Journal of Hazardous Materials 301 (2016) 462–470

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

A new integrated approach for dye removal from wastewater by polyoxometalates functionalized membranes

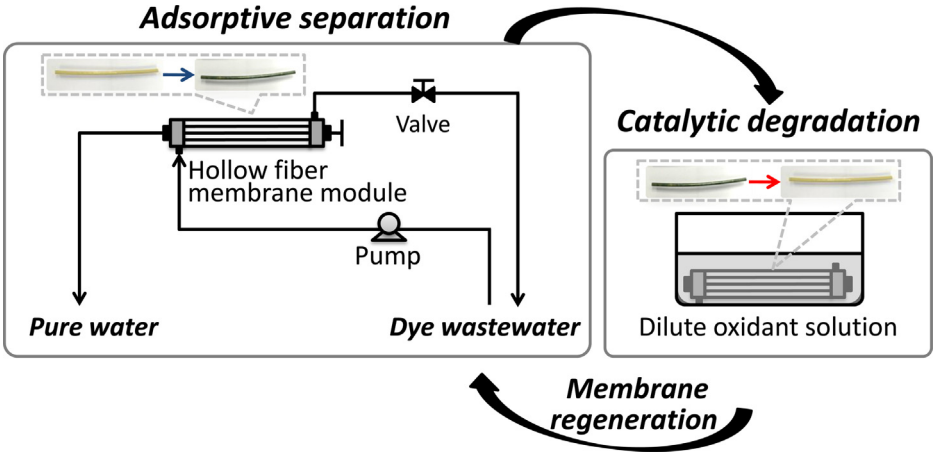
Lei Yao [a,b], Lizhi Zhang [b], Rong Wang [b,*], Shuren Chou [b], ZhiLi Dong [a,*]

[a] School of Materials Science and Engineering, Nanyang Technological University, Nanyang Avenue, Singapore 639798, Singapore
[b] Singapore Membrane Technology Centre, Nanyang Environment and Water Research Institute, Nanyang Technological University, 1 Cleantech Loop, Singapore 637141, Singapore

HIGHLIGHTS

- A new integrated approach for dye removal was developed.
- A POMs bi-functionalized (adsorptive and catalytic) membrane was fabricated.
- A novel sol–gel method was proposed for POMs incorporation with membrane.
- An excellent dye rejection with economic membrane regeneration was realized.
- The selection of POMs is flexible for the distinct design of catalytic degradation.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 6 July 2015
Received in revised form 1 September 2015
Accepted 13 September 2015
Available online 15 September 2015

Keywords:
Polyoxometalates
Membrane
Adsorption
Catalytic degradation
Dye removal

ABSTRACT

Membrane technique is a promising way for the removal of dyes from wastewater. A unique approach combining both the adsorptive and the catalytic membrane processes was proposed on the basis of a new functionalized membrane. The membrane integrating both the adsorptive and catalytic activities was developed by introducing polyoxometalates (POMs) as an ideal candidate for the membrane functionalization *via* a novel sol–gel method. A two-step protocol, adsorptive separation and catalytic degradation, was designed for dye removal, realizing an excellent dye rejection with easy and economic membrane regeneration through simply soaking the membrane in a limited volume of dilute oxidant solution. This approach is feasible and versatile owing to the flexible selection of distinct POMs and design of catalytic degradation routes as required. As a result, the current research provides insight into a new methodology of the membrane technique in dye removal applications.

1. Introduction

The intensive industrialization throughout the world has always been followed by increasing generation of wastewater. Industrial wastewater contains hazardous and refractory organic pollutants,

* Corresponding authors. Fax: +65 67909081.
E-mail addresses: rwang@ntu.edu.sg (R. Wang), zldong@ntu.edu.sg (Z. Dong).

