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Crystal violet and toxicity removal by adsorption and simultaneous photocatalysis in a continuous flow micro-reactor

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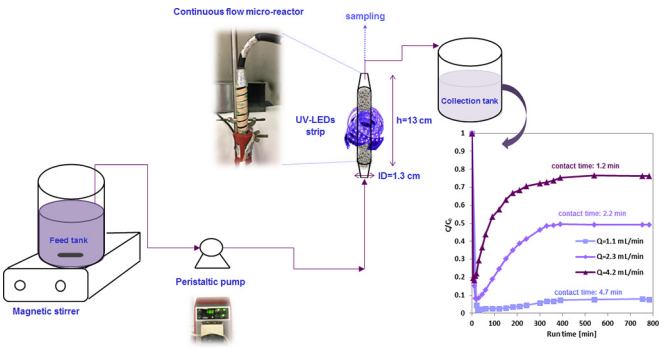
HIGHLIGHTS

- A continuous flow micro-reactor irradiated by UV-LEDs was developed.
- Removal of crystal violet dye through simultaneous adsorption and photocatalysis.
- ZnO/zeolite pellets were used as active material.
- Treated water showed a significant reduction of toxicity.
- A preliminary mathematical model was developed.

GRAPHICAL ABSTRACT



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ABSTRACT

A continuous flow micro-reactor irradiated by UV-LEDs was employed to treat coloured wastewater by adsorption and simultaneous photocatalysis. Zinc oxide (ZnO) immobilized on commercial zeolites pellets in spherical shape (ZEO) was used as catalytic material in a micro-reactor maximizing the photocatalyst exposition to light sources, irradiating uniformly the entire solution volume and improving the mass transfer phenomena. Experimental tests were carried out on crystal violet dye (CV) as one of the main dying agent present in textile wastewater. The comparison between adsorption and adsorption/photocatalytic tests showed that UV irradiation can achieve a steady state CV concentration value corresponding to an equilibrium condition between adsorption and photocatalytic oxidation. The higher removal efficiency (*i.e.* 93%) was observed with a liquid flow rate of 1.1 mL/min (contact time = 4.7 min; CV = 10 mg/L) under UV light irradiation. In the steady state, CV removal remained constant for the overall testing time. Bioassays evidenced that toxicity was not completely removed (*i.e.* final effluent ranked as "slight acute toxic") from wastewater suggesting its suitability for sewage collection discharge. A Dubinin Radushkevich (D-R) isotherm model was applied for studying the adsorption behaviour of ZnO/ZEO sample. CV adsorption constants were evaluated from experimental data carried out in dark conditions in a batch system. Kinetic expression of CV removal and the D-R adsorption were incorporated in the CV mass balance estimating the kinetic parameter. The model was validated comparing the calculated CV conversion with the experimental tests collected at different CV inlet concentration.

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1. Introduction

Several industries such as textiles, paint, ink, plastics, paper and cosmetics use different types of organic dyes and about 15% of them are lost during synthesis and processing with wastewater (Nagaveni et al., 2004; Robinson et al., 2001; Vacchi et al., 2017). The discharge of coloured wastewater in the environment is considered to be a major issue because conventional treatments such as biological methods, flocculation, coagulation, precipitation, adsorption, membrane filtration are not able to completely remove organic dyes in water (Ghaffar et al., 2018; Janoš, 2003; Pal et al., 2016; Sahoo et al., 2005). For this reason, advanced oxidation processes (AOPs) have received considerable attention in recent years to treat efficiently coloured wastewater (Li et al., 2018; Vaiano and Iervolino, 2018; Vaiano et al., 2017a). Among AOPs, heterogeneous photocatalytic methods are the most effective and attractive ones (Doong et al., 2010; Miranda et al., 2016). Photocatalysis is actually a very active area of scientific research, but its large scale implementation has not been successful so far. The main reason is attributed to the slow development of practical photocatalytic systems this means efficiently and economically viable for large-scale wastewater treatment application (Damodar and Swaminathan, 2008; Dionysiou et al., 2000). Other reasons are the absence of a proper reactor design and optimization because of the most studied photoreactors are in batch configuration (Chong et al., 2017; Liu et al., 2014a; Nguyen and Juang, 2015; Veisi et al., 2016). Reactors that could be operated in continuous mode could be a valid alternative because the main advantage is the easy scale-up of the system compared to batch processes and, therefore, they are being recently investigated by scientific literature (Damodar et al., 2010; Erdei et al., 2008; McCullagh et al., 2010). The scale-up of these types of reactors can be achieved by continuous introduction of wastewater into the reactor and by placing several devices in parallel (Cambié et al., 2016; Su et al., 2014). Among the continuous photoreactors, the use of flow micro-reactors received attention especially for photochemical applications (Schuster and Wipf, 2014). Specifically, the use of a photocatalytic micro-reactor allows to irradiate uniformly the entire solution volume and consequently, photocatalytic reactions can be substantially accelerated (from hours/days for batch process to seconds/mins in continuous-flow) (Cambié et al., 2016). Another advantage of micro-reactors is the improved mass transfer phenomena (Ray, 1999; Sengupta et al., 2001) due to the formation of a thin film of pollutant solution over the catalyst surface enabling an efficient penetration of UV radiation inside the core of the reactor too (Ollis and Turchi, 1990). In order to guarantee the continuous operation of the system, it is necessary to use semiconductors immobilized on macroscopic supports (Borges et al., 2015; Chanathaworn et al., 2014). Though the efficiency of the immobilized system may be less than that of the slurry system, the catalyst can be used continuously for a long time (Chen et al., 2001). Regarding to the immobilized systems, a variety of support materials (such as glass (Chanathaworn et al., 2014), ceramic (Vaiano et al., 2015b; Zhang et al., 2017) or polymeric substrate (Sacco et al., 2018a; Sacco et al., 2018c; Vaiano et al., 2017b)) has been studied in the last years (Kamble et al., 2004; Pozzo et al., 1997). Besides, a good choice could be the immobilization of photocatalyst on adsorbent materials to obtain hybrid catalysts (semiconductor deposited on zeolites) combining the adsorption properties of zeolite with the photocatalytic properties of the semiconductor. Several investigations have been carried out using TiO_2 or ZnO coupled with zeolites, evidencing an improvement of the photocatalytic performances compared to bulk photocatalysts (Fukahori et al., 2003; Liu et al., 2014b; Sarno et al., 2015; Susarrey-Arce et al., 2010). Most papers deal with the use of photocatalysts supported on zeolites in the powder form, thus making the development of photoreactors operating in continuous mode difficult.

