

The Degradation of Naproxen and Diclofenac by a Nano-TiO₂/diatomite Photocatalytic Reactor

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A study of the photodegradation of two pharmaceuticals---naproxen (NPX) and diclofenac (DCF) in aqueous medium at different intensities of ultraviolet irradiation and hydraulic retention times (HRT) by using a lab-scale photoreactor was carried out. A new nano-TiO₂/diatomite (NTD) composite was used as the photocatalyst, and its adsorption and photocatalysis of the two pharmaceuticals were observed owing to their hydrophilic/ hydrophobic character. It was found that the NTD photocatalytic reactor exhibited significant removals of the NPX and DCF with the supply of suspension and aeration. The variation of UV irradiation intensity plays more significant role in the degradation of DCF, compared with that of NPX.

Keywords: Nano-TiO₂/diatomite; naproxen; diclofenac; photocatalysis.

1. INTRODUCTION

Nowadays, many residues of pharmaceuticals and personal care products (PPCPs) can be detected in municipal wastewater effluent (MWW) because wastewater treatment plants were not designed to remove PPCPs from their effluents. Therefore, many residues of these compounds can be detected in both MWW and surface water bodies [1-4].

As a well-known anti-inflammatory and model hydrophobic drug[5, 6], naproxen (NPX), was chemically designated as (S)-6-methoxy-R-methyl-2-naphthaleneacetic acid [7] and its molecular formula is C₁₄H₁₄O₃. This pharmaceutical product is often present in wastewater treatment effluents, rivers and lakes [8]. Thus, how to adsorb or degrade this substance has been investigated. X. Zhao et

al. found that NPX can be degraded via photoelectrocatalytic process at Bi_2MoO_6 -boron-doped diamond hybrid electrode under visible light irradiation [9]. K. Kimura et al. [10], J.L. Tambosi et al. [5] and R. Reif et al. [11] drew a conclusion that the NPX could be removed with higher efficiency in membrane bioreactors. A. D'Haese et al. conducted the study on the trace organic solutes in closed-loop forward osmosis and found a negative influence of fouling on closed-loop forward osmosis rejection which was limited in most cases, while it was significant for some compounds such as paracetamol and naproxen, indicating specific compound-foulant interactions [12].

Diclofenac ($2'$ -[$2,6'$ -(dichlorophenyl)amino]phenylacetic acid) is a non-steroidal anti-inflammatory drug used to treat inflammatory and painful diseases of rheumatic and non-rheumatic origin. Nowadays this drug is ubiquitously present in the aquatic environment due to its resistance to biodegradation [13]. H. Yu et al. had studied the kinetics, degradation pathways and toxicity assessments of the diclofenac by advanced oxidation and reduction processes and found that advanced reduction process is more suitable for removing the toxicity, while the reduction processes generally need higher irradiation dose [14]. M. Soufan et al. had researched the aqueous chlorination of diclofenac and several degradation products formed during chlorination of DCF were identified [15].

TiO_2 is the most popular nanometer-scaled photocatalytic material because of its high oxidability, stable chemical properties and non-toxicity. However, TiO_2 also has the disadvantage of feeble thermal stability. Therefore, some research has focused on finding hierarchical porous materials to be the carrier for TiO_2 [16]. Diatomite is one of the most readily available supports due to its inherently hierarchical porosity [17]. A simple process has been reported for the production of efficient and hierarchically structured catalysts: nanometer-scaled TiO_2 which was coated on the surface of diatomite using multiple cycles with phytic acid as the molecular binder [16]. T. Haruthai et al. found that low pH electron transfer from carboxyl group to the TiO_2 valence band hole giving ketone and alcohol from ibuprofen and naproxen. Besides, $\text{HO}\cdot$ radical aromatic ring oxidation dominant at pH 5 and above for all compounds giving Cl ion from clofibric acid and diclofenac [18].

The main objective of this study is to better elucidate the adsorption and photodegradation of NPX & DCF by NTD, as well as the characteristics of NTD composite.

