Process Safety and Environmental Protection 116 (2018) 22–33

Contents lists available at ScienceDirect

Process Safety and Environmental Protection

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

Synthesis of ceramic ultrafiltration membrane and application in membrane bioreactor process for pesticide remediation from wastewater

Debarati Mukherjee[a,b], Priyankari Bhattacharya[b], Animesh Jana[a,b], Sandipan Bhattacharya[d], Subhendu Sarkar[b], Sourja Ghosh[a,b,*], Swachchha Majumdar[b], Snehasikta Swarnakar[c]

[a] Academy of Scientific and Innovative Research (AcSIR), CSIR-Central Glass and Ceramic Research Institute, India
[b] Ceramic Membrane Division, CSIR-Central Glass and Ceramic Research Institute, Kolkata 700032, India
[c] Drug Development Diagnostics & Biotechnology Division, CSIR-Indian Institute of Chemical Biology, Kolkata 700032, India
[d] Department of Environmental Science, University of Calcutta, 35 Ballygunge Circular Road, Kolkata 700019, India

ARTICLE INFO

Article history:
Received 4 July 2017
Received in revised form 4 January 2018
Accepted 14 January 2018

Keywords:
Ceramic ultrafiltration membrane
Green synthesized iron oxide nanoparticles
Membrane bioreactor (MBR)
Atrazine
Toxicity assay

ABSTRACT

The efficiency of membrane bioreactor (MBR) process involving indigenously developed ceramic membranes was explored for management of wastewater containing toxic pesticides like atrazine. Performance of the MBR process was compared for clay-alumina based ceramic microfiltration membranes (MF-MBR) with that of an indigenously developed new ceramic ultrafiltration membrane (UF-MBR). The UF membrane was prepared on the macroporous support tubes using iron oxide nanoparticles synthesized by green route from *Aloe vera* leaf extract, with chitosan as matrix and glutaraldehyde as cross-linker. The synthesized membrane was characterized in terms of X-ray diffraction, field emission scanning electron microscopy, Fourier transform infrared spectroscopy, pore diameter and molecular weight cut off, etc. Microorganisms isolated from activated sludge of a pilot scale MBR plant were optimized to enhance the biodegradation efficiency of atrazine. Compared to the MF-MBR process, the UF-MBR process showed about 15% increase in atrazine removal, lower membrane fouling and complete separation of the biomass in the synthetic system. Performance of the UF-MBR process was further analyzed with domestic and industrial wastewater simulated with atrazine. In addition, toxicity assay of the UF-MBR treated water was performed on an aquatic model, *Radix balthica* indicating that the permeate could be safely disposed into the environment.

1. Introduction

Pesticides, herbicides, pharmaceuticals and personal care products (PPCP) are detected in low level, usually in ng/L to mg/L in surface water, industrial wastewater treatment plants and even in groundwater (Lai et al., 2016). Pesticides like atrazine, DDT (dichloro diphenyl trichloroethane), DEET (N,N-diethyl-meta-toluamide), metolachlor, malathion and methoxychlor, etc. are one of the various types of emerging contaminants discharged into surface or ground water from agricultural runoff. Specific treatment is required for such type of contaminants and accordingly, various approaches had been employed which include adsorption by activated carbon, ozonation, photolysis, incineration and chemical degradation for removal of these toxic emerging contaminants. Granular activated carbon (GAC) based adsorbents (Yue et al., 2006) and modified clays (Zadaka et al., 2008) were reported to have efficiency of about 98% for atrazine removal (Borisover et al., 2001). Microbial biodegradation of different herbicides like clodinafop propargyl, atrazine, metolachlor, glyphosate and imazapyr, etc. was employed as an economical and ecofriendly option (Singh and Singh, 2016). The cell wall of Gram negative bacteria usually possesses contaminant binding property (Ahalya et al., 2003). However, most of these processes have several limitations like rapid saturation of adsorption sites and handling of toxic ozone which may cause irritation in body, are costly and often suffer with

* Corresponding author at: Ceramic Membrane Division, CSIR-Central Glass and Ceramic Research Institute, Kolkata 700032, India.
E-mail addresses: sourja@cgcri.res.in, sourja.g@gmail.com (S. Ghosh).

https://doi.org/10.1016/j.psep.2018.01.010
0957-5820/

production of other toxic by-products (Pathak and Dikshit, 2011; Saxena et al., 2014; Edward et al., 2015). Considering these factors, the recent focus has been shifted to membrane filtration technique in view of its simplicity, cost-effectiveness, ease of operation for longer duration and environment friendly nature (Kiso et al., 2000; Bellona et al., 2004).

Recently, membrane based separation processes show a new dimension for treatment of such emerging contaminants. Application of biopolymeric membranes developed from chitosan and alginate was employed for adsorption of glyphosate which indicated that chitosan membrane showed best adsorption followed by chitosan-alginate bilayer (Carneiro et al., 2015). Nanofiltration and reverse osmosis membranes were also used for removal of atrazine; however, these processes involve high pressure, thus making them expensive (Plakas et al., 2006). In addition, disposal of the concentrated retentate in the environment is often a big concern in the membrane processes (Abdelmelek et al., 2011). Membrane bioreactor process could be an effective option in this context since the application of ultrafiltration or microfiltration membrane ensures complete removal of the biosolids, thus yielding better quality of treated water and also overcomes the problem of associated sedimentation as required in the biological treatment process (Basile et al., 2011). Moreover, MBR process is cost-effective as it eliminates the need for secondary clarification and tertiary treatment steps unlike a conventional activated sludge process (Melin et al., 2006). MBR process involving the combination of biodegradation by genetically engineered microorganisms (GEM) and filtration by a polyethylene microfiltration membrane module resulted in about 94.7% removal of atrazine (Liu and Huang, 2008). GEM was prepared by cloning atrazine chlorohydrolase gene of *Pseudomonas* sp. ADP into the plasmid vector pACYC184 which was then transferred into *Escherichia coli* DH5a. Considerable removal of atrazine at low concentration was achieved in the MBR process (Buttiglieri et al., 2011).

