POSTER
Ph.D. Student: N
Journal: NONE

Fenton Process Integrated with Membrane Distillation for Textile Wastewater Treatment using Commercial Simulators

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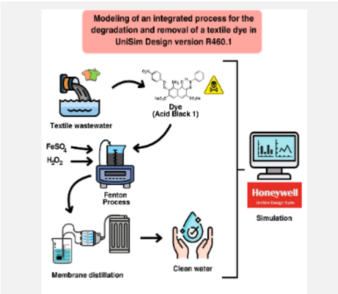


The simulation of integrated process is important for evaluating different scenarios and their interactions without risk to human life or the environment. In this study, the UniSim Design software was used to propose a model for simulating the Fenton process integrated with membrane distillation. Experimentally and simulated results of degradation rate and permeate flow obtained were used to validate the model, achieving an error < 5%. Additionally, a sensitivity analysis of the H_2O_2 concentration on the dye degradation was also evaluated, showing the optimal concentration limit for this reactant. This results confirm the reliability and utility of the simulation model for optimizing integrated processes in wastewater treatment.

Introduction

The integration of the Fenton process with membrane distillation offers relevant advantages both environmentally and economically. This integration combines the organic contaminants degradation capacity of the Fenton process with the selective separation efficiency provided by membrane distillation [1]. This approach reduces environmental impact by minimizing the presence of pollutants in the final effluent and also provides economic benefits, such as the recovery of valuable products and the reduction of costs associated with wastewater treatment [2].

Due to its built-in functionality, the use of commercial process simulations is both intuitive and user-friendly, enabling detailed analysis of system behavior, identification of optimization points, and adjustments to maximize the operational and economic efficiency. In contrast to conventional simulation methods, commercial simulators do not require programming skills, custom code or additional plugins which can be a challenge for integrated processes. Thus, the application of commercial simulators represent a promising approach to addressing these challenges and also that related to industrial wastewater treatment in a sustainable and effective manner.

While simulating the Fenton reaction for wastewater treatment is well-established, its integration with membrane distillation remains unexplored. Therefore, the objective of this study is to develop a simulation model using theuser-friendly interface of commercial simulations, to be a tool for predicting pollutant removal rates and identifying potential bottlenecks or constraints in the integrated process.

Material and Methods

UniSim Design software version R460.1 was used as commercial simulator. The simulation model was based on experimental data from previous works of the research group for the integrated process and degradation of synthetic black acid dye ($C_{20}H_{12}N_3O_7SNa$) in water [1].

Firstly, the input data for the base simulation environment was configured, followed by the definition of the input components, the fluid package and the efficiency and operational conditions used in the Fenton process (degradation and neutralization). Components not available in the software library were inserted with data regarding their molecular structures and physicochemical parameters. The fluid package model used was NRTL (Non-Random Two Liquids), used to accurately adjust phase equilibrium parameters to experimental data [3] and also to correlate the coefficients of the different components included in a simulation.

The degradation reactions were represented by intermediate reactions based on experimental data [4], as shown in Equations 1-3, with 1% conversion was considered for each reaction. Equation 4 describes the complete degradation of the wastewater, with 5% conversion was considered. The neutralization step was represented as Equation 5, and 100% conversion was considered.

$$12C_{20}H_{12}N_3NaO_7S + 12FeSO_4 + 79H_2 \rightarrow 25C_8H_6O_4 + 20C_2H_4O_2 + 6Na_2SO_4 + NH_4NO_3 + 6Fe_2(SO_4)_3 \quad (1)$$

$$2C_{20}H_{12}N_3NaO_7S + 2FeSO_4 + 19H_2O_2 \rightarrow 5C_6H_6O_3 + 10CH_2O_2 + Na_2SO_4 + 3NH_4NO_3 + Fe_2(SO_4)_3 \quad (2)$$

$$2C_{20}H_{12}N_3NaO_7S + 2FeSO_4 + 14H_2O_2 \rightarrow 5C_7H_6O_3 + 5CH_2O_2 + Na_2SO_4 + 3NH_4NO_3 + Fe_2(SO_4)_3 \quad (3)$$

$$2C_{20}H_3NaO_7S + 2FeSO_4 + 89H_2O_2 \rightarrow Na_2SO_4 + 3NH_4NO_3 + Fe_2(SO_4)_3 + 4CO_2 + 95H_2O \quad (4)$$