2. MATERIALS AND METHODS

2.1. Feed water

NPX and DCF were purchased from Sigma-Aldrich Company (USA). Stock solution of NPX and DCF was prepared with deionized water, respectively. All chemicals used were reagent grade and were used without further purification. The Stock solution was prepared the day before photocatalysis. And water samples were filtered through $0.45\ \mu\text{m}$ membrane filter to remove colloidal particles.

2.2. Composition of the NTD composite

The NTD photocatalysts were obtained from the China University of Mining and Technology. The NTD composite was prepared by hydrolysis, precipitation, filtration, lavation, arefaction and

roasting of the following materials: delegiert diatomite as the carrier; TiCl_4 as the precursor; and hydrochloric acid, ammonium sulfate and ammonium carbonate as assistant agents [19, 20].

2.3. Photocatalysis module and operation method

A photocatalytic reactor at laboratory-scale was projected and operated as shown in Fig. 1. In this study, the reactor was made of stainless steel with an effective volume of 7 L. And the suspended NTD concentration at the operating conditions was 0.5 g/L. Three low pressure UV lamps (16 W, Philips, Holland) with a wavelength of signally 254 nm were hanged vertically in the middle of the reactor. And a magnetic stirring apparatus was located under the reactor to guarantee the suspension homogeneously when the UV lamps worked. Coarse bubble aeration was set at the bottom of the reactor to supply continued aeration and effective completed turbulent flow. A constant temperature of 27 °C was maintained in the reactor by a condenser. The influent and effluent were maintained by two peristaltic pumps at a flux range of 0.6–3.00L/ h corresponding to the HRT 11.67–2.33h. The feed tank was loaded with the same concentration of catalyst in the reactor to ensure the constant catalyst amount in the reactor. Samples were taken from the outlet at predefined time, filtrated by 0.45 μm membranes and stored at 4 °C for subsequent analysis.

The main operation process of this experiment included two parts: (1) adsorption: mixing the feed water and NTD composite for 30 min in the dark to achieve a steady state conditions for the adsorption phenomena; (2) photocatalysis: turning on the UV lamps and opening the influent and effluent peristaltic pumps after 30 min, respectively. Samples were withdrawn at fixed time intervals in the whole process.

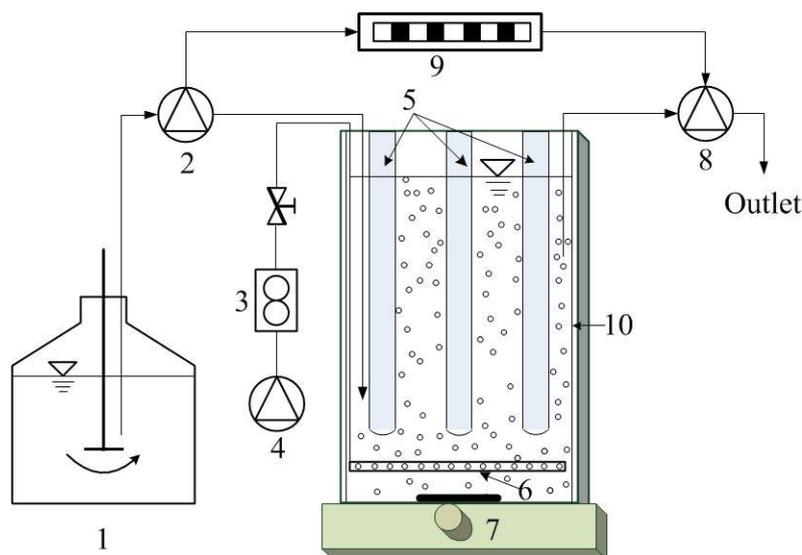


Figure 1. A schematic diagram of the photocatalytic reactor: 1. Feed tank, 2. Influent pump, 3. Flow meter, 4. Air pump, 5. UV lamp, 6. Air diffuser, 7. Magnetic stirrer, 8. Effluent pump, 9. Control system, 10. Condenser.

