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/TiO₂ photocatalytic process and submerged microfiltration module.
• AR1 decolorization, COD and TOC degradation and cake layer formation were evaluated.

GRAPHICAL 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 TiO₂ to find optimal conditions for a photocatalytic membrane reactor (PMR) operation. Furthermore, to separate and recover the anatase TiO₂ 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.

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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
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, complexometric 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 TiO2, ZnO or SrTiO3. Among these semiconductor catalysts, TiO2 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 TiO2 catalyst are used: suspended and immobilized [14]. In suspended or slurry type, TiO2 particles are dispersed in the reaction mixture. The immobilized reactor configuration is a fixed-catalyst type with TiO2 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 backwashing with permeate is necessary to remove it. Recently, several publications have appeared concerned with hybrid systems combining photocatalytic oxidation by TiO2 with submerged membrane processes [18], but only a few investigations have focused on membrane fouling caused by TiO2 particles [10]. The combination of MF and AOPs, such as ultraviolet (UV) irradiation/TiO2, 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/TiO2 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 C18H13N3Na2O8S2, 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 Prechezas 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 m2/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
extrusion, annealing and stretching. The fibers have typical slot-like pores with a mean size of 0.1 × 0.5 μm. Some nominal characteristics of the membrane itself and the membrane module are given in Table 1. The membrane was soaked at least overnight in isobutyl alcohol to remove soluble processing chemicals and to pretreat the hydrophobic membrane.

2.2. Analysis

The absorbance of aqueous solutions of AR1 was determined by a UV–visible spectrophotometer (Thermo Spectronic Helios alfa, United Kingdom) at a wavelength of 532 nm. The concentration of AR1 dye in the solution was determined by using a calibration curve (concentration vs. absorbance) prepared with dye of known concentrations. The oxygen equivalent of the organic matter of the samples was analyzed using a standard chemical oxygen demand (COD) method [20]. Values were determined using lab kits (Lange LC500) and analyzed with a spectrophotometer (Hach Lange DR/2800, Germany). Total organic carbon (TOC) was determined using a TOC/TN Analyzer (Skalar Formacs, Netherlands) via the standard method [21]. A digital pH meter Hanna Model HI 9124 was used to measure the pH. The turbidity of the samples was measured with a turbidity meter (WTW Turb 550 IR, Germany).

Samples of the reaction mixtures were withdrawn from the reactor regularly for UV–visible, COD and TOC analysis and immediately centrifuged for 5 min at a speed of 6400 rpm on a centrifuge Fisher Scientific Model S67601A, followed by filtration through a Sartorius 0.2 μm membrane (Minisart) to remove the suspended TiO2 particles before analysis.

2.3. Batch photocatalytic reactor

First the photocatalytic removal of AR1 was studied in bench scale tests in a 300 mL open-air double wall cylindrical glass reaction vessel with a reaction volume of 200 mL. The mixtures in the reactor were continuously mixed at 400 rpm using a magnetic stirrer that was selected from batch experiments. UV irradiation was provided by an 8 W UV lamp (Camag, Switzerland) positioned above the reactor that emitted light with an intensity of 62.91 mW/cm² at a wavelength of 254 nm. The lamp was placed in a quartz glass tube with a 50 mm outside diameter that was located concentrically in another tube with an 80 mm inside diameter, forming an annulus in which the reaction mixture was circulated. The total holdup of reaction mixture in the UV reactor was 0.5 L.

Before each experiment, the UV lamp was allowed to warm up for 10 min to ensure stable output. For safety purposes, the entire system was placed inside a dark box to avoid UV light escaping to the surroundings. Temperature was kept constant at 25 ± 1 °C through the outer wall of the reactor using a water bath control system (Thermo Haake C10-PS, Germany).

Fig. 2 shows the diagram of the experimental setup. It consisted of UV reactor and a circulation system equipped with a membrane unit. The reactor included an 18 W UV lamp that emitted light at a wavelength of 254 nm, which was selected from batch experiments. The lamp was placed in a quartz glass tube with a 50 mm outside diameter that was located concentrically in another tube with an 80 mm inside diameter, forming an annulus in which the reaction mixture was circulated. The total holdup of reaction mixture in the UV reactor was 0.5 L.