$$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + H_2O \quad (5)$$

After configuring the basic environmental data, the input streams of the Fenton process (Table 1) and flow sheet of the simulation was inserted (Figure 1).The proposed simulation model consists of three input streams: H_2O_2, $FeSO_4$, and wastewater, which are inserted in a mixer, resulting in an output stream (Feed reactor) that enters a conversion reactor (Fenton reactor) where the chemical degradation of the dye occurs. In this reactor, reactions 1-4 occurred simultaneously. The breaking of bonds, through the action of hydroxyls, released heat into the medium, which was represented as a heat stream added at a temperature of 50 ºC, and H_2SO_4 was added to represent the reaction medium at a pH ~ 3. Next, the neutralization reaction occurred in a conversion reactor unit (reaction 5). For the neutralization, the NaOH was added to reach pH ~ 7. In a sequence, there is the filtration stage, where solids were separated, and the liquid phase was directed to the membrane distillation process. Before, it was necessary to add a heater to reach the feed temperature of 60 ºC and another mixer, which represents a tank where retentate recirculation could occur. Since direct contact membrane distillation is unavailable in the simulator, a flash distillation representing the feed side and a cooler for the permeate side were proposed as model.

Table 1. Input streams of the Fenton process.

Streams	Mass flow (kg/h)
$FeSO_4$	$7.5x10^{-5}$
H_2O_2	0.0015
Wastewater	1.996

Results and Discussion

In order to validate the simulation, the degradation rate of the dye was defined, which can be calculated as the ratio between the remaining amount of dye in the membrane inlet stream (Feed membrane) and the initial amount of dye in the degradation reactor feed stream (Feed reactor). The resulting value, alongside the permeate flow rate of the simulation, was compared with the experimental data, as summarized in Table 2. In both parameters, the deviation from the experimentally values were small (>5%), indicating that the simulation can properly represent the integrated process. This confirms that the model proposed accurately predicts real-world behavior, resulting in adequate tool to help in designing processes that minimize environmental impact and enhance sustainability.

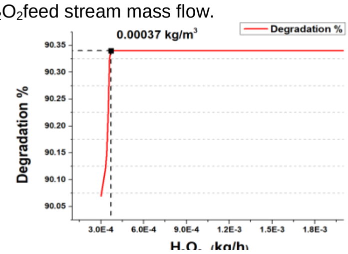
Table 2. Validation data for the simulation proposed.

Parameters	Degrada -tion rate (C_f/C_i)	Degradation percentage (%)	Permeate flow rate (kg/h)
Experimental	0.100	90.00	0.051
Simulation	0.096	90.34	0.050
Error (%)	3.540	-	3.320

[a]The initial mass flow rate of H_2O_2 was 0.0015 kg/h
Effective membrane area = $1.385x10^{-3}$ m^2

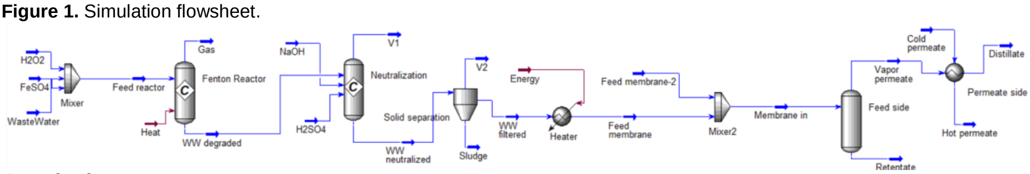
To evaluate the simulation's potential to predict different behaviors, a sensitivity analysis was carried out of the influence of H_2O_2 feed concentration´s impact over the degradation percentage of the dye (Figure 2).

Figure 2. Degradation percentage of the dye as a function of the H_2O_2feed stream mass flow.



It was observed that beyond $3.7x10^{4}$ kg/h, increasing H_2O_2 concentration does not enhance dye degradation, indicating an optimal concentration threshold for cost-effective operation. Excessive use of H_2O_2 would lead to unnecessary costs without additional benefits.

Figure 1. Simulation flowsheet.



Conclusions

In this study, a simulation of a Fenton process integrated with Membrane Distillation was successfully proposed and validated with an error of less than 5% using a commercial simulator. This obtained model is robust and can be applied to predict possible bottlenecks or restrictions in the integrated process. Also, enables to understanding of the system's behavior, mechanisms, and interactions, leading to better-informed modifications and innovations.

Acknowledgments

This study was supported by Honeywell, Federal University of Santa Catarina (UFSC), Higher Education Personnel Improvement Coordination (CAPES) and National Council for Scientific and Technological Development (CNPq).

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