparticles is a useful method in the purification and removal of organic substances due to the use of environmentally friendly chemicals and the removal of many organic substances in a shorter time (33,34).

AOPs, especially of the photocatalytic type, have many advantages over conventional water purification processes and reduce the production of sludge (35). Photocatalytic oxidation is an efficient way to purify water and air and remove pollutants and toxins from the above systems. The main advantage of this process is the complete mineralization of the desired pollutant, which is achieved by the non-selective oxidation mechanism of hydroxyl radicals (23,36-38). Catalysts play an important role in

the synthesis, degradation, and destruction of organic substances (39,40). Magnetic nanoparticles are one of the most important and widely used nanomaterials with unique properties that lead to their specific and potential applications (41). Titanium dioxide nanoparticles (TiO₂) are one of the most important usable photocatalysts that can be used alone or in combination with ultraviolet A (UVA) radiation (42). Among the semiconductor photocatalysts, TiO₂ has characteristics such as availability, cost-effectiveness, non-toxicity, high optical activity, high stability against chemical and optical decomposition, and high oxidization property, and is widely used and noticed. The possibility of recycling again without significantly reducing its photochemical efficiency, not being harmful to humans, chemically and biologically ineffective, and compatible with the environment are among its other characteristics (43-47). Several studies have reported the effectiveness of using TiO₂ for the photocatalytic degradation of HA (48-50). One of the advantages of the UV/TiO₂ process is the inactivation of *Escherichia coli* bacteria (51). Due to the high energy gap (3.2 electron volts), titanium dioxide is not able to produce electron holes in visible light, and the activity of this material takes place under UV light radiation. In other words, it is possible to stimulate the capacitance layers against UV radiation (52). Factors such as crystal structure, specific surface area and porosity, and shape and distribution of pores affect the photocatalytic activity of TiO₂ (44). The presence of a TiO₂ catalyst increases photodegradation due to the power of photocatalytic oxidation with ultraviolet radiation (53).

AOPs are oxidation-degradation reactions, in which free radicals, such as hydroxyl, break down organic materials into simpler inorganic compounds such as carbon dioxide and water (54,55). The photocatalytic degradation process involves the use of a semiconductor such as titanium dioxide. The energy of the electrons increases with the UV light radiation and the impact of the high-energy photons of the UV light on the electrons of the capacitance layer of nanoparticles. Therefore, it is transferred to the conduction band, which is higher in energy than the valence band. Because this band is empty, the electron can easily be transferred from one molecule to another. This causes the appearance of positive holes and negatively charged electrons that are far from each other, each of which can initiate a series of oxidation-reduction reactions, and ultimately, produce hydroxyl radicals. Hydroxyl radical is very active and quickly attacks the surrounding molecules, especially organic molecules, and oxidizes them (45). The schematic diagram of the degradation mechanism of HA and FA using TiO₂ in the presence of UV radiation is shown in [Figure S1 \(see Supplementary file 1\)](#).

In several studies, TiO₂/Fe⁺³ has been used as a heterogeneous nano-photocatalyst for the degradation

of antibiotics in aqueous solutions using UV-C radiation as an energy source (56). The research results of Zhou et al in 2019 on the photocatalytic degradation of HA by TiO₂ nanocomposite modified with rGO nanocomposite showed that the removal efficiency of HA increases with system temperature and light intensity. The removal efficiency of HA in the optimal conditions reached 88.7% (57). The results of the study by Derakhshan et al in 2022, on the efficiency of MnFe₂O₄@TiO₂ nanoparticles in the removal of HA from aqueous solutions under UV light, showed that under optimal experimental conditions (pH=3, nanocomposite dose=0.03 g/L⁻¹, HA initial concentration=2 mg/L⁻¹, and contact time=20 min), the maximum degradation of HA can be achieved (58). Although several experimental studies have been conducted in recent years regarding the removal of pollutants using nanoparticles from aqueous solutions, there is still a significant gap in the relevant literature concerning the investigation of TiO₂/UVC absorption capabilities for the removal of HA and FA from aqueous solutions.

In this research, the removal rate of HA and FA using titanium dioxide nanoparticles in a photocatalytic reactor and using experimental variables was investigated. In this study, in addition to the removal of HA, the removal of FA was also investigated, and few studies have been done in this field. Also, the conditions and efficiency of humic and FA removal from aqueous solutions were improved using the TiO₂/UV nano-photocatalytic process, and the performance of this system was analyzed as a new method to remove HA and FA as water pollutants. Therefore, this study aimed to investigate the possibility of using UV radiation on TiO₂ (TiO₂/UV) to decompose humic and FA from water.

Materials and Methods

Chemicals and reagents

Stock solutions (1000 mg L⁻¹) were prepared by dissolving sodium salt powder (Aldrich Chemical Co. Ltd). HA and FA analytical reagent grades (99.99%, 300 mesh) were obtained from Aldrich Chemical Co. Ltd (Sigma Aldrich USA). One gram of each HA and FA (Sigma Aldrich,

