



# Visible-light assisted photo-Fenton degradation of textile dye effluents using NiFe<sub>2</sub>O<sub>4</sub>/biochar nanocomposite

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## ABSTRACT

The rapid growth in industrialization increases the water pollution and impacts ecosystem and human health. The increasing dye pollutants discharged from textile industrial wastewater consistently accumulated in large amount in fresh water bodies. In recent years, biochar based nanocomposites have been utilized as eco-friendly materials for remediation of dye pollutants. In the present work, biochar derived from wood residues of sawmill (WRB) was utilized as support for the fabrication of NiFe<sub>2</sub>O<sub>4</sub>/WRB nanocomposites and investigated for photo-Fenton degradation of textile dye effluents, methylene blue (MB) and Acid Red 27 (AR27). Different wt% of WRB (25%, 50% & 75%) loaded over NiFe<sub>2</sub>O<sub>4</sub> to prepare NiFe<sub>2</sub>O<sub>4</sub>/WRB nanocomposites that shows higher degradation efficiency than pure NiFe<sub>2</sub>O<sub>4</sub>. These magnetic nanocomposites (NiFe<sub>2</sub>O<sub>4</sub>/WRB) were synthesized via hydrothermal method and characterized by comprehensive analytical techniques to study the structural, morphological and optical properties. X-ray diffraction (XRD) analysis revealed the average crystallite size of 7.35 nm while Brunauer-Emmett-Teller (BET) studies confirmed a mesoporous surface with high specific surface area of 187.63 m<sup>2</sup>/g, 0.25 cm<sup>3</sup>/g pore volume, and 3.85 nm average pore diameter for NiFe<sub>2</sub>O<sub>4</sub>/WRB3. FE-SEM analysis revealed high degree of particle agglomeration, while EDX analysis confirmed the presence of Ni, Fe, and O atoms, further confirming the absence of impurity elements. FT-IR spectra examined the presence of surface functional groups and chemical interactions between NiFe<sub>2</sub>O<sub>4</sub> and WRB while Raman spectrum shows the phase purity. UV-vis spectroscopy revealed the increase in band gap with increasing wt% ratio of WRB from 1.68 eV for pure NiFe<sub>2</sub>O<sub>4</sub> to 1.94 eV for NiFe<sub>2</sub>O<sub>4</sub>/WRB3 nanocomposite. The magnetic properties of pure NiFe<sub>2</sub>O<sub>4</sub> and optimized NiFe<sub>2</sub>O<sub>4</sub>/WRB3 were investigated by Vibrating Sample Magnetometry (VSM) at room temperature confirms the magnetic nature of composite by the obtained (M-H) hysteresis loop. Under the optimized conditions, the photo-Fenton reaction against MB, AR27 and real industrial effluent (RIE) using NiFe<sub>2</sub>O<sub>4</sub>/WRB3 revealed 95% for 5 ppm MB and 91.43% for 10 ppm AR27 degradation on exposure to visible irradiation within 90 min, while 64.52% of RIE and 87.6% of mixed dyes degraded in 90 min. Various operational parameters such as catalyst loading, pH of the dye solution, initial amount of H<sub>2</sub>O<sub>2</sub> critically influenced the photo-Fenton degradation process. All degradation reactions followed first-order kinetics (R<sup>2</sup> > 0.95), and the NiFe<sub>2</sub>O<sub>4</sub>/WRB3 demonstrated excellent stability over five cycles by maintaining >80% degradation efficiency in the fifth cycle. Radical scavenging experiments further revealed that •OH radicals and electrons were primary reactive species responsible for the photo-Fenton degradation process.

## 1. Introduction

The global industrial expansion and urbanisation over past few decades have significantly released hazardous pollutants in environment and widely disrupts the ecosystem [1,2]. Wastewater from textile industries have widely contributed in polluting water bodies by discharging untreated wastewater comprising persistent organic pollutants such as synthetic dyes [3]. Synthetic dyes extensively used in textile

industries have emerged as significant environmental contaminants due to their complex chemical structure, high stability, and resistance to biodegradation [4]. During textile dyeing and finishing operations, a considerable proportion of applied dyes remains unfixed to fibres and is discharged as industrial effluent into surrounding water bodies [5]. These dye-containing wastewaters impart intense coloration even at low concentrations, thereby reducing the light penetration and restricted the photosynthetic activity in aquatic ecosystems. Many synthetic dyes,

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particularly azo and reactive dyes, generate toxic, mutagenic, and carcinogenic degradation products that pose serious risks to aquatic organisms as well as human health through contaminated water resources [6,7]. The improper management of discharging untreated textile effluents was resulted from insufficient wastewater treatment infrastructure, high operational costs, and ineffective regulatory enforcement, especially in rapidly industrializing regions [8–10]. Consequently, dye pollution contributes to water quality deterioration, ecological imbalance, and long-term environmental persistence, highlighting the urgent need for efficient treatment technologies and sustainable dye management practices in textile industries [11].

In recent years, advanced oxidation processes (AOPs) are widely recognized as most efficient strategy for wastewater treatment [12,13]. AOPs such as ozonation, Fenton and Photo-Fenton are highly effective in degradation of complex organic contaminants. Among which, Photo-Fenton process holds a promising approach due to its simplicity, high performance and minimal generation of secondary pollutants on operating at even lower concentration of the catalyst, which resulted in reprocessing the treated water economically [14,15]. The efficiency of the photo-Fenton approach in degrading the dye pollutants widely depends upon the employed photocatalyst. In recent times, the iron oxide-based photocatalyst gains considerable attention due to higher surface area and magnetic recoverability [16]. Among which magnetic nanoparticles such as spinel ferrites shows interesting structural, optical and magnetic properties owing to the distinct crystallite structure with interstitial tetrahedral and octahedral sites [17]. These crystallographic sites significantly governs the structural configuration, magnetic and catalytic properties of spinel ferrite [18]. Nickel ferrite ( $\text{NiFe}_2\text{O}_4$ ) has been featured as magnetic material with excellent chemical stability, wide range pH applicability and intrinsic ferromagnetic properties. However, the relatively narrow bandgap led to the rapid recombination of photogenerated  $e^-/h^+$  pairs and thereby limiting the generation of ROS essential of degradation of pollutants. Furthermore, the lower specific surface area and strong dipole interactions tends to nanoparticles (NPs) aggregation and reduces the active sites. To overcome these limitations, the incorporation of biochar to support  $\text{NiFe}_2\text{O}_4$  emerged as an effective photo-fenton catalyst for degradation of dye pollutants. Biochar-supported photocatalyst outstand as an eco-friendly and low cost abundant material for the wastewater treatment owing to its porous structure, high specific surface area and surface reactivity [19]. Kaveh et al. fabricated a ternary nanocomposite of  $\text{NiFe}_2\text{O}_4/\text{Ag}_3\text{PO}_4/\text{Biochar}$  in the ratio (20:10:70) using hydrothermal method, exhibited a degradation rate constant  $0.028 \text{ min}^{-1}$  for the photocatalytic degradation of 10 ppm MB dye up to 94% using 2.6 g/L of catalyst at pH 7 within 90 min exposure to visible light irradiation [20]. Saleh et al. synthesized  $\text{NiFe}_2\text{O}_4/\text{AC}$  nanocomposite using hydrothermal method by employing activated carbon (AC) derived from willow catkins by chemical activation method and loaded on  $\text{NiFe}_2\text{O}_4$ . The optimized 45 wt%  $\text{NiFe}_2\text{O}_4/\text{AC}$  (45NFAC) employed for the photocatalytic degradation of RhB dye, achieved 99.7% degradation within 90 min of simulated sunlight while retained more than 90% efficiency even after five cycles [21]. Biochar derived from coconut husk was utilized to prepare magnetic  $\text{NiFe}_2\text{O}_4/\text{biochar}$  nanocomposite using one-step pyrolysis method, demonstrated the rate constant of  $0.016 \text{ min}^{-1}$  for the degradation of RhB dye. The photo-Fenton approach achieved 99.9% degradation of 4 ppm RhB dye by employing 2.0 g/L  $\text{NiFe}_2\text{O}_4/\text{biochar}$  at pH 3 within 30 min under UV irradiation [22]. The comparative analysis of  $\text{NiFe}_2\text{O}_4/\text{Biochar}$  photocatalyst reported in literature for dye removal was evaluated against the current study has been summarized in Table 8. The photocatalytic performance of synthesized catalyst was assessed by various factors such as catalyst loading, pH conditions, initial dye concentration, amount of  $\text{H}_2\text{O}_2$  and irradiation time in photo-Fenton process.  $\text{NiFe}_2\text{O}_4/\text{biochar}$  nanocomposites reported in literature have also shown higher removal of dye pollutants compared to pure  $\text{NiFe}_2\text{O}_4$ . Moreover, these composites investigated for the adsorption study of textile dye pollutants by employing higher adsorbent dosage and contact

time as compared to the present work.

In the present work, wood waste (residue) from sawdust mill was sourced for the preparation of high-value biochar (WRB) for the synthesis of  $\text{NiFe}_2\text{O}_4/\text{WRB}$  nanocomposites using hydrothermal method. Different wt% (25%, 50% and 75%) of WRB was utilized to support  $\text{NiFe}_2\text{O}_4$  NPs and their structural, optical and photocatalytic properties have been studied. The photo-Fenton degradation studies of MB, AR27 and mix dyes carried out under visible irradiation. To the best of author's knowledge, the detailed studies on  $\text{NiFe}_2\text{O}_4/\text{WRB}$  nanocomposites synthesized by utilizing wood residue from sawdust mill and investigated as a photocatalyst for the degradation of dye effluents has not been reported yet. While previous work have investigated the  $\text{NiFe}_2\text{O}_4/\text{biochar}$  nanocomposites for other dyes and pharmaceutical effluents. Additionally the facile hydrothermal synthesis conducted as an efficient and low-cost strategy to prepare  $\text{NiFe}_2\text{O}_4/\text{WRB}$  nanocomposite that ensures the uniform dispersion and precise control over crystallinity and particle size. Further, the research study does not only focused on the degradation of model cationic (MB) and anionic (AR27) dye but also emphasized on the degradation of real industrial dye effluents and mixture of dyes using photo-Fenton approach. The hydrothermally synthesized  $\text{NiFe}_2\text{O}_4/\text{WRB3}$  also exhibit excellent specific surface area ( $S_{\text{BET}}$ ) resulted in enhancing its photocatalytic activity and stability over several photo-fenton cycles, while also demonstrated remarkable magnetic properties for easy regeneration of catalyst that signifies its great potential in wastewater treatment.

## 2. Experimental

### 2.1. Materials and methodology

For the synthesis purpose, all AR-grade chemicals and double distilled water were utilized to ensure experimental procedure reproducibility. The chemicals utilized include Nickel Nitrate Hexahydrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) (Loba Chemie Pvt. Ltd.) CAS number 13478-00-7. Iron Nitrate Nonahydrate Purified (Merck) CAS number 7782-61-8, Urea (Fischer Scientific). Saw dust residue was collected from sawmill located in MIDC, Chakan, Pune. For evaluation of photocatalytic activity, MB ( $\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$ ) CAS number 61-73-4 and AR27 ( $\text{C}_{16}\text{H}_8\text{N}_2\text{Na}_2\text{O}_8\text{S}_2$ ) CAS number 915-67-3 procured from Loba Chemie were used. Real Industrial effluent (RIE) was collected from textile industrial wastewater located in MIDC Chakan, Pune, Maharashtra, India. Different Scavengers were employed for investigation of quenching experiments including p-Benzoquinone ( $\text{C}_6\text{H}_4\text{O}_2$ ), Silver Nitrate ( $\text{AgNO}_3$ ), Potassium Iodide (KI), all procured from Merck, and Isopropanol ( $\text{C}_3\text{H}_8\text{O}$ ) were sourced from Qualigens.

### 2.2. Synthesis of wood residue biochar (WRB)

Biochar was produced by pyrolysis of waste residue collected from saw mill. Initially, the wood residue was rinsed and washed with double distilled water to remove surface impurities and then dried overnight at  $80^\circ\text{C}$  in hot air oven. Further, it was grinded to powder in a mixer-grinder and sieved with  $50 \mu\text{m}$ -mesh molecular sieves. Initially, the biomass was washed several times with double distilled water and dried at  $100^\circ\text{C}$  for 24 h. The residual wood pieces was chopped in smaller size and crushed and grinded in mixer-grinder to reduce to powder form. Further, it was sieved through  $50 \mu\text{m}$  molecular sieves. The obtained powder was pyrolysis at  $600^\circ\text{C}$  with heating rate of  $5^\circ\text{C}/\text{min}$  under  $\text{N}_2$  atmosphere for 2 h.

### 2.3. Synthesis of $\text{NiFe}_2\text{O}_4$

The  $\text{NiFe}_2\text{O}_4$  NPs were synthesized by the hydrothermal method. In the experimental procedure 25 mL of 0.4 M iron nitrate solution and 25 mL of 0.2 M nickel nitrate solution were mixed. Urea and HCl solutions were utilized to monitor and adjust the pH 11–12 under continuous

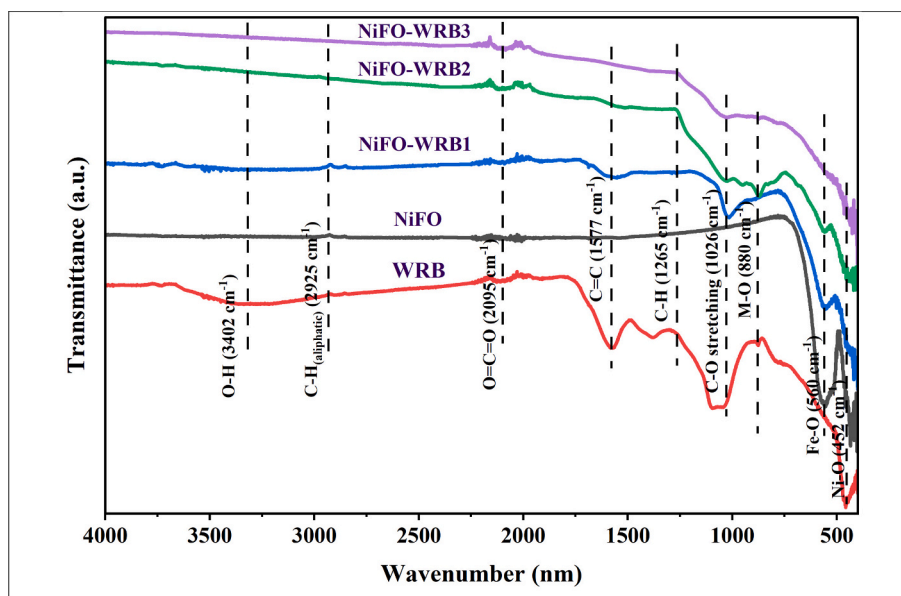


Fig. 1. FTIR Spectra of WRB,  $\text{NiFe}_2\text{O}_4$  and  $\text{NiFe}_2\text{O}_4/\text{WRB}$  nanocomposites.

temperature-controlled stirring and the solution was kept at 80 °C for 120 min and then naturally cool down to room temperature (25 °C). The precipitate obtained was washed several times with double distilled water and ethanol to eliminate any impurities and side products formed from chemical reaction. Lastly, the precipitate was dried and kept at 100 °C in vacuum oven and powdered with a mortar-pestle to separate the agglomerated nanoparticles.

