

Research Article

Comparison of membrane immobilized zero-valent iron nanoparticles for RED ME4BL azodye degradation

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Abstract

Textile industries are hailed as one of the major environmental polluters in the world, owing to their release of undesirable dye effluents. Synthetic dyes do not adhere to fabric firmly and are released into the aquatic ecosystem as effluent. Consequently, the consistent release of wastewater from numerous textile industries without previous treatment has detrimental effects on the ecosystem and human health. Treatment methods currently being used fail to degrade the dye effluents and have their own shortcomings. Immobilized nanoparticles have been extensively studied for dye remediation because of their many advantages over conventional methods. The present study aimed to compare the efficiency of two different carrier matrices [namely Poly (vinylidene fluoride) and Polyurethane] for iron nanoparticle and their decolorization activity on an azo dye (RED ME4BL). Scanning Electron Microscopy was carried out to show the deposition of iron nanoparticles on the membrane. The reaction kinetics of the bare nanoparticles were compared with that of the immobilized nanoparticles, and all were found to follow pseudo-second-order kinetics. Polyurethane immobilized iron nanoparticles showed a significant degradation of RED ME4BL than the Poly (vinylidene fluoride) immobilized iron and bare nanoparticles. This paper also demonstrates a relatively newer method for nanoparticle immobilisation using the synthetic polyurethane form.

Keywords: Azo dye, Dye degradation, Polyurethane, Poly(vinylidene fluoride), REDME4BL, Zerovalent iron nanoparticles

INTRODUCTION

Water, occupying nearly two-thirds of the earth's surface, is the most abundant resource on earth; however, due to unrestricted human activities, it is getting extremely polluted (Kalra and Gupta 2021; Tkaczyk *et al.*, 2020). Presently, one of the biggest issues affecting the entire world is water contamination brought on by textile factories' inability to adequately dispose of their waste water. More specifically, textile, plastic, paper, and cosmetic industries discharge substantial amounts of organic dyes, of which the textile industry effluents pose a major threat (Slama *et al.*, 2021; Shanker *et al.*, 2017).

Azo dyes constitute the most widely used dyes in the textile industry, accounting for more than 70% (nine million tonnes) of global manufacturing needs (Benkhaya *et al.*, 2020). Due to their chemical structures (azoic linkages, amino groups, and aromatic rings), azo dyes persist in water bodies for longer. The major concern related to the untreated disposal of azo dyes is that they and their byproducts, produced by the breakage of their azo bonds (aromatic amines), have been classified as highly carcinogenic compounds, representing a great risk to humans (Pinheiro *et al.*, 2022). The azo dye effluents discharged from factories cause various environmental, ecological and health

impacts. It is crucial to remove or degrade the dyes in industrial effluents before their disposal (Lellis *et al.*, 2019; Al-Tohamy *et al.*, 2022). Dyes dispersed into the water bodies cut light penetration, affecting the growth of aquatic plants. Furthermore, dyes consumed by aquatic animals are metabolized into toxic mediates, which can have an adverse impact on the health of their predators (Elgarahy *et al.*, 2021; Liang *et al.*, 2017). In humans, these effluents can bring about allergies, dermatitis, mutations, and other serious problems (Sarvajith *et al.*, 2018). Several physical and chemical methods are employed for effluent treatment with their own merits and demerits (Crini and Lichtfouse, 2019). At this juncture, nanoparticles are successfully exploited for the remediation of dye effluents because of their notable advantages over the other methods (Mehta *et al.*, 2021; Badvi and Javanbakht 2021; You *et al.*, 2021; Jadoun *et al.*, 2021; Saravanan *et al.*, 2021; Naseem and Durrani, 2021). Bare nanoparticles tend to aggregate easily because of the high energy, which results in a loss of their catalytic activity. Therefore, a proper matrix is essential to stabilize the metal nanoparticles and studies have successfully exploited several matrices for nanoparticle immobilization (Riaz *et al.*, 2022; Alani *et al.*, 2021; Zhu *et al.*, 2019; Arancibia-Miranda *et al.*, 2016; Chen *et al.*, 2016).