2.4. Analytical methods

The concentration of NPX and DCF were determined by a HPLC/ VWD FLD (Agilent 1200, USAHP1090) with an XBridge™ column (4.6×150mm) [21]. Methanol solution and 0.25 M acetic acid with the volume ratio of 3:1 were used as the mobile phase of NPX at a flow rate of 0.7 ml/min, and the quantity of the separated compounds were detected by UV absorbance at 280 nm and 30°C. As to the DCF, ammonium acetate (0.2M), acetic acid (1%) and Methanol solution with the volume ratio of 32:3:65 were used as the mobile phase at a flow rate of 0.4 ml/min. Quantity of the separated compounds were detected by UV absorbance at 280 nm and 30°C.

3. RESULTS AND DISCUSSION

3.1. NTD composite characterization

Fig. 2 shows the SEM images of NTD composite. It can be seen that copious nano-TiO₂ crystals were adhered to the surface of diatomite homogeneously and the unit of diatomite was intact and diameter-uniform, which stood for the high purity of the diatomite and the grain sizes were in the range of 20 to 30 μm mostly.

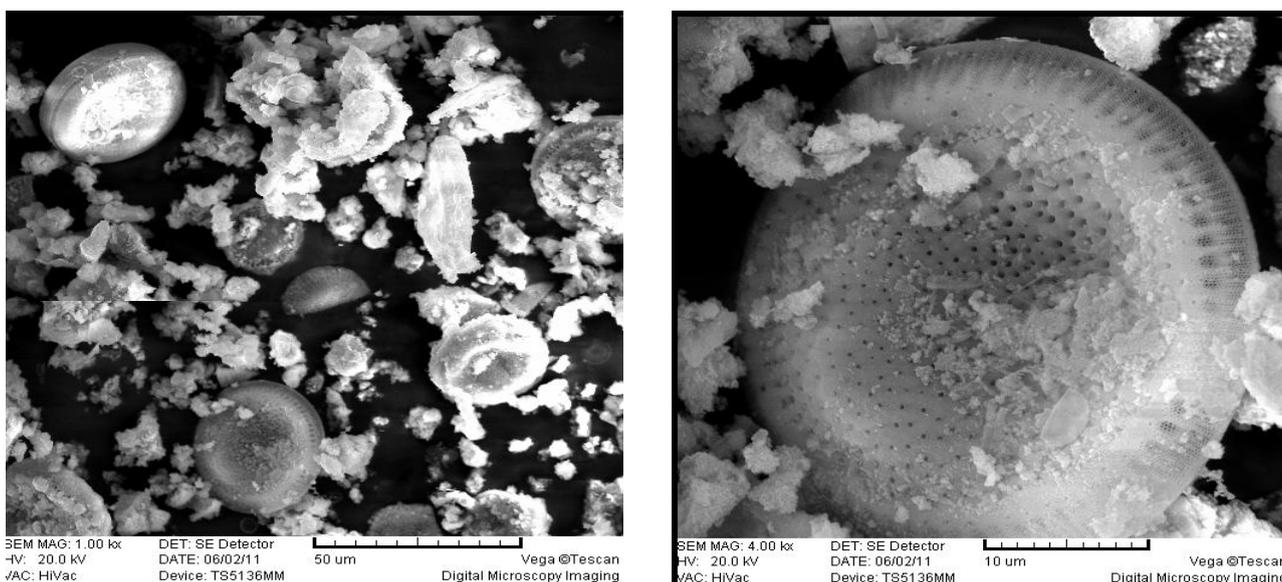


Figure 2. The SEM images of the NTD composite

3.2. Catalyst loss and control

The suspended catalyst concentration was measured based on turbidity. The NTD powder was mixed with deionized water to obtain the NTD suspension liquid. Six different concentrations of NTD particles (0, 0.2, 0.4, 0.6, 0.8 and 1.0 g/L) were evaluated to obtain the corresponding turbidity values

in Fig. 3. The turbidity and concentration of the NTD suspension liquid exhibited a strictly linear relationship ($R^2=0.9953$).