#### 2.4. Synthesis of $\text{NiFe}_2\text{O}_4/\text{WRB}$

The hydrothermal method has been employed for the synthesis of  $\text{NiFe}_2\text{O}_4$  and  $\text{NiFe}_2\text{O}_4/\text{WRB}$  nanocomposites. Initially, 30 mL of 0.2 M nickel nitrate solution and 30 mL of 0.4 M iron nitrate solution were dissolved and ultra-sonicated for 15 min. Meanwhile, certain amount of WRB i.e. 25 wt%, 50 wt% and 75 wt% has been added and ultrasonically dispersed in the above solution and labelled as  $\text{NiFe}_2\text{O}_4/\text{WRB1}$ ,  $\text{NiFe}_2\text{O}_4/\text{WRB2}$ ,  $\text{NiFe}_2\text{O}_4/\text{WRB3}$  respectively. The solution pH was adjusted to 11 using urea solution and then the mixture was transferred to a Teflon-lined stainless steel autoclave. Further, the autoclave was kept in hot air oven at a temperature of 160 °C for 12 h. After cooling down to room temperature, the obtained precipitate was filtered and washed three times with distilled water and ethanol and then kept in vacuum oven for drying at 80 °C for 12 h. The obtained powder was further activated in tubular furnace at 600 °C for 2 h. After natural cooling down to room temperature, the powder was filtered and washed several times with distilled water and ethanol and dried in vacuum oven at 80 °C for 12 h.

#### 2.5. Characterization

X-ray diffraction (XRD) analysis was conducted to identify the crystalline structure and phase formation of  $\text{NiFe}_2\text{O}_4$  and  $\text{NiFe}_2\text{O}_4/\text{WRB}$  nanocomposites using an X'PERT-Pro MPD (PANalytical Co.) with  $\text{Cu-K}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). Functional groups and formation of bonds on surface of nanocomposites were examined using Fourier transform infrared (FT-IR) spectroscopy (Shimadzu IR Affinity-1). UV-Vis absorption analysed using a Shimadzu UV-3600 spectrophotometer. Surface morphology and particle size of  $\text{NiFe}_2\text{O}_4$  and  $\text{NiFe}_2\text{O}_4/\text{WRB}$  nanocomposites were measured using field-emission scanning electron microscopy (FE-SEM, Nova NanoSEM) and high-resolution transmission electron microscopy (HR-TEM, JEOL JEM 2100F). Magnetic properties

of  $\text{NiFe}_2\text{O}_4$  and  $\text{NiFe}_2\text{O}_4/\text{WRB3}$  was examined using Vibrating Sample Magnetometer (VSM), MicroSense ADE- EV9 at room temperature within a magnetic field range of  $-20 \text{ kOe}$  to  $+20 \text{ kOe}$ . X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe III) was used to determine chemical state of elements and their corresponding binding energies. Specific surface area ( $S_{\text{BET}}$ ), pore radius and volume were calculated using Brunauer- Emmett-Teller (BET) method and Barrett-Joyner- Helenda (BJH) method on Quantachrome Nova 2200.

#### 2.6. Photocatalytic studies

The photo-Fenton degradation of MB and AR27 dyes and Industrial effluents were performed by employing synthesized  $\text{NiFe}_2\text{O}_4/\text{WRB3}$  as photocatalyst in a photochemical reactor. Different concentration (5, 10 and 15 mg/L) dye solutions of MB and AR27 were prepared. The catalyst dosage of 0.05, 0.1 and 0.15 g/L of  $\text{NiFe}_2\text{O}_4/\text{WRB3}$  nanocomposites were taken while 5, 10 and 15 mM amount of  $\text{H}_2\text{O}_2$  were added to 100 mL MB dye and 100 mL AR27 dye solutions while RIE was used directly without any treatment, in different pH condition i.e. pH 4, pH 7 and pH 9. The reactor setup consists of 250 W visible light source with broad spectral range of 400 nm–800 nm. The visible light source was positioned at a fixed distance from the reaction suspension in quartz container for all experiments. The intensity of visible light irradiation was measured using digital lux meter and found to be 104,000 lx approximately. Initially the reaction mixture was magnetically stirred for 30 min in the dark without exposure to visible light irradiation to attain the adsorption-desorption equilibria and also to facilitate homogenous dispersion of catalyst in the reaction media. The certain amount (5 mL) of reaction mixture was withdrawn at an interval of 15 min and centrifuged to remove the catalyst, while the change in absorbance value was recorded on spectrophotometer (Equiptronics EQ-826). The %degradation efficiency was calculated using equation 1:

$$\% \text{degradation} = \frac{A_0 - A_t}{A_0} \times 100 \quad (1)$$

Where  $A_0$  is the initial absorbance at  $t = 0$  (before exposed to visible light) while  $A_t$  corresponds to absorbance at reaction time 't'.

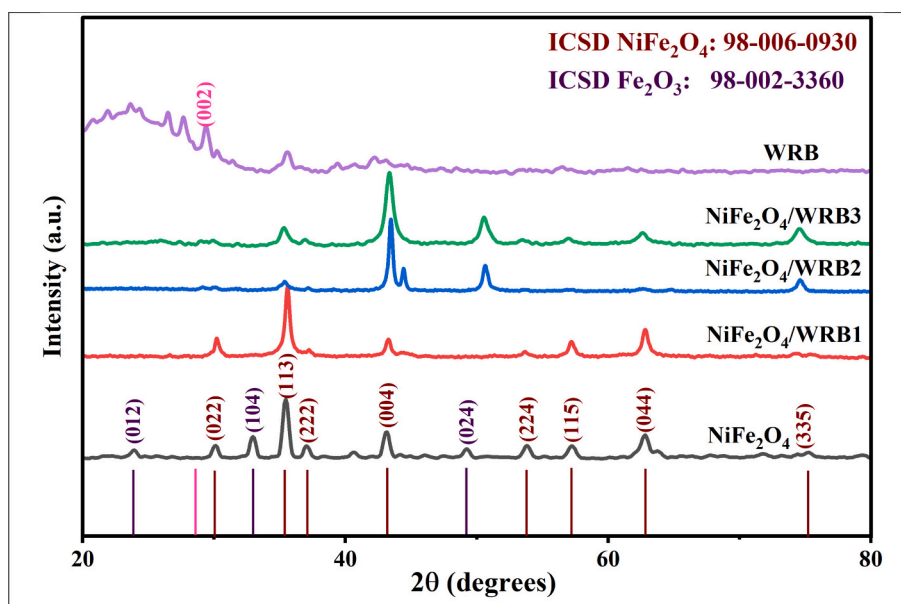


Fig. 2. XRD patterns of synthesized  $\text{NiFe}_2\text{O}_4$ , WRB and  $\text{NiFe}_2\text{O}_4/\text{WRB}$  nanocomposites.

### 3. Results and discussions

#### 3.1. Characterization

##### 3.1.1. FTIR

FT-IR spectrometric analysis was performed in the range of  $400\text{--}4000\text{ cm}^{-1}$  to determine various functional groups present on the surface of  $\text{NiFe}_2\text{O}_4$  and  $\text{NiFe}_2\text{O}_4/\text{WRB}$  nanocomposites, as shown in Fig. 1. The appearance of sharp band in FTIR spectrum at  $452\text{ cm}^{-1}$  and  $560\text{ cm}^{-1}$  correspond to the Ni—O and Fe—O vibrations whereas the band at  $880\text{ cm}^{-1}$  also associated to M—O bond present in  $\text{NiFe}_2\text{O}_4$  and  $\text{NiFe}_2\text{O}_4/\text{WRB}$  nanocomposites [20,23]. The adsorption band observed at  $1026\text{ cm}^{-1}$  and  $1265\text{ cm}^{-1}$  and  $1577\text{ cm}^{-1}$  attributed to C—O stretching vibration, C—H bending and C=C vibrations respectively corresponding to the existence of aromatic lignin in biochar (WRB) while also facilitate the adsorption of dye molecules through  $\pi\text{--}\pi$  interactions [24]. The broad band at  $\sim 3402\text{ cm}^{-1}$  correspond to O—H bending vibration by the adsorbed  $\text{H}_2\text{O}$  in nanocomposite while also associated with hydroxyl group of WRB [25]. The presence of all characteristics peaks indicates the successful fabrication of  $\text{NiFe}_2\text{O}_4/\text{WRB}$  nanocomposites with surface functional groups that facilitate the adsorption as well as catalytic active sites for degradation of MB and AR27 dyes.

##### 3.1.2. XRD

Fig. 2 shows the XRD pattern of  $\text{NiFe}_2\text{O}_4/\text{WRB}$  nanocomposites synthesized using hydrothermal method. The observed reflections for the synthesized  $\text{NiFe}_2\text{O}_4/\text{WRB}$  correspond to the (0 2 2), (1 1 3), (0 0 4), (2 2 2), (0 0 4), (2 2 4), (1 1 5), (0 4 4) and (3 3 5) planes matched with the pattern of cubic spinel  $\text{NiFe}_2\text{O}_4$  (ICSD ref. # 98-006-0930) and affiliated to the space group Fd-3m with a space group number 227 [20,21]. Additionally, the observed pattern at (0 1 2), (1 0 4) and (0 2 4) planes was attributed to the minor secondary phase of hexagonal  $\text{Fe}_2\text{O}_3$  (ICSD ref. # 98-004-1058) present within the  $\text{NiFe}_2\text{O}_4$  [23,26,27]. This secondary phase of  $\text{Fe}_2\text{O}_3$  phase arises due to the incomplete diffusion of  $\text{Ni}^{2+}$  ions into the crystal lattice of Fe—O. However the presence of  $\text{Fe}_2\text{O}_3$  could be advantageous in harvesting visible-light as well as to regulate  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox cycle, but since its minor secondary phase was observed in pure  $\text{NiFe}_2\text{O}_4$  while negligible suggests that its contribution to the overall photo-Fenton activity is limited. The broad peak located at  $20^\circ\text{--}26^\circ$  associated to C (0 0 2) plane of graphitized carbon in WRB. The

Table 1

Structural parameters and band gap relation of  $\text{NiFe}_2\text{O}_4$  and  $\text{NiFe}_2\text{O}_4/\text{WRB3}$ .

| Catalyst                              | a (Å)  | c (Å)  | V (Å) <sup>3</sup> | D (nm) | Band gap (eV) |
|---------------------------------------|--------|--------|--------------------|--------|---------------|
| $\text{NiFe}_2\text{O}_4$             | 8.3370 | 8.3370 | 579.46             | 6.8953 | 1.62          |
| $\text{NiFe}_2\text{O}_4/\text{WRB3}$ | 8.3370 | 8.3370 | 579.46             | 7.3564 | 1.94          |

intensity of diffraction peaks observed in  $\text{NiFe}_2\text{O}_4/\text{WRB}$  samples was progressively declined with decrease in Ni and Fe concentration while the increasing carbon support in  $\text{NiFe}_2\text{O}_4/\text{WRB3}$  reflects the displacement of oxygen ions from cationic A-sites due to the increase in tetrahedral interstices and this shows successful incorporation as well as stoichiometric regulation of  $\text{NiFe}_2\text{O}_4$  and WRB. In addition, the XRD pattern of reused  $\text{NiFe}_2\text{O}_4/\text{WRB3}$  nanocomposite after photo-Fenton process is shown in Figure S1.

The average crystallite size 'D' was calculated using the Debye-Scherrer method as per equation 2:

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (2)$$

where 'k' represent Scherrer constant generally taken as 0.94 and  $\lambda$  is the wavelength of Cu- $\alpha$  radiation ( $\sim 0.154\text{ nm}$ ),  $\beta$  is full width of peak at half maxima (FWHM) and  $\theta$  is the angle of diffraction. The average crystallite size was calculated as approximately 6.89 nm for pure  $\text{NiFe}_2\text{O}_4$  and 7.35 nm for  $\text{NiFe}_2\text{O}_4/\text{WRB3}$  nanocomposite. The inter-planar distance (d) corresponding to the identified peaks was calculated using Bragg's equation 3, whereas the lattice parameters were determined using equations 4 and 5 as given below.

$$2d \sin \theta = n\lambda \quad (3)$$

The unit cell volume (V) for cubic and hexagonal system mentioned in Table 1 was determined using equations 6 and 7, respectively.