The application of zero-valent iron nanoparticles (nZVI) for textile effluent remediation seems promising in recent years because iron nanoparticles exhibit a highly responsive activity towards the pollutant. They are safe, toxicity free, and reasonable. The nanoscale iron particles can agglomerate together swiftly with respect to time. To address this, supports such as nickel, zinc, bentonite, kaolin, rectorite, cellulose, biochar, graphene, and clinoptilolite are added to amplify the stability of iron nanoparticles (Raman and Kanmani, 2016; Kgatle *et al.*, 2021; Thakare *et al.*, 2022). The present study aimed to determine the best immobilization carrier for iron nanoparticles, which in turn will be successful and efficient degradation of the azo dye, RED ME4BL.

MATERIALS AND METHODS

Chemicals and reagents

RED ME4BL, a reactive azo dye, was procured from Sun Dye Chem in the Tirupur district, Tamil Nadu and used as such without any additional treatments. Sodium borohydride (NaBH₄), ferric chloride (FeCl₃) and palladium acetate [Pd(O₂CCH₃)₂] were obtained from Hi-Media. Absolute alcohol (ethanol) was purchased from Merck.

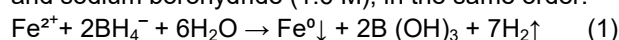
Immobilization of bimetallic nanoparticles in modified PVDF Membrane with PAA

The PVDF [poly(vinylidene fluoride) membranes] activated with Poly Acrylic Acid (PAA) was set up by coat-

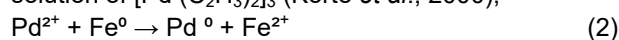
ing the surface pores with the acrylic acid monomer solution, thus causing a free radical polymerization reaction through thermal treatment (Gabriel and Gillberg, 1993). Toluene was used as the solvent to pull off the ability to soak the hydrophobic PVDF membrane. The monomer solution was made ready by blending the acrylic acid (30 wt %), benzoyl peroxide (0.5 wt %, initiator), trimethylolpropane triacrylate (TMPTA - 1 wt %, crosslinking material) in toluene. The solution was de-aerated by purging with ultra-high pure nitrogen for 2 hours. The PVDF membrane was immersed into the prepared monomer solution for 2 minutes, hurriedly placed between teflon plates, and then kept in the oven at 90 ± 2°C with continuous nitrogen purging for thermal activation (Gabriel and Gillberg, 1993). After 4 hours, the membranes were removed from the Teflon setup and washed with absolute ethanol to wash off the unbound monomers, followed by rinsing with deionized water. PAA coated PVDF membranes were immersed in sodium hydroxide (0.1 M) solution overnight. After rinsing, the excess sodium hydroxide was washed off using deionized water. The membrane was treated with a deoxygenated solution of 5.5 mM ferrous chloride (pH 4.8~5) with nitrogen purging for about 12h. After washing with deoxygenated deionized water, the membrane was exposed to sodium borohydride (0.07 M) to reduce Fe²⁺ embedded in the PAA/PVDF membrane. After rinsing with deoxygenated deionized water and absolute ethanol, the membrane immobilized zero-valent iron nanoparticle was exposed to a hydro-ethanolic solution (90/10 vol.% ethanol/water) of [Pd(C₂H₃)₂]₃ (0.12 mM) for 45 minutes, which lead to the sedimentation of palladium on iron surface through a redox reaction. To minimize the corrosion reaction, the PAA/PVDF membrane with the immobilized bimetallic (Fe/Pd) nanoparticles was rinsed with 90% ethanol and stored in 100% ethanol until use (Xu and Bhattacharyya, 2007).

Immobilization of bimetallic nanoparticles in modified Polyurethane membrane

The commercial polyurethane (PU) foams were washed with acetone and distilled water to remove the previous industrial treatments carried out. The cleaned material was then soaked in 4% HCl for about 8 – 12 hours. The pre-treated membrane was cut into uniform cubes (1 cm³) (Domènech *et al.*, 2016). Nano zero-valent iron was synthesized by reducing sodium borohydride (Wang and Zhang, 1997). The pre-treated PU membrane was let to react with ferric chloride (1.0 M) and sodium borohydride (1.6 M), in the same order.



The zero valent iron nanoparticles were then dusted with palladium acetate by dispersion with an ethanolic solution of [Pd (C₂H₃)₂]₃ (Korte *et al.*, 2000),



The deposition of iron nanoparticles on the individual

membrane was visualized using an electron microscope (SEM). To prevent oxidation, the PU membranes were stored in air-tight containers until further use.

Characterization of bimetallic nanoparticles

The deposition and size of the iron nanoparticles were observed using a Scanning Electron microscope (SEM) JEOL: JSM-6390.