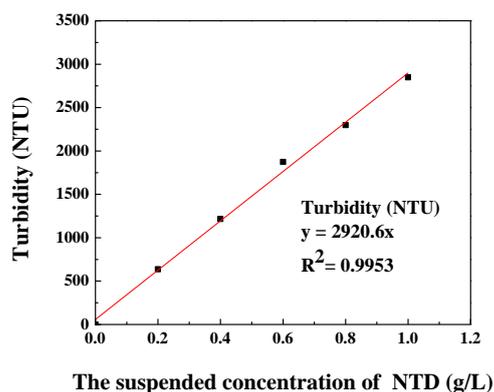


Figure 3. The calibration curve for the suspended NTD concentration as a function of the turbidity

3.3. NPX and DCF degradation

Fig. 4 shows the relation about the suspended NTD concentration and the decrease of NPX concentration with and without aeration after the same photocatalytic time (conditions in operating: NTD, 0.8 g/L; influent and effluent flux, 3.0 L/ h). Under the assist of coarse bubble aeration, only 11% of the catalyst concentration decreased after 10 h of photocatalysis and the final naproxen concentration reduced to 23 μ g/L corresponding to the removal rate of 94%. However, a sharp decrease of the suspended NTD concentration appeared without aeration, and the decomposition rate of naproxen was less than 80%. Wei et al. found that coarse bubble aeration below the flat membrane module not only could reduce TiO₂ deposition on the membrane surface but also maintained the TiO₂ in suspension. [22] Thus, magnetic stirring and coarse bubble aeration were employed in this study.

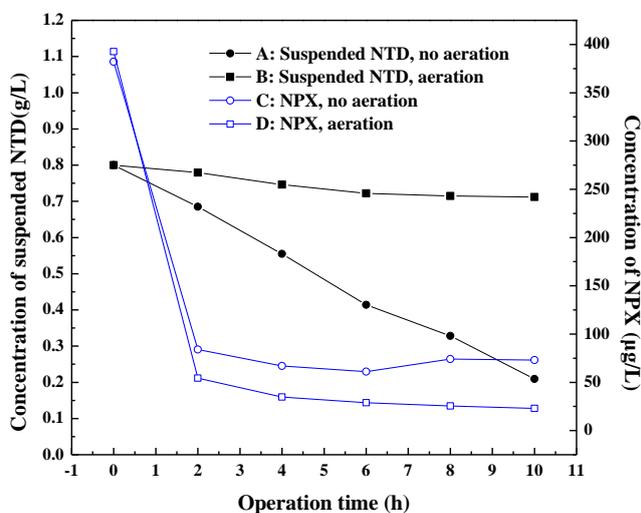


Figure 4. Variations of NTD concentration and NPX concentration during the catalytic process.

Fig. 5 showed the percentages removal of NPX and DCF at different initial concentrations (C_{NPX} & C_{DCF} , 400 & 800 $\mu\text{g/L}$) and ultraviolet irradiation intensities (I_{UV} , 0.39 & 1.17 mw/cm^2) when the influent flux was 3.0 L/h. Fig. 5a showed that the NPX removal efficiencies by NTD adsorption under the four operating conditions were all below 7%, and the highest NPX removal for each NTD photodegradation condition was 100, 97.42, 99.75 and 98.84%. It was obvious that when the initial NPX concentration was 800 $\mu\text{g/L}$ and UV irradiation intensity was 0.39 mw/cm^2 , the NTD photodegradation was the least efficient in the four operating conditions. These results could indicate that the initial NPX concentration of the feed water might exert negative effect on the naproxen removal and a lower UV irradiation intensity would reduce the photocatalytic degradation of the NPX. As for Fig. 5b, the removal efficiencies of the DCF by NTD adsorption under the four operating conditions were all below 5%, and when the initial DCF concentration was 400 $\mu\text{g/L}$, the DCF could be degraded completely in 30min under UV irradiation intensity of 1.17 mw/cm^2 . Besides, it seems that the variation of UV irradiation intensity plays more significant role in the degradation of DCF, compared with that of NPX. The experiment of identification of byproducts by M. Fabiola et al. shows that demethylation and decarboxylation are the principal initial processes in the degradation of NPX[23]. P. Calza, et al. found that the DCF photomineralization of the chlorine ions release was rather a quick process (less than 1 h), while the amino moiety is mainly transformed into NH_4^+ and in a lesser extend into NO_3^- ions[24]. And J. Hartmann considered that the diclofenac degradation could take place in the homogeneous phase governed by a precipitation-redissolution-degradation process[13].

