Chapter 15
Greywater Treatment in Continuous Flow Solar Photocatalytic Reactor Using Graphite Supported Nitrogen-Doped TiO_2

Kumari Priyanka, Neelancherry Remya, and Manaswini Behera

Abstract The increasing water demand has been one of the major global issues for the past decades. An enormous amount of potable water is required for household, industrial and agricultural activities, which led the water authorities to look-out for suitable alternatives. Treated greywater reuse and recycling is an economically viable and attractive option for meeting a portion of future water demand. The feasibility of a continuous mode solar photocatalytic system in greywater treatment was explored in this study. The solar photocatalytic tests were employed with graphite-supported nitrogen-doped titanium dioxide (N-TiO_2). The effect of flow rate (20–70 mL/min) was investigated under pH-3, H_2O_2 dosage-1 g/L, catalyst dosage-5 g/L in a continuous reactor. These tests revealed that the maximum removal efficiency in terms of COD, TOC and NH_4-N was accomplished at 20 mL/min, while the lowest removal efficiencies were found at 70 mL/min. The removal efficiencies of COD, TOC, and NH_4-N were progressively reduced from a flow rate of 20 to 50 mL/min, followed by a sharp drop at a flow rate of 70 mL/min. The reactor operation at the lowest flowrate i.e. 20 mL/min showed the removal efficiencies of 71.8, 65.1 and 63.7% for COD, TOC and NH_4-N, respectively. The result showed that a solar photocatalytic system with GT-NTiO_2 could be effectively used for greywater treatment under continuous mode operation.

Keywords Greywater · Graphite-supported catalyst · Continuous-mode reactor · Solar photocatalysis · Pollutant degradation

15.1 Introduction

The need for consumable/non-consumable water supplies for domestic, industrial and agricultural utilization has been magnified considerably over the last decades with the rapid increase of populace and reduction in freshwater sources. To meet

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this demand, the water authorities and policymakers are contributing to alternative sources of water like reused water, rainwater and greywater. Greywater accounts for 50–75% of the total domestic wastewater (Palmquist and Hanæus 2005). The domestic greywater originates from showers, kitchen sinks, laundry machines and hand washbasins but excludes wastewater from toilets. Greywater usually has lower infectious agent content and organic matter load, henceforth, its treatment and reuse are acquiring a lot of attention (Benami et al. 2016; Oteng-Peprah et al. 2018).

The treatment and reuse of greywater could dramatically reduce the demand for domestic potable water, but caution must be taken to ensure that treatment should be done without damaging public health and the environment. Some common problems associated with greywater reuse without treatment are oxygen depletion (as in eutrophication), the domination of anaerobic conditions, plant toxicity, and hygiene risks (Eriksson et al. 2002; Wiel-Shafran et al. 2006). Treated greywater has various reuse potential such as flushing toilets, cleaning floors, washing cars, and industrial cooling and cleaning applications (Al-Jayyousi 2004; Ghaitidak and Yadav 2013). The guidelines and standards for greywater reuse and recycling based on safety, sanitation, esthetics and ecological tolerance have been established by various nations (Li et al. 2009; Vuppaladadiyam et al. 2019).

Numerous greywater treatment options are applied in the past such as physical (membrane filtration), chemical (coagulation/flocculation, electrochemical process) and biological methods (constructed wetlands, rotating biological contractors) (Pidou et al. 2007). In the last decades, the utilization of advanced oxidation processes (particularly solar photocatalysis) in greywater treatment has been viewed as a potential method. In comparison to the previous greywater treatment methods, solar photocatalytic systems offer numerous merits such as (1) high efficiency in degrading emerging pollutants, (2) high stability of photocatalysts, and (3) removal or mineralization of a wide variety of aqueous pollutants (Prieto-Rodriguez et al. 2012).

In this work, photocatalytic degradation of greywater using nitrogen-doped titanium dioxide (N-TiO_2) supported on graphite is investigated in a continuous solar photocatalytic reactor. The effect of different flow rates was evaluated for treating greywater.