Dye degradation studies

The batch experiment was conducted using RED ME4BL, in the presence of the nanoparticle-immobilized membranes and compared with the unimmobilized nanoparticles. The dye solution was prepared at a concentration of 100mg/L. From this stock solution, 10 ml was transferred to 30ml air-tight bottles and treated with 1 piece of each of the membranes. At predetermined intervals of time (0, 30, 60, 90, 120 and 150 minutes), the supernatant of the dye solution was read in UV- visible Spectrophotometer at 520 nm. The experiments were performed in triplicate at room temperature.

Dye degradation kinetics

The kinetic removal rate of membrane-bound bimetallic nanoparticles was determined using the following equation (Meyer *et al.*, 2004),

$$-dC = kC^n/dt \quad (3)$$

where C is dye concentration at time t,

k is the rate constant (min^{-1})

n is the order of the reaction.

RESULTS AND DISCUSSION

SEM characterization of the membrane immobilized iron nanoparticles

The membranes were observed by SEM to identify the structural disparity between the support membrane and the composite membrane coated with bimetallic nanoparticles. As shown in Fig. 1a, the PVDF support membrane was found to have a pore size of 200nm with extreme porosity. The pore size was reduced after the PAA solution coating (Fig. 1b). After treatment with FeCl_3 , NaBH_4 and $[\text{Pd}(\text{C}_2\text{H}_3)_2]_3$, the membrane surface and pores were found to be covered with bimetallic (Fe^0/Pd) nanoparticles (Fig. 1c). The SEM image depicted well-dispersed bimetallic nanoparticles with an average particle size of 20 nm. SEM characterization of the polyurethane membrane showed that the immobilized nanoparticles exhibited a size range of 100 - 200 nm with a greater surface area (Fig. 2).

Dye degradation studies

The reactivity of the bare nanoparticles and the bimetallic nanoparticles in pore-modified PVDF/PAA membrane and PUF membrane were evaluated for the decolorization of RED ME4BL, at different time intervals (0 minutes – 100 minutes). The unimmobilized nanoparticles showed a degradation of 50% in 80 minutes, following which the results plateaued. This could be attributed to the clumping of the nanoparticles, which reduced the number of active sites and caused a reduced catalytic activity. The high surface area and the

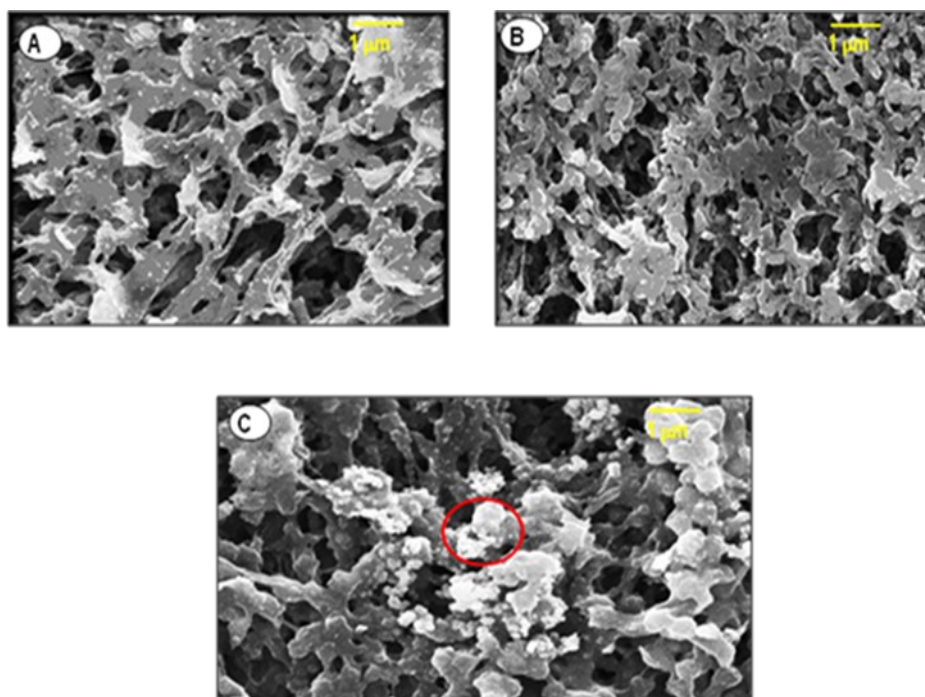


Fig. 1. SEM surface images of the unmodified PVDF support membrane (A), PAA functionalized PVDF membrane (B), bimetallic nanoparticle (Fe^0/Pd) immobilized in PVDF PAA membrane (C) (circled part show the presence of nanoparticles)