The membrane separation system consisted of a 5 L feed tank into which the hollow fiber membrane module was immersed and suction was applied by a permeate pump (Heidolph 5025, Germany) with driver capable of reversing direction. This pump provides relatively constant output regardless of changes in pressure and can easily be used for membrane backflushing. In standard operation an outside-in direct dead-end constant flow rate filtration was realized in which no cross flow was applied. The transmembrane pressure in all experiments was measured by a pressure gauge placed in the permeate line. During the photocatalytic membrane experiments intensive (∼ 40 L/m² h) short (5 s) backflushing was carried out periodically using permeate by reversing the direction of permeate flow. Bubbling of air was also used with an intensity of 3 L/min by means of a porous flexible tube to achieve saturation of oxygen and promote photodegradation reactions as well as to remove stray TiO2 particles from the surface of the fibers. The experiments were carried out in recirculation mode and permeate was recycled back to the tank.

3. Results and discussions

Before using the membrane photoreactor, some tests were performed to determine the optimum values of the operating parameters that influence the reaction rate.

3.1. Effect of process parameters on decolorization of AR1

First, an experiment was carried out to determine the photostability of AR1 under the conditions of photolysis without catalyst. Absorbance at 532 nm, TOC and COD contents were measured and it was observed that after 3 h of UV-illumination of the dye solution the measured parameters were practically constant. This meant that no degradation of the model compound took place, so it can be said that in the presence of catalyst a true heterogeneous catalytic regime takes place. In heterogeneous photocatalysis, the catalyst loading, initial dye concentration,
pH, oxygen saturation, homogenization, type of UV irradiation and intensity all play important roles. The experimental results were assessed in terms of decolorization (absorbance at 532 nm) and reductions in COD and TOC with a normalized dye concentration \(c/c_0\) to determine the overall treatment efficiency of the degradation processes.

### 3.1.1. Effect of catalyst loading

The amount of TiO\(_2\) catalyst loading is one of the main parameters for dye degradation studies from an economics point of view. The optimum catalyst concentration depends on the nature of the compounds and the photoreactor geometry.

The results for the system investigated are shown in Fig. 3. The normalized dye concentration, given as a ratio of actual and initial concentration \(c/c_0\), sharply decreases with increasing catalyst loading, especially up to a catalyst concentration of 0.5 g/L. This can be ascribed to the increase in the number of active sites on the TiO\(_2\) particles. However, the reason for the slight decrease in color removal at higher catalyst concentrations may be due to aggregation of the TiO\(_2\) particles, which would lead to a decrease in the number of surface active sites. On the other hand, a high catalyst concentration increases the opacity of the suspension and UV light scattering, and thus should result in a decrease in the passage of irradiation through the reaction mixture [22,23].

Galindo et al. [24] reported an empirical power law relationship between the initial decolorization rate and TiO\(_2\) concentration, where the exponent was less than 1 for all the dyes studied. In our work, the dependence of the initial decolorization rate \(r_0\) on the TiO\(_2\) concentration \(c_{TiO2}\) follows a similar relationship for TiO\(_2\) concentrations less than 0.5 g/L in Eq. (1):

\[
r_0 = -0.5638 \times c^{0.372}_{TiO2} \text{ [mg L/min; g/L]} \tag{1}
\]

#### 3.1.2. Effect of initial dye concentration

Initial dye concentration \(c_0\) is an important parameter because large variations in azo dyes concentrations exist in wastewater effluents. The effects of initial dye concentration on photocatalytic decolorization were investigated by varying the initial dye concentration from 15 to 75 mg/L with an optimum catalyst loading of 0.5 g/L as shown in Fig. 4. It can be seen that nearly complete color removal was obtained after a certain exposure time in all cases. Since the lifetime of hydroxyl radicals is very short (only a few nanoseconds), they can only react at or near the location where they are formed. Thus, higher dye concentrations should enhance the probability of collisions between the organic matter and the oxidizing species, leading to an increase in the decolorization rate. According to a great number of studies [1,19,25–27] the influence of the actual concentration of the solute \(c\) on the photocatalytic decolorization rate \(r\) of most organic compounds can be described by pseudo-first-order kinetics, which is the simplified form of the Langmuir–Hinshelwood reaction model for low solute concentrations [1,28]:

\[
r = \frac{dc}{dt} = -kc \tag{2}
\]