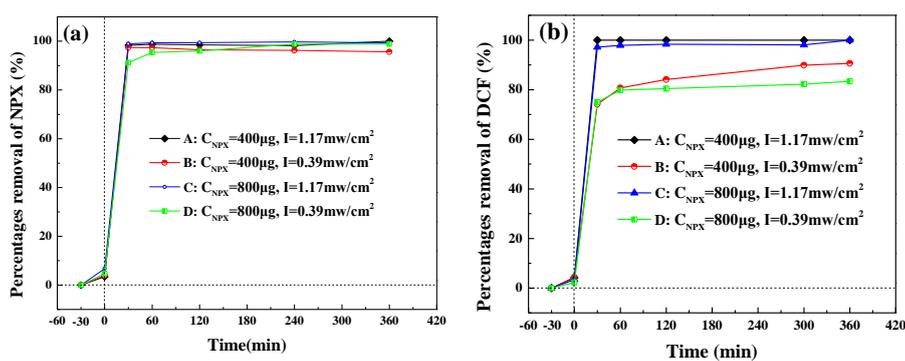


Figure 5. The percentages removal of NPX and DCF at different initial NPX concentrations and ultraviolet irradiation intensities: (a) NPX; (b) DCF.

Fig. 6 showed the percentage removal of NPX and DCF at an initial concentration of 800 $\mu\text{g/L}$ when the UV irradiation intensity was 0.39 mw/cm^2 . The percentages of NPX removal happened at the influent flux of 3.0, 4.5 and 6.0 L/h (HRT=1.17, 1.56, 2.33h). During 360 min photocatalytic time, the removal efficiencies of NPX and DCF grow regularly with the time extension of photocatalysis and the flux decrease. Compared the degradation curves of NPX and DCF under the same flux, the degradation of NPX is more effective than that of DCF by the photocatalysis of NTD under the operating condition of a high concentration and low UV irradiation intensity.

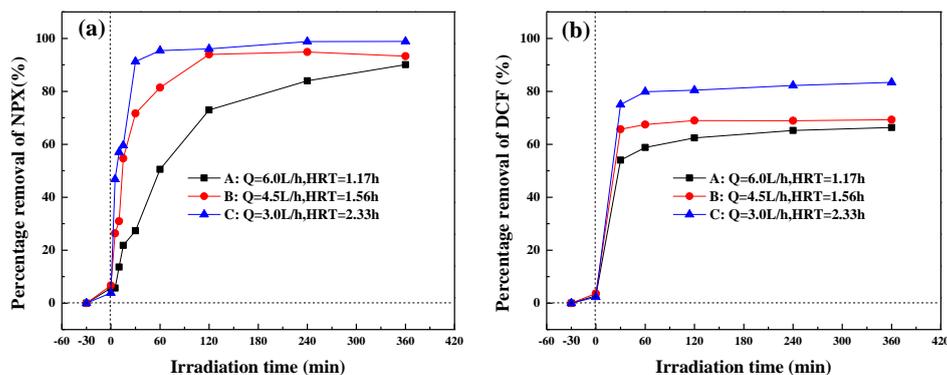


Figure 6. Percentage removal of NPX and DCF under different continuous fluxes: (a) NPX; (b) DCF.

4. SUMMARY

The NTD photocatalytic reactor exhibited significant removals of the NPX and DCF. Under the condition of a higher UV irradiation intensity and a lower initial concentration, NPX and DCF can be degraded completely at a flux of 3.0 L/h when the photocatalytic time was 360min and 30min, respectively. And the supply of suspension and aeration has a significant impact on the photocatalytic effect. The variation of UV irradiation intensity plays more significant role in the degradation of DCF, compared with that of NPX.

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