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Photodegradation of 4-nitrophenol using an impinging streams photoreactor coupled with a membrane

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ABSTRACT

In the present work, degradation of 4-nitrophenol (4-NP) in a novel configuration of an axial radial impinging streams photoreactor coupled with a membrane microfiltration was proposed. The influences of initial 4-NP concentration, catalyst loading, slurry flow rate and pH were investigated as the most important operating parameters. Firstly, the performance of axial radial impinging streams photoreactor was evaluated in a batch recirculation mode and optimum conditions for pertinent parameters were determined. Complete decomposition of a 30 ppm batch solution of 4-NP was obtained within almost 180 min under optimal conditions and the decrease in COD and TOC were 71% and 62%, respectively. The experimental data of 4-NP degradation with an initial concentration in the range of 10–50 ppm accorded well with pseudo-first order model. Finally, the photoreactor was equipped with a membrane and applied in the continuous degradation of 4-NP. A combination of pH 4, 2 g/L TiO_2 and 2.24 L/min flow rate were determined to be the optimized conditions for degradation of 30 ppm 4-NP in the continuous membrane impinging streams photoreactor. In this reactor, an increased performance capability, a less membrane fouling, a higher permeate flow rate and subsequently a higher efficiency compared to conventional processes can be seen.

1. Introduction

Nitrophenols are some of the most refractory fatal pollutants with a high solubility in water. Due to the presence of a nitro group in their aromatic ring, adverse features of such a compound such as toxicity, non-biodegradability and high persistence in the environment become severe [1]. 4-NP is normally discharged from textile, pesticides, insecticides and herbicides plants to surface and ground water resources [2]. Hence, effective elimination of these organic pollutants becomes an essential priority in order to avoid dangerous increase of COD and TOC in effluent [3]. Removal of 4-NP from industrial effluents has several traditional techniques, such as biological treatment, adsorption, ozonation and catalytic oxidation, with certain limitations and disadvantages. Classical methods for clean up waters, instead of degrading the pollutants, usually transfer such compounds from a phase to another one. Therefore, it is necessary to develop some advanced techniques for industrial wastewater treatment.

Advanced oxidation processes (AOPs) are comparatively new and intensively developing technique, with the characteristic of high efficiency, low energy consumption and a wide range of application, which can decompose a large number of organic compounds and mineralize them to small inorganic molecules, without using chemicals and thus, avoiding sludge production and its disposal. This process is based on the electronic excitation of a molecule or solid caused by light absorption (usually UV light) that drastically alters its ability to lose or gain electrons and promote decomposition of pollutants to harmless by-products [4]. Among AOP technologies, UV/TiO_2 process regarding the following advantages is one of the most effective ways to degrade contaminants [5]: (i) Complete oxidation of a wide range of organic and inorganic pollutants at ambient temperature and pressure without generating any harmful byproducts (ii) reduction of pollutants concentration down to a ppb range (iii) catalyst adaptability to specially designed reactor system.

Application of TiO_2 in suspension instead of immobilizing on solid carriers has shown an improvement in organic degradation efficiencies due to the uniform distribution and large specific surface area [6]. However, the inherent disadvantage of a slurry batch reactor is the catalyst separation after treatment. Therefore, the recovery of photocatalysts is one of the main concerns affecting its engineering application on a large scale [7]. This may be overcome by implementation of degradation process in a

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continuous reactor with simultaneous separation of TiO_2 particles [8,9]. Photocatalysis-membrane separation coupling technology, which has been a heavily studied area in water and wastewater treatment during recent years, can solve the problem mentioned above effectively. Purification processes, utilizing methodologies that integrate photocatalytic reactions with membrane-separation processes, taking the advantage of synergy of both technologies, have been found to be very fascinating [10]. The experimental results from literatures demonstrated that the hybrid photocatalysis-membrane systems could be also very interesting from an economic point of view by means of confining or recycling the photocatalyst particles within the treatment module. Furthermore, in the area of membrane separation, microfiltration is a solid–liquid separation process useful when colloids and fine particles in the micro-range (i.e. from 0.1 to 5 μ) are involved (the TiO_2 particles meet such size requirements) and may be the only process for a complete recovery of TiO_2 particles from liquids. In comparison with ultrafiltration, microfiltration offers further advantages of needing relatively low transmembrane pressure for operation and of providing a relatively high filtration rate with a consequent reduction of equipment and operating costs [11,12].

