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Photocatalytic degradation of drugs by supported titania-based catalysts produced from petrochemical plant residue

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ABSTRACT

A series of eleven drugs, namely, atorvastatin calcium, diclofenac sodium, fluoxetine, ketoconazole, ibuprofen, dexamethasone, tioconazole, naphazoline hydrochloride, valsartan, guaifenesin and paracetamol, were comparatively degraded under UV and visible radiation in the presence of a supported photocatalyst generated from the catalyst residue from a Ziegler–Natta catalyst petrochemical plant. The presence of Mg (4.4%) and Ti (2.5%) afforded a catalyst that was active over the UV and visible spectral regions. For comparative reasons, commercial P25 (titania) was also evaluated. Among the tested systems, the highest drug degradation was observed under UV (48.6%) and visible (45.2%) radiation with the synthesized photocatalyst, whereas under the same conditions, the commercial P25 catalyst achieved 66.3% and 50.2% degradation, for UV and visible radiation, respectively. Despite the comparable degradation capability, the proposed photocatalyst could be reused five times without losing catalyst activity.

1. Introduction

A wide variety of pollutants have been found in aquatic environments, such as effluent from sewage treatment plants and surface waters. Among these pollutants, compounds identified as emerging contaminants include certain drugs of different classes, such as analgesics, anti-inflammatory drugs, psychiatric drugs, antibiotics and antilipemics, which may be present in wastewater, especially in the case of hospital effluents. There have been certain reports of the presence of emerging pollutants in water sources in several countries [1–5]. Pharmaceutical compounds have been detected in environmental samples, and concentrations at the ng L^{-1} and mg L^{-1} levels have already been reported [6].

The absence of appropriate treatment processes combined with the diversity of these contaminants found in domestic and industrial effluents created demand for the development of new treatment methods to ensure efficient removal of these emerging pollutants. Many of these contaminants are not removed by conventional water treatment systems; therefore, they can cause irreversible damage to human health.

Physical processes (i.e., sedimentation, flotation, filtration, and adsorption) are characterized by phase transfer of the contaminant without causing its degradation. These processes tend to be relatively efficient and may be useful as pre-or post-treatment steps [7–9]. Chemical processes are based on the oxidation of contaminants by reactions with strong oxidants, such as hydrogen peroxide (H_2O_2), chlorine (Cl_2), chlorine dioxide (ClO_2) and permanganate (MnO_4^-). However, in most cases, the use of this type of treatment does not result in the complete mineralization of the contaminant to CO_2, with the formation of a wide variety of degradation by-products, particularly organic acids (oxalic, tartaric, formic, and acetic acid).

The presence of substances in wastewater is a reflection of the low efficiency of their removal by conventional treatment processes, which leads to contamination of surface waters. This situation has encouraged the search for more efficient methods capable of promoting mineralization of these contaminants or at least their transformation into products without adverse environmental effects. In this context, the Advanced Oxidation Processes (AOPs) have attracted significant interest due to their potential alternative or complementary approach to conventional sewage treatment processes. AOPs are processes based on the formation of hydroxyl radicals (HO•), which are highly oxidizing agents that can react with a wide variety of classes of compounds [10]. Among the AOPs, it is worth highlighting heterogeneous photocatalysis, which is a process involving redox reactions induced by radiation on the surface of a semiconductor (catalysts).

In parallel, industrial activities have generated increasing amounts of solid waste, including inorganic materials, which are generally fated for landfills and function as another type of pollutant. Conventionally, the removal of metals from industrial wastes has been performed using certain approaches, such as biological treatment techniques, liquid–liquid extraction, precipitation, reverse osmosis, activated carbon adsorption and reduction to an elemental form. These techniques often use potentially dangerous or polluting materials, and most of these techniques are

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not destructive. Thus, the management of waste generated by industrial activity is also a challenge for a sustainable world. Attempts to determine alternative uses for industrial wastes have been reported in the literature. For example, mesoporous spherical silica has been prepared using photonic industrial waste as the silica source [11], sorbents have also been prepared from industrial waste materials [12,13], zero-valent iron nanoparticles have been prepared from food industry wastes [14], and bioethanol has been produced from sago pith waste [15].

In a previous study, we investigated the potentiality of different types of industrial and academic wastes as sources for the preparation of supported photocatalysts [16]. These systems were evaluated in the degradation of Rhodamine B [16] and nicotine [17]. As an extension of our previous study, a series of drugs was selected because many of these drugs are emerging pollutants. The criteria to select these analytes were the polluting potential of these drugs in the environment and the presence of residues with these drugs. Studies have reported the presence of antidepressants and analgesics, such as fluoxetine [19] and paracetamol [20–22], in surface water, domestic sewage and sediment [18]. Other types of drugs are continuously consumed, serving as sources of environmental probes, such as diclofenac sodium [23–26], morphine [27], ibuprofen [28–30] and dexamethasone [31].