$$a = \sqrt{(h^2 + k^2 + l^2)} d \quad (4)$$

$$\frac{1}{d^2} = \frac{4}{3a^2} (h^2 + hk + k^2) + \frac{l^2}{c^2} \quad (5)$$

$$V = a^3 \quad (6)$$



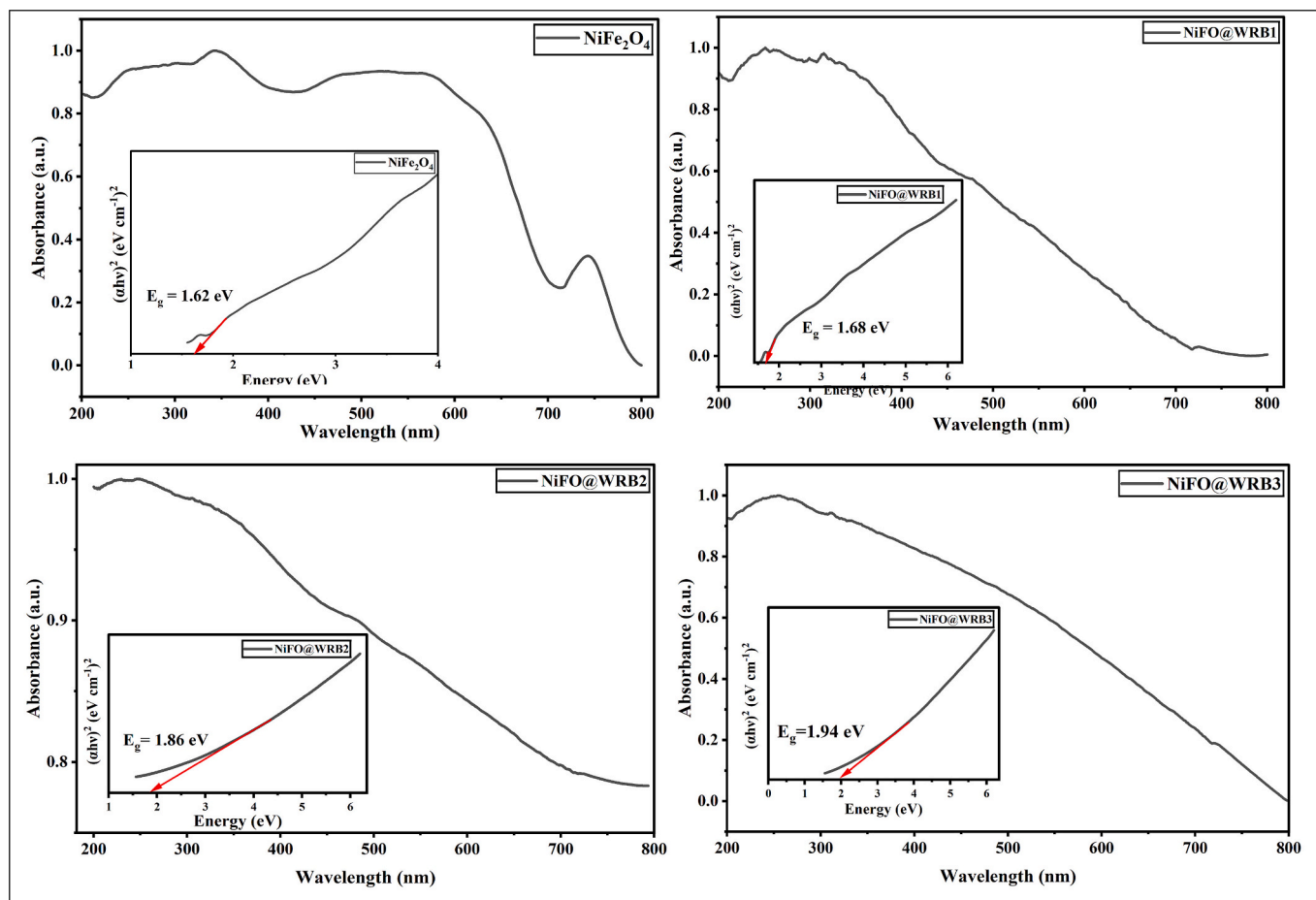


Fig. 3. UV-Vis absorbance spectra and inset tau's plot of  $\text{NiFe}_2\text{O}_4$ ,  $\text{NiFe}_2\text{O}_4/\text{WRB1}$ ,  $\text{NiFe}_2\text{O}_4/\text{WRB2}$ ,  $\text{NiFe}_2\text{O}_4/\text{WRB3}$ .

$$V = \frac{\sqrt{3}}{2} (a^2 c) \quad (7)$$

### 3.1.3. UV-Vis

The optical properties of  $\text{NiFe}_2\text{O}_4$  and  $\text{NiFe}_2\text{O}_4/\text{WRB}$  nanocomposites was investigated by UV-DRS spectroscopy. The band gap energy ( $E_g$ ) was determined by the Tauc plot corresponding to absorption spectrum as shown in Fig. 3. The absorbance of  $\text{NiFe}_2\text{O}_4$  and  $\text{NiFe}_2\text{O}_4/\text{WRB}$  nanocomposites observed to be higher in the visible region that could efficiently harness visible light. The absorbance peaks of  $\text{NiFe}_2\text{O}_4$  observed at 226 nm and 567 nm while the decrease in absorbance reflected for  $\text{NiFe}_2\text{O}_4/\text{WRB}$  nanocomposite on increasing wt% from 25% to 75% of biochar along the wavelength region. From the energy equation,  $E = hc/\lambda$  the calculated band gap energy from tauq plot found to be 1.62 eV for pure  $\text{NiFe}_2\text{O}_4$  and 1.68 eV, 1.86 eV and 1.94 eV for  $\text{NiFe}_2\text{O}_4/\text{WRB1}$ ,  $\text{NiFe}_2\text{O}_4/\text{WRB2}$  and  $\text{NiFe}_2\text{O}_4/\text{WRB3}$  respectively. Although the band gap of  $\text{NiFe}_2\text{O}_4/\text{WRB1}$  (1.68 eV) and  $\text{NiFe}_2\text{O}_4/\text{WRB3}$  (1.94 eV) both lie within the visible region, but  $\text{NiFe}_2\text{O}_4/\text{WRB3}$  exhibit superior photocatalytic activity owing to higher biochar ratio that provides larger surface area while the highly conductive carbon matrix accommodate photogenerated electrons and prevents rapid recombination of electron-holes. Since the photocatalytic activity of  $\text{NiFe}_2\text{O}_4/\text{biochar}$  nanocomposite was not merely governed by the band gap alone, rather it was combined effect of charge separation efficiency, interfacial electron transfer and generation of ROS radicals. The increasing of band gap energy can be attributed to several factors such as particle size, atomic charge interactions and ionic size effect. Herein, the incorporation of biochar enhances the adsorption edge and apparently lead to the widening of band gap. Biochar acts as an electron reservoir while the

potential energy of graphitic layers of carbonaceous biochar facilitate the migration of photogenerated electrons from conduction band of  $\text{NiFe}_2\text{O}_4$  to the empty p-orbital of graphitic carbon through  $\pi$ -conjugation and suppressed the rapid electron-hole recombination. Furthermore, increasing biochar loading could also enhance large specific surface area as well as accessibility to active sites to enhance the degradation process.

### 3.1.4. Morphological studies

The morphology of the synthesized  $\text{NiFe}_2\text{O}_4$  and  $\text{NiFe}_2\text{O}_4/\text{WRB}$  nanocomposites were investigated using FE-SEM and TEM analysis. FE-SEM images and EDS spectra were obtained at a resolution of 5  $\mu\text{m}$  and 500 nm, as shown in Fig. 4(a-i). In addition, the FE-SEM image of reused  $\text{NiFe}_2\text{O}_4/\text{WRB3}$  nanocomposite after photo-Fenton process was also obtained, and is shown in Figure S1. From the FE-SEM images, it is evident that the  $\text{NiFe}_2\text{O}_4$  and  $\text{NiFe}_2\text{O}_4/\text{WRB}$  nanocomposites are highly porous and exhibit spherical irregular morphologies while the biochar (WRB) surface reflects multilayer porous structure. The highly porous structure as well as the support of WRB to  $\text{NiFe}_2\text{O}_4$  evidenced by deposition of nano-spherical particles over biochar surface while the high agglomeration attributed to strong magnetic interactions of  $\text{NiFe}_2\text{O}_4$  nanoparticles confirm the successful formation of  $\text{NiFe}_2\text{O}_4/\text{WRB}$  nanocomposite. The energy-dispersive X-ray spectroscopy (EDS) analysis revealed the elemental composition of  $\text{NiFe}_2\text{O}_4$  and  $\text{NiFe}_2\text{O}_4/\text{WRB}$  nanocomposites. The elemental composition was normalized by excluding the carbon contribution arising from the carbon tape used during SEM analysis. The EDS analysis confirms the presence of Ni, Fe, and O elements in the synthesized  $\text{NiFe}_2\text{O}_4/\text{WRB}$  nanocomposites without any impurities. The measured atomic percentages and weight percentages were influenced by several factors such as surface

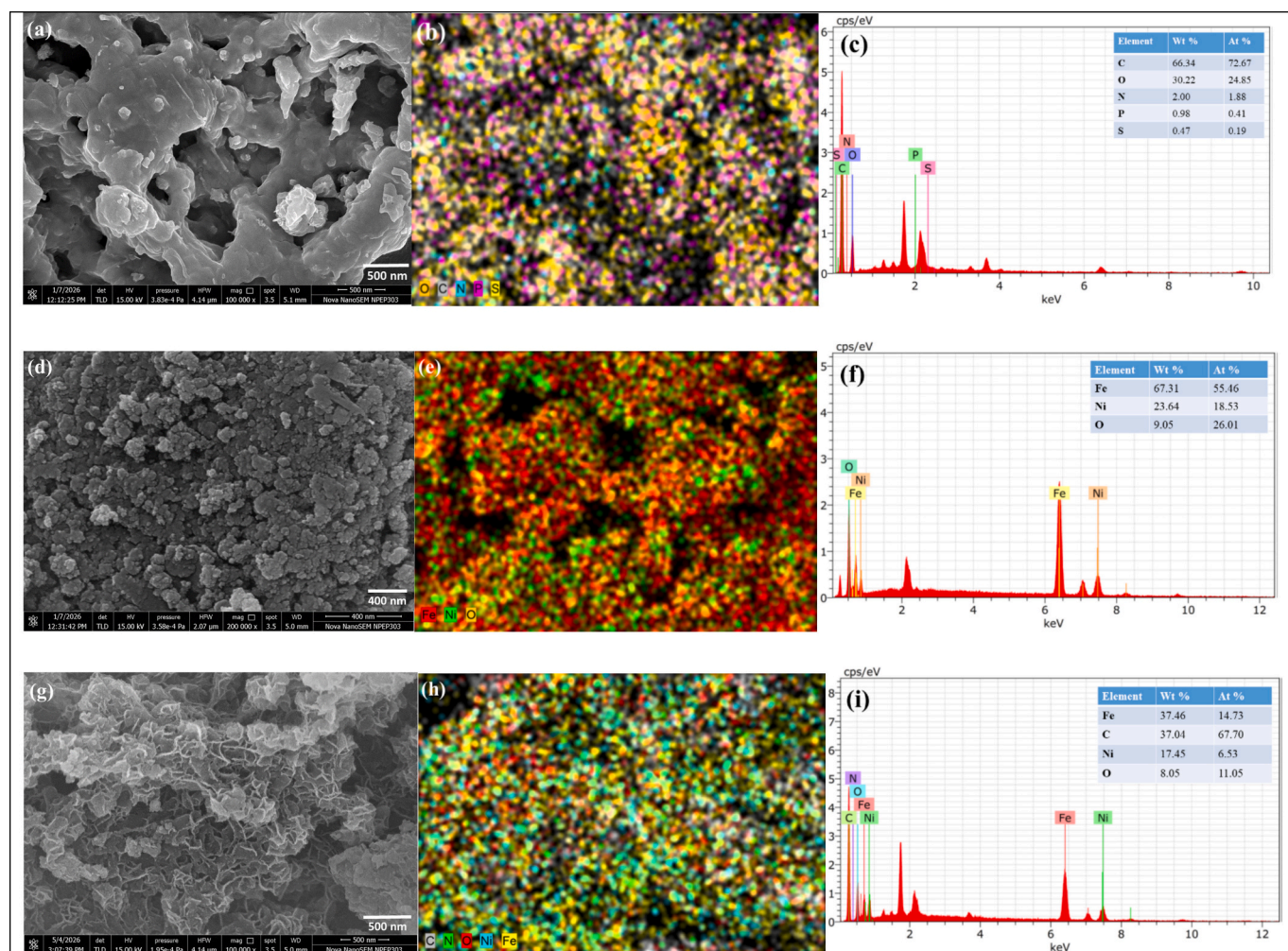


Fig. 4. FE-SEM image, elemental mapping and EDS spectra of (a–c) WRB, (d–f) NiFe<sub>2</sub>O<sub>4</sub>, (g–i) NiFe<sub>2</sub>O<sub>4</sub>/WRB3.

sensitiveness, morphology of biochar matrix as well as the presence of a minor Fe<sub>2</sub>O<sub>3</sub> secondary phase and therefore exhibit slight deviation from ideal stoichiometry. TEM analysis revealed that the individual particles mostly exhibit polymorph irregular spherical shapes as shown in Fig. 5(a, d) TEM image also used to evaluate the average particle size analysis using ImageJ software of NiFe<sub>2</sub>O<sub>4</sub> and NiFe<sub>2</sub>O<sub>4</sub>/WRB3 as Fig. 5 (b, e) which revealed that the average particle size of 27.24 nm for pure NiFe<sub>2</sub>O<sub>4</sub> and 20.56 nm for NiFe<sub>2</sub>O<sub>4</sub>/WRB3.

### 3.1.5. Raman analysis

Raman spectrum provides valuable insights of cationic distribution, lattice distortions, crystal symmetry and presence of structural defects. Fig. 6 shows the Raman spectra of NiFe<sub>2</sub>O<sub>4</sub>, WRB, and NiFe<sub>2</sub>O<sub>4</sub>/WRB nanocomposites (NiFe<sub>2</sub>O<sub>4</sub>/WRB1, NiFe<sub>2</sub>O<sub>4</sub>/WRB2, NiFe<sub>2</sub>O<sub>4</sub>/WRB3) with two vibrational peaks at 470 cm<sup>-1</sup> and 620 cm<sup>-1</sup> represented as D band and G band and the vibrational mode F<sub>2g</sub> and A<sub>1g</sub> respectively. These peaks correspond to the presence of defects in NiFe<sub>2</sub>O<sub>4</sub> and NiFe<sub>2</sub>O<sub>4</sub>/WRB nanocomposites and their ratio expressed in terms of degree of defect. The I<sub>D</sub>/I<sub>G</sub> ratio of NiFe<sub>2</sub>O<sub>4</sub> and NiFe<sub>2</sub>O<sub>4</sub>/WRB3 found to be 1.28 and 1.32 respectively indicating higher defect density in the NiFe<sub>2</sub>O<sub>4</sub>/WRB3 nanocomposite which enhances the active sites and electron charge transfer for faster degradation [28].

### 3.1.6. XPS

The elemental composition, valence states and surface chemical bonds of constituent elements in NiFe<sub>2</sub>O<sub>4</sub>/WRB can be determined by using X-ray Photoelectron spectroscopy. The characteristic peaks in XPS

spectra correspond to the Ni, Fe, O and C as shown in Fig. 7. The high resolution XPS spectra of Ni 2p revealed the two characteristic peaks of Ni 2p<sub>1/2</sub> and Ni 2p<sub>3/2</sub> as well as the presence of satellite peaks. The Ni 2p<sub>3/2</sub> spin-orbital further exhibited Ni<sup>+2</sup> and Ni<sup>+3</sup> peaks with binding energies 854.90 eV and 861.27 eV respectively while Ni 2p<sub>1/2</sub> shows the peak at 872.16 eV accompanied by satellite peaks at 864.30 eV, 867.87 and 879.43 eV [29]. The Fe 2p spectrum also displayed the two characteristic peaks i.e. Fe 2p<sub>3/2</sub> and 2p<sub>1/2</sub> at 710.19 eV and 724.59 eV respectively results from the spin-orbital interaction along with satellite peak at 712.36 eV that confirms the Fe<sup>+3</sup> in NiFe<sub>2</sub>O<sub>4</sub>/WRB spinel nanocomposite [30]. The deconvoluted spectra of O1s reflects the characteristic peaks at 529.80 eV and 531.18 eV attributed to lattice oxygen (O<sup>2-</sup>), oxygen vacancies and surface functional carbonyl ((C=O), (C=O)) and hydroxyl groups (C-OH) [31]. The C1s spectra shows peaks with binding energies 284.93 eV, 286.57 eV and 288.23 eV attributed to the chemical interaction of graphitized carbon in WRB with oxygen-containing functional groups [32].

