Separation and Purification Technology 72 (2010) 186–193

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Ozonation of dye wastewater by membrane contactor using PVDF and PTFE membranes

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ARTICLE INFO

Article history:
Received 2 November 2009
Received in revised form 2 February 2010
Accepted 3 February 2010

Keywords:
Decolorization
Dyes
Membrane contactor
Ozonation
PTFE membrane
PVDF membrane

ABSTRACT

This work aimed to study the decolorization of dye wastewater by ozonation membrane contacting process. Three different dyes, i.e., Direct red 23, Acid blue 113 and Reactive red 120 were selected to be used in this work. The effects of operating parameters which were gas and liquid velocity, liquid phase temperature, dye auxiliary reagents were investigated along with the mass transfer study. Membranes used in this work were PVDF and PTFE hollow fiber membranes. The ozone mass transfer performance and long term performance in ozonation by these two different types of membrane were studied. In addition, decolorization performance and kinetic study of ozonation in the batch system with various operating parameters and dye types were investigated.

From the results, the ozone mass transfer increased with increasing liquid velocity, liquid phase temperature, and with the presence of Na_2CO_3. On the contrary, the ozone flux was not influenced by gas velocity. PVDF membrane provided higher ozone flux than PTFE, but PTFE membrane gave more stable and higher flux than PVDF for a long operation period. The ozone flux of different types of dye was in the following order: Direct red 23 > Reactive red 120 > Acid blue 113. Conversely, the decolorization performance of Acid blue 113 was higher than those of Direct red 23 and Reactive red 120. Kinetic analysis showed that decolorization of dyes followed the first order kinetics and the rate constants were in the following order: Acid blue 113 > Reactive red 120 > Direct red 23.

1. Introduction

Textile industry generates large amount of wastewater which varies greatly in quantity and compositions. Treatment of textile wastewater by chemical coagulation and biological methods can usually reduce biological oxygen demand (BOD) and chemical oxygen demand (COD) satisfactorily, except for the removal of dye color. A direct solution to this problem is treatment by chemical oxidation. Bouwers [1] reported the comparison between different oxidants such as Cl_2, H_2O_2, $KMnO_4$ and O_3. It was found that ozone generally produced non-toxic breakdown products which were finally converted to CO_2 and H_2O if the conditions were drastic enough. Excess ozone decomposes after a few minutes to oxygen without harmful residue, as opposed other inorganic oxidants.

Ozone is a powerful oxidant for water and wastewater treatment. Depending on the pH of the liquid phase, ozone may react with a great number of organic compounds by direct oxidation as molecular ozone or by indirect reaction through formation of secondary oxidants like hydroxyl radical [2]. Conventional ozone contacting methods include bubble column, impellers, and others. The conventional reactors to perform ozonation mentioned above are easy to set up and operate as reported in the literature [3–5]. However, there are the problems that hinder the use of those techniques such as, flooding, uploading, and foaming. Further study is needed to enhance the mass transfer rate and to avoid those problems. Due to the low solubility of ozone in water a high contact area would increase the ozone transfer from the gas to liquid phase. A recent study of Chu et al. [6] on the application of microbubble technology in ozonation process reported that a specific surface area, mass transfer, and oxidation of ozone were enhanced. However, they concluded that the total energy cost should be further analysed.

As far as the specific surface area for mass transfer is concerned, the application of a bubbleless membrane contactor system for ozonation is the potential approach, especially when the hollow fibers are used. A gas–liquid membrane contactor is a membrane process in which the hydrophobic porous membrane acts as a barrier separating gas phase and liquid phase. The mass transfer in a membrane contactor for absorption gas into the liquid phase consists of a transport of the interested gas from the bulk of gas phase to the interface between gas phase and a membrane, transport of gas through the membrane pores, and the dissolution of a gas

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1383-5866/$ – see front matter
doi:10.1016/j.seppur.2010.02.006

Nomenclature

a	parameter in Eq. (3)
C	concentration of dye at any reaction times, mol m^{-3}
C_0	initial dye concentration, mol m^{-3}
D	diffusion coefficient of ozone in the liquid phase, $m^2\,s^{-1}$
D_A	continuum gas diffusion coefficient, $m^2\,s^{-1}$
D_K	Knudsen diffusion coefficient, $m^2\,s^{-1}$
$D_{g,eff}$	effective diffusion coefficient of gas in the pores, $m^2\,s^{-1}$
d_i	inside diameter of membrane, m
d_{ln}	logarithmic mean diameter of membrane, m
d_o	outside diameter of membrane, m
E	enhancement factor
H	Henry's constant
K_{ol}	overall mass transfer coefficient, m s^{-1}
k	pseudo-first-order rate constant, min^{-1}
k_l	individual mass transfer coefficient of liquid phase, m s^{-1}
k_m	individual mass transfer coefficient of membrane, m s^{-1}
k_g	individual mass transfer coefficient of gas phase, m s^{-1}
L	effective length of the membrane module, m
l_m	thickness of the hollow fiber, m
R	gas constant, 8.314 Pa $m^3\,mol^{-1}\,K^{-1}$
Re	Reynolds number
r_p	membrane pore size, m
Sc	Schmidt number
Sh	Sherwood number
T	temperature, K
t	time, min
V	velocity, m s^{-1}
Greek letters	
α	parameter in Eq. (3)
β	parameter in Eq. (3)
ε_m	membrane porosity
σ_{AB}	characteristic length, Å
τ_m	membrane tortuosity
Ω_D	collision integral