Although polymeric membrane based MBR have been reported, application of ceramic membranes for such types of pesticides removal has been scantily available. The ceramic membranes may be potential candidate due to their high thermal, chemical and mechanical stability, better longevity, and lower fouling properties compared to the polymeric membranes (Sarkar, 2014). The present study hence, focuses on remediation of atrazine, a persistent organic pollutant, from contaminated water using ceramic UF membrane based MBR process. A new UF membrane was synthesized involving green synthesized iron oxide nanoparticles (Mukherjee et al., 2016a) over macroporous clay-alumina based ceramic support and its application was studied in MBR process for the removal of atrazine from contaminated water. The performance efficiency was compared with that of the MBR process integrated with the MF membrane. Atrazine (2-chloro-4-ethylamino-6-isopropyl-s-triazine), a member of s-triazine group of herbicides, is one of the most widely used herbicides that has been detected in very high concentrations in groundwater and surface water because of its longer half life and slow rate of degradation (Tappin et al., 2012). Concentration of this herbicide found in surface water, especially in agricultural areas, is found to be as high as 2.5 mg/L (Graymore et al., 2001; Scott et al., 2010; Stein, 2006). Atrazine concentration in well water near loading or mixing sites may range from 0.024 to 22 mg/L (Long, 1987). In India also, there is wide usage of atrazine (Geed et al., 2017). Ground water samples of Delhi were detected with mean atrazine concentration in the range of 0.72 μg/L to 0.0173 mg/L (Aslam et al., 2013). The maximum contaminant level (MCL) of EPA for atrazine in water is 3 μg/L (Bezbaruah et al., 2009). In this study bacterial strains identified to be potential in atrazine removal were isolated from the activated sludge collected from a pilot scale MBR plant for domestic wastewater treatment. Evaluation of the toxicity effect of the atrazine containing simulated wastewater samples on environment before and after the MBR treatment was studied by using aquatic snails (*Radix balthica*) as animal model.

2. Materials and methods

2.1. Membrane preparation

The microfiltration (MF) membranes were prepared from kaolinite and alumina using organic additives as binders (Banerjee et al., 2014). These tubes were of single channel configuration having 150 mm length, 10 mm outer diameter and 7 mm inner diameter. The ultrafiltration membrane was prepared on the MF membrane using green synthesized iron oxide nanoparticles (Fe (III) NP) as coating material prepared from ferric chloride as the initial precursor and *Aloe vera* leaf extract (Mukherjee et al., 2016a). The nanoparticles were mixed with different concentrations of chitosan [Sigma–Aldrich, Germany] solution prepared in 2 wt% acetic acid (Merck, India). The mixture was stirred at 110 rpm for 2 h under clean and dust free environment following which 5% glutaraldehyde (Merck, Germany) was added. The slurry formed was stirred at 110 rpm for 30 min for attainment of proper crosslinking.

The substrate tubes were ultrasonicated with acetone for 30 min to remove any impurities present which may hamper the formation of homogenous coating layer, followed by drying at 105 °C for 1 h and then coated with the prepared slurry by dip coating with 5 min contact time. The coated tubes were oven dried at 110 °C for 6 h for complete removal of the moisture. Unsupported films of the membranes were also prepared at the aforementioned conditions for detailed characterizations.

2.2. Characterization of membranes

Microstructure of the membranes was observed using Field Emission Scanning Electron Microscopy [FESEM, Zeiss, Germany] to analyze the surface morphology before and after MBR treatment. The pore diameter, specific surface area and porosity of the unsupported film were determined by adsorption–desorption of nitrogen with multipoint Braunauer–Emmett–Teller (BET) method using Quantachrome Autosorb Automated Gas Sorption System, (USA). The clean water permeability of the MF and UF membrane and the molecular weight cut-off (MWCO) of the prepared UF membrane were determined by standard procedure (Mukherjee and De, 2015). For MWCO estimation the rejection (%) of polyethylene glycol (PEG) with different molecular weights, viz. 0.4, 0.6, 2, 4, 6, 10 and 20 kDa was analyzed using the prepared membrane. The unsupported UF membrane was characterized by X-ray diffraction [Phillips 1710 Diffractometer] with copper (α = 1.541 Å) as the anode material and scanning range of 2θ as 5–80°. Fourier transform infrared spectroscopy [FTIR, Perkin Elmer, USA] of the unsupported membrane was performed for identification of the various functional groups in the wave number range of 400–4000 cm^{-1}. The stability of the prepared membrane was characterized in terms of pH resistivity, iron oxide leaching, degree of cross linkage (DC) and degree of swelling (DS) following standard procedures (Budianto et al., 2015). For this unsupported membrane was weighed (W_0), immersed in acetic acid for 24 h followed by oven drying at 100 °C and again weighing of the mixed matrix membrane (W_g) to obtain the degree of crosslinking (Eq. (1)).

$$DC(\%) = \frac{W_g}{W_0} \times 100 \quad (1)$$

The degree of swelling of the unsupported membrane was determined by weighing the sample (W_0) and after immersed in distilled water for 30 min followed by removing the excess water using fil-