USA) was dissolved separately in 100 mL of 0.1 normal sodium hydroxide solution. Using 1000 mL of distilled water, the primary standard of HA and FA separately with a concentration of 100 mg L⁻¹ was prepared. Then, by diluting each of the obtained mixtures separately with 0.1 normal sodium hydroxide solution, more diluted standards (1-20 mg L⁻¹) were prepared (Figure S2). Afterward, using the TOC analyzer (TOC, Shimadzu, Japan) and the line obtained from the regression analysis of these standards' charts, the correlation coefficient was shown as high as 98%. Two UVC lamps were used at different times in the photocatalytic degradation experiments with a nominal power rating of 8 and 16 W (Philips, China), and their respective energy intensities (irradiances) were determined by radiometry as 8 and 16 W/cm² at a 5 mm distance from the light source. Titanium dioxide (TiO₂, anatase, 99.9%) prepared by a US company (US Research Nanomaterials, Inc), with a specific surface of 200-240 m²/g and mean particle size of 25 nm was used as a catalyst in the photocatalysis process. High mechanical, thermal, and chemical resistance, and no change after participating in a catalytic cycle have caused the widespread and successful use of this catalyst in water and wastewater treatment. Titanium dioxide is a very active photocatalyst with photon energy in the range of 300 nm < λ < 390 nm (59,60). In Figure 1, TEM photo and chemical composition of the TiO₂ catalyst are shown. TiO₂ nanoparticles have an apparent density of 0.24 g/cm³ and a real density of 3.9 g/cm³. Its manufacturing method is by combustion at high temperatures. Sodium hydroxide and hydrochloric acid (Germany, >99% purity) were used for adjusting pH during the experiment. All the chemical compounds used to prepare the reagent solutions (Merck and Sigma Chemical, MO, Germany) were of analytic reagent grade and employed without further purification.

Reactor design

The reactor used in this research was a cylinder with a volume of 1 L. A magnetic stirrer was used to completely mix the sample inside the reactor. A mercury lamp was placed inside the cylindrical reactor as the UV light source.

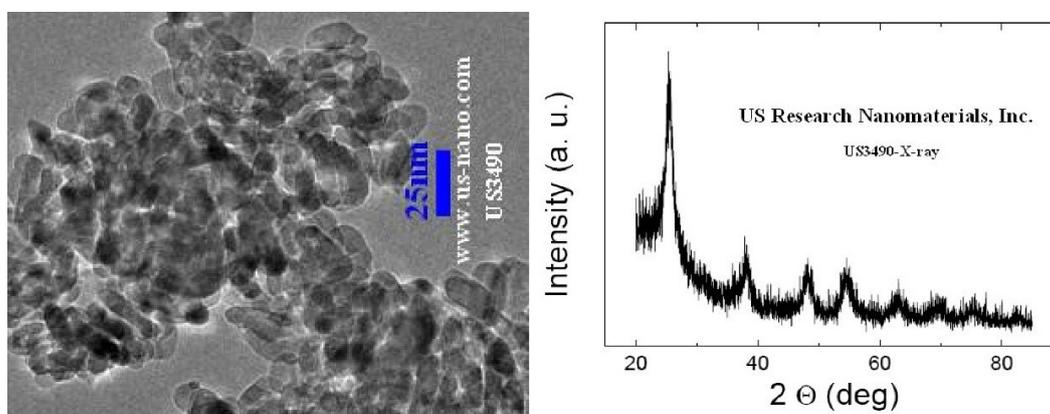


Figure 1. TEM photo and chemical composition of Titanium dioxide powder

Due to the high temperature caused by the UV lamp, coolant (water) was used to regulate the temperature. For this purpose, the system (a 1-L cylindrical reactor and the UV lamp placed inside it) was placed inside a pre-prepared pilot (a 3-L cylinder with a larger diameter, about 20 cm), and the space between the system and the pilot was filled with water and the temperature of the sample was kept constant at the ambient temperature of the laboratory using a thermometer. Also, to prevent the effect of UV rays and the possibility of reflecting the ultraviolet rays coming out of the reactor and increasing the efficiency of the photocatalytic oxidation process, the surrounding of the pilot was covered by thick aluminium sheets (Figure S3).

Experimental method

Batch tests were performed to investigate the effect of various parameters such as contact time (15, 30, 45, 60, and 75 minutes), initial pH (4, 7, and 9), initial HA and FA concentration (0.5, 1, 2, 5, and 7 mg/L⁻¹), TiO₂ dose (5, 10, 15, and 20 mg/L⁻¹), and different UV irradiation (8 and 16 W) for the removal of HA and FA from aqueous solutions using TiO₂/UV at room temperature (20 ± 3 °C). This was done in a reactor equipped with a magnetic stirrer. Experimentation was continued by applying a 60-minute celebration time at an agitation speed of 150 rpm. Afterward, the solution was filtered with a 0.45-µm membrane filter and was analyzed by a TOC analyzer.

Statistical analysis

The data were analyzed using the multivariate regression analysis method and based on the regression equation to obtain the predicted response variable (Y) for humic and FA removal using TiO₂/UV photocatalyst.

Results

Effect of initial pH on nano-photocatalytic degradation

Initial pH is one of the essential factors in the photocatalytic removal of organic pollutants in chemical oxidation processes (61,62). Considering the importance of the pH effect of the aqueous solution on the decomposition and removal process, to determine the optimal pH value for the maximum degradation of HA and FA acids, the laboratory operations for each of these two natural organic substances (NOM_s) at pH 4, 7, and 9. The experiments were carried out by changing the pH and keeping other parameters constant in a closed reactor. The results show that as the pH increases from 4 up to 9, the rate of decomposition and destruction of HA and FA decreases during the nano TiO₂/UV photocatalytic process (Figure 2a, b). The maximum and minimum photodegradation was obtained at pH=4 (89%) and pH=9 (26%) for HA concentration and pH=4 (92%) and pH=9 (38%) for FA concentration, respectively. The optimum pH for the removal of HA and FA was 4.