strong, attractive nanoparticle interaction result in their aggregation. The nanoparticle aggregation thus reduces the potential enhancement of mechanical properties in nanocomposites concerning interfacial area restriction (Esbati and Irani, 2018; Chen *et al.*, 2015). The PVDF/PAA membrane-supported nanoparticles were shown to remove the dye color in 60 minutes. After 1-hour, RED ME4BL of 100mg/L concentration was decolorized to 93%. However, the PUF-bound bimetallic nanoparticles demonstrated a maximum decolorization percentage of 95% at 30 minutes, after which the pattern linearized (Fig. 3).

Our results are in accordance with Sikhwivhilu and Moutloali (2015), who applied bimetallic Fe nanoparticles immobilized on an industrial PAA/PVDF filtration membrane for methyl orange dye (MO) degradation. They observed an increased MO degradation at pH 4 compared to pH 7, with more than 80% of the degradation happening within 120 min in acidic conditions. Their findings demonstrated the membrane's in-situ polymerisation, which was credited to the method's uniform metal distribution. The present results can also be corroborated by a recent study by Shin *et al.* (2022). They developed functionalized polyvinylidene fluoride membranes altered with chitosan-coated iron oxide nanomaterials (Fe-PVDF) for the remediation of dye-polluted water. The group applied the Fe-PVDF membrane to remove a number of anionic dyes, including Acid Yellow 25, Congo red, Acid Green 25, and methyl blue. Under acidic conditions, the decolorization of anionic dyes was accomplished more evidently in comparison to the neutral conditions. This phenomenon shows the electrostatic interaction mechanism for the removal of anionic dyes.

However, in the present study, the PUF bound bimetallic nanoparticles demonstrated a maximum decolorization percentage of 95% at 30 minutes, after which the pattern linearized (Fig. 3). The outcome showed that the polyurethane immobilized iron nanoparticles were much better for RED ME4BL degradation. Similarly, Inderyas *et al.* (2020) showed that metal oxide immobilized on a polyurethane foam showed promising degradation efficiency against Acid black 1. The study also demonstrated that polyurethane immobilized nanoparticles could possibly be used to treat wastewater and dye effluents. In comparison with other results, the present results assert that polyurethane foam, with its exceptional chemical resistance, porous nature, and stability, is a robust carrier for immobilization (Atmianlu *et al.*, 2021).

Polyurethane foam's high surface area to volume ratio is the key feature that makes it an outstanding matrix for immobilizing iron nanoparticles. Since polyurethane foam has a large surface area, it provides plenty of room for iron nanoparticles to settle and become immobilized. These particles are then used as a catalyst to

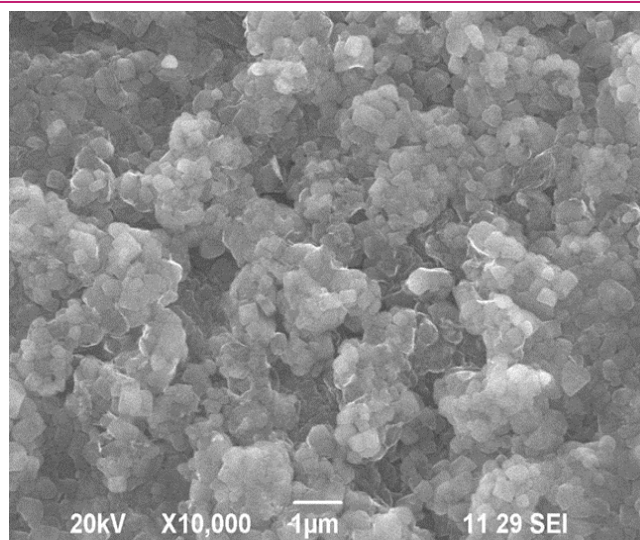


Fig. 2. SEM surface image of the bimetallic nanoparticle (Fe^0/Pd) immobilized in polyurethane membrane

degrade the dyes in wastewater. Furthermore, the porosity of polyurethane foam makes it easier for reactants and products to diffuse, assuring effective catalytic activity (Satria and Saleh, 2022). On the other hand, while PVDF membranes are traditionally used for nanoparticle immobilization, they suffer a few shortcomings compared to the polyurethane membrane. Limited chemical compatibility, mechanical strength, and insubstantial pore size range could be the reasons attributed to the poor performance of the PVDF membrane. Additionally, application of PVDF immobilization of iron nanoparticles for dye remediation can be hampered in the presence of aggressive chemicals, high pressure, or mechanical stress (Alyarnezhad *et al.*, 2020).