component into a liquid (with or without the reaction). The mass transfer in the hollow fiber membrane contacting process is shown in Fig. 1. Membrane contactors have been widely studied for the process such as liquid–liquid extraction, gas–liquid absorption, for example, the absorption of CO_2 [7,8].

Most studies on the application of membrane contactors for ozonation involve liquid feeds which were solutions of NOM (natural organic matter) [9,10] and humic substance [11]. We recently published our work [12] on ozonation membrane contacting system for dye wastewater treatment using PVDF (polyvinylidene fluoride) hollow fiber membrane (UMP-153, Pall Corperation). In that study the ozone mass transfer, the effects of HRT (hydraulic retention time) on color removal were investigated.

The polymer membranes which have been used as contactors are usually made from PP (polypropylene), PVDF (polyvinylidene fluoride), and PTFE (polytetrafluoroethylene). In general, the hydrophobicity is in the order of PTFE > PVDF > PP [13]. For ozonation by membrane contactors it is important that the membranes are resistant to ozone which is a strong oxidant. Mori et al. [14] reported that the ozone resistance was in the following order; PTFE > PVDF > PE (Polyethylene). However, in previous research [9–12] only PVDF membranes were selected for the study and there has been no investigation on the comparison of the long-term performance of PVDF and PTFE membranes for ozonation of dye wastewater. Accordingly, the main objective of this work was to study the performance of both PVDF and PTFE membranes for decolorization of dye wastewater by ozonation. Three types of azo dye, i.e., Reactive red 120, Direct red 23, and Acid blue 113 were selected for the study. The effects of auxiliary reagents (NaCl, Na_2SO_4) were also investigated. In addition, this study also included the reaction kinetics of these dyes with ozone.

2. Basic principle of mass transfer in gas–liquid membrane contactor

The mass transfer mechanism in the gas–liquid membrane contacting process can be described by using the resistance-in-series model. Fig. 1 demonstrates the mass transport of gas in dry operating mode of membrane contactors, i.e., diffusion from the bulk gas through the membrane pores and dissolution in the liquid absorbent. The resistance-in-series model can be expressed as Eq. (1).

$$\frac{1}{K_{ol}} = \frac{1}{Ek_l} + \frac{d_o}{Hk_m d_{ln}} + \frac{d_o}{Hk_g d_i} \quad (1)$$

where K_{ol} is the overall mass transfer coefficient based liquid phase (m/s), E is the enhancement factor which is included to account for the effect of the reaction. k_l, k_m, k_g are the individual mass transfer coefficients of the liquid phase, membrane and gas phase, respectively. d_i, d_o, d_{ln} are the inner, outer and logarithmic mean diameters of the fibers, respectively. H represents Henry's constant. For the dissolution of ozone in water at 295 K, the Henry's constant is 3.823 $(mg/l)_g/(mg/l)_l$ [12].

In the operation of a membrane contactor, either the gas phase or liquid phase can be fed through the shell side or tube side of the hollow fiber membrane module. In our work liquid was fed through the tube while gas was fed into the shell side. The well-known Graetz-Lévêque mass transfer correlation was widely used to predict the tube side mass-transfer coefficient [7,15];

$$Sh = \frac{k_l d_i}{D} = 1.62\left(\frac{d_i^2 V}{LD}\right)^{1/3} \quad (2)$$

where Sh is Sherwood number, D is the diffusion coefficient, L is the tube length and V is the fluid velocity.

Many correlations have been proposed to determine the shell side mass transfer coefficient [15–17]. However, each of them is applicable to a certain limited range of operation. In general, it can be expressed in the following form:

$$Sh = aRe^{\alpha}Sc^{\beta} \quad (3)$$

where Re and Sc are Reynolds and Schmidt numbers, respectively. The membrane mass transfer coefficient can be calculated independently using the pore structure properties [18]:

$$k_m = \frac{D_{g,eff}\varepsilon_m}{\tau_m l_m} \quad (4)$$

where ε_m is the membrane porosity, l_m is the membrane thickness, and τ_m is tortuosity which can be calculated from the following empirical correlation [19].

$$\tau_m = \frac{(2-\varepsilon_m)^2}{\varepsilon_m} \quad (5)$$

Eq. (5) is recommended and has been successfully employed for polymer membrane manufactured by phase inversion method. In Eq. (4), $D_{g,eff}$ is the diffusion coefficient of gas in the membrane