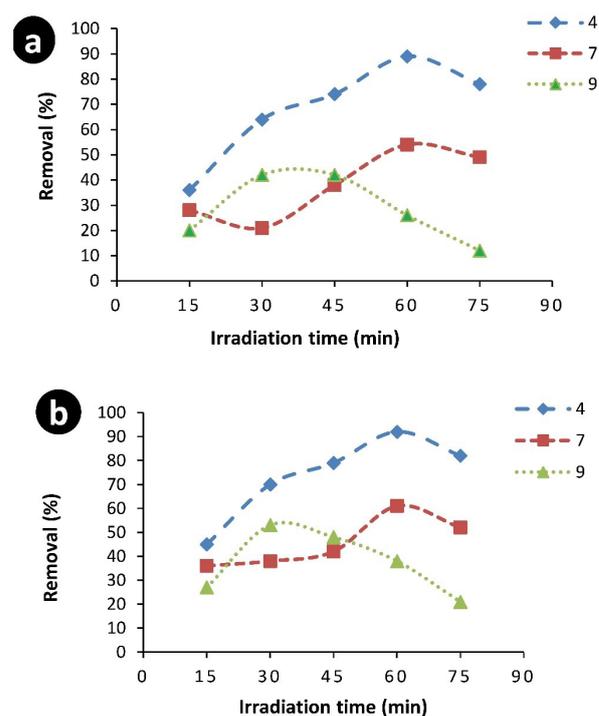


Figure 2. Effect of pH on humic acid (a) and fulvic acid (b) degradation in TiO₂/UV process over 60 min (catalyst concentration) anatase TiO₂(= 10 mg/L⁻¹, Humic acid concentration=2 ppm, fulvic acid concentration=5 ppm, UV LAMP= 16 W)

Effect of catalyst dosage at different irradiation times

To determine the effect of titanium dioxide nanoparticle dose concentration on the removal and photocatalytic degradation of humic and FA, experiments with different concentrations of this nanoparticle (5, 10, 15, and 20 mg/L⁻¹) at different contact times and different concentrations of HA and FA were performed in aqueous solution (Figure 3a, b). The experiments were performed by changing the catalyst dosage and keeping other parameters constant in a closed reactor. After each photocatalytic test, the parameters related to NOMs (HA and FA) were measured separately by determining the total organic carbon (TOC) concentration using the total organic carbon device by the TOC analyzer (TOC, Shimadzu, Japan).

At different contact times (15, 30, 45, 60, and 75 minutes), the removal of HA and FA in the initial dose of catalyst was 5 mg/L⁻¹ (contact time: 45 minutes) and 10 mg/L⁻¹ (contact time: 60 minutes), respectively, for HA to about 61% and 89% and reached 74% and 92% for fulvic acid. At concentrations of more than 10 mg/L⁻¹ of titanium nanoparticles, the removal efficiency of HA and FA decreases by process TiO₂/UV. Therefore, the concentration of 10 mg/L⁻¹ was chosen as the optimal number of nanoparticles.

Effect of HA and FA concentration

By increasing the concentration of HA and FA, the removal efficiency increased. This increase for HA up to 2 mg/L⁻¹

and folic acid up to 5 mg/L⁻¹ was 89% and 92%, respectively (Figure 4). This removal value was obtained at an optimum pH of 4, catalyst dosage of 10 mg/L⁻¹, and maximum optimum time of 60 minutes for humic and fulvic acid organic substances separately in an aqueous solution.

Effect of UV intensity

After examining the effect of UV intensity (8 and 16 watts) at different times (15, 30, 45, 60 and 75 minutes), different doses of titanium dioxide catalyst (0.5, 10, 15 and 20 mg/L⁻¹), the concentration of humic substances and fulvic acid (0.5, 1, 2, 5 and 7 mg/L⁻¹) and at the initial pH (4, 7 and 9) in the aqueous solution, the results showed that at the UV intensity of 16 watts, more efficiency was obtained in the decomposition of humic substances

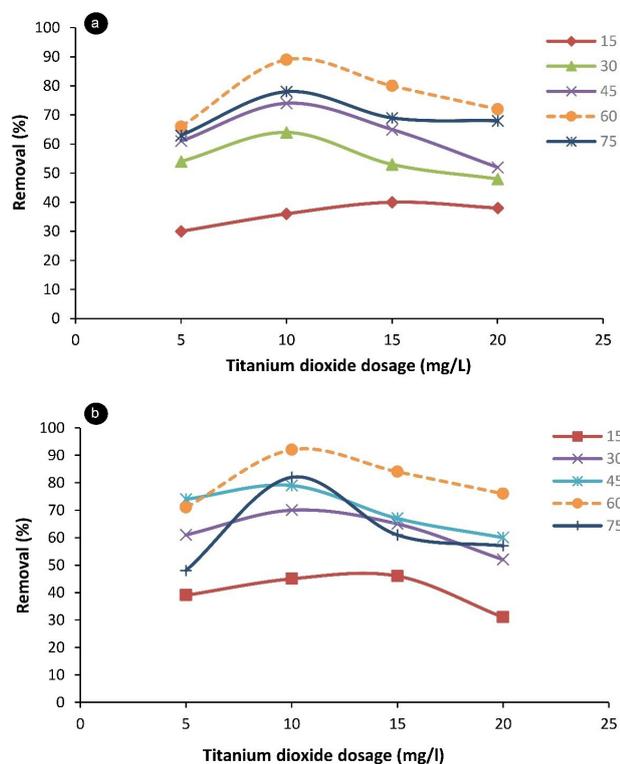


Figure 3. Effect of different TiO_2 /UV catalyst concentrations on humic acid (a) and fulvic acid (b) photodegradation (pH=4, Anatase TiO_2 =10 mg/L⁻¹, Humic acid concentration=2 ppm, fulvic acid concentration=5 ppm, UV LAMP=16 W, contact time: 15, 30, 45, 60, and 75 min)

