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Submerged hollow fiber microfiltration as a part of hybrid photocatalytic process for dye wastewater treatment

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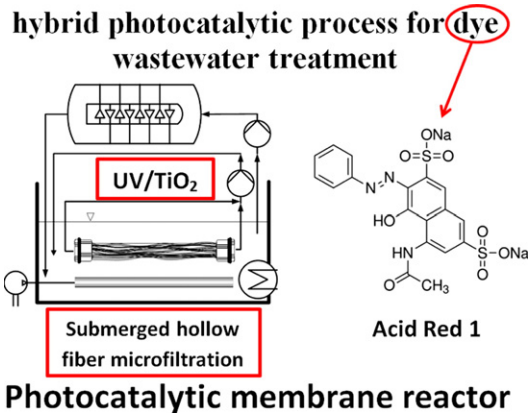
HIGHLIGHTS

- The photocatalytic activity of BR was determined by degradation of AR1 monoazo dye.
- PMR was investigated using the optimal parameters determined from batch experiments.
- PMR contained UV/TiO_2 photocatalytic process and submerged microfiltration module.
- AR1 decolorization, COD and TOC degradation and cake layer formation were evaluated.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, photocatalytic degradation of an organic azo dye, Acid Red 1, has been measured under UV irradiation in an aqueous dispersion of TiO_2 to find optimal conditions for a photocatalytic membrane reactor (PMR) operation.
Furthermore, to separate and recover the anatase TiO_2 photocatalyst, low-pressure microfiltration using hollow fiber membranes was applied. Since the main limitation in dead-end microfiltration with hollow fibers is the formation of an external specific deposit on the outer surface of the membrane, cake layer formation was also studied.
The changes in various parameters, including decolorization, chemical oxygen demand, total organic carbon, pH and turbidity of the solution were measured and analyzed during the process. Experimental results indicate that the solutions containing the model azo dyes could be successfully decolorized using the photocatalytic process studied.

1. Introduction

Dyes are widely used in many industries, including the textile, leather, plastic, cosmetic, and food industries. Textile industries in particular have shown a significant increase in the use of synthetic complex organic dyes to color their final products. Among the various types of dyes, azo dyes are extensively used and are the largest group of synthetic

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colorants, still dominating the dyestuff market with a share of approximately 60–70% [1]. Azo dyes are characterized by containing one or more azo groups (–N = N–) [2]. These dyes are widely used in industries because they are relatively cheap to synthesize, and are available in a great variety of colors compared with natural dyes [3]. Significant losses of these dyes can occur during the operations, which are released as effluents into the environment [4]. Wastewater containing azo dyes and their intermediates is usually toxic and carcinogenic to aquatic life and causes serious environmental and esthetic problems [5]. The presence of azo dyes in water reduces light penetration and has a negative impact on photosynthesis. They are resistant to biodegradation due to their toxicity and refractory nature [6]. Furthermore, color is usually the first contaminant to be recognized in a wastewater, so very small amounts of synthetic dyes in water are highly visible, affecting the transparency, gas solubility and oxygen transfer of bodies of water [7]. Treatment of colored wastewaters is a serious problem that has attracted the attention of many researchers in recent decades. Generally, methods for colored wastewater treatment can be grouped as physical, biological and chemical methods. Traditional methods to treat colored effluents are physical methods including coagulation, flocculation and sedimentation [8]; adsorption and filtration [9]; and ion exchange and membrane separation [10], which are based on transfer of contaminants from one phase to another. However these methods are useful but non-destructive, since they transfer the pollution from wastewater to secondary products that still need to be processed further [11]. Conventional biological treatment methods are often ineffective for the structure degradation of azo dyes, predominantly due to their complex aromatic structure and the stability or toxicity of the dyes or their by-products. Among chemical methods, there are processes such as reduction, oxidation, complexiметric methods, and neutralization [12]. Advanced oxidation processes (AOPs) have also been proposed among the chemical methods to treat colored wastewater. These are relatively new, powerful, and very promising techniques [1]. AOPs are based on the generation of strong oxidizing species and radicals that have one unpaired electron. They trigger a sequence of reactions that breaks down the dye molecules into smaller and less harmful substances, and in many cases completely mineralizes them into water, carbon dioxide, nitrates, sulfates and chlorides. Among AOP technologies, semiconductor-based photocatalytic technology has been demonstrated to be very effective and uses photocatalysts such as TiO_2, ZnO or $SrTiO_3$. Among these semiconductor catalysts, TiO_2 has become a very active field of research and received much attention due to its high physical and chemical stability and activity, non-toxicity, non-environmental impact and relatively low cost [13]. In photocatalytic processes two forms of TiO_2 catalyst are used: suspended and immobilized [14]. In suspended or slurry type, TiO_2 particles are dispersed in the reaction mixture. The immobilized reactor configuration is a fixed-catalyst type with TiO_2 fixed on a carrier material. Fixed-catalyst type reactors have the intrinsic advantage of not requiring a catalyst recovery operation, but they have several drawbacks such as possible catalyst deactivation and wash out, reduced processing capacity due to mass transfer limitations, low surface area to volume ratio and low UV light utilization efficiency due to scattering of the catalyst [15]. However, the suspended form has several advantages, like its faster mass transfer and larger reaction area for the same quantity. To solve these problems, recover the catalyst and obtain a good quality effluent, photocatalytic membrane reactors have been utilized [16,10].

