TREATMENT OF TEXTILE WASTEWATER BY SULFATE RADICAL BASED ADVANCED OXIDATION PROCESSES (SR-AOPS)

Rajeev Kumar[1], Subhalaxmi Sahoo[2], Prateeksha Mahamallik[1, *]

[1]Department of Civil Engineering, National Institute of Technology, Rourkela, Odisha, India 769008

[2]Department of Civil Engineering, National Institute of Technology, Rourkela, Odisha, India 769008

Corresponding author's E-mail address: mahamallikp@nitrkl.ac.in

ABSTRACT

In wastewater from the textile industry, there are many substances like the ones found in dyes, metals, and organics that are very harmful and the conventional treatment methods that are being used in the industry, cannot get rid of them. But it's different with the advanced oxidation processes (AOPs), particularly sulfate radical-based (SR-AOPs), they are very good at removing these hazardous pollutants. This article focuses on the study of Fe/Mn-biochar as a catalyst in persulfate (PS) for the treatment of textile effluent. Its porous structure, large surface area, and redox activity play a crucial role in the promotion of radical production and the abasement of the pollutant. Using XRD and FTIR, they announced the results showed that this element was workable. The Fe/Mn-biochar effectively decomposed Rhodamine B by applying a second-order kinetic model. It could be used more than one time and still work fine for three cycles, but on the third cycle, the efficiency will decrease and it can be regenerated. In brief, Fe/Mn-biochar is a new, eco-friendly, and relatively cheap option for industrial wastewater treatment using SR-AOPs which could be the new possible solution for future large cuts in industrial water pollution**.**

Key words: Adsorption, degradation, PMS, FeMn/Biochar.

1. INTRODUCTION

Textile wastewater containing persistent Rhodamine B (RhB) resists conventional treatment. Sulfate radical-based AOPs (SR-AOPs) using activated persulfate/peroxymonosulfate generate potent $SO_4^{\bullet-}$ radicals for effective RhB degradation and the typical treatment methods are not enough for full removal (Li et al., 2020). Advanced oxidation processes (AOPs) have been proven to be an efficient way of treating wastewater degrading the recalcitrant pollutants. They involve sulfate ($SO_4^{\bullet-}$) radicals that oxidize recalcitrant pollutants. These radicals have higher oxidation potential and are more effective at degrading recalcitrant organics than hydroxyl radicals (•OH) have (Wang et al., 2022). Fe/Mn-biochar is a catalyst made from biochar (BC) which is modified by the iron (Fe) and manganese (Mn). Fe/Mn-biochar can be used as a catalyst to enhance persulfate activation, and help in the degradation of pollutants. Fe/Mn-biochar is a promising catalyst because of its high surface area, porosity and redox-active sites which can produce radicals and adsorb pollutants for effective degradation, also it is an eco-friendly technology (Zhang et al., 2021). A number of research papers have reported that the doping of the Fe/Mn-biochar catalyst is an effective strategy for degrading dyes and organic pollutants. This implies its great potential usefulness in a large scale.

2. MATERIALS AND METHODS

2.1. Chemicals and Instrumentation

Ferric chloride hexahydrate and manganese chloride tetrahydrate were purchased from Oxford. Biochar prepared from wood is used for preparing the composite catalyst. Muffle furnace was used to calcinate the material. Absorbance was measured using a UV-vis spectrophotometer with a 1cm cuvette. A magnetic stirrer with a hot plate was used to mix the sample, and a hot air oven was used to dry the material. A centrifuge was used to separate solids from liquids by centrifugation.

2.2. Preparation of modified Fe/MnBC

The Fe/MnBC were prepared as follows:1g of Biochar was dissolved in 50ml deionized water and then the add 0.0407 g of $FeCl_3$ and 0.1977g of $MnCl_2.4H_2O$. After that the crucible was covered properly with foil paper, and then it was put into the muffle furnace at 600°C for 30 mins. After cooling they were put into hot air over at 80°C for 30 minutes.

2.3. Experimental procedures for RhB Degradation

Degradation experiments were conducted in 100 mL flasks with 30 mL RhB solution, PMS, and Fe/MnBC. The solution was kept in the dark for 1 hour for adsorption equilibration, then stirred for degradation. Samples were taken at intervals, centrifuged at 25°C, 4000 rpm for 5

min, and the liquid was analysed for absorbance to determine RhB concentration using the calibration curve.

2.4. Analysis of RhB

RhB concentration was measured using a spectrophotometer. Standard solutions (0-20 mg/L) were prepared by diluting a 100 mg/L stock solution. Absorbance was measured at λ_{max}=551 nm. A calibration curve was created with the equation: Concentration (mg/L) = 0.156 + 0.148x, and a correlation coefficient (R^2) of 0.9834. This equation was used to calculate unknown RhB concentrations from their absorbance values.