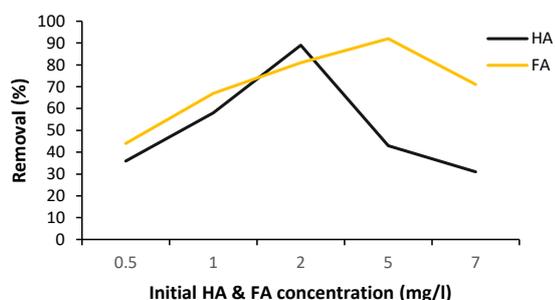


Figure 4. Effect of initial concentration of HA and FA on the removal efficiency in the optimum condition (pH: 4, anatase TiO_2 : 10 mg/L⁻¹, irradiation time: 60 min, and UV: 16 W)

and fulvic acid. Photodegradation of HA and FA under optimal conditions (pH: 4, anatase TiO_2 : 10 mg/L⁻¹, irradiation time: 60 minutes, initial HA concentration: 2 mg/L⁻¹, and initial FA concentration: 5 mg/L⁻¹) in aqueous solution, was 89% and 92%, respectively. This effect (photodegradation of HA and FA) at the UV=8 W and under other similar conditions for each of the HA and FA substances in aqueous solution was 64% and 73%, respectively. Therefore, the comparison of different UV intensities shows that the effect of UV=16 W is greater in humic and fulvic acid photodegradation. The removal efficiency of HA and FA increased with increasing time. This increase continued up to 60 min, then, the removal efficiency did not increase significantly (Figure 5a, b).

Elimination of TOC

The removal efficiency of TOC and HA and FA was investigated under optimal conditions including anatase TiO_2 : 10 mg/L⁻¹, HA concentration: 2 mg/L⁻¹, FA concentration=5 mg/L⁻¹, pH: 4, and reaction time: 60 minutes. The results are displayed in Figure 6a, b. The 76% TOC removal efficiency compared to 89% of HA and 83% TOC removal efficiency compared to 92% of fulvic acid suggests the high efficiency of this process in the removal of HA and FA. In the studied pH range, the maximum removal of TOC occurred at time =60 minutes in the presence of 10 mg/L⁻¹ TiO_2 . Also, acidification (pH=4) leads to better TOC removal.

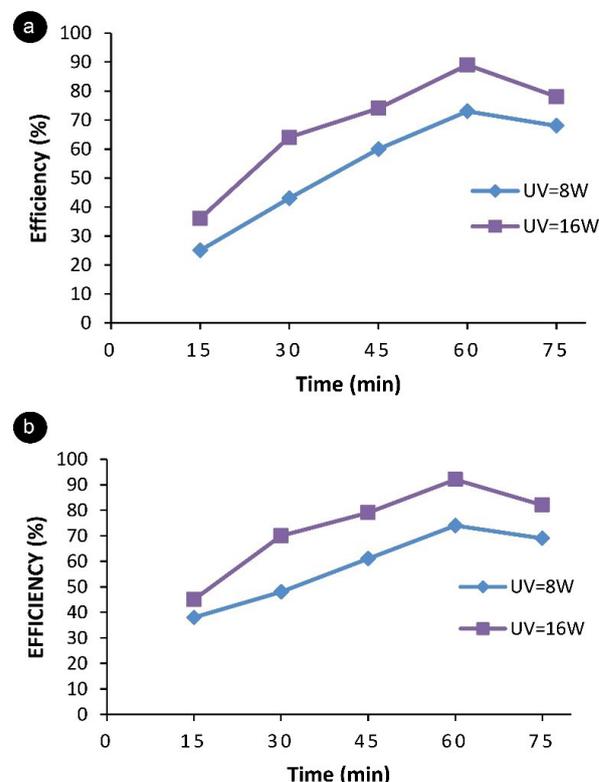


Figure 5. Relative photonic efficiencies of photocatalytic degradation of HA (a) and FA (b) with different UV (8 W and 16 W) and versus irradiation time

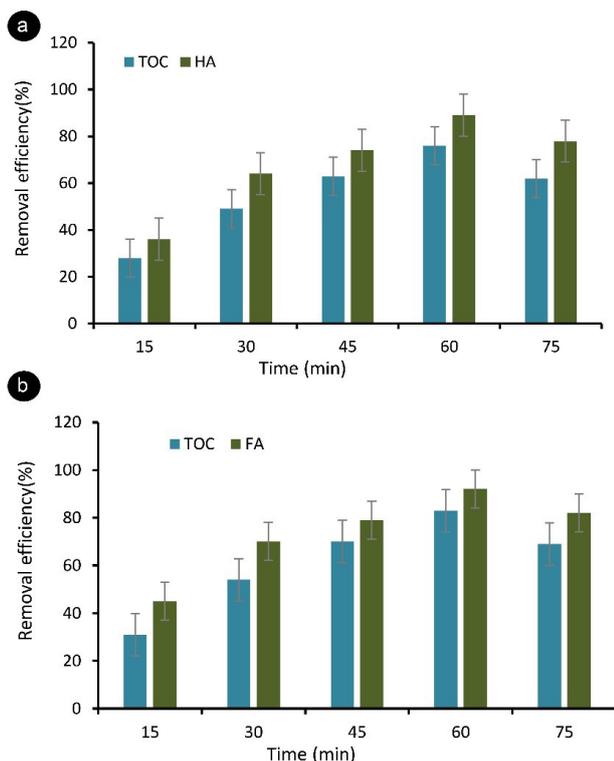


Figure 6. The removal efficiency of humic acid (a) and fulvic acid (b) and TOC using the photocatalytic process in optimal conditions (pH=4, Anatase TiO₂=10 mg/L⁻¹, Humic acid concentration=2 ppm, fulvic acid concentration=5 ppm, UV LAMP=16 W)

