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**Immobilized Nanopillars-TiO2 in the efficient removal of micro-pollutants from aqueous solutions: Physico-chemical studies**

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**Highlights**

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Nano-pillars TiO2 immobilize onto [borosilicate glass](https://www.sciencedirect.com/topics/earth-and-planetary-sciences/borosilicate-glass) using sol–gel template method.

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[Thin films](https://www.sciencedirect.com/topics/earth-and-planetary-sciences/thin-films) with and without filler (PEG) is well characterized.

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[Thin films](https://www.sciencedirect.com/topics/earth-and-planetary-sciences/thin-films) are utilized in the [photocatalytic degradation](https://www.sciencedirect.com/topics/earth-and-planetary-sciences/photocatalytic-degradation" \o "Learn more about photocatalytic degradation from ScienceDirect's AI-generated Topic Pages) of micro-pollutants.

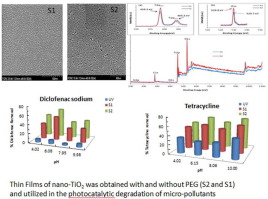
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Physico-chemical studies enabled to deduce mechanism of degradation.

**Abstract**

Nanopillars-TiO2 was immobilized onto a [borosilicate glass](https://www.sciencedirect.com/topics/earth-and-planetary-sciences/borosilicate-glass) disk using sol–gel template method. The TiO2 film was immobilized with and without polyethylene glycol as filler media and annealed at 500 °C. The prepared films were characterized by the IR, XRD, XRF and XPS analytical methods. The surface morphology was obtained using FE-SEM and AFM images of these thin films and the BET specific surface area was obtained. Further, the Nanopillars TiO2 was employed in the [photocatalytic degradation](https://www.sciencedirect.com/topics/earth-and-planetary-sciences/photocatalytic-degradation" \o "Learn more about photocatalytic degradation from ScienceDirect's AI-generated Topic Pages) of micro-pollutants *viz*., diclofenac sodium and tetracycline hydrochloride from aqueous solutions using UV-light under batch reactor operations. Various physico-chemical parametric studies *viz*., effect of pH, pollutant concentration and interfering ions was studied to deduce the mechanism involved in photocatalytic degradation of these pollutants. The time dependence degradation of these pollutants provided kinetics of degradation of these pollutants from aqueous solutions. The studies were further extended with total organic carbon measurement using TOC analyser to demonstrate an apparent mineralization of these pollutants. The photocatalytic degradation was assessed in presence of scavengers and several co-existing ions to simulate the data for real wastewater matrix. The hydroxyl radical scavengers 2-propanol and sodium bicarbonate greatly suppressed the catalytic activity of the thin films. However, the singlet oxygen scavenger sodium azide could not affect significantly the catalytic activity of these thin films at least the degradation of diclofenac sodium and tetracycline from aqueous solutions.

**Graphical abstract**



1. [Download : Download full-size image](https://ars.els-cdn.com/content/image/1-s2.0-S1385894715009985-fx1.jpg)

**Introduction**

Presence of organic micro-pollutants, in particular variety of pharmaceuticals and personal care products (PPCPs), seemingly pose serious environmental concerns during recent past; since several micro-pollutants are persistent, low biodegradable and toxic even at low level. A widespread occurrence of PPCPs is demonstrated by a number of monitoring agencies and measurable concentration of many of the PPCPs are detected in the wastewater, surface water, sediments, groundwater, and even in drinking water [1]. PPCPs enter into the terrestrial environment through direct runoff and excretion of un-metabolized drugs or active metabolites and/or degradation by-products [2]. It was reported that *Ca* 70% of consumed pharmaceuticals were excreted through human urine as active ingredients or metabolites [3], [4]. The normal sewage treatment system is insufficient to eliminate such pollutants completely, which results in presence of residual load of pollutants in the effluent water [5].

Tetracycline (TC; Structure 1) is an antibiotic drug widely prescribed for the treatment of bacterial infections [6]. TC is employed in aquaculture and livestock industry as one of typical antibiotic [7], food additives and growth promoters in farming and animal husbandry [8]. The consumption of tetracycline for veterinary purposes is higher than for other classes of antibiotics [9]. Similarly, diclofenac (2-[-2′,6′-(dichlorophenyl)amino]phenyl acetic acid) (Structure 2), used mostly to its sodium salt, is a non-steroidal anti-inflammatory drug (NSAID) widely employed for the treatment of inflammatory and painful diseases of rheumatic, nonrheumatic and antiarthritic origin. It is recommended to reduce menstrual pain, dysmenorrhea etc. An annual consumption of diclofenac is *Ca* 940 tons globally with a recommended dose of 100 mg/day [10], [11]. The continued intake of diclofenac, at low level, by humans shows several adverse biochemical effects e.g., cytotoxicity to liver, kidney and gill cells as well the renal lesions even at a concentration of 1.0 μg/L [12], [13], [14], [15]. It may also influence the biochemical functions of fish which leads to tissue damage [16].

