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Research article

Nanocomposite thin films Ag^0(NP)/TiO_2 in the efficient removal of micro-pollutants from aqueous solutions: A case study of tetracycline and sulfamethoxazole removal

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ABSTRACT

The aim of this communication is to synthesize novel Nanocomposite thin film materials (Ag^0(NP)/TiO_2) using the template process. Surface morphology of materials was obtained by the Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) analyses. The presence of doped Ag-nanoparticles was confirmed by the TEM images along with the SEM-EDX analyses. The Atomic Force Microscopic images were demonstrated the surface roughness and thickness of Nanocomposite thin films. X-ray diffraction analysis confirmed that TiO_2 was predominantly present to its anatase mineral phase. The Fourier Transform Infra-red analysis conducted to obtain the functional groups present with the solid. The specific surface area and pore sizes of Nanocomposites were obtained by the BET (Brunauer, Emmett, and Teller) analysis. Further, the Nanocomposite thin film photocatalysts were successfully employed in the degradation of emerging micro-pollutants *viz.*, the antibiotics tetracycline and sulfamethoxazole from aqueous solutions using less harmful UV-A light (λ_{max} 330 nm). The effect of solution pH (pH 4.0–8.0) and pollutant concentrations (1.0 mg/L-20.0 mg/L (for tetracycline) and (0.5 mg/L-15.0 mg/L (for sulfamethoxazole)) was extensively studied in the photocatalytic removal of these antibiotics. A significant decrease in percentage of non-purgeable organic carbon removal indicated that the micro-pollutants was substantially mineralized by the photocatalytic treatment. The stability of thin film was assessed by the repeated use of Nanocomposite thin films and results were indicated that the degradation of tetracycline or sulfamethoxazole was almost unaffected at least for six cycles of photocatalytic operations. The presence of several cations and anions in the degradation of these antibiotics was studied. Additionally, the presence of 2-propanol and EDTA inhibited significantly the degradation of these micro-pollutants i.e., the percentage of degradation was decreased by 31.8 and 24.2% (for tetracycline) and 42.8 and 39.9% (for sulfamethoxazole), respectively. This indicated that the degradation of tetracycline or sulfamethoxazole was predominantly proceeded by the ·OH radicals; generated at the valance and conduction band of semiconductor. Similarly, the presence of sodium azide inhibited the percentage removal of these antibiotics.

1. Introduction

The presence of several micro-pollutants including pharmaceuticals, endocrine disrupting chemicals and personal care products in aquatic environment has posed potential threat to the ecological system. These micro-pollutants are found to be emerging water pollutants that need to be addressed adequately for its efficient removal/treatment in aquatic environment. Furthermore, a widespread and enhanced use of these chemicals with uncontrolled release into the aquatic environment resulted an increased and additional load to the water bodies (Jafari Kang et al., 2017; Michael et al., 2013; Saleh, 2001; Tuzen et al., 2018). Moreover, the existing wastewater treatment plants are insufficient to treat effectively these micro-pollutants at the required low level hence; these residual micro-pollutants are easily escaped and entered into the aquatic environment. This eventually contaminates the river, ground, drinking water or even the sludge (Peiris et al., 2017; Saleh and Gupta, 2016).

The antibiotics are known to be the most important therapeutic advances of the twentieth century that destroys selectively or inhibits the growth of microbes, especially the pathogens, however; keeping human cells and tissues unaffected (Lou et al., 2017). These compounds are physiologically active and widely used in livestock farms to inhibit