3. RESULTS AND DISCUSSION

3.1. Characterization of Fe/Mn Biochar

3.1.1. X-Ray Diffraction (XRD)

XRD analysis showed a broad amorphous peak at 2θ = 24.2° (crystalline carbon fibres) and a strong peak at 29.5°, with weaker peaks at 36.1°, 39.4°, 43.3°, 47.6°, and 49.5°, indicating Ca, K, and Mg. After Fe-Mn loading, a new peak at 35.5° (α-Fe_2Os_3) appeared, while MnO_2 peaks were absent, suggesting an amorphous FeMn/BC phase.

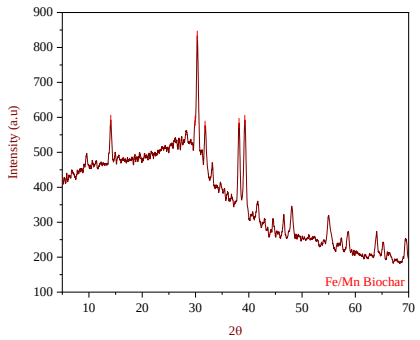

Figure 1: XRD analysis graph of Fe/MnBC.

3.1.2. Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectrum of Fe/Mn biochar shows multiple functional groups. The peak at 2981 cm^{-1} indicates C-H stretching, suggesting aliphatic hydrocarbons (Socrates et al., 2004). The 1754 cm^{-1} peak corresponds to C=O stretching, representing carbonyl groups like ketones, aldehydes, or esters, which are crucial for adsorption and reactivity (Pavia et al., 2015). A peak at 1567 cm^{-1} signifies C=C stretching, confirming aromatic rings or conjugated systems typical of biochar (Nakamoto et al., 2009). The broad band at 877.04 cm^{-1} results from aromatic C-H bending, further validating the biochar's aromatic structure (Stuart et al., 2004).

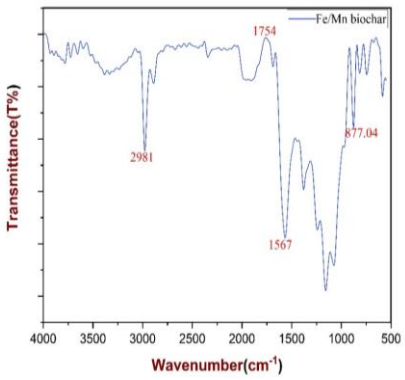

Figure 2: FTIR analysis graph of Fe/Mn Biochar.

4. EFFECT OF OPERATIONAL PARAMETERS ON RHB DEGRADATION USING PMS

4.1. Effect of RhB Concentration Variation

RhB removal can be observed at different concentrations (5–25 mg/L) in Fig. 3(a) with time. At 5 mg/L, removal reaches its climax of 70% in 10 min, and then it is stabilized. 10 mg/L, it reaches ~40% by 60 min, while 15 mg/L and 25 mg/L reach 35% and 30%, respectively. The decrease in adsorption efficiency at higher concentrations is because of the capacity limitation, which makes material more effective at low concentration pollution (Gupta et al., 2010). From Fig. (b), it can be verified that RhB removal increases over time with 99.01% efficiency at 5 mg/L due to fast initial adsorption. Lower effectiveness at higher concentrations might be associated with saturation. The first 10 min see the fastest removal; thus, it can be said that the strong initial adsorption/degradation is largely determining upon whether the treatment is effective for wastewater.

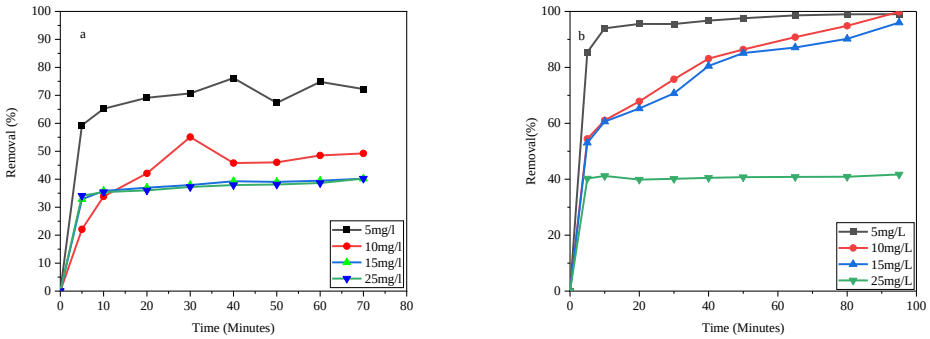

Figure 3: (a) Adsorption for RhB concentration variation: PMS = 0.009g, FeMn/BC = 0.015g. (b) RhB degradation with different materials (initial conc.=10 mg/L; catalyst dose =1 g/L; PMS = 0.5 mmol).