Integration of Eq. (2) leads to:

\[
\frac{c}{c_0} = e^{-kr} \tag{3}
\]

If this model is valid for the data presented in Fig. 4, the experimental points should fit only one curve, with \(k\) as the apparent reaction rate constant. It can be seen from Fig. 4 that the decolorization rate is considerably influenced by the value \(c_0\) of the initial dye concentration, thus the value of \(k\) is decreasing with increasing concentration. It is likely that at high dye concentrations the path length of photons entering the catalyst decreases due to the UV-screening effect of the AR1 dye itself. Furthermore, the dye molecules may absorb a significant amount of UV radiation rather than the catalyst and this may also reduce the efficiency [29].

Similarly, Damodar et al. supposed that [30] the breakdown of molecules in higher concentrations of dye solution leads to the formation of intermediate compounds that, tend to compete with the existing dye molecules for active sites, resulting in lowering the decolorization at later stages.

#### 3.1.3. Effect of agitation speed

Mixing is very important in photocatalytic reactions in order to keep the catalyst in the dispersion, i.e. in preventing sedimentation as well as improve the mass transfer of dye to the catalyst surface and ensure sufficient oxygen in the mixture during the decolorization process. The experiments were carried out by varying the agitation speed from 0 to 800 rpm while keeping all other factors constant. The initial reaction rates \(r_0\) at varying agitation speeds are shown in Fig. 5. It confirms that the photocatalytic decolorization of the AR1 dye is highly dependent on the intensity of mixing. A critical agitation speed of 400 rpm was found, above which further increases do not affect the reaction rate. Similar results were reported in another kinetics study conducted with a peach red azo dye [31]. They found that the effect of increasing the mass transfer on dye degradation kinetics is negligible for agitation speeds greater than a critical value of 600 rpm.

#### 3.1.4. Effect of UV irradiation

A short wave UV light at 254 nm and a long wave UV light at 366 nm were examined and compared. From Fig. 6 it can be concluded that no decolorization of the aqueous AR1 solution occurs in the absence of catalyst using short wave UV irradiation. Complete decolorization of the...
AR1 could only be observed with the simultaneous presence of catalyst and UV irradiation. The decolorization rates were nearly equal at both wavelengths. Slightly faster initial degradation was observed at 254 nm, but at the end of the irradiation experiments the two decolorizations were nearly equal. Akyol et al. reported similar results in a comparative study conducted with photocatalytic degradation of Remazol Red F-3B in a batch slurry reactor. Their results showed that TiO2 irradiated under 254 nm UV successfully degraded both benzene and naphthalene derivatives. Under 254 nm UV, some derivatives began to appear in detectable quantities at the end of 5 min, while others required 10 min to be detectable. With a 366 nm UV source, these periods were almost doubled [32].

3.1.5. Effect of initial pH

In photocatalytic decolorization reactions the initial pH of the solution is a very important parameter, because it dictates the surface charge properties of the particles, which affects the sorption of dye on the catalyst surface. Furthermore, the structures of the dye and products, such as acids and amines and stereoisomers, also change as a function of pH.

The effect of pH on decolorization of AR1 after 30 min is presented in Fig. 7. It shows the efficiency of dye decolorization of AR1 at pH 3.0, 7.0 and 11.0. During the 30 min of UV irradiation, the highest ratio reached was 93.78% at pH 3, while the lowest ratio of 48.79% was observed at pH 11. The catalyst surface is positively charged and can effectively adsorb the negatively charged AR1 dye anion at pH 3. At higher pH the repulsion of the AR1 dye anion by the negatively charged catalyst surface results in a reduction in efficiency of photocatalytic decolorization. Ilinoiu et al. also found that the optimal pH for the best discoloration and aromatic ring-opening was pH 3 during degradation of a Reactive Yellow 125 (RY 125) dye solution [33].

3.2. Effect of process parameters on mineralization of Acid Red 1

The main objective of a photocatalytic process is the complete mineralization of all organic compounds, because some of the intermediates generated during the degradation could be more toxic than the parent AR1. Therefore the oxidative degradation process was evaluated using COD and TOC measurements. COD is a measure of the oxygen required for oxidation of azo dye to be completely mineralized into water, carbon dioxide, nitrates and sulfates. On the other hand, the total quantity of the CO2 produced from organic matter is determined by TOC measurements.