Recently (Sacco et al., 2018b), the use of the simultaneous adsorption and photocatalytic processes (adsorption/photocatalysis) for the removal of caffeine was studied using zinc oxide (ZnO) photocatalyst immobilized on commercial zeolite (ZEO) as pellets (ZnO/ZEO), thus providing a suitable structured photocatalyst formulation to be used in a continuous-flow photocatalytic reactor. At our knowledge, scientific literature about the employment of a continuous-flow reactor for water depollution through the dual effect of adsorption and photocatalysis is still limited (Li et al., 2010).

This work investigated a continuous-flow micro-photoreactor using ZnO/ZEO as catalytic material. Crystal violet (CV) was selected for technology validation and assessment as one of the main widespread dying agents and its related toxicity (Adak et al., 2005; Sahoo et al., 2005; Yu et al., 2012).

2. Materials and methods

2.1. Preparation and characterization of ZnO/ZEO samples

ZnO nanoparticles (NP) has been immobilized in commercial Na-ZSM5 zeolite spherical pellets (ZEOcat Z-400, pellets size: 1.2–2 mm, SiO_2/Al_2O_3 ratio: 400, provided by ZEOCHEM) by wet impregnation method starting from $Zn(NO_3)_2 \cdot 6H_2O$ (Sigma-Aldrich) dissolved in aqueous solutions. The experimental procedure is described in our previous published work (Sacco et al., 2018b). The final ZnO loading in ZnO/ZEO composites was found to be 6.1 wt%. From the chemical-physical characterization results it was found that ZnO NPs are in wurtzite phase and incorporated in the mesoporous structure of ZEO pellets (Sacco et al., 2018b).

2.2. Photocatalytic tests using a batch reactor

The photocatalytic removal of CV was preliminarily studied in a cylindrical batch photoreactor using ZnO powder obtained from $Zn(NO_3)_2$ by thermal treatment in air at 450 °C for 2 h. A photocatalytic test, using 3 g/L of ZnO, was carried out in a Pyrex cylindrical reactor (ID = 2.6 cm, L_{TOT} = 41 cm and V_{TOT} = 200 mL). During the test an air flow rate of 144 Ncc·min^{-1} was continuously bubbled inside the suspension. A UV-LEDs strip (*LEDlightinghut*, nominal power: 12 W/m; main emission: 365 nm) was used as light source and positioned around the external surface of the photoreactor. The initial CV concentration was 10 mg/L while the solution volume, at the spontaneous pH (about 5.5), was 100 mL. Liquid samples were collected at fixed times and analyzed to measure the CV concentration through UV–Vis spectrophotometer (Thermo Evolution 201) at the wavelength of 583 nm (Ameen et al., 2013).

In addition to the measurement of CV concentration, mineralization of CV was evaluated in terms of total organic carbon (TOC) concentration decrease through the measurement of CO_2 obtained by catalytic combustion at T = 680 °C. CO_2 produced in gas-phase was monitored by continuous analyser (Uras 14, ABB) (Sannino et al., 2013).

2.3. Experimental tests using the continuous flow micro-reactor

The micro-reactor, which operates in continuous mode, is a cylindrical pyrex reactor (ID = 1.3 cm, L_{TOT} = 10 cm and V_{TOT} = 7 mL) because this type of geometry is the simplest configuration for a photoreactor, allowing a possible scale-up of photocatalytic systems for water and wastewater treatment.

The stock solutions containing the CV dye (at 5, 10, 15 and 25 mg/L initial concentration) were prepared and collected in the feed tank (3 L). The feed tank is equipped with a magnetic stirrer to assure the complete homogenization of the stock solution. The feed solution was pumped from the feed tank to the micro-reactor using a peristaltic pump (*Watson Marlowe 120 s*). The used liquid flow rates were 1.1, 2.3 and 4.2 mL/min. The overall liquid stream is fed from the bottom of the reactor and liquid stream passes through the catalytic bed and finally comes out from the top of the reactor, being conveyed in a tank where the treated solutions were collected. The liquid sample was withdrawn