4.2. Effect of Dose (Fe/Mn Biochar) Variation

Figure 4(a) shows pollutant removal using FeMn/BC at dosages of 0.2, 0.5, 0.8, and 1.2 g/L. Higher dosages improve removal efficiency, with 1.2 g/L reaching ~80%, 0.8 g/L ~60%, 0.5 g/L ~50%, and 0.2 g/L ~40%. Figure (b) confirms that increasing FeMn/BC dosage enhances dye removal. At 0.2 g/L, removal reaches ~60% in 90 minutes, while 0.5 g/L and 0.8 g/L achieve 85–95%, with 0.8 g/L slightly better. The highest dosage, 1.2 g/L, achieves ~100% removal within 30 minutes. Higher dosages improve degradation efficiency, with diminishing returns beyond 0.8 g/L.

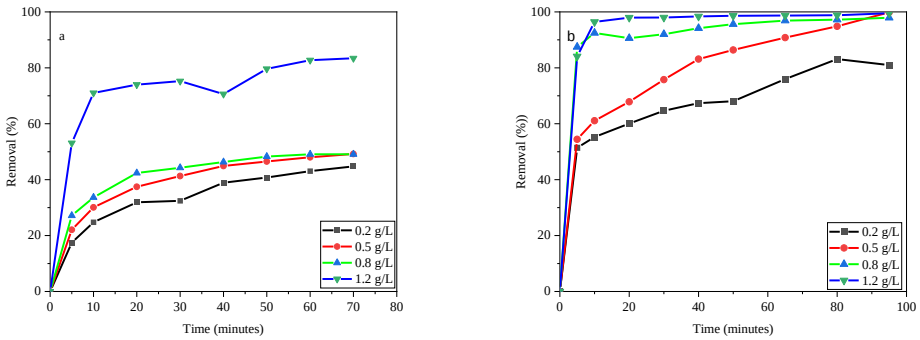

Figure 4: (a) Adsorption for Fe/MnBC dose variation (RhB = 3 mL, D.W = 27 mL, PMS = 0.0092 g). (b) Degradation with Fe/MnBC dose variation (RhB = 10 mg/L, catalyst = 1 g/L, PMS = 0.5 mmol).

4.3. Temperature variation

Dye removal efficiency using FeMn/biochar increases with temperature, reaching ~80% at 45°C vs. ~60% at 35°C in 90 min. The reaction follows second-order kinetics (k = 0.0572 min^{-1}) with an activation energy (E_a) of 34.76 kJ/mol, indicating moderate temperature dependency. Higher temperatures enhance reaction kinetics, diffusion, and catalytic efficiency. Operating above 35°C is recommended for optimal performance.

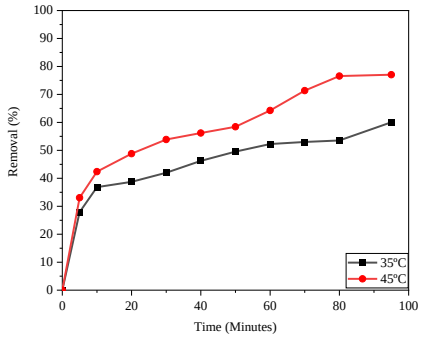

Figure 5**:** Effect of Temperature on Dye Removal Efficiency Using FeMn/Biochar Catalyst.

4.4. pH Variation

The graph shows Fe/Mn biochar performance under different pH conditions. At pH 7, removal reaches ~95-100% by 180 min, indicating effective adsorption and degradation. At pH 3,

removal rises quickly to ~70% in 80 min but then declines, suggesting instability. At pH 11.43, removal is slower, reaching only ~50% by 180 min, likely due to reduced reactivity. Neutral pH is optimal, while acidic and basic conditions lower efficiency.