### 3.1.7. BET analysis

The adsorption capacity of NiFe<sub>2</sub>O<sub>4</sub>/WRB nanocomposites was determined by the surface properties and investigated through N<sub>2</sub> gas adsorption-desorption conducted at 77 K. The specific surface area (S<sub>BET</sub>) was calculated by BET method, while the pore size distribution and pore volume were calculated by Barrett-Joyner-Halenda (BJH) method. The adsorption-desorption isotherms and pore size distribution curves are shown in Fig. 8, which indicates a rapid inclination in N<sub>2</sub> adsorption at higher P/P<sub>0</sub> for NiFe<sub>2</sub>O<sub>4</sub>/WRB3, which shows



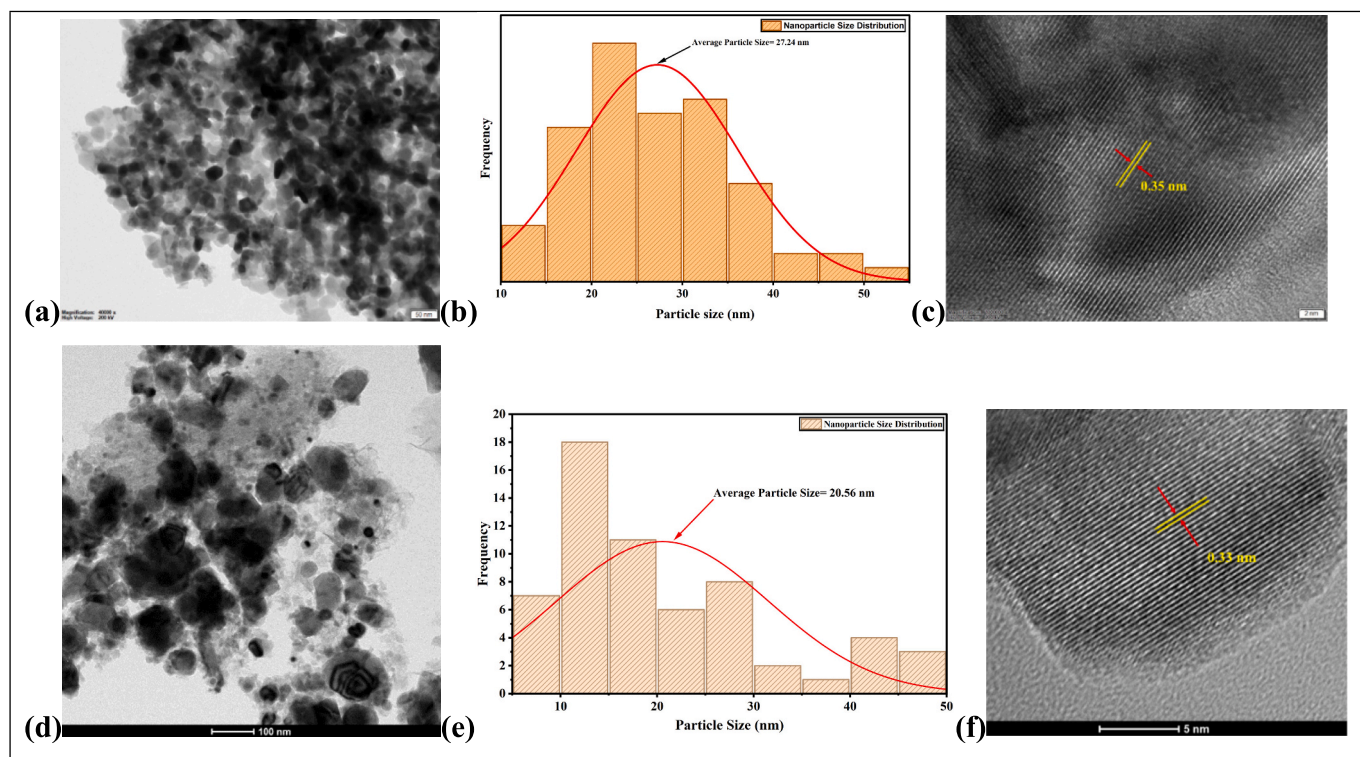


Fig. 5. TEM image, particle's size distribution, HRTEM analysis of (a–c) NiFe<sub>2</sub>O<sub>4</sub> and (d–f) NiFe<sub>2</sub>O<sub>4</sub>/WRB nanocomposites.

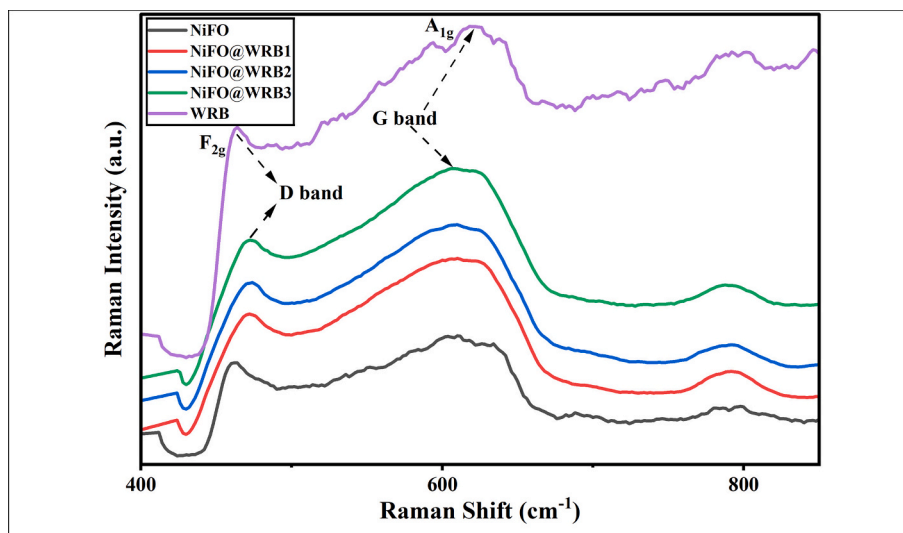


Fig. 6. Raman spectra of WRB, NiFe<sub>2</sub>O<sub>4</sub> and NiFe<sub>2</sub>O<sub>4</sub>/WRB nanocomposites.

enhancement in mesoporosity. In contrast, pure NiFe<sub>2</sub>O<sub>4</sub> exhibit significantly lower N<sub>2</sub> adsorption, suggesting limited mesoporosity. As a result, NiFe<sub>2</sub>O<sub>4</sub>/WRB3 was found to exhibit high specific surface area and shows higher adsorption capacity as compared to pure NiFe<sub>2</sub>O<sub>4</sub>. The S<sub>BET</sub> and pore volume were found to be 187.630 m<sup>2</sup>/g and 0.25 cm<sup>3</sup>/g respectively for NiFe<sub>2</sub>O<sub>4</sub>/WRB3, which were much higher than pure NiFe<sub>2</sub>O<sub>4</sub> (9.465 m<sup>2</sup>/g and 0.025 cm<sup>3</sup>/g) attributed to the particle aggregation and limited particle growth in pristine NiFe<sub>2</sub>O<sub>4</sub> as observed in FE-SEM [20]. The observed adsorption-desorption isotherm curve closely relates to type IV according to the IUPAC classification, whereas the hysteresis loop strongly resembled a distinct H3 hysteresis loop, which confirmed the mesoporous surface characteristic of all NiFe<sub>2</sub>O<sub>4</sub>/WRB via slit-shaped mesopores generated by the layered carbon

framework of biochar and aggregated NiFe<sub>2</sub>O<sub>4</sub> NPs. These interconnected mesoporous pathway facilitate rapid migration of dye molecules as well as reactive oxygen species in photo-Fenton degradation process attributed to the enhanced the catalytic performance of NiFe<sub>2</sub>O<sub>4</sub>/WRB3 [33] Table 2 summarized the S<sub>BET</sub>, Pore diameter and Pore volume obtained from BET analysis.

### 3.1.8. VSM

The magnetic properties of pure NiFe<sub>2</sub>O<sub>4</sub> and optimized NiFe<sub>2</sub>O<sub>4</sub>/WRB3 nanocomposite were investigated by vibrating sample magnetometry (VSM) and the corresponding magnetization–magnetic field (M–H) hysteresis curve obtained at room temperature are represented in Fig. S2. The magnetization rapidly increased by the increase in applied

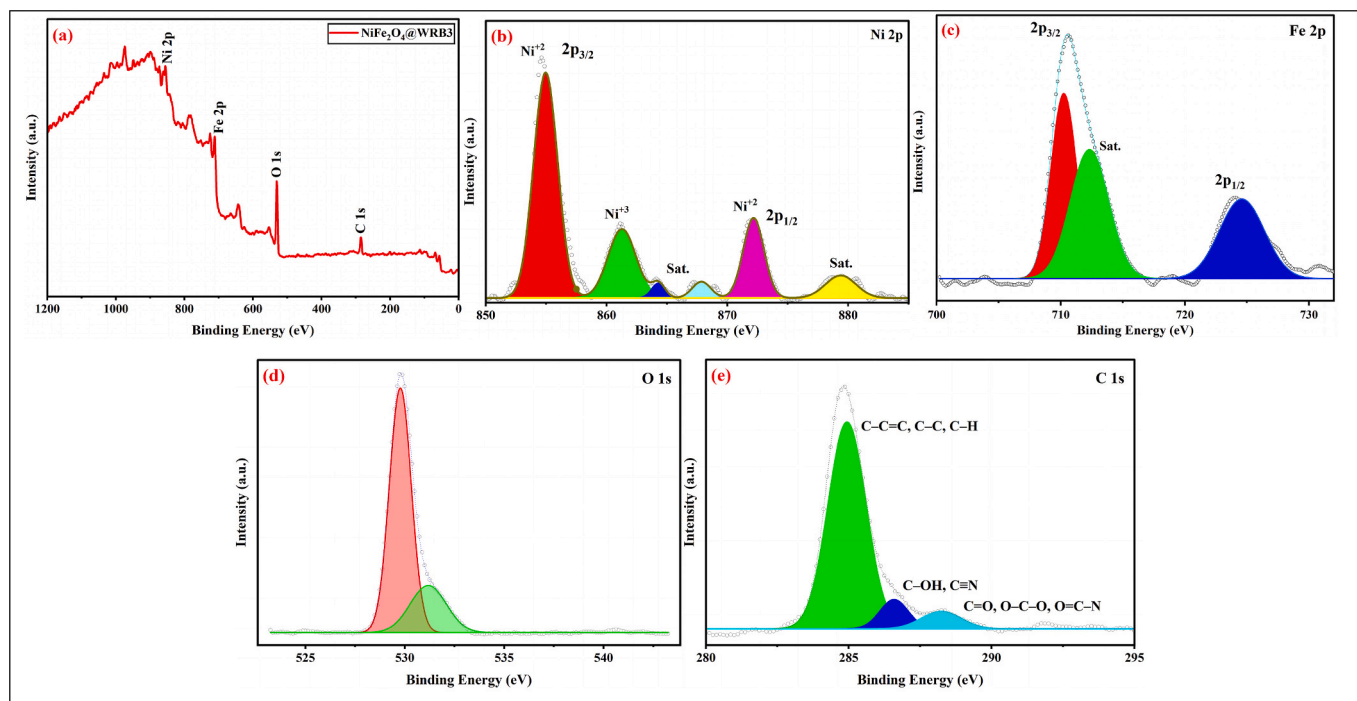


Fig. 7. (a) XPS spectra of NiFe<sub>2</sub>O<sub>4</sub>/WRB3 nanocomposite, (b) Ni 2p spectrum, (c) Fe 2p spectrum, (d) O 1s spectrum and (e) C 1s spectrum.

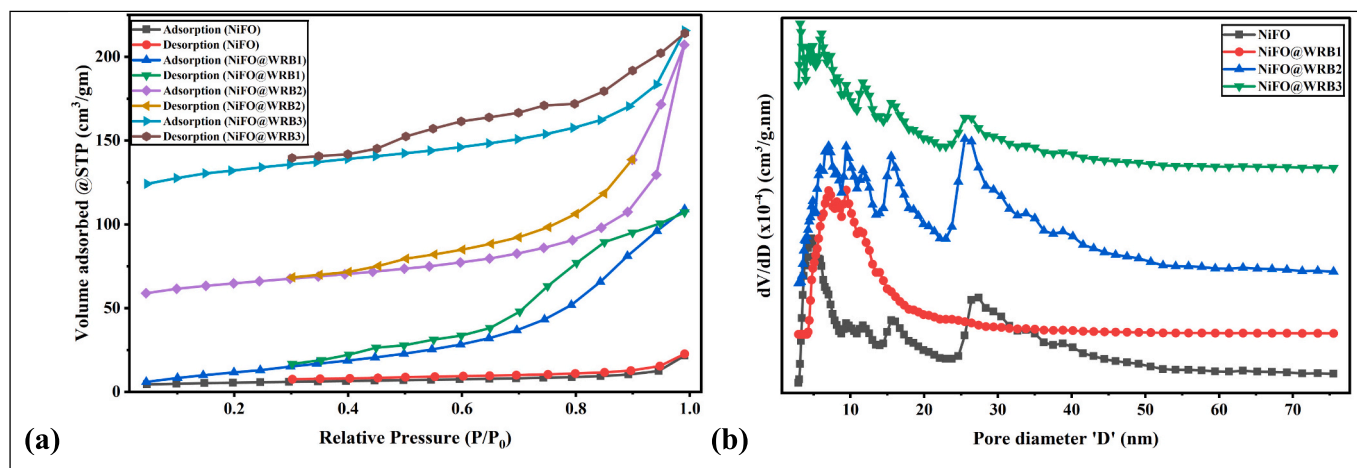


Fig. 8. BET N<sub>2</sub> adsorption-desorption isotherms and pore size distribution curve of NiFe<sub>2</sub>O<sub>4</sub>, NiFe<sub>2</sub>O<sub>4</sub>/WRB1, NiFe<sub>2</sub>O<sub>4</sub>/WRB2 and NiFe<sub>2</sub>O<sub>4</sub>/WRB3.