Therefore, there is greater attention of effective and efficient remediation of aquatic environment contaminated with micro-pollutants. The low solubility, high log *Kow* values, low dipole moments and negative charges makes high rejection values for diclofenac in the nano-filtration unit [17]. The unit operations associated with ozonation [18], adsorption on activated carbon [19], [20] and membrane filtration as nano-filtration and reverse osmosis [21], [22] are some of possible ways as employed in the removal of several pharmaceuticals (>99%). The degradation of diclofenac from aqueous solutions as a combination of membrane TiO2/UV-A catalysis-ultrafiltration with photolysis could allow an effective and efficient diclofenac degradation [23]. The oxygen and free radical promoters are investigated in the photolysis (UV-254) of diclofenac [24]. Chlorine dioxide (ClO2) is employed in degradation of diclofenac under the simulated water disinfection condition. Results reveal that rapid and significant degradation of diclofenac occurs during initial few minutes but much longer time is needed for its complete mineralization [25]. Similarly, photocatalytic ozonation (O3/UVA/TiO2) is assessed in the degradation of diclofenac and shows that a complete elimination of diclofenac is achieved within 6 min and from 60% to 75% of TOC is removed within 60 min of operation [26]. An advanced oxidation/reduction process is conducted using a pulse radiolysis having 8 MeV accelerator which produces 2 ns electron pulse causes a production of high concentration of radicals i.e., 1 mM per pulse. The kinetics, degradation pathways along with the toxicity is obtained for diclofenac with this study [27]. The presence of different forms of nitrogen is studied in the photo degradation of diclofenac under the simulated sunlight. Results show that the degradation of diclofenac proceeds with pseudo-first order rate kinetics [28]. *In vivo* and *in vitro* studies conducted on the white-rot fungus *Trametes versicolor* pellets show almost a complete oxidative removal of diclofenac is obtained within short period of time [29].

On the other hand, tetracycline is having a 4-ring system. It contains multiple ionisable functional groups. TC possesses three *pKa* values due to the tricarbonylamide, phenolic diketone and dimethylamino groups, respectively. Literature reveals that various methods were demonstrated in the degradation of tetracycline from aqueous solutions. A boron doped diamond electrode was used in a complete degradation of TC using electrochemical reactor operated at constant current density of 300 A/m2 [30]. Similarly, Electrochemical Oxidation (EO) and Electro-Fenton (EF) processes were assessed in the oxidation of TC. It was reported that the EO process contained with carbon-felt cathode was relatively more efficient than the stainless steel cathode. Further, almost a total mineralization (TOC removal up to 98%) of 100 mg/L of TC was obtained with 6 h operation using either EO and/or EF treatment using a BDD anode [31]. A photo-electro-Fenton process was proposed using a fabricated Fe3O4–graphite cathode and a high degradation of TC was achieved and interestingly the electrode could be reused with a similar efficiency [32]. Fe(III) via complexation with the TCs promotes the degradation of several TCs even in absence of light sources [33]. Similarly, the combined application of nano-TiO2 and corona discharge plasma was utilized in the catalytic degradation of TC (50 mg/L) from aqueous solutions and the TC removal was achieved to 85.1% using the input discharge power of 36.0 W [34]. The nano-TiO2(P25) was introduced in the photocatalytic reactor for the oxidation of TC and one of the end products NH4+ was detected [35]. Photooxidation of TC was enhanced in presence of H2O2. Moreover, the presence of dissolved organic matter greatly enhanced the degradation of TC possibly due to the formation of radical species OH which acted as strong photosensitizer [36]. The visible light driven photocatalysts *viz*., Ag-decorated K2Ta2O6 nanocomposite, Ni(1−*x*)Cu(*x*)Fe2O4 or Sr–Bi2O3 were assessed in the photocatalytic degradation of TC from aqueous solutions and found to be efficient in the treatment process [2], [37], [38]. Although, the use of nano-TiO2 in the photocatalytic degradation of several micro-pollutants is found to be efficient however; separation of catalyst from the bulk phase or repeated use of catalyst restricts its wider implication in the wastewater treatment plants.

Therefore, the present investigation deals to immobilize the Nanopillars-TiO2 onto a borosilicate glass substrate using the template sol–gel synthetic process. Further, the materials were utilized in the photocatalytic degradation of micro-pollutants *viz*., diclofenac sodium and tetracycline hydrochloride from aqueous solutions.

**Section snippets**

**Chemical and materials**

Titanium (IV) isopropoxide, poly(ethylene glycol), diclofenac sodium salt and tetracycline hydrochloride were procured from the Sigma Aldrich. Co., USA. Acetylacetone (assay ⩾ 99%), ethanol anhydrous, hydrochloric acid, sodium hydroxide, zinc chloride, cupric sulfate pentahydrate, cadmium nitrate tetrahydrate, ethylenediaminetetraacetic acid, sodium nitrate, sodium nitrite, oxalic acid, glacial acetic acid, HPLC water, sodium azide, sodium bicarbonate, 2-propanol and acetonitrile (HPLC grade)

**Characterization of thin films**

XRD results were obtained for the S1 and S2 samples and returned in Fig. 1S or elsewhere [40]. The samples S1 and S2 showed characteristics peaks at the 2*θ* values of 25.39, 37.84, 48.14, 53.44 and 54.59 which is well matched with the anatase phase of TiO2. No characteristic peak of rutile phase was observed. It was mentioned that among the crystalline phases of TiO2, anatase is most active photocatalyst [41].

The average particle size (*D*) of the TiO2 was calculated using the Debye–Scherrer

**Conclusions**

The Nanopillars of TiO2 are obtained onto borosilicate glass substrates. The sol–gel template synthesis was conducted using PEG as modifier. The two thin films i.e., S1 and S2 were obtained with and without PEG. XRD data revealed that anatase phase of Nanopillar TiO2. The IR analysis indicated the presence of –OH group with both the catalyst samples. The XRF data enabled the presence of titanium element in the S1 and S2 samples. Moreover, the XPS analysis indicated the presence of Ti and O

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