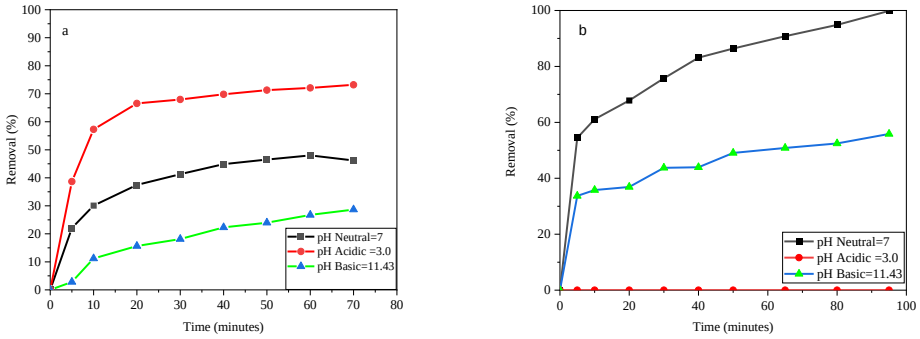

Figure 6: PH variation for (a)Adsorption and (b)degradation Graph for Fe/MnBC (0.015g), PMS (0.009g), D.W (27ml), RhB (3ml).

4.5. Degradation kinetics

Second-order degradation kinetics was analysed using sample data, yielding a linear plot with equation $y = 0.0572x + 0.7303$ and $R^2 = 0.945$, indicating a strong fit. The rate constant $k = 0.0572$ confirms a second-order reaction, with an increasing slope over time, showing concentration-dependent degradation.

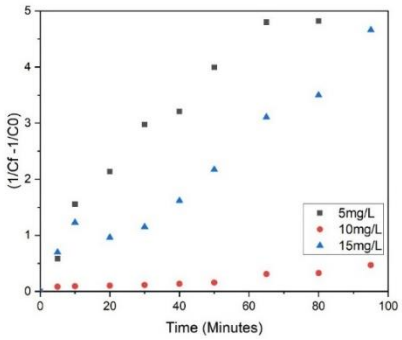

Figure 7: Linear second order Kinetics graph (Initial concentration: 10mg/L).

4.6. Quenching with Radical scavengers

Quenching studies with STS and EtOH identify dominant reactive species in FeMn/Biochar-catalysed dye degradation. STS inhibits $SO_4^{\bullet-}$, confirming sulfate radicals as primary oxidizers, while EtOH (quenching $SO_4^{\bullet-}$ & $\bullet OH$) has a lesser effect, indicating a minimal hydroxyl radical role. The catalyst effectively activates persulfate for SR-AOPs, proving its potential for efficient wastewater treatment.

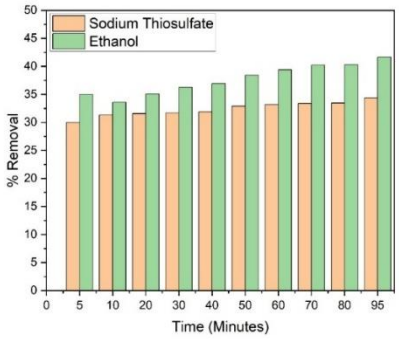

Figure 8: Effect of various radical scavengers' effect on removal of RhB (sodium thiosulfate=0.0047g, RhB=3ml, D. W=27ml).

4.7. Recyclability of Modified Fe/Mn Biochar

The FeMn/biochar catalyst remains effective for three cycles of dye degradation. First cycle: ~95-100% removal. Second cycle: drops to ~65-70%. Third cycle: further declines to ~30-35%, indicating significant activity loss. While reusable, effectiveness decreases with each cycle, requiring regeneration or replacement after the second cycle for optimal performance.

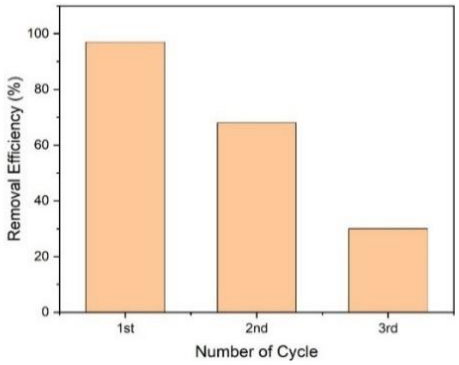

Figure 9: Recyclability of FeMn/Biochar (RhB=3ml, D. W=27, FeMn/BC=0.015, PMS=0.009g).

5. CONCLUSION

Results showed efficient RhB and pollutant degradation via PMS-activated sulfate radicals ($SO_4^{\bullet-}$). Characterization (XRD, FTIR) confirmed high surface area, porosity, and redox-active sites for effective radical production. Catalyst dosage, dye concentration, pH, and temperature influenced degradation, with neutral pH and higher temperatures enhancing performance. Quenching tests confirmed sulfate radicals as primary oxidizers. Recyclable for three cycles, but efficiency declined. Fe/Mn-biochar is a sustainable, efficient catalyst, with potential for large-scale use, regeneration strategies, and industrial optimization in eco-friendly wastewater treatment.

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