In the present study, we investigated the potentiality of a heterogeneous photocatalyst prepared from petrochemical industrial waste containing Ti and Mg for the degradation of a series of drugs, namely, atorvastatin, diclofenac, fluoxetine, naphazoline hydrochloride, valsartan, guaifenesin, ketoconazole, ibuprofen, dexamethasone, tioconazole and paracetamol. The structures of these drugs are shown in Scheme 1.

These drugs were selected because they represent classes of pharmaceuticals that are typically consumed, and their structures possess chemical functionalities commonly present in synthetic drugs. For comparative reasons, commercial titania (Degussa P25) was also evaluated as a photocatalyst.

2. Materials and methods

2.1. Materials

Catalytic residue (Ziegler–Natta catalysts) from a petrochemical company was used as the source for the production of the photocatalyst. TiO_2 (Degussa P25) was used as a reference catalyst. Atorvastatin calcium (Lipiton), diclofenac sodium (Multilab®), fluoxetine (Genix), ketoconazole (Multilab®), ibuprofen (Multilab®), dexamethasone (Multilab®), tioconazole (Multilab®), naphazoline hydrochloride (Multilab®), valsartan (Multilab®), guaifenesin (Multilab®) and paracetamol (Multilab®) were used in the photocatalytic tests.

2.2. Synthesis and characterization of the supported catalyst

In a typical preparation, 3 mL of petrochemical residue (Ziegler–Natta catalyst) was added to 1.0 g of fumed silica (Wacker HDKN20), and the solution was maintained under stirring for 90 min and then calcinated (450 °C for 4 h). The resulting catalyst was labeled as TiO_2ZNSiO_2. More details and characterization data are reported elsewhere [16].

The specific surface area, pore diameter and pore volume of the samples were calculated from nitrogen measurements performed on a Micromeritics Gemini 2375 instrument. The energy band gap was determined by diffuse reflectance spectroscopy (DRS-UV) in a UV–visible spectrophotometer (Cary 100 Scan Spectrophotometers). Scanning electronic microscopy (SEM–EDX) analyses were performed on a scanning electron microscope–energy dispersive spectrometer (X-ray JEOL model JSM 5800). Rutherford backscattering spectroscopy (RBS) analyses were performed using a 3 MV Tandetron particle accelerator. Zeta potential (ZP) was measured on a Malvern Zetasizer® nanoZS-style. The analyses were performed at the small angle X-ray scattering (SAXS) line D11A at the National Synchrotron Light Laboratory (LNLS, Campinas, Brazil) using the Irena routine evaluation [32] implemented in Igor Pro (WaveMetrics, Portland, USA) software [33]. Details are reported elsewhere [16].

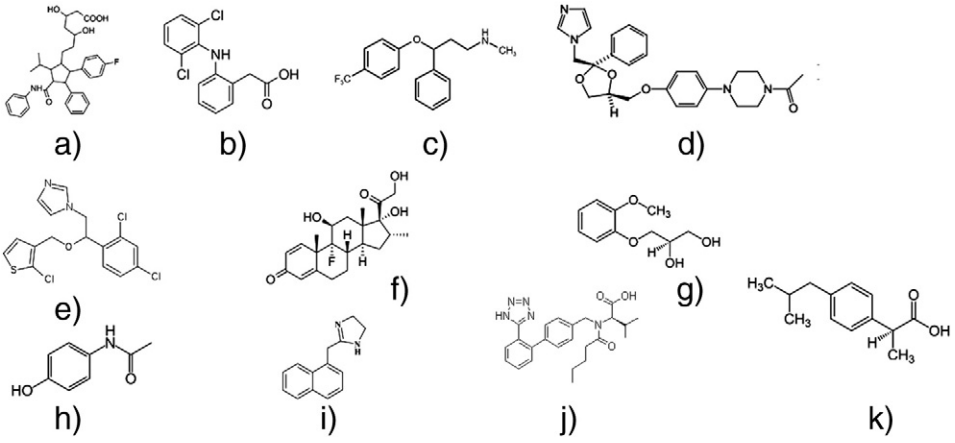
2.3. Computational methodology

The molecular volume of the employed drugs was estimated using the molecular geometry obtained from an unconstrained optimization performed using the DFT method defined by the B3LYP hybrid functional formed by the three parameter fit of the exchange–correlation potential suggested by Becke [34] and the gradient corrected correlation functional of Lee, Yang and Parr [35] with the 6-31G(d,p) basis set. The molecular volume was defined as the solvent-excluded volume [36] calculated using the GEPOL algorithm [37,38].

2.4. Photocatalytic activity

For the photocatalyst tests, the drug solutions were prepared by dissolving the drug (powder) in distilled water. All of the solutions were prepared at a concentration of 20 mg L^{-1}.

The photocatalytic activity tests were performed in a 50-mL reactor immersed in a water bath at 30 °C. The visible light source was a mercury vapor lamp of 125 W. A similar ultraviolet lamp was employed but



Scheme 1. Chemical structures of the investigated drugs: atorvastatin (a), diclofenac (b), fluoxetine (c), ketoconazole (d), tioconazole (e), dexamethasone (f), guaifenesin (g), paracetamol (h), naphazoline hydrochoride (i), valsartan (j) and ibuprofen (k).