15.2 Materials and Methods

15.2.1 Greywater

Greywater was simulated by using analytical grade chemicals (sucrose, urea, soluble starch, ammonium chloride, potassium dihydrogen phosphate) and other ingredients (toothpaste, utensil cleaning gel and shower gel). All the chemicals in a certain amount were added to the tap water to prepare the simulated greywater. The different physicochemical parameters of greywater were analyzed and tabulated in Table 15.1.

Table 15.1 Physicochemical characteristics of greywater

	Simulated greywater characteristics									
			Solids (mg/L)		Organics (mg/L)			Nutrients(mg/L)		
Parameters	pH	Turbidity (NTU)	TDS	TSS	COD	BOD	TOC	PO_4^{3-}-P	NH_4-N	TKN
Values	7.3	6	625	102	285	142	131	19.5	22.3	51.4

15.2.2 Materials

Analytical grade titanium (IV) isopropoxide ($C_{12}H_{28}O_4Ti$, >98%), used as a precursor of titanium dioxide (TiO_2), was obtained from Sigma Aldrich. Other chemicals used for greywater preparation such as sucrose ($C_{12}H_{22}O_{11}$), soluble starch ($(C_6H_{10}O_5)_n$), ammonium chloride (NH_4Cl), potassium dihydrogen phosphate (KH_2PO_4) and urea (CH_4N_2O) were obtained from Avra Synthesis Private Ltd, Hyderabad. Emerging pollutant (Benzophenone-3, 98% purity) (BP) and standard titanium (IV) dioxide (99%) (P-25) were procured from HIMEDIA. Chemicals such as acetic acid glacial (>99.99%, Rankem, India), acetonitrile (Avra Synthesis, India), and HPLC water (Avra Synthesis, India) were obtained for the high-performance liquid chromatography (HPLC) analysis. Ethane-1,2-diyldinitrilotetraacetic acid (EDTA, $C_{10}H_{16}N_2O_8$, >99.9%), and hydrogen peroxide (H_2O_2, 30%) were obtained from Merck and Avra Synthesis, respectively.

15.2.3 Synthesis of Graphite-Coated N-Doped Catalyst

Titanium isopropoxide (TTIP) and urea were used as TiO_2precursors and nitrogen sources, respectively for the preparation of this photocatalyst as described in (Priyanka et al. 2020). To achieve a N/Ti ratio of 2:1, a certain quantity of urea and TTIP was added slowly to distilled water (about 20 mL). This mixture was stirred at 650 rpm using a magnetic stirrer for one hour. Next, the mixture was treated with ultrasonication for 30 min and then, dried at 100 °C in an oven for one day. The obtained pre-calcined powder was ground and heated at 5 °C/min upto 300 °C for 3 h in a muffle furnace. The material was then labelled as N-TiO_2.

The resulted powder N-TiO_2 was characterized with several techniques. X-ray diffraction (XRD) was performed on D8 Advance (Bruker, Germany) between 20° and 70° at room temperature with Cu-Kα radiation (voltage-40 kV, current-40 mA) and XRD patterns were identified using DIFFRACSUITE software. Surface properties were evaluated by scanning electron microscopy (SEM) (MERLIN compact, Carl Zeiss). And the elemental composition of N-TiO_2 nanoparticles was determined by electron dispersive energy spectroscopy (EDS) (51XMX 1004, Oxford Instruments). A UV–visible spectrophotometer (U-2900, Hitachi) was used to obtain spectra at a range of 200–800 nm.

Graphite was used as the substrate for the coating of N-TiO_2 particles through dip coating (Rao et al. 2012) with some changes. The pre-treatment of graphite (size-2 mm, seived) was carried out before the deposition of N-TiO_2 particles. Initially, about 1500 g of graphite was cleaned under the running tap water to get rid of the soil from the surface. Then, graphite was immersed in 1 N H_2SO_4 and kept in the shaker at 180 rpm for 12 h and rinsed again with tap water to keep neutral pH. Afterward, cleaned graphite was heated at 70 °C for 12 h. Then, the dried graphite was cooled to room temperature. 2% N-TiO_2 particles were added to the solvent solution (in a ratio