Table 2

S<sub>BET</sub>, Pore diameter and Pore volume of NiFe<sub>2</sub>O<sub>4</sub> and NiFe<sub>2</sub>O<sub>4</sub>/WRB nanocomposites.

| Sample                                 | S <sub>BET</sub> (m <sup>2</sup> /g) | Pore diameter (nm) | Pore volume (cm <sup>3</sup> /g) |
|----------------------------------------|--------------------------------------|--------------------|----------------------------------|
| NiFe <sub>2</sub> O <sub>4</sub>       | 9.465                                | 3.84               | 0.026                            |
| NiFe <sub>2</sub> O <sub>4</sub> /WRB1 | 75.462                               | 3.41               | 0.15                             |
| NiFe <sub>2</sub> O <sub>4</sub> /WRB2 | 162.304                              | 3.83               | 0.18                             |
| NiFe <sub>2</sub> O <sub>4</sub> /WRB3 | 187.630                              | 3.85               | 0.25                             |

magnetic field and gradually approached the saturation at 5000 Oe. The steep initial increase in magnetization correspond to the progressive movement of magnetic domain walls and the alignment of magnetic domains along the direction of the applied magnetic field. The magnetic parameters obtained from the hysteresis loop confirmed the magnetic nature of NiFe<sub>2</sub>O<sub>4</sub> and NiFe<sub>2</sub>O<sub>4</sub>/WRB3 nanocomposite, originates predominantly from the spinel NiFe<sub>2</sub>O<sub>4</sub> phase. The M-H curve exhibited a

well-defined, narrow hysteresis loop with an S-shaped profile, yielding a saturation magnetization (M<sub>s</sub>) of pure NiFe<sub>2</sub>O<sub>4</sub> was found to be 36.374 emu/g, while the corresponding remanent magnetization (M<sub>r</sub>) and coercivity (H<sub>c</sub>) were 6.29 emu/g and 125 Oe, respectively, while NiFe<sub>2</sub>O<sub>4</sub>/WRB3 nanocomposite exhibited M<sub>s</sub> of 16.17 emu/g, M<sub>r</sub> of 5.39 emu/g, and H<sub>c</sub> of 417 Oe. The substantial lowering of M<sub>s</sub> in NiFe<sub>2</sub>O<sub>4</sub>/WRB3 compared to pure NiFe<sub>2</sub>O<sub>4</sub> could be attributed to the incorporation of non-magnetic biochar, which tends to reduce the magnetic NiFe<sub>2</sub>O<sub>4</sub> phase. However, the dispersion of NiFe<sub>2</sub>O<sub>4</sub> NPs over the surface of biochar WRB led to the magnetic exchange interactions and its domain structure, thereby reducing the overall magnetization of NiFe<sub>2</sub>O<sub>4</sub>/WRB3 nanocomposite. Similarly, the magnetic parameters, remanent magnetization (M<sub>r</sub>) and coercivity (H<sub>c</sub>) obtained from the M-H curve demonstrated that, with the reduced fraction of magnetic-phase in NiFe<sub>2</sub>O<sub>4</sub>/WRB3 nanocomposite, the M<sub>r</sub> value decreased slightly from 6.29 emu/g (for pure NiFe<sub>2</sub>O<sub>4</sub>) to 5.39 emu/g. Additional parameters such as squareness ratio (S = M<sub>r</sub>/M<sub>s</sub>), magnetic moment (μ<sub>B</sub>) and



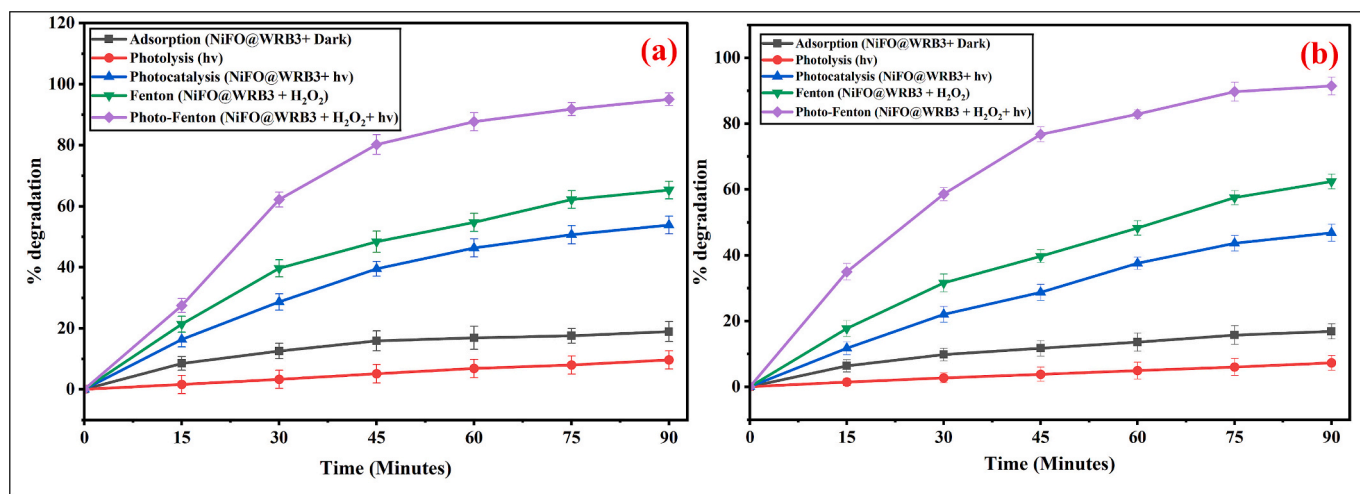


Fig. 9. Comparative study of % dye removal from adsorption, photolysis, photocatalysis, Fenton and photo-Fenton of (a) 5 ppm MB and (b) 10 ppm AR27 dye using  $\text{NiFe}_2\text{O}_4/\text{WRB3}$  nanocomposite.

Table 3

Magnetic parameters of pure  $\text{NiFe}_2\text{O}_4$  and  $\text{NiFe}_2\text{O}_4/\text{WRB3}$  nanocomposite.

| Sample                                | $M_r$ (emu/g) | $M_s$ (emu/g) | Hc (Oe) | Squareness ( $M_r/M_s$ ) | Magnetic moment ( $\mu_B$ ) | Anisotropy constant (K) |
|---------------------------------------|---------------|---------------|---------|--------------------------|-----------------------------|-------------------------|
| $\text{NiFe}_2\text{O}_4$             | 6.29          | 36.374        | 125     | 0.1729                   | 0.0409                      | 47.3619                 |
| $\text{NiFe}_2\text{O}_4/\text{WRB3}$ | 5.39          | 16.179        | 417     | 0.3331                   | 0.0156                      | 70.2384                 |

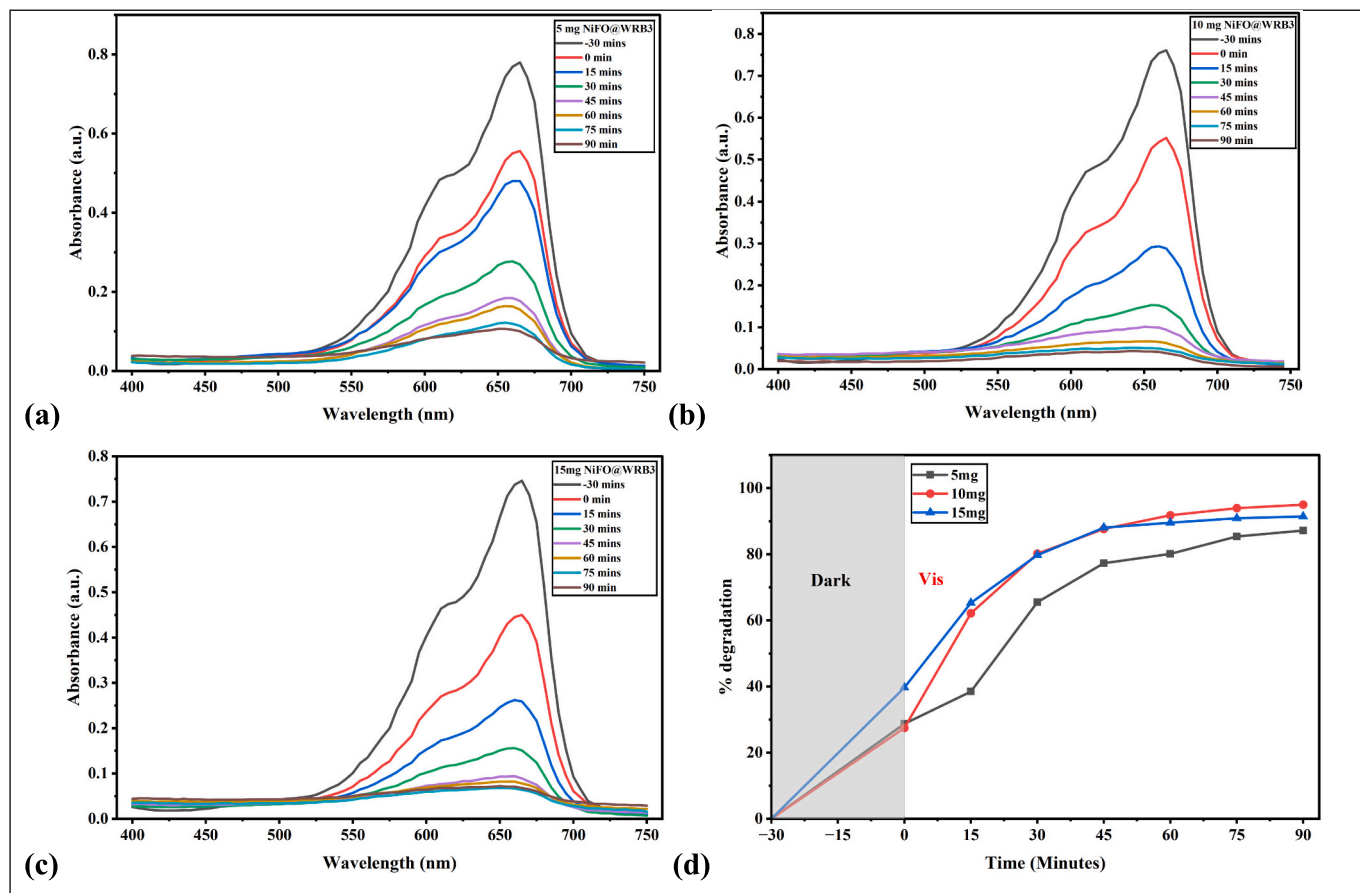
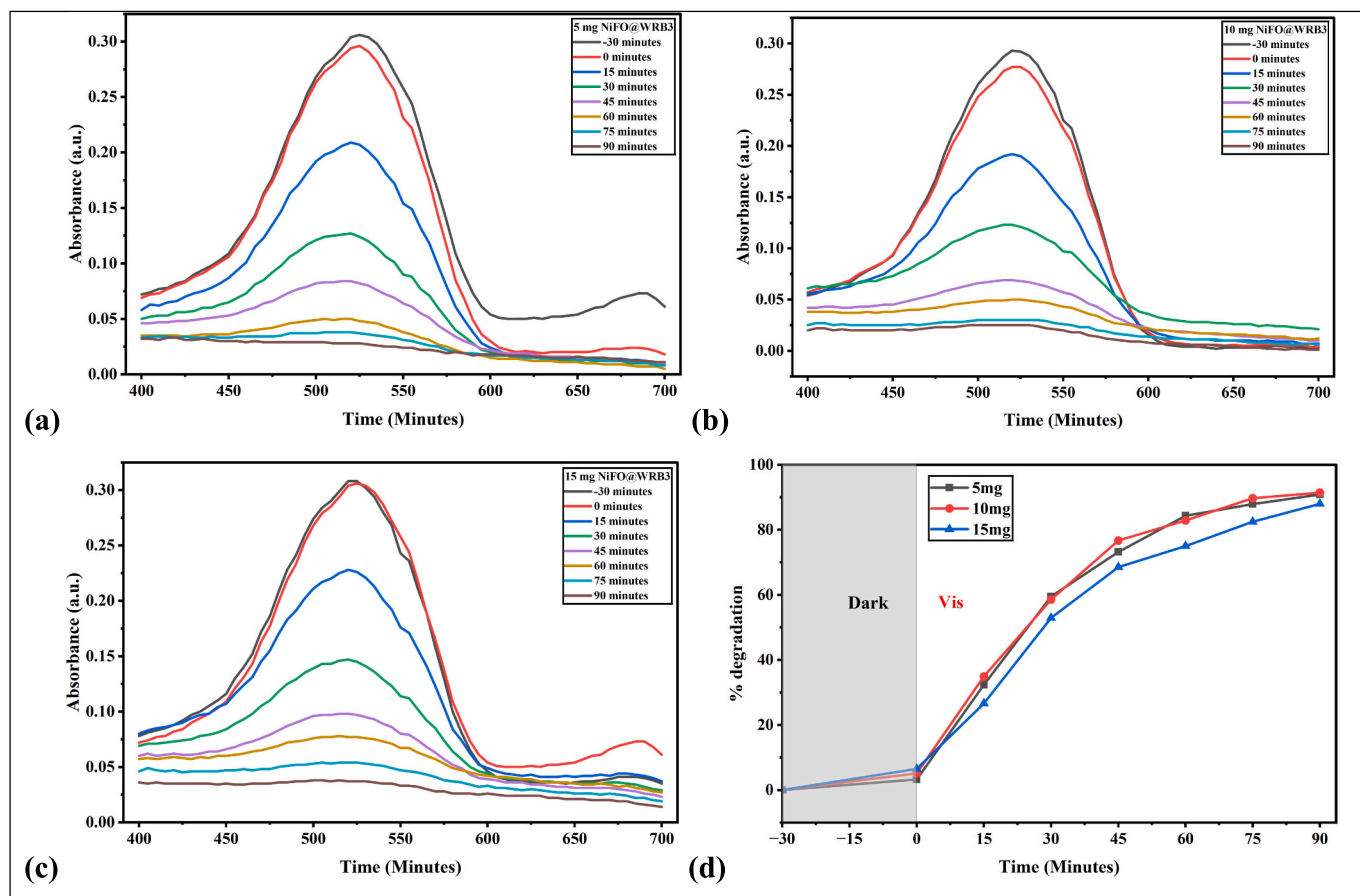


Fig. 10. UV-Vis absorbance spectra for MB dye degradation at different dosage of  $\text{NiFe}_2\text{O}_4/\text{WRB3}$  (a) 0.05 g/L, (b) 0.10 g/L, (c) 0.15 g/L, (d) overall % degradation. Reaction conditions: conc. of MB dye = 5 ppm, amount of  $\text{H}_2\text{O}_2$  = 1 mM, pH = 7.