The use of readily available polyurethane membrane for iron nanoparticle immobilization and their application for dye degradation has been less documented. The present work also demonstrates that polyurethane immobilized nanoparticles were better suited for azo dye degradation (Krishnan *et al.*, 2021). Therefore, further investigations are required to study the effectiveness and adaptability of this method.

Degradation kinetics

Kinetic study revealed that dye decolorization followed pseudo-first-order kinetics for both the PVDF/PAA membrane and PUF membrane (Fig. 4). The degradation kinetics for dye removal depends on the type of dye, the characteristics of the membrane, and the properties of the iron nanoparticles used. The obtained results were in correlation with the finding of Satapanajaru *et al.* (2011), who reported that the decolourization of RB5 and RR198 using nZVI was following pseudo-first order reaction. The results clearly indicated that the reactivity of membrane-immobilised nanoparticles was higher than that of bare nanoparticles.

Jadaa *et al.* (2021) studied the degradation kinetics of a

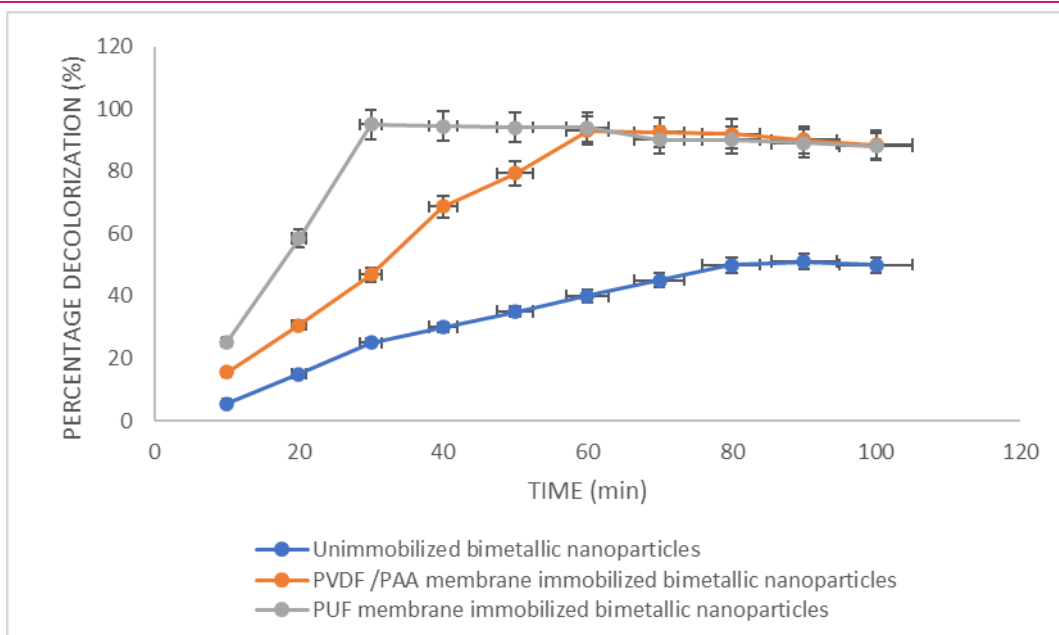


Fig. 3. Degradation percentage of RED ME4BL by the un-immobilized nanoparticles, PVDF/PAA immobilized bimetallic nanoparticles and PUF immobilized bimetallic nanoparticles. The values are expressed as Mean \pm SEM ($P < 0.05$)