Fig. 15.1. Photographic image of GT-NTiO_2 **a** Before coating **b** After coating

of ethanol-80: water-20). The coated graphite was air-dried (<70 °C) with the help of a blow drier (HP8142/00, Philips). The same procedure was repeated for the second layer of coating with dip-coating and drying methods. Lastly, the graphite-coated N-TiO_2 material was oven-dried at 100 °C and cooled to obtain coated photocatalyst (GT-NTiO_2). GT-NTiO_2 was leached using distilled water to confirm the coating of the N-TiO_2. The graphite was weighed before and after coating to measure the actual amount of N-TiO_2 coated on it (Fig. 15.1). And it was found that about 0.8–1 g catalyst coated per 100 g of graphite.

15.2.4 2.4. Solar Photocatalytic Activity

Continuous-mode photocatalytic experiments were carried out using a tray-type solar photocatalytic reactor (Heber scientific, MODEL: HP-SLJV16254). A tungsten-halogen lamp (Heber scientific) of 150 W was employed as a visible light source with a wavelength varied from 400 to 700 nm. Tray-type solar photocatalytic reactor (25 cm × 35 cm × 8 cm) was filled with N-TiO_2 nanoparticles immobilized on graphite (as one layer uniformly). Peristaltic pump (PP-20-EX, MICLINS) and submersible water pump (WP3200, Sobo) were used for regulating flow rate (to maintain flow rate) and circulating cooling water, respectively. The flow rate was maintained between the ranges of 20–70 mL/min. The N-TiO_2 photocatalytic activity tests were carried out in the solar photocatalytic reactor (SPCR) with greywater. The initial BP concentration in greywater was 11 mg/L. The reactors were operated at optimal conditions (pH-3, H_2O_2 dosage-1 g/L, catalyst dosage-5 g/L) as provided in previous work (Priyanka et al. 2019). The schematic diagram of continuous-mode photocatalytic systems was provided in Fig. 15.2.

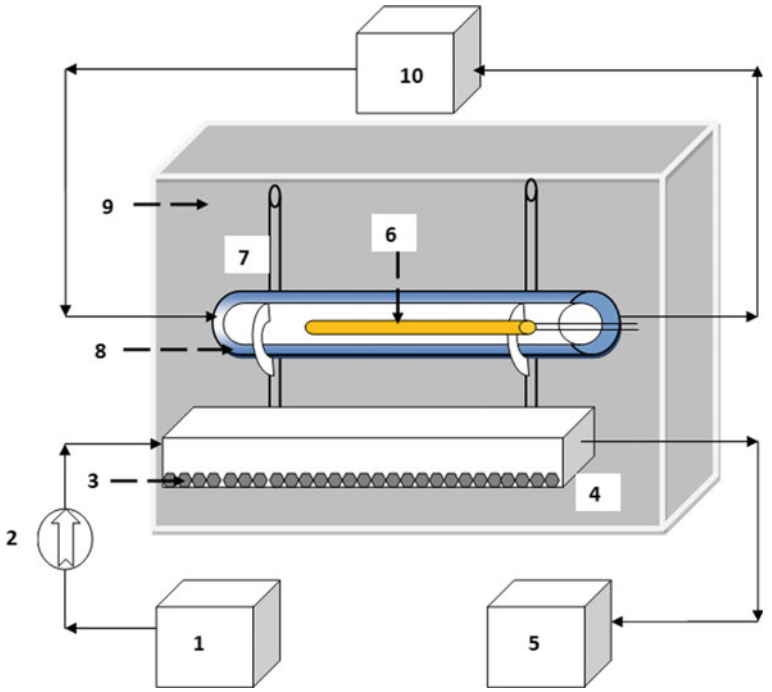

Fig. 15.2 Schematic representation of continuous solar photocatalytic reactor (1-greywater inlet tank, 2-peristaltic pump, 3-graphite coated NT-TiO_2, 4-tray-type photocatalytic reactor, 5-effluent tank, 6-visible lamp, 7-stand, 8-lamp holder, 9-protection hood, 10-cooling water tank, 11-pump for water recirculation)