**Fig. 11.** UV-Vis absorbance spectra for MB dye degradation at different dosage of NiFe<sub>2</sub>O<sub>4</sub>/WRB3 (a) 0.05 g/L, (b) 0.10 g/L, (c) 0.15 g/L, (d) overall % degradation. Reaction conditions: conc. of AR27 = 5 ppm, amount of H<sub>2</sub>O<sub>2</sub> = 1 mM, pH = 7.

anisotropy constant ( $K$ ) were calculated using equations 8 and 9 (summarized in Table 3):

$$\mu_B = \frac{M^* M_s}{5585} \quad (8)$$

$$K = \frac{H_c * M_s}{0.96} \quad (9)$$

Interestingly, the increase in  $H_c$  value from 125 Oe in pure NiFe<sub>2</sub>O<sub>4</sub> to 417 Oe in NiFe<sub>2</sub>O<sub>4</sub>/WRB3 can be attributed to the increased nanoparticles interaction or surface coupling between WRB and NiFe<sub>2</sub>O<sub>4</sub> NPs that led to increase domain-wall pinning at the interface of NiFe<sub>2</sub>O<sub>4</sub>/WRB3. However, the  $H_c$  value of 417 Oe still correspond to the soft magnetic behaviour of material and advantageous in magnetic separation using external magnetic field.

### 3.2. Photocatalytic studies

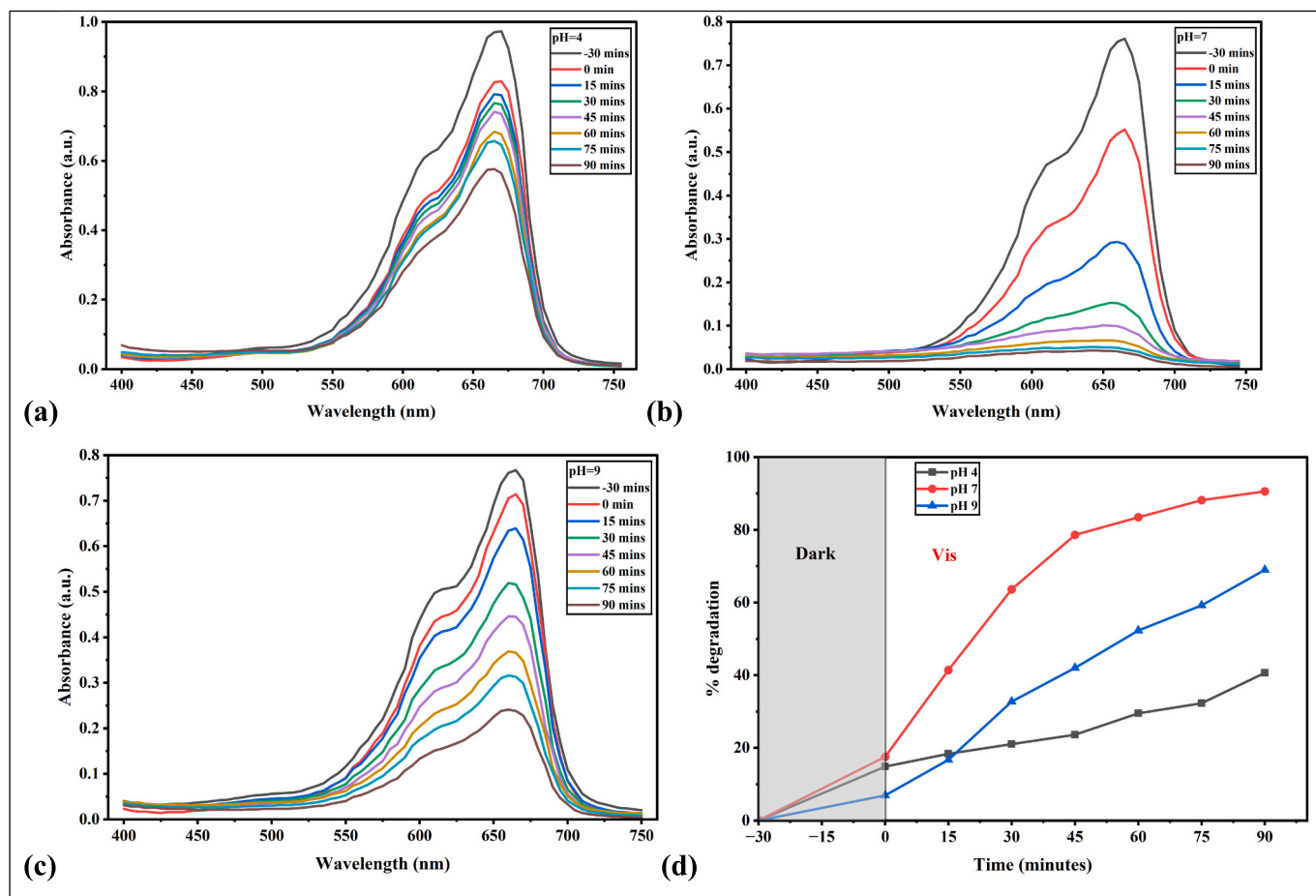
#### 3.2.1. Mechanistic insights into comparative dye removal of MB and AR27 by adsorption, photolysis, Photocatalysis, Fenton and photo-Fenton process

Various reaction pathways have been investigated to compare their contribution in degradation of MB and AR27 dyes under identical experimental conditions: Adsorption (NiFe<sub>2</sub>O<sub>4</sub>/WRB3+ dark), Photolysis (hv), Photocatalysis (NiFe<sub>2</sub>O<sub>4</sub>/WRB3+ hv), Fenton (NiFe<sub>2</sub>O<sub>4</sub>/WRB3+ H<sub>2</sub>O<sub>2</sub>), photo-Fenton (NiFe<sub>2</sub>O<sub>4</sub>/WRB3+ H<sub>2</sub>O<sub>2</sub>+ hv), as shown in Fig. 9. In case of photolysis, the 5 ppm MB and 10 ppm AR27 dye solutions were exposed to visible irradiation, resulted in just 9.63% degradation of MB and 7.23% degradation of AR27 dye within 90 min and demonstrated negligible photochemical oxidation of dye pollutants. However, the adsorption reaction was carried out in dark without using

any light source and shows 18.92% adsorption of MB and 16.82% adsorption of AR27. The photocatalysis reaction involved the exposure of NiFe<sub>2</sub>O<sub>4</sub>/WRB3 surface to visible irradiation and shows maximum degradation of 53.82% of 5 ppm MB and 46.78% for 10 ppm AR27 dye. However, the Fenton reaction involved the interaction of H<sub>2</sub>O<sub>2</sub> with MB and AR27 dye molecules as well as with the surface functional groups of NiFe<sub>2</sub>O<sub>4</sub>/WRB3, resulted in increasing the degradation of MB to 65.26% while AR27 to 62.39% within 90 min. The photo-Fenton process shows enhanced degradation by the combining effect of H<sub>2</sub>O<sub>2</sub> and visible light over NiFe<sub>2</sub>O<sub>4</sub>/WRB. Among all the processes, photo-Fenton reaction shows maximum degradation of 95% for 5 ppm MB while 91.43% for 10 ppm AR27. Therefore, photo-Fenton reaction was employed to further investigate the degradation process by varying reaction parameters such as catalyst load, amount of H<sub>2</sub>O<sub>2</sub>, concentration of MB and AR27 and at different pH conditions.

#### 3.2.2. Effect of catalyst dosage on degradation of MB and AR27 dyes

The concentration of Fe<sup>+2</sup>/Fe<sup>+3</sup> directly influences the efficiency of the photo-Fenton process, as it is primarily responsible for the generation ROS (\*OH) radicals [34]. Moreover, In photo-Fenton process, the effective Fe<sup>+2</sup>/Fe<sup>+3</sup> redox cycle is directly proportional to the NiFe<sub>2</sub>O<sub>4</sub>/WRB3 catalyst dosage; therefore, optimizing the NiFe<sub>2</sub>O<sub>4</sub>/WRB3 dosage is critical in enhancing the number of active iron sites for efficient photo-Fenton process. The experimental observation indicate that the catalyst (NiFe<sub>2</sub>O<sub>4</sub>/WRB3) concentration significantly affects the MB and AR27 dye degradation as shown in Fig. 10. and Fig. 11. Increasing the NiFe<sub>2</sub>O<sub>4</sub>/WRB3 concentration enhances the photo-Fenton degradation of MB and AR27 dye and achieved maximum degradation of 95% for 5 ppm MB while 91.33% degradation for 10 ppm AR27 dye using optimum catalyst dose of 0.1 g/L within 90 min on exposure to visible



**Fig. 12.** UV-Vis absorbance spectra for MB degradation at different pH of  $\text{NiFe}_2\text{O}_4/\text{WRB3}$  (a) pH 4, (b) pH 7, (c) pH 9, (d) overall % degradation. Reaction conditions: catalyst dosage = 0.1 g/L, conc. of dye = 5 ppm, amount of  $\text{H}_2\text{O}_2$  = 1 mM.

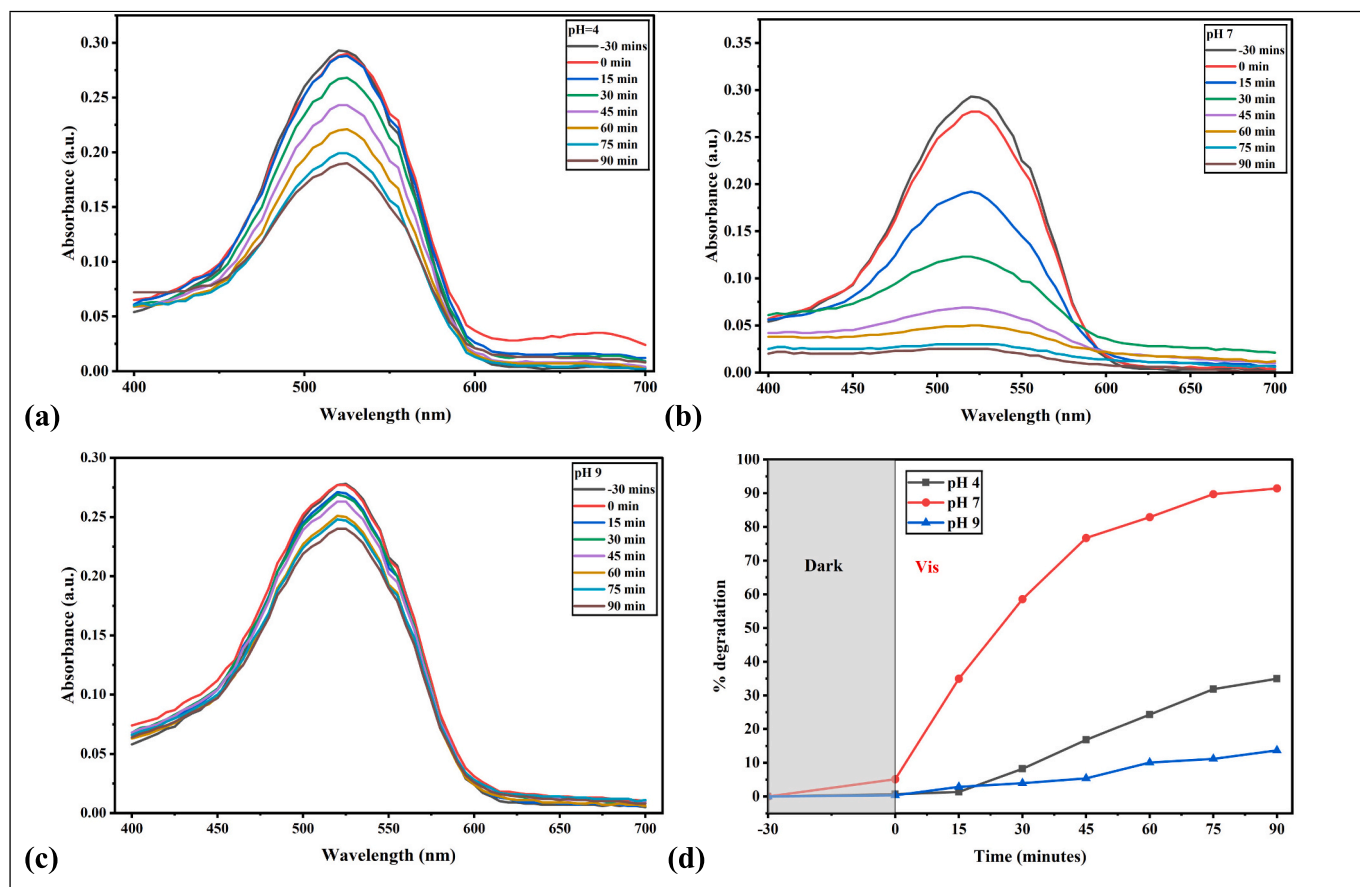
irradiation. At lower concentration of 0.05 g/L, 87.17% degradation of MB and 91.43% degradation of AR27 was observed, however slightly increase in concentration to 0.15 g/L led to decrease the MB degradation to 91.42% while AR27 to 87.98%. The lower %degradation at catalyst loading of 0.05 g/L occurred due to limited availability of active catalytic  $\text{Fe}^{+2}/\text{Fe}^{+3}$  sites to react with  $\text{H}_2\text{O}_2$  for generation of  $\cdot\text{OH}$  radicals. Hence, an increase in concentration from 0.05 g/L to 0.1 g/L enhances the catalytic active sites and generates higher  $\cdot\text{OH}$  radicals to degrade MB and AR27 dye pollutants. However, it was observed that further increase in concentration from 0.1 g/L to 0.15 g/L lead to decrease the degradation efficiency, as excess iron concentration generates the ferric hydroxide precipitation and decreases the availability of active  $\text{Fe}^{+2}/\text{Fe}^{+3}$  sites while excess  $\text{Fe}^{+2}$  also scavenges the ROS ( $\cdot\text{OH}$ ) radicals. Additionally, the higher concentration of catalyst also intensifies particle-particle interaction that leads to screening effect due to agglomeration and hinders the incoming photon from irradiation source to reach the active sites on the catalyst surface and thereby reducing the overall degradation of MB and AR27 dyes.