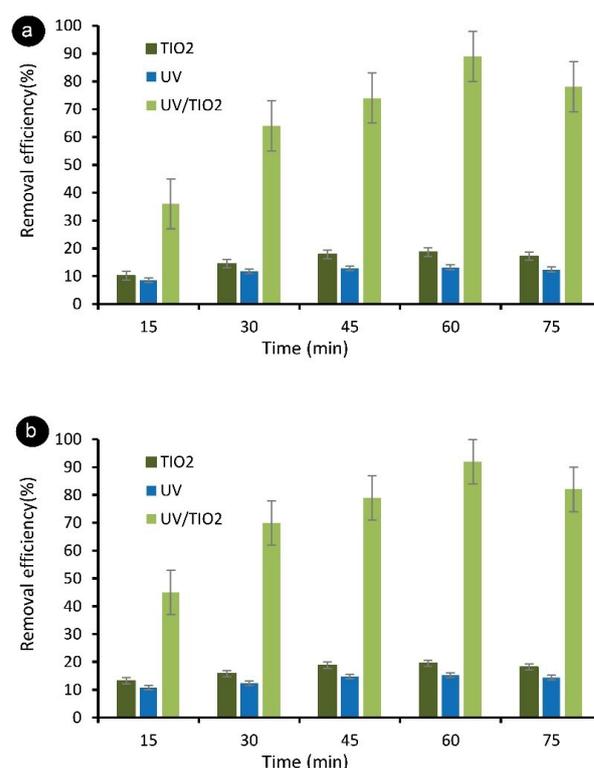


Figure 7. Removal efficiency of different processes involved in photocatalytic degradation of HA (a) and FA (b) (pH=4, Anatase TiO₂=10 mg/L⁻¹, Humic acid concentration=2 ppm, fulvic acid concentration=5 ppm, UV LAMP=16 W)

Examination of real sample

Some of the physical and chemical characteristics of the water network distribution of Sari, Iran, are reported in Table S1. The test was performed on the real aqueous solution in the optimal conditions obtained from the synthetic sample. The removal efficiency of humic and fulvic acid was 75% and 81%, respectively.

Reusability of immobilized TiO₂

From the environmental and economic point of view, the recovery of catalysts and their sustainability is very important in the evaluation of AOPs (63). In this study, recovery and reuse of stabilized TiO₂ nanoparticles and their catalytic activity were investigated (Figure S4a, b). For each new cycle, the stabilized TiO₂ nanoparticles were washed with water and ethanol, dried, and used to decompose a solution containing fresh HA under the same optimal conditions as the previous experiments. In the first stage of use, the titanium dioxide catalyst was effective up to 89% and 92% for the removal of HA and FA in an aqueous, respectively. After several stages of recycling, it was used in the fourth stage to remove HA and FA, and according to Figure 7, the removal efficiency was 81% and 83.5% for each, respectively.

Comparison of humic and fulvic acids degradation in different processes

Comparing the results of photolysis, absorption, and

photocatalytic mechanisms in photocatalytic processes is of great importance and has been emphasized in many studies (29,64-66). To compare the effect of titanium dioxide nanoparticles and ultraviolet rays (UV), and also, the combined effect of UV plus TiO₂ nanoparticles on the removal efficiency of HA and FA in aqueous solutions, each one separately with 2 mg/L⁻¹ of HA and 5 mg/L⁻¹ of FA, at different times (15, 30, 45, 60, and 75 min) and other equal conditions (pH: 4, anatase TiO₂: 10 mg/L⁻¹, UV: 16 W) were investigated. According to Figure 7a, b, the efficiency of HA removal using titanium dioxide, ultraviolet rays, and the process of combining titanium dioxide nanoparticles and ultraviolet rays in the reaction time of 60 minutes was 18.6%, 13.2%, and 89%, respectively. Also, the effectiveness of FA removal using TiO₂, UV, and the process of combining TiO₂/UV in the reaction time of 60 minutes was 19.5%, 15.2%, and 92%, respectively. The maximum removal efficiency of HA and FA was obtained in 60 minutes of reaction time in the photocatalytic process (TiO₂/UV). The band gap of TiO₂ (3.2 eV) is excited due to the intensity of ultraviolet radiation, and with the penetration of ultraviolet light, more free radicals are formed and the rate of degradation of organic substances increases (67). In the combined process and the presence of TiO₂/UV-C rays, the removal efficiency increased, indicating the effective role of the catalyst and the process combination used in pollutant photodegradation (68,69).

Kinetics studies

Adsorption kinetics is used to predict the rate of adsorption and adsorption mechanisms. The degradation kinetics of reactions are applied to describe the photocatalytic degradation process of organic compounds (22,56,70). To investigate the adsorption kinetics, two pseudo-first-order and pseudo-second-order kinetic equations were analyzed separately for both organic substances, HA and FA. After determining the equilibrium time by conducting a preliminary kinetic experiment, Langmuir and Freundlich models of the adsorption of HA and FA onto TiO₂/UV were investigated. In this study, the Langmuir isotherm and the first-order reaction best fit the experimental data. The R² obtained for the pseudo-first-order model with TiO₂/UV and HA and FA was observed to be 0.8572 and 0.7974, respectively. Figures 8a and 8b show the Langmuir plot and pseudo-first-order kinetics curves, respectively. R² obtained for the Langmuir isotherm model for HA and FA, and TiO₂/UV were 0.8012 and 0.939, respectively. The pseudo-first-order kinetic model is based on adsorbent capacity and is applied when adsorption using diffusion mechanism occurs within a boundary layer while the pseudo-second-order kinetic model shows that chemical adsorption is a dominant and controlling mechanism in the process of adsorption (71,72).