http://dx.doi.org/10.1016/j.jhazmat.2015.09.027
0304-3894/

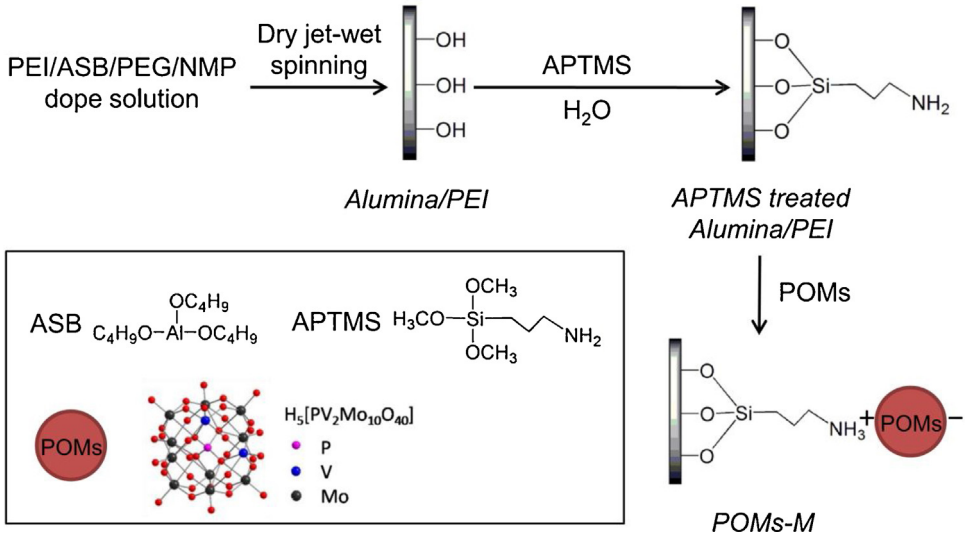


Fig. 1. Proposed route for fabrication of the POMs functionalized membrane (POMs-M).

causing severe environmental problems. One of the typical organic pollutant species, synthetic dyes with an annual production of more than 700,000 tonnes are widely used in textile, leather, paper, paint, plastic and other industries [1]. It has been estimated that more than 10–15% of the total dyestuff was released into the environment during their synthesis and dyeing process [2], which is a serious threat to aquatic ecosystem as well as public health. The removal of dyes from wastewater is hence of great importance before discharging into the environment.

For the removal of dyes from wastewater, researchers in the past few decades have made great efforts, and various techniques such as adsorption [3–5], coagulation/flocculation [6,7], membrane separation [8–12], catalytic oxidation [4,13,14], *etc.* have been well developed. Each of these techniques has its specific advantages. At the same time, specific disadvantages are also accompanied. For example, adsorption or coagulation/flocculation is highly efficient and flexible for dye removal from wastewater, while the high sludge production as well as the post-treatment of the toxic sludge is all the time a big issue for large-scale applications [15]. Similarly, membrane separation technique such as nanofiltration (NF) and reverse osmosis (RO) is promisingly attractive for the removal of dyes from wastewater because of its production of high-quality effluent without the generation of sludge, while the major disadvantage of this technique is the low water permeability with the high energy cost [16,17]. In addition, catalytic oxidation (*e.g.*, Fenton reaction) is able to generate highly reactive radicals driving the mineralization of dyes in wastewater within a short duration, while there are great issues in terms of the recycling and recovery of catalysts from wastewater and the high cost due to the employment of a large amount of oxidants (*e.g.*, H_2O_2) in a large volume of effluents. In order to make best use of the advantages and bypass the disadvantages, researchers in recent years have begun to focus on the development of integrated techniques for the removal of dyes from wastewater.

Adsorptive membranes, which integrate the membrane separation and the adsorption process in one device, have drawn increasing attention for dye removal from wastewater. For example, Lin et al. prepared poly(methyl methacrylate)/Na^+–montmorillonite membranes for the adsorptive removal of methyl violet [18]. Chiu et al. fabricated quaternary ammonium groups functionalized glass fiber membranes for the adsorptive removal of Cibacron blue 3GA [19]. In addition, Daraei et al. employed organoclay/chitosan-

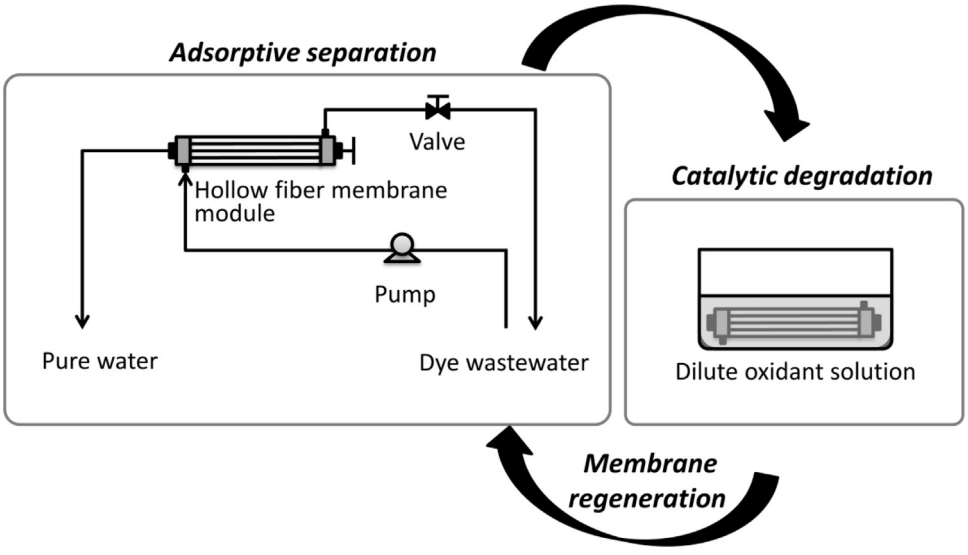


Fig. 2. Schematic diagram of the dye removal process.