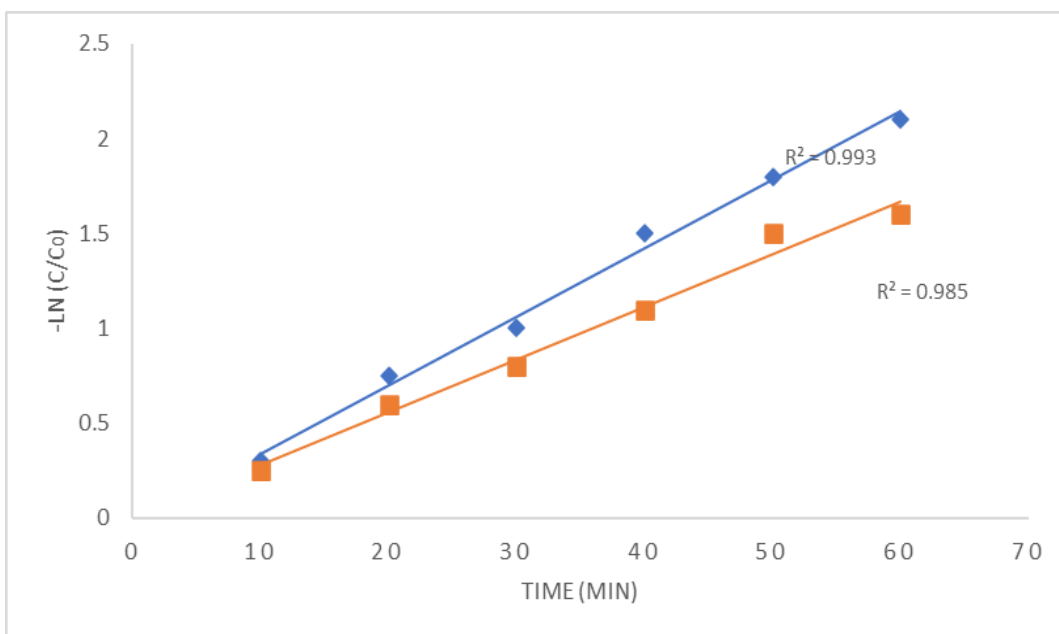


Fig. 4. Pseudo second order rate constants for RED ME4BL degradation by (a) PUF immobilized bimetallic nanoparticles and (b) PVDF/PAA immobilized bimetallic nanoparticles

diazo dye (Direct Blue 15) over immobilized TiO_2 catalyst and found it to follow a pseudo-first-order mechanism. The present results can also be comparable to Alkaykh *et al.* (2020), wherein $MnTiO_3$ nanoparticles were used for the photocatalytic degradation of methylene blue dye.

The present finding is supported by the result of Cho and Choi (2010), who reported a faster transformation of TCE by membrane-supported nanoparticles. Zero valent iron nanoparticles are known to degrade a broad range of contaminants (Mukherjee *et al.*, 2016; He *et al.*, 2020), but the agglomeration restricts the availabil-

ity of surface area on the nanoparticle and hence accessible active site for contaminant degradation is reduced (Khan *et al.*, 2019; Mohtar *et al.*, 2021). The increase in the rate of the reaction of immobilized bimetallic nanoparticles may be due to the less agglomeration of nanoparticle in the membrane phase than in the solution phase which in turn lead to the exposure of more active sites (Chekli *et al.*, 2014; Abbas *et al.*, 2020).

The rate of surfactant-modified zeolite/nZVI for perchloroethylene reduction was higher than that of nZVI, according to the report of Zhang *et al.* (2002). TCE re-

removal was high in the case of the membrane-supported bimetallic nanoparticle (Wu and Ritchie, 2006; Xu and Bhattacharyya, 2005). Many other reports also prove that membrane immobilization is a good technique for enhancing the activity of nanoparticles (Sikhwivhilu and Moutloali, 2015; Li *et al.*, 2021; Dube *et al.*, 2020). Therefore, the membrane immobilized bimetallic nanoparticle is expected to be successful for a broad range of pollutants and contaminants.

Conclusion

Zero valent iron nanoparticles for textile effluent remediation are receiving huge attention in the recent times. Preferential adsorption or mineralization occurs using nanoscale iron particles in textile dye remediation. The present study degraded a recalcitrant azo dye, RED ME4BL, using bimetallic zerovalent iron nanoparticles. The nanoparticles were further immobilized on two different matrices to prevent them from self-agglomeration and their dye degradation activity was monitored. The PUF immobilized iron nanoparticles demonstrated a maximum dye degradation of 95% in the shortest time interval compared to the PVDF/PAA membrane. Further membrane properties and reaction kinetics analysis are essential for scaling the bench scale results to a real-time scenario.

Conflict of interest

The authors declare that they have no conflict of interest.

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