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the parasites, prevent diseases, and increase productivity (Silbergeld et al., 2008). It was reported that the global antibiotic use was exceeded to 70 billions of standard units (i.e., tablets) in 2010 for human consumption (Gelbrand et al., 2015; Norvill et al., 2017), and over 63,000 tons were employed for livestock production (Boeckel et al., 2015). Since antibiotics are partly absorbed or metabolized in biological systems once administered therefore; *Ca* 30–90% administered antibiotics are excreted through urine or feces and eventually entering into the receiving water bodies. This causes an enhanced growth of antibiotic resistance genes (ARGs) and leads to the prevalence of antibiotic resistance in the environment and human commensal microbes (Su et al., 2017). Since the conventional waste water treatment plants showed inefficient towards the effective removal of these persistent pollutants hence; are often detected in several matrices (Ahmed et al., 2015) and poses a serious and widespread threat to the aquatic life or even to the human health (Li and Hu, 2016; Rodriguez-Mozaz et al., 2015). The group of tetracycline antibiotic includes with chlorotetracycline, oxytetracycline and doxycyclinehyclate antibiotics. These are widely prescribed for the aquaculture, human and veterinary medicines in prevention and treatment of bacterial infectious diseases (Ahmed et al., 2015). Additionally, it is good growth promoters of livestock-farming (Chang and Ren, 2015; Nasseri et al., 2017; Yahiaoui et al., 2013). The $LogK_{OW}$ and pK_a values of tetracycline was reported to be −1.37 and 3.3, respectively (Ahmed et al., 2015). The low value of $logK_{OW}$ enables it to escape readily in water bodies having with high hydrophilic nature. It is further pointed that tetracycline quickly hydrolyze in water due to, relatively, low pK_a value (Wu and Fassihi, 2005). The photolysis of tetracycline results even more toxic by-products than the parent compound (Jiao et al., 2008; Leng et al., 2016). On the other hand, sulfamethoxazole is a sulfonamide type of antibiotic. It includes with sulfadiazine, sulfamerazine, sulfamethazine sulfathiazole and sulfapyridine. Sulfamethoxazole possesses the $LogK_{OW}$ and pK_a values of 0.89 and 1.6/5.7, respectively. Sulfamethoxazole is an excellent bacteriostatic agent and frequently supplemented in human and veterinary medicines (Hu et al., 2007). Sulfamethoxazole is widely prescribed as a synergistic additive with trimethoprim to treat urinary tract infections (Dias et al., 2014). Both these antibiotics are therefore, widely used and found to be ubiquitous water pollutants. It was reported previously that these pollutants were removed only 12–80% by the conventional treatment plants. Therefore, causing widespread contamination of water resources (Maroga Mboula et al., 2012; Palominos et al., 2009).

The existing urban WWTPs (Waste Water Treatment Plants) are seemingly reported the main source of releasing the antibiotics in the terrestrial environment since these plants are not adequately designed to eliminate completely the antibiotics from aqueous wastes. Hence, there is an emergent concern to upgrade the existing treatment plants in order to eliminate completely the emerging and important class of water pollutants. In a line, efforts are made and suggested to couple the existing wastewater treatment plants with the membrane filtration (microfiltration, ultrafiltration, nano-filtration and reverse osmosis) (Bagheri and Julkapli, 2017; Koyuncu et al., 2008; Riquelme Breazeal et al., 2013), activated carbon or advanced materials adsorption (Carabineiro et al., 2012; Kaur, 2017; Liu et al., 2016; Putra et al., 2009; Saleh, 2015a; Saleh et al., 2017), advanced oxidation processes (AOPs) or Nano-filtration with AOP (De la Cruz et al., 2013; Liu et al., 2014; Sousa et al., 2012).