### 3.2.3. Effect of pH on MB and AR27 dye degradation

The pH of the solution is the critical operational parameter in photo-Fenton dye degradation as it influences the surface charge of photocatalyst, ionised state of dye pollutants their interaction with the surface of catalyst. Additionally in photo-Fenton process, pH of the solution also affects the redox  $\text{Fe}^{+2}/\text{Fe}^{+3}$  cycle that directly influence the generation of  $\cdot\text{OH}$  radicals. Therefore, to better evaluate the effect of pH on photocatalytic activity, experimental studies were conducted in acidic (pH 4), basic (pH 9) and neutral (pH 7) media at optimum catalyst loading of 0.1 g/L of  $\text{NiFe}_2\text{O}_4/\text{WRB}$  and 1 mM  $\text{H}_2\text{O}_2$  for 5 ppm MB and 10 ppm

AR27 dyes in exposure of visible irradiations for 90 min. Fig. 12 and Fig. 13 shows the absorbance spectra of MB, AR27 at different pH conditions. In neutral medium, at pH 7, the faster degradation of MB and AR27 was observed, achieving 95% degradation of MB and 91.43% degradation of AR27 dye upon exposure to visible irradiation within 90 min. The decrease in degradation to 68.97% at pH 9 while a substantial decrease to 40.61% was observed at pH 4. However, in case of AR27, the degradation was decreased to 34.93% at pH 4 while a gradual decrease in degradation to 13.66% was observed at pH 9. The pH-dependent photo-Fenton process is primarily governed by the surface charge characteristics of the catalyst which has been determined by its pHpzc (point of zero charge pH), pHpzc correspond to the pH value at which net surface charge of catalyst is zero [25]. The pHpzc was calculated using the earlier reported method and found to be 6.4. At  $\text{pH} < \text{pHpzc}$ , the surface of the catalyst undergoes protonation and facilitate the higher interaction of anionic dye (AR27) molecules while repulsion to MB dye molecules, as a result 10 ppm AR27 was degraded to 34.93% while 5 ppm MB was degraded to 40.61% using 0.1 g/L  $\text{NiFe}_2\text{O}_4/\text{WRB3}$  at pH 4 ( $< \text{pHpzc}$ ), within 90 min. However at  $\text{pH} > \text{pHpzc}$ , the deprotonation of surface functional groups led to the higher interaction of cationic dye (MB) molecules and generates negatively charged sites on the catalyst, resulted in 68.97% degradation of 5 ppm MB while just 13.66% degradation of AR27 dye within 90 min exposure to visible irradiation. The maximum degradation of MB and AR27 dye was observed at pH close to pHpzc, that shows 95% degradation of 5 ppm MB and 93.41% of 10 ppm AR27, which can be attributed to the proton availability that facilitates  $\text{Fe}^{+2}/\text{Fe}^{+3}$  redox cycle in photo-Fenton process, and ultimately generates higher hydroxyl radicals and minimum leaching of active sites. Under basic conditions, at pH 9, the decrease in





**Fig. 13.** UV-Vis absorbance spectra for AR27 degradation at different pH of  $\text{NiFe}_2\text{O}_4/\text{WRB3}$  (a) pH 4, (b) pH 7, (c) pH 9, (d) overall % degradation. Reaction conditions: catalyst dosage = 0.1 g/L, conc. of AR27 = 10 ppm, amount of  $\text{H}_2\text{O}_2$  = 1 mM.

degradation to 68.97% for MB observed as due to increase in  $\text{OH}^-$  concentration as well as the deprotonation of  $\text{H}_2\text{O}_2$  that generates hydroperoxyl radicals ( $\text{OOH}^\cdot$ ), together affects the generation of  $\text{OH}^\cdot$  radicals that are primarily responsible for the degradation of MB and AR27 dye pollutants. The decomposition of  $\text{H}_2\text{O}_2$  into water and  $\text{O}_2$  molecules also suppresses the catalytic activity of redox  $\text{Fe}^{+2}/\text{Fe}^{+3}$  cycle in generation of  $\text{OH}^\cdot$  radicals. In addition to these, excess of  $\text{OH}^-$  ions also scavenge the generated  $\text{OH}^\cdot$  and forms singlet oxygen  $^1\text{O}_2$ . On the other hand, at pH 4 the lower degradation observed due to repulsive charge phenomenon occurred between the positively charged  $\text{NiFe}_2\text{O}_4/\text{WRB}$  surface and cationic dye (MB) ions. Although AR27 is an anionic dye that dissociate negatively charged ions and electrostatically attracted to the positively charged surface of the photocatalyst ( $\text{NiFe}_2\text{O}_4/\text{WRB}$ ) but the unavailability of  $\text{OH}^\cdot$  radicals in acidic conditions resulted in lesser degradation as compared to the degradation at neutral conditions.

### 3.2.4. Effect of $\text{H}_2\text{O}_2$ on MB and AR27 dyes degradation

The photo-Fenton degradation of MB and AR27 dyes are directly influenced by the concentration of  $\text{H}_2\text{O}_2$  as it regulates the generation of ROS ( $\text{OH}^\cdot$ ) radicals [35]. At optimum concentration (1 mM), the  $\text{H}_2\text{O}_2$  effectively activate the catalytic  $\text{Fe}^{+2}/\text{Fe}^{+3}$  redox cycle in  $\text{NiFe}_2\text{O}_4/\text{WRB}$  to produce  $\text{OH}^\cdot$  radicals, which are primarily responsible for the dye pollutants degradation. However, it is worth to note that the deficiency as well as excessive amount of  $\text{H}_2\text{O}_2$ , both affect the photo-Fenton degradation process [36,37]. The photo-Fenton reactions were conducted at different  $\text{H}_2\text{O}_2$  concentration varying from 0.5 mM, 1 mM and 1.5 mM as in Fig. 14 and Fig. 15. The lower concentration of  $\text{H}_2\text{O}_2$  (0.5 mM) produces limited  $\text{OH}^\cdot$  radicals and ultimately decreases the degradation rate of 5 ppm MB to 90.06% and 10 ppm AR27 to 69.60% at

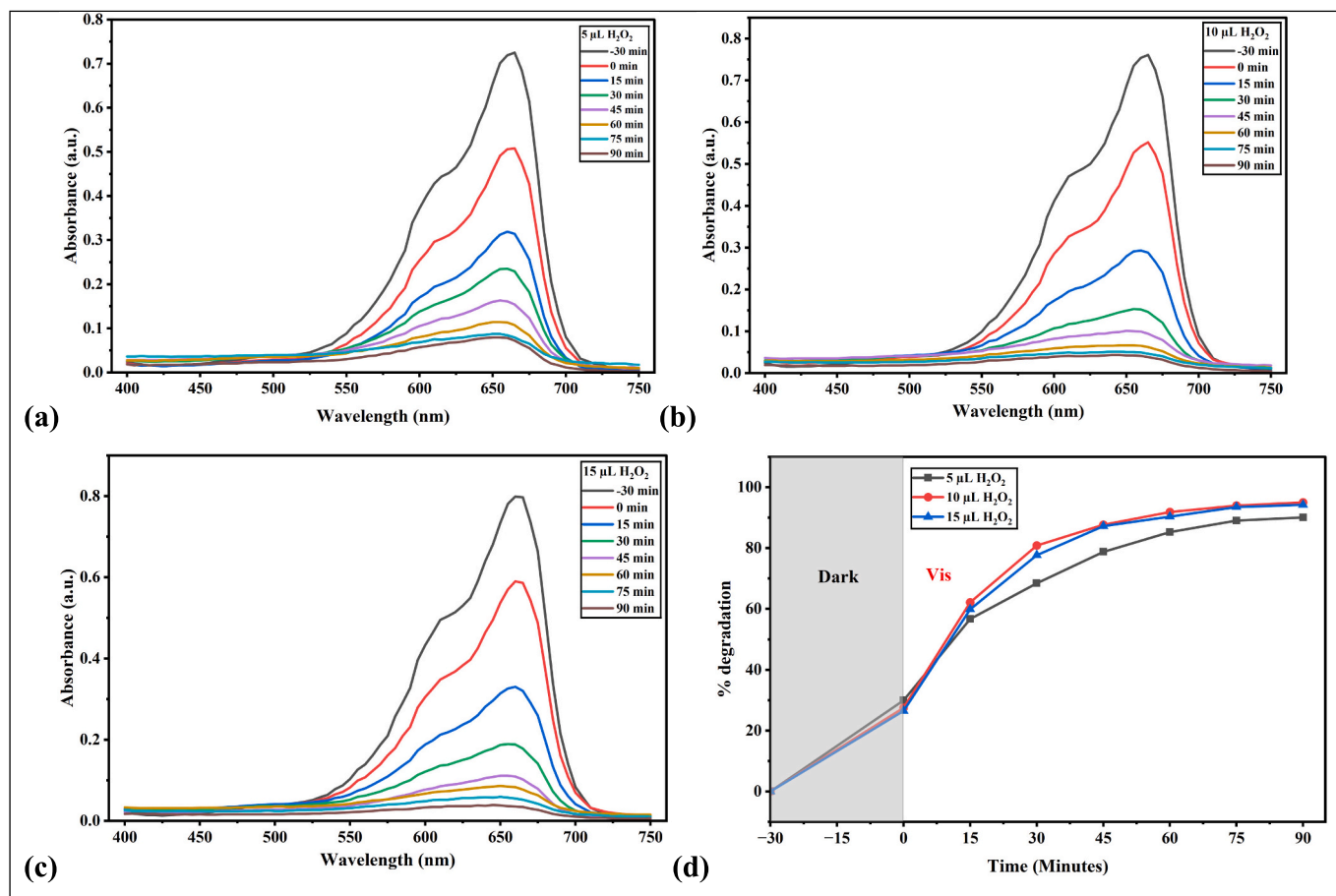
optimum catalyst dose of 0.1 g/L. The maximum degradation of 95% was achieved for 5 ppm MB and 91.78% for 10 ppm AR27 by employing 0.1 mM  $\text{H}_2\text{O}_2$  and using 0.1 g/L  $\text{NiFe}_2\text{O}_4/\text{WRB3}$ . As optimal concentration of  $\text{H}_2\text{O}_2$  facilitate the catalytically active redox  $\text{Fe}^{+2}/\text{Fe}^{+3}$  cycle to generate  $\text{OH}^\cdot$  radicals. However, beyond the optimum concentration, i.e. increase in  $\text{H}_2\text{O}_2$  from 0.1 mM to 0.15 mM led to decrease the degradation of MB to 94.23% and AR27 to 91.05%. Although, 0.15 mM  $\text{H}_2\text{O}_2$  also reflects higher degradation rate of MB as well as AR27 dye but employing minimal amount of  $\text{H}_2\text{O}_2$  holds equivalent importance to control the operational cost as well as the potential toxicity caused in utilizing higher  $\text{H}_2\text{O}_2$  concentration. It was also observed that excess of  $\text{H}_2\text{O}_2$  also scavenges the  $\text{OH}^\cdot$  produced and reduces overall photo-Fenton degradation efficiency.

### 3.2.5. Photo-Fenton degradation of RIE and mixed dyes

The evaluation of photocatalytic activity of  $\text{NiFe}_2\text{O}_4/\text{WRB3}$  nanocomposite has been also investigated by photo-Fenton degradation of real industrial effluents (RIE) and solution of mixed cationic dye (MB) and anionic dye (AR27) for the applicability in treatment of real textile industrial wastewater. The photo-Fenton experiment was conducted under optimized conditions by employing 0.1 g/L  $\text{NiFe}_2\text{O}_4/\text{WRB3}$  and 1 mM  $\text{H}_2\text{O}_2$  at pH 7 achieved 64.52% degradation of RIE and upto 90% degradation for mixture of 5 ppm MB and 10 ppm AR27 dyes as represented by UV-Vis absorbance spectra in Fig. 16.

### 3.3. Evaluation of photo-Fenton degradation kinetics

The kinetics of photo-Fenton degradation have been studied using zero-order, first-order and second-order reaction kinetics by equations 10, 11, and 12, respectively.



**Fig. 14.** UV-Vis absorbance spectra for MB dye degradation at different  $\text{H}_2\text{O}_2$  concentration of  $\text{NiFe}_2\text{O}_4/\text{WRB3}$  (a)  $5 \mu\text{L H}_2\text{O}_2$ , (b)  $10 \mu\text{L H}_2\text{O}_2$ , (c)  $15 \mu\text{L H}_2\text{O}_2$ , (d) overall % degradation. Reaction conditions: catalyst dosage =  $0.1 \text{ g/L}$ , conc. of MB =  $5 \text{ ppm}$ ,  $\text{pH} = 7$ .

$$C_0 - C_t = k_0 \cdot t \quad (10)$$

$$\ln\left(\frac{C_0}{C_t}\right) = k_1 \cdot t \quad (11)$$

$$\left(\frac{1}{C_t}\right) - \left(\frac{1}{C_0}\right) = k_2 \cdot t \quad (12)$$

where,  $C_0$  = initial dye pollutant concentration,  $C_t$  = concentration of dye pollutant at time 't',  $k_0$  = rate constant for zero-order reaction,  $k_1$  = rate constant for first-order reaction and  $k_2$  = rate constant for second-order reaction. For all the photo-degradation reaction, the correlation coefficient ' $R^2$ ' value obtained from first order kinetic model represent the best fit compared to the zero-order and second-order kinetic model as evidenced by correlation coefficient, ' $R^2$ ' value ( $R^2 > 0.95$ ) obtained for all reactions were close to unity. Importantly, the experimental trends observed across all the variable parameters shows excellent consistency over the rate constant and corresponding  $t_{1/2}$  (half-lives) to the first-order kinetic model. Various parameters such as rate constant ( $k_1$ ),  $R^2$  values and  $t_{1/2}$  associated with the first order kinetic model are calculated and shown in Table 4 and Table 5 for MB dye while Table 6 and Table 7 for AR27 dyes. Fig. 17 shows the corresponding plots of  $\ln \frac{C_0}{C_t}$  against reaction time. Moreover the rate constant ( $k_1$ ) in photocatalytic degradation is strongly influenced by catalyst dose, dye pollutant concentration and pH. Higher value of rate constant correspond to the faster degradation rate and thereby results in more generation and utilization of ROS radicals.