15.2.5 Analytical Methods

The characteristics of the synthetic greywater samples were analysed as per the standard methods (USEPA 2012). The analytical instrument to measure the turbidity of the water sample was a turbidimeter (HACH, 2100 N (USA)). Nitrate values were assessed using a nitrate meter equipped with a nitrate probe (Thermo Scientific, EUTECH ION 2700). And pH measurement was carried out using a pH meter (ADWA Bench meter, AD800). A total organic carbon (TOC) analyzer (TOC-L, Shimadzu) was utilized for measuring TOC concentration. The total Kjeldahl nitrogen (TKN) analyzer with a digester (Kelplus, Kelvac-VA (India)) and a distillation unit (Kelplus, Classic DX VATS (E)) was used for TKN measurement. The strength of the visible lamp was calculated and noted using a photometer (HTC instruments, LX-101A).

About 1 mL sample from the continuous photocatalytic reactor was withdrawn at a different time interval. Greywater effluent was filtered through a 0.22 μm filter paper before BP measurement. BP concentration was measured in a C-18 column (250 mm × 4.6 mm) (HYPERSIL GOLD 5UM, Thermo scientific) with a UV absorbance of

287 nm using HPLC (Ultimate 3000, DIONEX, USA). Acetonitrile and 0.1% acetic acid mixture were used in a ratio of 70:30 (v/v) as mobile phase at a flowrate of 1 mL/min. BP was detected at a retention time of 6.71 min. Chromeleon 7 software was employed for processing the data of BP.

15.3 Results and Discussion

15.3.1 Characterization

The characterization of N-TiO_2 nanoparticles was discussed in our previous study (Priyanka et al. 2019). The peaks of the anatase phase were dominated in the XRD image of conventional TiO_2 (P-25) and N-TiO_2. Figure 15.3 reveals the crystalline peaks at 25.69, 38.22, 48.47, 54.52, 55.46, 63.10, and 69.15° of 2ϴ, which represented anatase phase of TiO_2 (Nguyen et al. 2018). The N-doped TiO_2 formation in the present study can be corroborated with previous findings in the literature (Sacco et al. 2018; Senthilnathan and Philip 2010). Figure 15.4a-b illustrates the SEM and EDS graphs for P-25 and N-TiO_2powders. Upon doping with nitrogen, the average grain sizes of N-TiO_2 nanoparticles were decreased from 120 to 118 nm. EDS graphs (Fig. 15.4b) confirms the doping of N into the TiO_2 structure. Further, UV-visible spectra were investigated for both P-25 and N-TiO_2 (Fig. 15.5). A remarkable redshift in N-TiO_2 nanoparticles was detected towards the wavelength of 400 to 600 nm that demonstrated an improvement of visible light absorption property.

