Ultrasound-assisted Fenton-like degradation of methylene blue using electrospun nanofibrous membranes

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Abstract. New materials supported by Green Chemistry have been receiving widespread attention because they are fulfilling the sustainable development goals (SDGs) agenda, for which clean water development is a top priority. Recently, electrospun nanofibers membranes are being frequently used to decontaminate organic pollutants such as dyes because of their easy operation, flexibility, economic feasibility and high removal efficiency. In the present study, green polyvinyl alcohol-based electrospun nanofibers membranes (PVA NF) were produced at room temperature and applied for efficient capturing methylene blue as a common organic pollutant. A series of experiments were conducted to affirm their catalytic activity. In particular, dye degradation studies were initiated by dissolving a selected amount of Fe (III), H_2O_2, PVA NF membrane and ultrasound (ULTS). Results showed that ultrasound could generate hydroxyl (•OH) radical and triggers dye removal percentages, which are of significant contribution in terms of peroxide-free Fenton-like catalysis. Finally, this study has proven that electrospun nanofibrous membranes could be a potential economic and efficient carrier for the Fenton catalytic process to capture large amounts of organic pollutants from industrial effluents.

Keywords: Electrospun nanofiber membrane, Green Chemistry, clean water, Fenton-like, methylene blue

1. Introduction

Dyes are considered as one of the major pollutants in wastewater because of their adverse effects on human health and the ecosystem. Methylene blue (MB) is a common dye used in various industrial sectors such as textile, food, paper, leather, etc. However, it is identified as highly toxic and carcinogenic (Kaya-Özkiper et al. 2021; Pervez et al. 2020a). Therefore, several technologies have been applied for the removal of MB from wastewater. Among them, electrospun nanofiber membranes exhibit great promises in wastewater treatment (e.g., dyes removal). This performance was obtained due to their high specific surface area, porosity, and removal efficiency (Hosseini et al. 2018; Pervez and Stylios 2018b). Usages of water-soluble polymers are getting attention for the fabrication of electrospun-based nanofibers membranes because of the following Green Chemistry principle, which are one of the potential requirements towards environmental sustainability development (Horzum et al. 2019; Pervez and Stylios 2018a; Rylkova et al. 2012).

Polyvinyl alcohol (PVA) is a water-soluble polymer, and the PVA-based electrospun nanofibers membrane shows high chemical resistance, thermal and mechanical stability and hydrophilicity that makes them a suitable candidate for water treatment (Pervez et al. 2020c; Yin et al. 2020; Zhao et al. 2015). However, the dye removal performance of the pure electrospun nanofiber membrane could be moduled by the addition of a catalytic process. Fenton reaction has long been used to capture recalcitrant-based organic pollutants from wastewater due to its easy operation, rapid processing and high degradation efficiency (Liu et al. 2017; Pervez et al. 2019; Telegin et al. 2016). Fenton reaction mainly works on the generation of powerful hydroxyl (•OH) radicals, and in recent years, it is reported that ultrasound (ULTS) could generate •OH radicals and accelerate the Fenton reaction,

Keeping in mind the above considerations, in this study, we proposed a robust dye removal process by the combination of ULTS-assisted nanofibers membrane and Fenton reaction. This work has paved the way to open up an innovative avenue for fabricating membrane–catalytic process to treat dye-containing wastewater effluent.

2. Experimental

In this study, polyvinyl alcohol (PVA,115,000 Mw) was bought from BDH Ltd Poole, UK. Methylene blue (Dye content, ≥82%), $FeCl_3$ and H_2O_2 (30%) were received from Merck. The PVA electrospun nanofiber membrane was prepared according to the previous study (Pervez et al. 2020c). Dye degradation experiments were conducted using an ultrasound bath (Elma Schmidbauer GmbH, Germany). Typically, 100 mL beaker containing 50 mL of 15 ppm MB solution and 0.8 g membrane. An appropriate amount of $FeCl_3$ was added, and experiments were also conducted with and without H_2O_2 in order to compare the degradation efficiency. The mixture was sonicated for 40 min with 35 kHz and 80 W power. After that, 1 mL samples were withdrawn at certain reaction intervals and subjected to UV/visible spectrophotometry (Perkin Elmer, USA) to measure the decolourization percentage (Eq.1).

$$\text{Decolorization}\ (\%) = \frac{C_o - C_t}{C_o} \times 100 \qquad (1)$$

Where, C_0 and C_t are the concentrations of MB initially and at time t, respectively.