The changes in COD and TOC are shown as a function of UV irradiation time in Fig. 8. Initial values of 6.1 mg/L and 11.5 mg/L were obtained for TOC and COD, respectively. Although the 15 mg/L aqueous AR1 solution was totally decolorized after 90 min of UV irradiation, the oxidative degradation of other parts of dye molecule apart from the azo groups (–N=N–) and characterized by changes in COD and TOC were significantly slower processes. Only 78% and 63% decreases in COD and TOC, respectively, were observed after 90 min. This means that decolorization provides a visually aesthetic treatment of wastewater, but is far from representing total purification due to the produced by-products. Interestingly, the TOC decreases nearly linearly as a function of the UV irradiation whereas COD exhibits faster degradation initially and then slows, similar to decolorization. Probably in the first part of the photocatalytic process the destruction of azo bonds is supported, resulting in faster decolorization and reductions in COD for the first 60 min. Further irradiation resulted in slower depreciation of the absorbance and COD values probably due to the lower probability of

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**Fig. 5.** Effect of agitation speed on initial dye decolorization rate ($c_0 = 15$ mg/L, $c_{{TiO}_2} = 0.5$ g/L, pH = 7, $T = 25\ ^\circ\mathrm{C}$, $\lambda_{UV} = 254$ nm, $l_{UV} = 62.9$ mW/cm²).

**Fig. 6.** Influence of UV irradiation wavelength on the decolorization process ($c_0 = 15$ mg/L, $c_{{TiO}_2} = 0.5$ g/L, pH = 7, $T = 25\ ^\circ\mathrm{C}$, $n = 400$ rpm, $l_{UV} = 62.9$ mW/cm²).

**Fig. 7.** Effect of initial pH on decolorization efficiency ($c_{{dyne}} = 15$ mg/L, $c_{{TiO}_2} = 0.5$ g/L, $n = 400$ rpm, $T = 25\ ^\circ\mathrm{C}$, $\lambda_{UV} = 254$ nm, $l_{UV} = 62.9$ mW/cm²).

**Fig. 8.** Absorbance, changes in COD and TOC versus irradiation time ($c_{{dyne}} = 15$ mg/L, $c_{{TiO}_2} = 0.5$ g/L, pH = 7, $T = 25\ ^\circ\mathrm{C}$, $n = 400$ rpm, $l_{UV} = 62.9$ mW/cm²).
3.3 Membrane reactor experiments

3.3.1 Microfiltration experiments

The first microfiltration experiments in a TiO₂ based slurry reactor were performed with TiO₂ water dispersions in order to investigate membrane retention, cake layer formation, backflushing efficiency and membrane fouling.

To determine the retention characteristics of the microfiltration membrane used, the membrane was challenged with catalyst feed dispersion at different transmembrane pressure differentials as well as concentrations and the permeate was tested for its turbidity. It was found that the initial rejection of catalyst particles was greater than 90% in all cases. After several minutes of the separation process the permeate was TiO₂ free; thus, total rejection was observed. Probably retention by the membrane is based on combined steric and electrostatic mechanisms followed by the creation of a retentive filter cake acting as a secondary membrane.

While the submerged membrane was operated in a constant pressure mode the tendency for membrane fouling was monitored through decreases in the permeate flux (J) (Fig. 9). Rapid flux decline was observed after the TiO₂ particles formed a cake layer on top of the membrane. The modified critical flux concept, initially proposed for steady state cross-flow systems, was used in describing fouling of the dead-end system tested [34]. The sustainable permeate flux found in this study was 40 L/m² h [35]. Up to this value, reversible membrane fouling was detected that was easily removed by a strong shear force of membrane backflushing with permeate. Above this value the operation resulted in irreversible fouling, in which permeate flux was not restored after backflushing, as shown for example in Fig. 9 for an initial permeate flux of 100 L/m² h.

With the submerged membranes operated in a constant flux mode, the tendency for membrane fouling was monitored through the increase in suction pressure during microfiltration. Since the produced permeate was circulated back to the feed tank, the concentration in the bulk dispersion decreased continuously until both it and the suction pressure became constant after a certain filtration time.