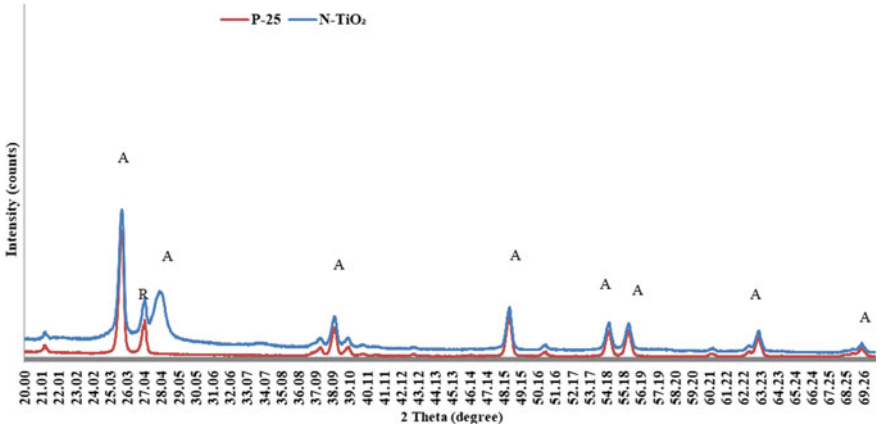

Fig. 15.3 XRD patterns of undoped TiO_2 (P-25) and N-TiO_2

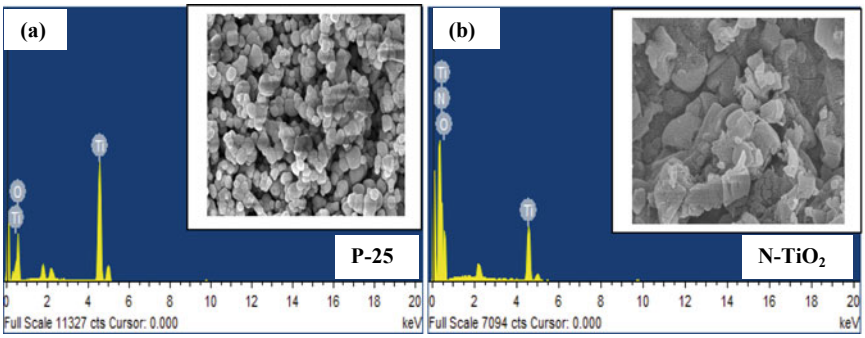

Fig. 15.4 SEM and EDS images of **a** P-25 and **b** N-TiO_2

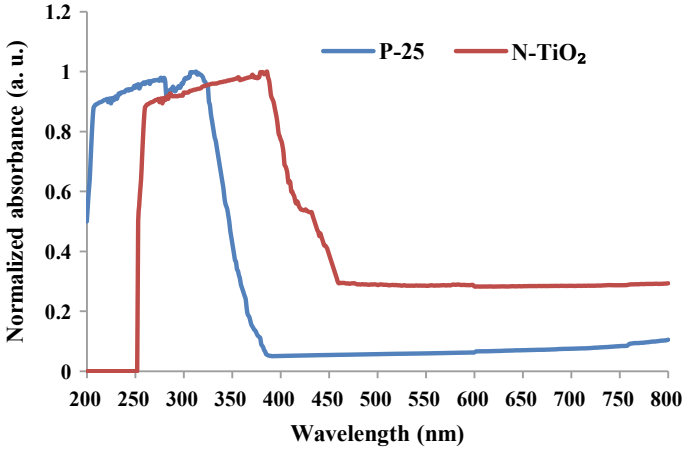

Fig. 15.5 Normalized UV visible spectra of P-25 and N-TiO_2

15.3.2 Photocatalytic Activity of Continuous Solar Photocatalytic Reactor

The treatment efficiency of the continuous solar photocatalytic reactor was evaluated in terms of COD, TOC, and ammonia. The effect of flow rates at 20, 25, 35, 50 and 70 mL/min was investigated. The flowrate was maintained up to 20 mL/min because the further decrease in flow rate would result in incomplete GT-NTiO_2 immersion.

Table 15.2 provides the continuous reactor performance for treating greywater at different flow rates. The removal efficiencies of COD, TOC and NH_4-N decreased with an increase in flow rate. From Table 15.2, it can be seen that the highest COD and TOC degradation of 71.8% and 65.1%, respectively was obtained at a flow rate of 20 mL/min. A similar trend was observed for NH_4-N removal efficiency (63.7% at 20 mL/min). The decrease in flow rate provides sufficient interaction time for the

Table 15.2. Performance of GT-NTiO$_2$ photocatalytic system operated at various flow rates

Flow (mL/min)	Hydraulic residence time (HRT)(h)	Removal efficiency (%)		
		COD	TOC	NH_4-N
20	8.33	71.8	65.1	63.7
25	6.67	62.91	60.55	59.24
35	4.75	58.76	47.24	43.62
50	3.33	44.83	33.3	39.86
70	2.38	11	8.1	16.57

pollutants with GT-NTiO$_2$ in the continuous flow reactor. Also, the reactor operating at a high flow rate (70 mL/min) showed a removal efficiency of COD (11%), TOC (8.1%) and NH_4-N (16.57%). The removal efficiencies of COD, TOC and NH_4-N were gradually decreased from 20 to 50 mL/min flowrate and next there was a sudden decrease in removal efficiencies at a flow rate of 70 mL/min. Asha et al. (2015) reported a similar study with different flowrates (60–100 mL/min) was carried out using GAC-TiO$_2$ in a continuous photocatalytic reactor. So, the optimum flow rate was found to be 20 mL/min. The graphs of COD, NH_4-N and pH variation were plotted for continuous flow reactor with respect to time (Fig. 15.6a-c). The final pH after the treatment time was obtained to be 4.9 (Fig. 15.6c). On the other hand, BP removal of 96.3% from greywater was accomplished on the completion of the treatment period.