3. Results and discussion

Here, methylene blue was chosen as a model organic pollutant due to its non-volatility and charged properties, in which it is available in the gas phase reactions. Previous reports suggested that the ultrasound-assisted degradation process generally occurred in gas phases, and MB degradation process also undergoes gas-phase oxidation medium (Minero et al. 2005; Yu et al. 2014).

In order to examine the catalytic activity of as-prepared PVA nanofiber membranes (PVA NF), the mixed dye solution was irradiated for 60 min in the ultrasonic bath to achieve dye equilibrium conditions. Afterward, the dye removal efficiency was assessed by UV-Vis, and all results are depicted in Figure 1.

Undoubtedly the introduction of ultrasound enhanced the removal efficiency, as shown in Figure 1 (a), (b) and (d). Notably, the highest dye degradation percentage achieved (96%) in the presence of the full combination process (PVA NF+Fe(III)+H_2O_2+ULTS) (Figure 1a). This result may be attributed to the synergistic effects of ultrasound and PVA NF membrane on the successful decomposition of peroxide into •OH radicals under Fenton's reagents.

Usually, ultrasound is a cavitation technique and possesses two pronounced effects: generate radicals and higher shearing into the reactor. Among them, radicals generation is mainly focused on water treatment applications (Fraiese et al. 2020; Naddeo et al. 2010; Naddeo et al. 2020). Ultrasonic power has generated some collapsing bubbles that may lead to the formation of •OH radical (Khataee et al. 2015a; Khataee et al. 2015b). Also, ultrasound power is responsible for higher turbulence in the mixed solution, which facilitated the mass transfer rate of MB, produced radicals and degradation by-products between the PVA NF membrane surface and the initial mixed solution (Eren and O'Shea 2019; Hou et al. 2013). Another reason can be explained by the evolution of active sites of nanofiber membrane in the presence of ultrasound and collectively contributes to a better removal efficiency. The size of the nanofiber membrane surface was significantly reduced due to the thermal and kinetic energy produced through ultrasound, resulting in a small diameter based nanofiber membrane formed, and it was firmly documented that a minor diameter baed membrane with a higher specific surface area is suitable for pollutants capture sites (Asrofi et al. 2018; Das et al. 2017; Zhang et al. 2021).

While in the absence of ultrasound (PVA NF+Fe(III)+H_2O_2), the degradation percentage showed a decreased trend to 87% (Figure 1c). This result is accounted for by the conventional Fenton process with an as-prepared PVA NF membrane. In this system, the conversion of Fe (III) to Fe (II) by H_2O_2, HO_2•, and •O_2^- contributes to the rate-determining step for MB degradation (De Laat and Gallard 1999; Yang et al. 2013). These results clearly demonstrated that the sonication process played an essential role in the degradation process.

Interestingly, the removal efficiency of MB was increased to 92% in the presence of PVA NF+Fe(III)+ULTS (Figure 1b). Although this experiment was carried out without H_2O_2, the degradation percentage of MB was dramatically enhanced. These can be discussed by the generation of •OH radicals upon sonication with PVA NF membrane, which likely to be the principal reason for MB degradation in the absence of H_2O_2. During the ultrasonication process with water, hydroxyl radicals are formed and simulated the Fenton reactions, accelerates the degradation process of MB (Eq. 1-4) (Naddeo et al. 2010).

$$H_2O +))) \longrightarrow \bullet H + \bullet OH \qquad (1)$$

$$MB + \bullet OH \longrightarrow \text{metabolities} + \bullet OH \longrightarrow \text{end-products} \qquad (2)$$

$$\bullet OH + \bullet OH \longrightarrow H_2O_2 \qquad (3)$$

$$H_2O_2 + \bullet H \longrightarrow H_2O + \bullet OH \qquad (4)$$

Where ')))' denotes the ultrasound waves.

It appears that Fe (III) also contributes to the degradation process (Figure 1b and c). Fe (III) act as a scavenger for hydrogen atoms, thereby inhibiting the recombination process and promotes the yield of •OH radicals (Pervez et al. 2020b). Also, Fe (III) supplies the source of catalyst development during sonochemical Fenton reactions, in which the degradation percentage of MB enhanced. However, the degradation efficiency was not so convinced using only Fe (III)+ PVA NF membrane (Figure 1e). It could be the reason that the formation of iron-complex inhibited the degradation efficiency. The previous study has emphasized that Fe-complex was formed in acidic media and reduced the degradation kinetics and efficiency (Park and Choi 2003; Ran et al. 2013).