Based on the Langmuir isotherm model, the maximum capacities of humic and fulvic adsorption on TiO₂

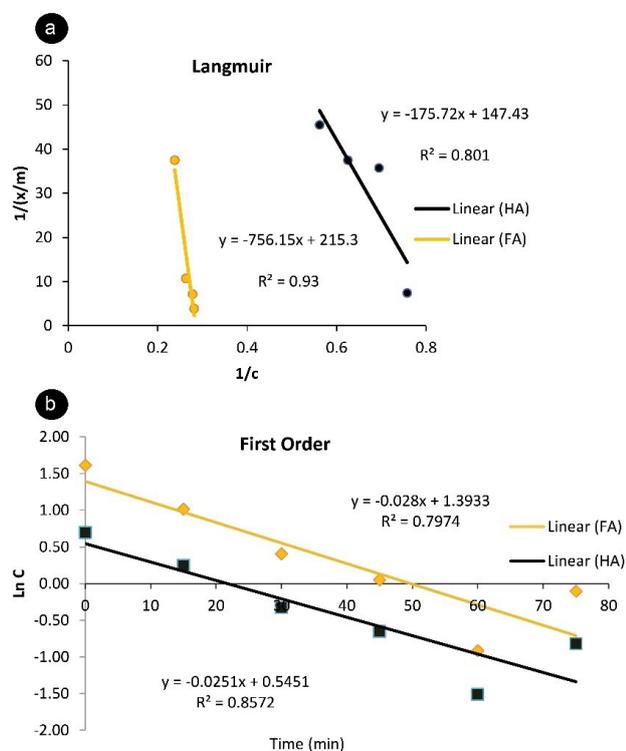
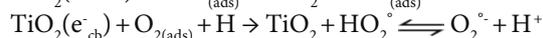
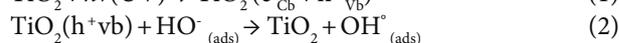
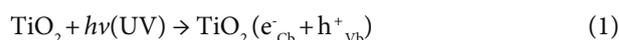


Figure 8. (a) Langmuir plot for the adsorption of HA and FA onto TiO₂/UV (b) First-order reaction plot for the adsorption of HA and FA onto TiO₂/UV (Time: 60 minutes, pH=4, T=25°C, Humic acid concentration=2 ppm, fulvic acid concentration=5 ppm, UV LAMP= 16 W)

nanoparticles are 1.3 and 1.9 mg/g, respectively. In addition, according to two common kinetic models (pseudo-first-order and second-order kinetic), the calculated parameters show that pseudo-first order the kinetic model can provide a better fit with the experimental data of HA and FA adsorption (Table 1).

Discussion

According to the literature, the decomposition of contaminants (FA, HA) on the bare TiO₂ surface proceeds probably according to the following mechanism (73,74). Electron-hole pairs are formed after the excitation of TiO₂ with light energy higher than the band gap. Continuous band-gap irradiation [E_{bg}= 3.2 eV]390 nm(in anatase] of an aqueous semiconductor dispersion excites an electron from the valence band (VB) to the conduction band (CB), creating an electron-hole pair (Eq. 1) (75). Holes, water, or surface hydroxyls are oxidized by light-induced carriers that participate in redox reactions by migrating to the particle surface, while electrons reduce dissolved oxygen (Eq. 2) (74). Through a complex sequence of reactions, the heterogeneous photocatalytic process is carried out, which can be expressed by the following set of equations (68,75):



Strong oxidizing hydroxyl radicals produced from reactions 1 and 5, may in turn attack organic materials (76). OH, radicals are strong oxidizing agents that can degrade organic substances such as HA and FA (Eq. 6). Also, the breakdown of HA and FA is obtained through the direct reaction of the created holes (Eq. 7). In addition to the mentioned possible degradation pathways, including holes, photogenerated electrons can decompose and remove HA and FA or interactively mineralize HA

Table 1. Adsorption kinetics and isotherm model for adsorption of HA and FA on the TiO₂/UV photocatalyst nano-photocatalytic

| Adsorption model | | Kinetic model | | | |
|------------------|-----------------------|---------------|--------------------|---|--------|
| Parameters | | Parameters | | | |
| HA | K _L (L/mg) | -0.814 | Pseudo-first-order | k _i (h ⁻¹) | 0.0127 |
| | q _m (mg/g) | 1.32 | | q _{e, cal} (mg g ⁻¹) | 651.36 |
| | R ² | 0.801 | | R ² | 0.857 |
| FA | K _L (L/mg) | -0.653 | Pseudo-first-order | k _i (h ⁻¹) | 0.0198 |
| | q _m (mg/g) | 1.94 | | q _{e, cal} (mg g ⁻¹) | 851.12 |
| | R ² | 0.939 | | R ² | 0.797 |

and FA with an electron acceptor to create superoxide O_2^- (Eqs. 8 and 9) (73,77). The TiO_2 catalyst is more important in the process of photocatalytic degradation by ultraviolet rays due to its cheapness, insolubleness, nontoxicity, and better activation than other catalysts (78,79).

According to the results of the study, by increasing pH from 4 to 9, the rate of degradation of HA and FA decreases during the nano TiO_2 /UV photocatalytic process. Due to the effect of surface charge at higher pH, OH^- ions increase in the solution, and due to its competition with HA and FA for positive surface charge adsorption sites of TiO_2 , the decomposition of HA and FA decreases (80). Another effective factor that causes protonation and deprotonation in acidic and alkaline conditions is the ionization of the photocatalyst surface (81). The relationship between HA decomposition and pH increases with decreasing pH.