It was reported that aerobic granules and conventional activated sludge were inoculated with the anoxic/anaerobic/oxic SBRs (Sequencing Batch Reactors) for sulfamethoxazole spiked (2 µg/L) wastewaters and results were indicated that the granules could remove *Ca* 84% of total triclosan which was significantly higher than the removal efficiency obtained by the suspended sludge (73%) (Prieto-Rodríguez et al., 2013). On-site removal of several antibiotics along with the antibiotic resistance genes (ARGs) from the leachate was carried out using the aged refuse bioreactor and indeed a total antibiotic removal efficiency was found to be 76.75%, and sulfanilamide and macrolide were removed at very high efficiencies (> 80%) (Su et al., 2017). A green synthesis was conducted to obtain nitrogen doped reduced graphene oxide (N-rGO) which could efficiently activate the persulfate (PS) to produce reactive radicals that efficiently degrade the sulfachloropyridazine (SCP) from aqueous solutions (Jafari Kang et al., 2017). The rejection of forward osmosis (FO) was contained with trace antibiotics which was treated efficiently by the electro-oxidation process operated at a current density J = 1 mA/cm^2. This enabled to remove almost 99% of total antibiotics from the rejection water of FO (Liu et al., 2015). A chemical reduction method was carried out to obtain the Ce^0/Fe^0-reduced graphene oxide ($Ce^0/Fe^0/RGO$) and the material was employed in the adsorptive degradation of sulfonamide (SMT) antibiotic from aqueous solutions under the Fenton-like process. Various parametric studies enabled to deduce the mechanism involved in the degradation process and the stability of catalyst was additionally ascertained with the repeated operation of catalyst (Wan et al., 2016). A similar photo-Fenton process was carried out in the degradation of gemifloxacin antibiotic from aqueous solutions. The study revealed that the optimum conditions for the maximum degradation of antibiotic was achieved at an optimum pH 3 having initial ferrous concentration 30 mg/L and H_2O_2 dose 200 mg/L for the initial gemifloxacin concentration of 200 mg/L (Shankaraiah et al., 2017). Two important antibiotics sulfamethoxazole (SMX) and trimethoprim (TMP) were efficiently treated at near neutral pH conditions using ferrioxalate complexes in a photo-Fenton process. It was pointed that the photo-Fenton reaction with ferrioxalate complexes inhibited significantly the formation of Fe(III)-antibiotic complexes, that eventually promoted the degradation efficiency of antibiotics at near neutral pH conditions (5.0) (Dias et al., 2014). Amino-containing iron trinitro phthalocyanine (FeMATNPc) was covalently immobilized onto the activated carbon fibers by deamination process to obtain the hybrid catalyst ACF-FeTNPc. The hybrid material which possessed with π-conjugated macrocyclic molecule was capable of degrading the sulfamethoxazole (SMX) in the ACFs-FeTNPc/H_2O_2 system (Wang et al., 2018). Similarly, modified photo-Fenton process using Nano zerovalent iron oxide (nZVI) was optimized for the degradation of ciprofloxacin from aqueous solutions. Results indicated that almost 100% removal efficiency was achieved within 30–40 min at around neutral pH conditions (Mondal et al., 2018). The degradation of ofloxacin antibiotic was degraded under the Fenton process using composite material obtained by sodium alginate and cyclohexane dinitrilo tetraacetic acid (CDTA). The optimum condition of degradation of ofloxacin was suggested to be 0.05 g of composite material granules, initial ofloxacin concentration 10 mg/L, 25 µL of 10 mmol/L H_2O_2. This was resulted to achieve almost 94% of pollutant degradation (Titouhi and Belgaied, 2016).

Advanced oxidation process integrated with TiO_2 photocatalyst is an effective method to degrade the stable and potentially emerging micro-pollutants. The process includes with *in situ* generation of highly reactive radical species that are predominantly responsible for the degradation/or even mineralization of micro-pollutants from wastewaters. The treatment is based on the 'no-waste' concept and the non-reactive and chemically stable TiO_2 catalyst enhances the useful applications in the area of high catalytic activity and wastewater treatment strategies (Babić et al., 2017). A heterogeneous photocatalyst as combined with ozonation and hydrogen peroxide was employed in the falling film reactor to degrade efficiently the *Flumequine* and *Clarithromycin* antibiotics. The results indicated that relatively a high mineralization of these antibiotics was achieved (Lou et al., 2017). Similarly, graphene-based TiO_2 composite photocatalyst was introduced in the visible light degradation of antibiotics sulfamethoxazole (SMX), erythromycin (ERY) and clarithromycin (CLA) along with the inactivation of antibiotic-resistant bacteria *E. coli* (Karaolia et al., 2018). In a line, the TiO_2 heterogeneous thin film photocatalyst along with the H_2O_2 was enabled to reduce the two antibiotic resistant bacteria (ARBs) *viz.*, mecA and ampC within the host ARB, methicillin-resistant *Staphylococcus aureus* (MRSA) and *Pseudomonas aeruginosa*, respectively