Identifying the role of H_2O_2 in dye degradation efficiency, some experiments were conducted in the presence of Fe (III) and absence. The addition of H_2O_2 accelerates the degradation efficiency, as presented in Figure 1 a, c, and d. However, slight degradation efficiency was noticed when Fe (III) absence (Figure 1 f), thic could be underlined that no direct reaction takes place between MB and H_2O_2 in the presence of PVA NF membrane (Minero et al. 2005).

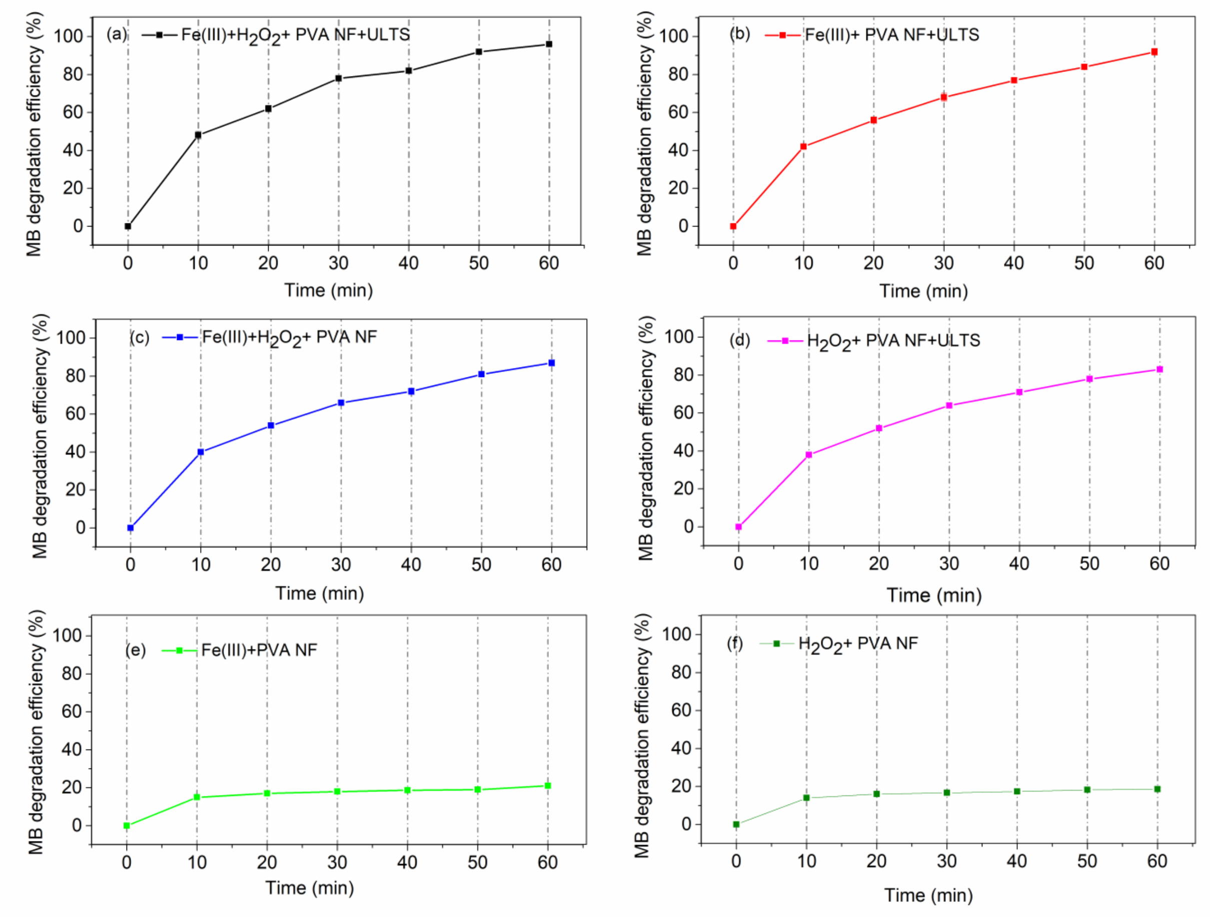

Figure 1. The degradation percentage of MB using different conditions

4. Conclusion

In this study, polyvinyl alcohol (PVA)-based green electrospun nanofibers membranes was prepared and applied as a novel heterogenous Fenton catalyst for dye removal from aquous solution. Results showed that addition of ultrasound significantly enhanced the degradation efficiency and entire process. It should be mentioned that •OH radical was mainly responsible for MB degradation. It was noticed that the ultrasound process has generated •OH radical and accelerates MB degradation percentages under PVA NF membrane and Fe (III) (without H_2O_2), which is more exciting and we optimistic that our study provides a foundation for the development of electrospun nanofiber membrane-based peroxide free Fenton-like catalyst to produce clean water sources.

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