Based on the conducted studies, the removal of HA by nanoparticles is done by electrostatic decomposition and ligand exchange between HA and the surfaces of nanoparticles. Phenolic functional groups in HA were responsible for ligand exchange with nano- TiO_2 (82,83). The structural orientation of the molecule is favorable for the attack of reactive species at acidic pH (83). The electrostatic attraction between TiO_2 and HA increased at acidic pH and led to increased efficiency of the photocatalytic degradation process (84). Similar studies have shown that pH changes in the range of 3-6 have little effects on the TOC reduction rate. But at pH=9, after reducing 70% of the initial concentration, the rate of decomposition slows down due to the formation of small species with a negative charge (carboxylate) (85). In many studies conducted on the removal of HA from aqueous solutions, the optimal pH range is between 3 and 5, and the maximum removal of HA is obtained at low and acidic pH (58,86-88), which is consistent with the results of this study. HA has the maximum rate of degradation in an acid environment (pH = 3) since there are more hydrogen ions (H^+) in the acidic environment and the nanoparticle surface becomes positively charged due to H^+ ions (86,89). According to Figure 2, the nano photocatalytic degradation efficiency of HA and FA increased with increasing time in the TiO_2 /UV photocatalysis reactor. The efficiency of photocatalytic decomposition of nano HA and FA was increased by increasing the concentration of titanium dioxide up to 10 mg/L⁻¹, increasing the time up to 60 minutes, and the concentration of 2 mg/L⁻¹ for HA and 5 mg/L⁻¹ for FA in the TiO_2 /UV photocatalysis reactor. It seems that the increase in turbidity caused by HA solution with the reduction of UV light absorption is effective in reducing the efficiency of the TiO_2 /UV photocatalysis process at higher concentrations of HA.

This finding confirmed and showed the previous observations. In related studies, it was found that increasing the contact time and catalyst dosage has a

positive effect on increasing the removal efficiency of organic substances, but pH has a negative effect (90). The rate of removal and degradation of HA and FA increases with the increase of the catalyst dose (TiO_2 up to 10 mg/L⁻¹), which is related to the heterogeneous photocatalysis properties of this catalyst (91-93). The photocatalytic degradation efficiency of HA increases with increasing catalyst dose due to the increase in surface area and the number of active places on the catalyst surface. So with ultraviolet radiation, more electron holes are generated, which leads to increased production of oxidate radicals and further disintegration of HA (43). In the special high concentration of catalyst, turbidity prevents further penetration of light in the reactor, leading to a decrease in the photodegradation efficiency (94). By increasing the amount of nano-catalyst to more than 0.03 g/L⁻¹, the turbidity increases, and the ability to remove HA decreases. This opacity makes the ultraviolet light not able to penetrate well. Another reason for the reduction of HA removal with increasing nano-catalyst dosage is that in high doses of this nano-catalyst, due to the increase in magnetic properties, the nano-catalyst condenses, which reduces the speed of photon absorption on its surface (95,96). In the research of Babel et al in 2016, using a catalyst dose of 0.3 g/L⁻¹, 100% HA removal efficiency was achieved in 3 hours (97). It is necessary to save time and use the minimum dose of catalyst. Therefore, when the dose of titanium oxide is 10 mg/L⁻¹, the concentration of HA and FA are 2 and 5 mg/L⁻¹, respectively, and the irradiation time is 60 minutes, the best removal efficiency occurs. The results of this study are consistent with the findings of a study by Huang et al in 2008. The findings showed that with increasing doses of TiO_2 , the number of reactive sites increases, and the rate of oxidation increases. At the same time, the turbidity of the system increases, and the effective radiation of ultraviolet rays decreases, which negatively affects the reaction speed. In this study, the optimal concentration of TiO_2 nanoparticles was in the range of 0.1-1 g/L⁻¹, and the removal efficiency decreased with an increase in nanoparticle dosage (98). The results of the study of Abdollahi et al in 2019 showed that the photocatalytic degradation of HA using MnFeN-tridoped TiO_2 increased with increasing catalyst dosage and decreased with increasing initial pollutant concentration and pH (99).

The reason for increasing the removal efficiency of HA at higher initial concentrations is its molecular weight. The high molecular weight of HA can act as electron-donating centers (oxidation) and as electron-accepting centers (reduction) in the photodegradation process (100). Therefore, at a high concentration of HA, due to the successive electron transfer of HA to the conduction band of TiO_2 , molecular bonding is established, leading to HA internalization (101).

The reason for the decrease in efficiency with the

increase in the initial concentration of HA and FA is that at lower concentrations there is more surface on the absorber that absorbs organic substances. On the other hand, the repulsive forces between the molecules of organic substances absorbed on the surface of the absorber increase (102). Due to the equal concentration of radicals produced in all solutions, a solution with a low concentration of HA with the same amount of hydroxyl radical has more decomposition than a solution with a higher concentration. The results of this study are consistent with the results of other studies. All these studies confirmed the reduction of removal with increasing concentration of organic substances in an aqueous solution (98,99,103). Photocatalytic degradation of an organic pollutant depends on its concentration, its nature such as structure, molar mass, functional groups, and other compounds present in the aqueous solution (104,105). The photo degradation rate of HA and FA varies due to the chemical structure of organic substances, which significantly impacts their speed of photodegradation (106).

This study confirms the results of other similar studies in increasing the efficiency of HA removal with increasing time and UV intensity (88,97,98). At concentrations higher than 2 mg/L⁻¹ of HA and 5 mg/L⁻¹ of FAs, due to the increase in turbidity, the effect of UV intensity on the photodegradation and removal of organic substances is reduced (98). Excessive UV radiation may harm the photodegradation properties of nanoparticles (107). At higher intensity radiation (UV=16 W), the nanoparticle catalyst absorbs more photons, which leads to the formation of more electron pairs, so the hydroxyl radical provides a higher efficiency in the photocatalytic mineralization and removal of NOMs (108). The results of various studies by examining the similar parameters used in this study to eliminate NOMs from natural waters, including the reservoir water (under conditions pH~7, TOC_M=10.6 mg/L, TOC_W=3.5 mg/L, [TiO₂]=0.1 g/L⁻¹, UVA—20 W (λ=365 nm), 150 minutes) with 80% TOC removal efficiency (109), Pre-treated (coagulation flocculation) water (under conditions pH~6.7, P25: TOCI=7.8 mg/L [TiO₂]=0.5 g/L⁻¹, 220 minutes) with 80% TOC removal efficiency (110), extracted river NOM (under conditions pH~8.2, TOCI=10 mg/L [TiO₂]=1 g/L⁻¹, UVC=8 W, 120 minutes) with 80% TOC removal efficiency (111), treatment plant inlet water in immersed ultrafiltration module (pH~7 DOC=5.48 mg/L, [TiO₂]=0.1 g/L⁻¹, UVC=15 W, 120 minutes) with 60% DOC (112) removal efficiency indicates that the use of the nanotechnology process has the efficiency needed to eliminate NOM in natural waters and in the presence of other water compounds. Photocatalysis has received increasing attention worldwide, especially in the last decade, as various investigated processes have been regularly reported to be one of the best water treatment

technologies for removing NOM from drinking water sources and reducing the formation of disinfectants by-products (113).