15.4 Conclusions

In this study, a continuous flow solar photocatalytic reactor was successfully for greywater treatment with graphite coated nitrogen-doped (GT-NTiO$_2$) catalyst. Continuous mode operation displayed significant degradation of COD, TOC and NH_4-N from greywater. An enhancement in degradation efficiency in all pollutants was observed with a decrease in flowrate. The maximum reduction of COD-71.8%, TOC-65.1% and NH_4-N-63.7% was attained at the flow rate of 20 mL/min. Continuous flow solar photocatalytic reactor has proven to be an efficient system for degrading organics and nutrients from greywater. Further research work in the modification of photocatalysts such as doping with multiple elements, etc. is required to enhance the photocatalytic degradation of organics and nutrients. Additionally, the greywater effluent could be utilized for non-consumable applications (gardening, floor cleaning, cooling water in industries, etc.) with the elimination of pathogens, heavy metals, surfactants, etc.

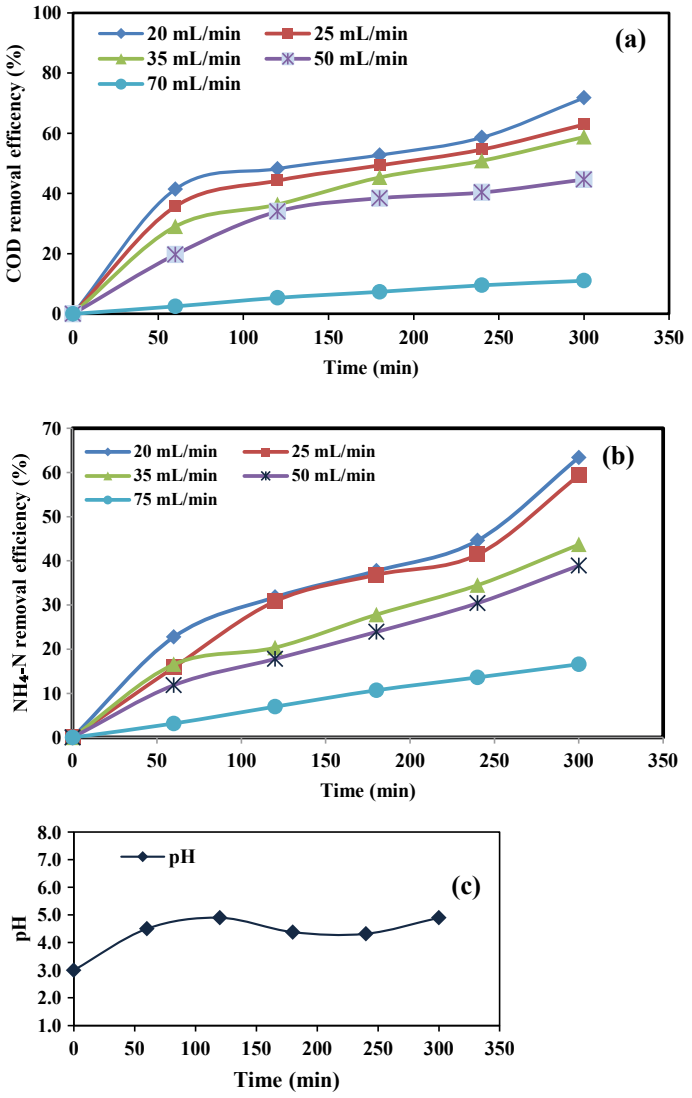

Fig. 15.6 Profiles of (**a**) COD, (**b**) NH_4-N and (**c**) pH variation for the treatment of greywater using the continuous flow solar photocatalytic reactor

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