Accumulation of catalyst on the membrane surface indirectly indicated the loss of suspended TiO₂ from the reaction mixture and thus reductions in the overall active sites of TiO₂ available for photocatalytic reaction. Therefore, by varying the frequency of membrane backflushing, fouling of the submerged membrane can be controlled; simultaneously, it is possible to optimize the backflush frequency to maintain the required catalyst concentration in the reaction mixture. For the system investigated a frequency of 0.5 h⁻¹, duration 5 s and intensity 40 L/m² h were found to be optimal [35].

3.3.2 Photocatalytic degradation in PMR

Operationally significant dye decolorization rates require specific reactor construction for desirable surface-to-volume ratios, while reaction completion dictates large reactor volumes to provide sufficiently long residence time, i.e. the average time that a particle spends in a particular system. On the other hand, direct contact of the membrane with UV light shortens the useful lifespan of the polypropylene membrane. For practical utility there should be an in-line recirculation set up (as in Fig. 2) that gives a desirable decolorization as well as permeate rate without compromising the life of the membrane. The distribution of the PMR’s capacity between the photocatalytic reactor zone and the membrane separation zone of the PMR is an important design parameter that needs to be optimized.

Fig. 10 presents the changes in permeate composition during the photocatalytic process realized in the membrane reactor equipped with submerged hollow fiber membranes. The ratio of the volume of the separation zone to the photocatalytic reactor volume was 10:1. For an initial dye concentration equal to 15 mg/L, the solution was colorless after 6 h. Similar to the batch experiments, COD and TOC analysis revealed the presence of organic carbon in the solution even after complete discoloration of the liquid. Nevertheless, the total decolorization time was approximately four times longer in comparison to the batch experiments. Therefore the actual permeate composition was compared with theoretically calculated dye concentrations and both COD and TOC values were based on results obtained in batch experiments.

Assuming $V_1$ to be the volume of the separation feed tank and $V_2$ the inner volume of the UV reactor, the correction factor for the active process time $t_A$ in the photocatalytic reactor zone should be calculated as

$$t_A = t \frac{V_2}{V_1} \quad (4)$$

Then for a given PMR system the estimate of the ratio $c_0/c_s$ at process time $t$ can easily be evaluated from batch experimental data as the value corresponding to active process time $t_A$ calculated from Eq. (4). A comparison of the experimental data and the theoretical predictions is given in Fig 10. Good agreement can be seen for decolorization and COD as well as TOC data.

4. Conclusions

Experimental results indicate that wastewaters containing the model azo dye Acid Red 1 could be successfully decolorized using the photocatalytic process studied. It was found that the decolorization rate of the photocatalytic degradation is considerably influenced by the value of the initial dye concentration and the complicated reaction system cannot be described by pseudo-first-order kinetics. Chemical oxygen demand and total organic carbon analysis revealed the presence

![Fig. 9. Constant suction pressure microfiltration of TiO₂ dispersion (concentration 5 g/L) with permeate backflushing after each filtration cycle (duration 5 sec and intensity 40 L/m² h) (pH = 7, T = 25 °C).](image1)

![Fig. 10. Decolorization, COD and TOC changes in a photocatalytic membrane reactor (PMR). Comparison of experimental data and theoretical predictions based on batch experiments ($c_{inj} = 15$ mg/L, $c_{TiO2} = 0.5$ g/L, pH = 3, T = 25 °C, h_{UV} = 254 nm).](image2)
of organic carbon in the solution even after complete discoloration of the wastewaters studied. Application of immersed hollow fibre modules together with the photocatalytic process resulted in complete separation of the photocatalyst from the treated reaction mixture. The sustainable permeate flux found for the system investigated was 40 Lm⁻² h⁻¹. Up to this value reversible membrane fouling was detected, which was easily removed by a strong shear force of membrane backflushing by the permeate. By varying the membrane backflushing frequency, fouling of the submerged membrane was controlled and simultaneously it was possible to optimize the backflush frequency to keep the required catalyst concentration in the reaction mixture. It was found that the distribution of the photocatalytic membrane reactor’s capacity between the photocatalytic reactor zone and the membrane separation zone is an important design parameter that needs to be optimized.

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