At the beginning of the reaction, the amount of TOC decreases slowly. The evolution of TOC demonstrates the ability of TiO₂ to act as an efficient catalyst in the photodegradation of HA. The reason for the initial reduction is related to the amount of TiO₂, so the lower the amount of TiO₂, the longer the duration of this stage (114). The classic saturation phenomenon is expressed for TiO₂ above 1 g/L⁻¹ (115). The evolution of the reaction is due to surface degradation of the carboxylate, which leads to a shorter HA chain, followed by the resorption of the macromolecule. It has been proven in various studies that photodegradation can be carried out on the surface through oxidation by holes, and this mechanism is suitable for adsorbed molecules (108,116,117). Surface degradation of adsorbed HA through carboxylate surface groups leads to photopolymerization. In the continuation of the process, the HA is decomposed through the surface oxidative mechanism, and it is the dominant mechanism until the macromolecules exported from the HA remain, and then, it gradually decreases with the evolution of carbon dioxide from the surface oxidation of the adsorbed carboxylate (114).

Changing the ratio of base cations to strong acid anions changes the alkalinity of the solution (118). Photocatalytic degradation depends on various functional parameters such as pH, anions, cations, etc (119). In the real sample, in addition to HA, there are other organic compounds (TOC), interfering factors, and physicochemical factors (pH, temperature, etc), so a part of the generated hydroxyl radicals and holes caused by electronic excitation decomposes these compounds (120).

The results of various studies have shown that TiO₂ nanoparticles have significant stability (68). In the fourth step, the use of a recycled catalyst reduces the strength between HA and titanium dioxide due to the occupation of active sites on the catalyst, so it is better not to use more than 4 steps to prevent the reduction of efficiency. The number of catalyst recovery times also depends on other process conditions. The catalyst's lifetime is one of the important parameters of the photocatalytic process because its use for a long time leads to a significant reduction in the cost of purification (121).

Comparisons with literature data

Some data from related studies used for different photocatalyst absorbers and operating conditions for HA and FA adsorption are summarized in Table 2. The data shows that different types of nano-catalyst materials such as TiO₂ have been used for the degradation of organic materials in a wide range of operating conditions. This study indicated that the TiO₂/UV nano-photocatalytic method is suitable for photodegradation and removal

Table 2. Comparative evaluation of the photocatalytic activity of various nano-catalysts at different initial pollutant concentrations

| Catalyst used | Organic pollutant | Initial pollutant concentration | Catalyst dose | Irradiation time (min) | Degradation efficiency (%) | References |
|--------------------------------|-------------------|---------------------------------|------------------------|------------------------|----------------------------|---------------|
| TiO ₂ | Humic acids | 100 mg/L ⁻¹ | 1.0 g/L ⁻¹ | 60 | 88 | (50) |
| TiO ₂ -Degussa 25 | Fulvic acid | 10 g/dm ³ | 1.0 g/dm ³ | 30 | 70 | (122) |
| TiO ₂ | Humic acid | 14.2 mg/L ⁻¹ | 0.1 g/L ⁻¹ | 34 | 50 | (73) |
| TiO ₂ | Fulvic acid | 13.5 mg/L ⁻¹ | 0.25 g/L ⁻¹ | 34 | 50 | (73) |
| TiO ₂ | Humic acid | 1.3 mg/L ⁻¹ | 1 g/L ⁻¹ | 60 | 95 | (120) |
| MnFeN-tridopedTiO ₂ | Humic acid | 10 mg/L ⁻¹ | 1.5 g/L ⁻¹ | 120 | 86.72 | (99) |
| TiO ₂ | Fulvic acid | 5 mg/L ⁻¹ | 10mg/L ⁻¹ | 60 | 92 | This research |
| TiO ₂ | Humic acid | 2 mg/L ⁻¹ | 10mg/L ⁻¹ | 60 | 89 | This research |

of humic and fulvic acids in aqueous solutions. The efficiency of the nano TiO₂/UV photocatalytic process under optimal conditions to remove HA and FA in artificial and real samples was 89%, 92%, and 75%, 81%, respectively.

Conclusion

This study shows that the TiO₂/UV nano-photocatalytic process is suitable for the photo-degradation and removal of HA and FA in aqueous solutions. The efficiency of this process in optimal conditions (pH=4, catalyst concentration=10 mg/L⁻¹, irradiation time=60 min, UV=16 W) for removing HA and FA) initial HA concentration=2 mg/L⁻¹, and initial FA concentration=5 mg/L⁻¹(was 89% and 92%, respectively. This process is simple and affordable. This technology is probably effective for decomposing and removing other organic substances (NOM₃) in aqueous solutions.

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Competing interests

The authors declare that they have no conflict of interests.

Ethical issues

The authors certify that all data collected during the study are as stated in the manuscript, and no data from the study has been or will be published separately elsewhere.

Supplementary files

Supplementary file 1 contains Figures S1-S4 and Table S1.

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