There are a small number of studies referencing the problem of separating a photocatalyst from treated water. Microfiltration (MF) has been widely applied in drinking water and wastewater treatment for the removal of particulates, turbidity and microorganisms as an alternative to conventional water treatment processes. Hollow fiber membranes have been used extensively for the treatment of different types of synthetic and industrial wastewaters [17]. Hollow fiber low-pressure microfiltration systems are typically operated in dead-end mode. The modules are immersed into a tank opened to the atmosphere and a gentle suction is applied to draw permeate through the hollow fibers. The applied pressure difference between the two sides of the membrane is limited to several dozens of kPa. Hence, a cake layer is forming during the filtration and backflushing with permeate is necessary to remove it. Recently, several publications have appeared concerned with hybrid systems combining photocatalytic oxidation by TiO_2 with submerged membrane processes [18], but only a few investigations have focused on membrane fouling caused by TiO_2 particles [10]. The combination of MF and AOPs, such as ultraviolet (UV) irradiation/TiO_2, could be very effective for the complete destruction of pollutants [19]. Such a system enables the retention of photocatalyst in the reaction mixture by means of a membrane, the realization of a continuous process with simultaneous separation of the products from the reaction medium and control of the retention times of particles in the reactor. The other benefit from this should be energy savings and a reduction in the size of the installation. One possible drawback of this combined technology is the fouling of the membrane by impurities. Such fouling often results in a decrease in permeate flux or an increased pressure drop.

Therefore, the main objective of this study was to analyze the photocatalytic degradation of Acid Red 1 organic azo dye in a UV/TiO_2 batch photocatalytic reactor to find the optimal conditions for photocatalytic membrane reactor (PMR) operation.

2. Materials and methods

2.1. Materials

The parent compound, Acid Red 1 azo dye (AR1), Egacid Red G 200, was obtained from Synthesia (Czech Republic) and used as a model pollutant without further purification. The formula, molecular weight and wavelength of maximum light absorption of AR1 are $C_{18}H_{13}N_3Na_2O_8S_2$, 509.42 g/mol and 532 nm, respectively. Fig. 1 displays the structure of AR1. Experiments were performed using model dye wastewater with AR1 (over a range of concentrations from 15 to 75 mg/L). The pH of the studied systems was adjusted to constant values (3.0; 7.0 or 11.0) using hydrochloric acid (c = 0.1 mol/L) or sodium hydroxide (c = 0.1 mol/L).

A commercially available titanium dioxide photocatalyst AV-01 with the crystalline structure of anatase was obtained from Precheza a.s. (Czech Republic). The particles were analyzed with a particle analyzer (Malvern Mastersizer 2000, United Kingdom). Particle sizes from 0.08 to 3.30 μm, with an average of 0.83 μm, were obtained and the particle zeta potential was +2.2, −14.8 and −38.1 mV at pH 3.0, 7.0 and 11.0, respectively. The surface area of 11 m^2/g was obtained by BET analysis (Asap 2020, USA). Experiments were performed with the catalyst concentration in the range from 0.01 to 2.0 g/L.

Microfiltration experiments were performed with a shell-less polypropylene hollow fiber membrane module (Zena, Czech Republic). The membrane was prepared by a technology based exclusively on

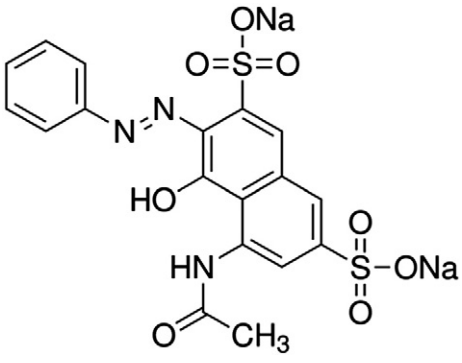

Fig. 1. Structure of Acid Red 1.