Several attempts have been made to develop suitable photocatalytic membrane reactors for treatment of organic pollutants in water. However, there are three essential problems in photoreactors which need to be overcome [13,14]: photon transfer limitations, mass transfer limitations and formation of cake resistance on membrane surface. An ideally intensified reactor should be able to integrate both maximized light efficiency and mass transfer process along with reducing formation of cake layer on membrane within a single piece of equipment. Recently, impinging streams configurations have attracted research efforts in academic and industrial fields [15–17]. In such a device, two feed streams entering the reactor either parallel or counter-currently collide with each other in the impingement zone. On account of their collision, a relatively narrow zone of high turbulence intensity is formed, which offers excellent conditions for enhancing heat and mass transfer rates [18].

The main purpose of the present study is to design an impinging streams membrane photocatalytic reactor as a novel apparatus. Owing to the following reasons, it is expected that by application of such a reactor, the mentioned problems in photoreactors can be overcome [19]:

a) Increase in the relative velocities between the phases.
b) Complete mixing within the impingement region enhances the effective area for mass and heat transfer leading to the increase in overall mass transfer rates.
c) Increase in the residence time of particles due to oscillatory motion within the impingement zone.
d) Intense mechanical agitation prevents agglomeration of TiO_2 particles and exerts shear forces to remove TiO_2 particles from the membrane surface.

A few studies have been performed on impinging streams photoreactors [20]. However, such a new design of the multi stage impinging streams membrane photoreactor proposed in the present work for continuous degradation of 4-NP, to the best of our knowledge, has not yet been designed and investigated. After construction the photoreactor, an experimental design analysis was first employed in order to determine and optimize the significant factors affecting 4-NP degradation. Then, in order to evaluate the performance of the reactor, a series of experiments using optimum conditions were carried out.

In this reactor type, an increased performance capability, a less membrane fouling, a higher permeate flow rate and subsequently a higher efficiency compared to conventional processes can be seen.

2. Experimental

2.1. Materials

The P25 TiO_2 used for the experiments was provided by Degussa, Germany. The BET specific surface area of TiO_2 was $50 \pm 15\, m^2\, g^{-1}$ with an average particle size of 21 nm. 4-NP (99%), sodium hydroxide (98%) and sulfuric acid (99.9%) were purchased from Merck Chemicals. The microfiltration membrane made of cellulose acetate (CA) with an average pore size of 0.22 μm was provided by Millipore Co. The pH of all solutions were adjusted using sodium hydroxide and sulfuric acid. All solutions were prepared using deionized water.

2.2. Analytical measurements

The visible spectrophotometer (Dr 2800Hach Co.) was employed for determination of 4-NP concentration. COD of solution was measured at a wavelength of 445 nm applying COD vials of Merck Co. In addition the mineralization of the substrate was monitored by determining the total organic carbon (TOC) with a TOC vials of Merck Co. at a wavelength of 605 nm according to instructions provided by the supplier. The turbidity of samples were measured by a HACH 2100P turbidity meter.

2.3. Batch photocatalytic reactor

Before applying the reactor in a continuous mode, a series of batch experiments were carried out to specify the optimum operating conditions. A schematic diagram of the axial radial impinging streams photoreactor used in this step is shown in Fig. 1. The innovative apparatus was constructed from a vertical Plexiglass cylinder with an internal diameter of 7 cm and the overall length of 24 cm. In each impingement zone, two coaxial nozzles were tangentially mounted opposite each other on the wall of the photoreactor. Injection of slurry feed to each reaction region, created a rotational flow around the UV lamp. As a result, eddy current or turbulence was generated in the impingement zones. Another feature of the present photoreactor was a continuous flow of the feed stream from the feed reservoir along the height of the reactor. Such a stream, passing through the reaction zones, was being recycled to the feed reservoir. The reactor was equipped with a light source consisted of a low-pressure U shaped UV lamp placed at the center of the vessel (Philips Co., 18 W) emitting UV-C radiation at 254 nm as irradiation source. In a typical experiment, a

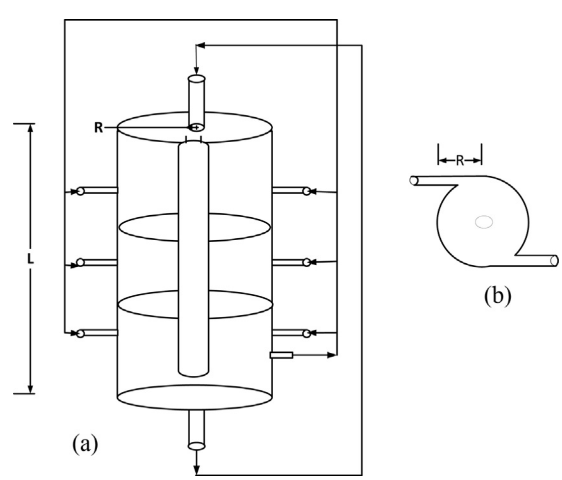

Fig. 1. Schematic diagram of the axial radial impinging streams photoreactor in batch mode (a) front view, (b) top view.