### 3.4. Reusability studies

In order to maintain the achieved photocatalytic activity of the synthesized  $\text{NiFe}_2\text{O}_4/\text{WRB3}$  nanocomposite over multiple photo-Fenton reactions, the stability and reusability are critical parameters for their practical applicability. The reusability of  $\text{NiFe}_2\text{O}_4/\text{WRB3}$  nanocomposite was investigated by its utilization in consecutive photo-Fenton cycle under identical experimental conditions while also evaluated by its magnetic separation from the treated reaction mixture using bar magnet. The recovered  $\text{NiFe}_2\text{O}_4/\text{WRB}$  nanocomposite was washed several times with DI water and ethanol to remove adsorbed MB and AR27 dyes and dried in vacuum oven and utilized for the next 5 cycles. The results of reusability of  $\text{NiFe}_2\text{O}_4/\text{WRB3}$  nanocomposite over 5 successive cycles are shown in Fig. 18. Initially, the degradation efficiency of  $\text{NiFe}_2\text{O}_4/\text{WRB3}$  was observed as 95% in the first cycle and gradually decreased in degradation to 86.58% in the fifth cycle for 5 ppm MB while in case of AR27, 91.34% degradation observed in first run that declined to 83.22% in the fifth cycle. These slightly decrease in degradation efficiency over multiple cycle was attributed to partial blocking of active catalytic sites, limited oxidation of surface functional groups and minor leaching of  $\text{Fe}^{+3}/\text{Fe}^{+2}$  at surface of  $\text{NiFe}_2\text{O}_4/\text{WRB3}$ . Overall, the  $\text{NiFe}_2\text{O}_4/\text{WRB3}$  exhibit excellent stability, easy magnetic separation and efficient photocatalytic activity over multiple photo-Fenton degradation cycles and holds promising performance and economically viable for long-term practical wastewater treatment.

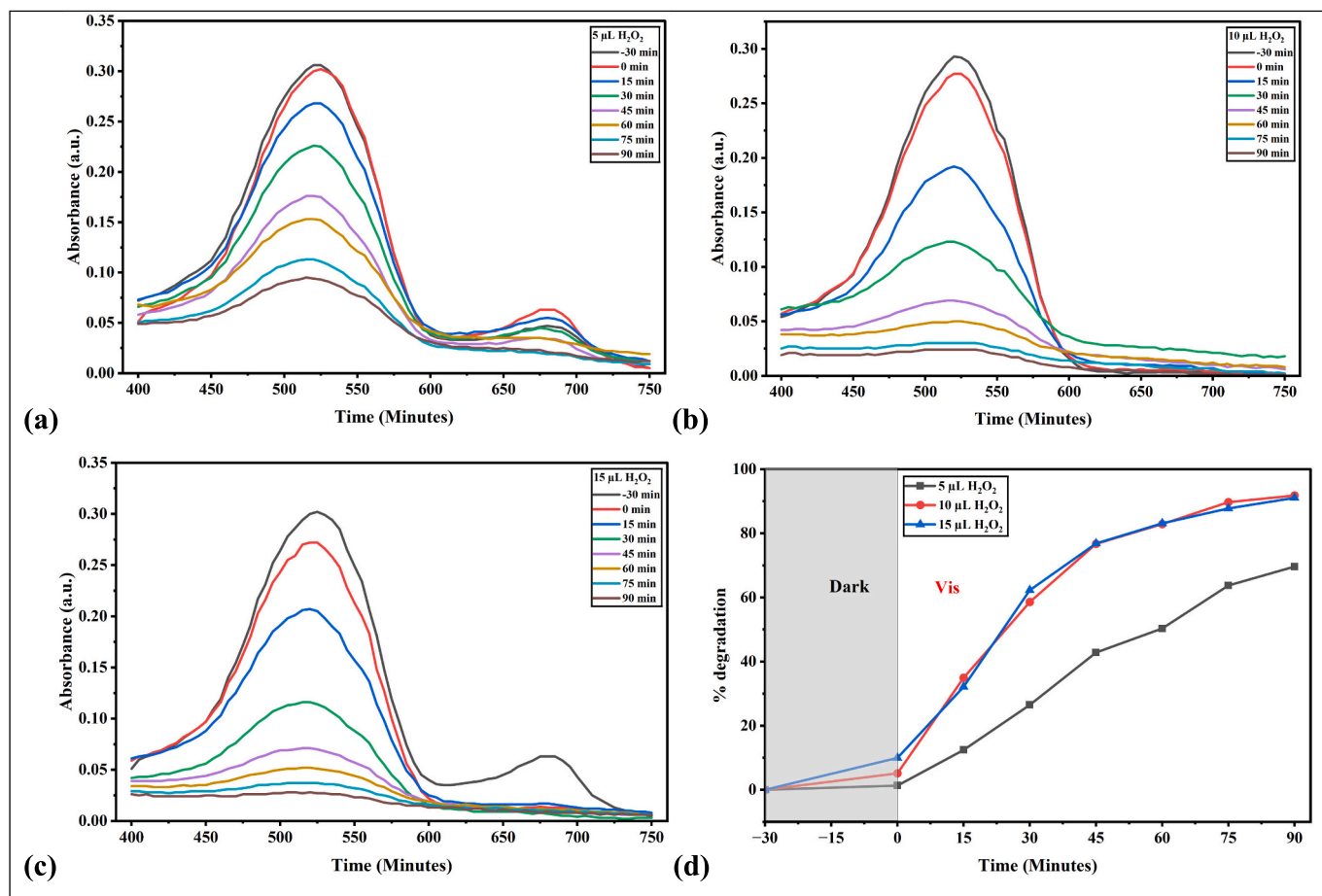


Fig. 15. UV-Vis absorbance spectra for AR27 dye degradation at different  $\text{H}_2\text{O}_2$  concentration of  $\text{NiFe}_2\text{O}_4/\text{WRB3}$  (a) 5  $\mu\text{L}$   $\text{H}_2\text{O}_2$ , (b) 10  $\mu\text{L}$   $\text{H}_2\text{O}_2$ , (c) 15  $\mu\text{L}$   $\text{H}_2\text{O}_2$ , (d) overall % degradation. Reaction conditions: catalyst dosage = 0.1 g/L, conc. of AR27 = 10 ppm, pH = 7.

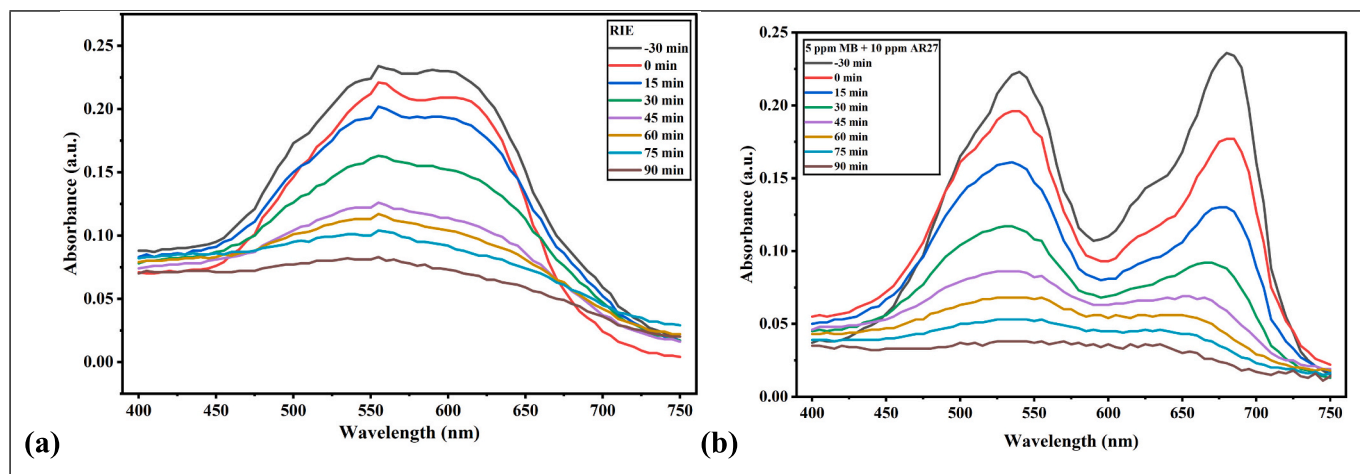


Fig. 16. UV-Visible absorbance spectra of (a) RIE and (b) mixture of dyes recorded under reaction conditions: 0.1 g/L  $\text{NiFe}_2\text{O}_4/\text{WRB3}$ , 0.1 mM  $\text{H}_2\text{O}_2$ , pH = 7.

### 3.5. Identification of ROS radical and proposed photo-Fenton degradation mechanism for MB and AR27 dye effluents

To determine the predominant ROS primarily responsible for the degradation of MB and AR27 dyes, photo-Fenton experiment for radical scavenger was performed using equimolar concentration of  $\text{AgNO}_3$  ( $e^-$  scavenger), KI ( $h^+$  scavenger), IPA ( $\cdot\text{OH}$  scavenger) and p-BQ ( $\cdot\text{O}_2^-$  scavenger). The rate of degradation by the effect of different scavengers

for 5 ppm MB and 10 ppm AR27 are shown in Fig. 19(a) and (b) respectively. The photo-Fenton degradation of MB and AR27 dyes without any scavengers observed to be 95% for 5 ppm MB and 91.43% for AR27 dyes using 0.1 g/L  $\text{NiFe}_2\text{O}_4/\text{WRB3}$ , 1 mM  $\text{H}_2\text{O}_2$  at pH 7. However, under similar conditions, the maximum decline in degradation efficiency to 40.99% was observed upon the addition of IPA while 43.71% on addition of  $\text{AgNO}_3$ . However, the lower decline in %degradation to 67.27% and 87.95% was observed on adding p-BQ and KI



**Table 4**

Reaction kinetics of photocatalytic MB dye degradation.

| Reaction parameters                                                                                                               | R <sup>2</sup> for 0th order | R <sup>2</sup> for 1st order | R <sup>2</sup> for 2nd order |
|-----------------------------------------------------------------------------------------------------------------------------------|------------------------------|------------------------------|------------------------------|
| <b>Effect of NiFe<sub>2</sub>O<sub>4</sub>/WRB catalyst load (g/L): 5 ppm MB, 1 mM H<sub>2</sub>O<sub>2</sub>, pH 7</b>           |                              |                              |                              |
| 0.05 g/L                                                                                                                          | 0.95296                      | 0.98603                      | 0.9837                       |
| 0.10 g/L                                                                                                                          | 0.90011                      | 0.98292                      | 0.98302                      |
| 0.15 g/L                                                                                                                          | 0.90223                      | 0.95849                      | 0.97769                      |
| <b>Effect of change in pH: 0.1 g/L NiFe<sub>2</sub>O<sub>4</sub>/WRB, 1 mM H<sub>2</sub>O<sub>2</sub>, 5 ppm MB</b>               |                              |                              |                              |
| pH 4                                                                                                                              | 0.97552                      | 0.9858                       | 0.98876                      |
| pH 7                                                                                                                              | 0.94826                      | 0.98292                      | 0.97002                      |
| pH 9                                                                                                                              | 0.99549                      | 0.99479                      | 0.95801                      |
| <b>Effect of MB dye concentration (in ppm): 0.1 g/L, NiFe<sub>2</sub>O<sub>4</sub>/WRB, 1 mM H<sub>2</sub>O<sub>2</sub>, pH 7</b> |                              |                              |                              |
| 5 ppm                                                                                                                             | 0.90272                      | 0.98292                      | 0.98024                      |
| 10 ppm                                                                                                                            | 0.99087                      | 0.99033                      | 0.91044                      |
| 15 ppm                                                                                                                            | 0.99317                      | 0.98678                      | 0.97287                      |
| <b>Effect of H<sub>2</sub>O<sub>2</sub> concentration: 0.1 g/L NiFe<sub>2</sub>O<sub>4</sub>/WRB, 5 ppm MB, pH 7</b>              |                              |                              |                              |
| 0.5 mM                                                                                                                            | 0.93892                      | 0.99093                      | 0.98093                      |
| 1.0 mM                                                                                                                            | 0.90272                      | 0.98292                      | 0.98024                      |
| 1.5 mM                                                                                                                            | 0.91443                      | 0.99289                      | 0.93658                      |

**Table 5**Rate constants 'k<sub>1</sub>' and half-life times 't<sub>1/2</sub>' values calculated using first-order kinetic model for degradation of MB dye in various reaction conditions.

| Reaction parameters                                                                                                              | R <sup>2</sup> | k <sub>1</sub> (min <sup>-1</sup> ) | t <sub>1/2</sub> (min) | % degradation, time (in minutes) |
|----------------------------------------------------------------------------------------------------------------------------------|----------------|-------------------------------------|------------------------|----------------------------------|
| <b>Effect of NiFe<sub>2</sub>O<sub>4</sub>/WRB catalyst load (g/L): 5 ppm MB, 1 mM H<sub>2</sub>O<sub>2</sub>, pH 7</b>          |                |                                     |                        |                                  |
| 0.05 g/L                                                                                                                         | 0.98603        | 0.009                               | 77                     | 82.01%, 90                       |
| 0.10 g/L                                                                                                                         | 0.98292        | 0.014                               | 49.5                   | 93.11%, 90                       |
| 0.15 g/L                                                                                                                         | 0.95849        | 0.011                               | 63                     | 85.77%, 90                       |
| <b>Effect of change in pH: 0.1 g/L NiFe<sub>2</sub>O<sub>4</sub>/WRB, 1 mM H<sub>2</sub>O<sub>2</sub>, 5 ppm MB</b>              |                |                                     |                        |                                  |
| pH 4                                                                                                                             | 0.9858         | 0.002                               | 346.5                  | 40.61%, 90                       |
| pH 7                                                                                                                             | 0.98292        | 0.014                               | 49.5                   | 93.11%, 90                       |
| pH 9                                                                                                                             | 0.99479        | 0.004                               | 173.25                 | 66.67%, 90                       |
| <b>Effect of MB dye concentration (in ppm): 0.1 g/L NiFe<sub>2</sub>O<sub>4</sub>/WRB, 1 mM H<sub>2</sub>O<sub>2</sub>, pH 7</b> |                |                                     |                        |                                  |
| 5 ppm                                                                                                                            | 0.98292        | 0.014                               | 49.5                   | 93.11%, 90                       |
| 10 ppm                                                                                                                           | 0.99033        | 0.007                               | 99                     | 82.63%, 90                       |
| 15 ppm                                                                                                                           | 0.98678        | 0.002                               | 346.5                  | 40.59%, 90                       |
| <b>Effect of H<sub>2</sub>O<sub>2</sub> concentration: 0.1 g/L NiFe<sub>2</sub>O<sub>4</sub>/WRB, 5 ppm MB, pH 7</b>             |                |                                     |                        |                                  |
| 0.5 mM                                                                                                                           | 0.99093        | 0.010                               | 69.3                   | 85.82%, 90                       |
| 1.0 mM                                                                                                                           | 0.98292        | 0.014                               | 49.5                   | 93.11%, 90                       |
| 1.5 mM                                                                                                                           | 0.99289        | 0.0144                              | 48.125                 | 94.19%, 90                       |

**Table 6**

Reaction kinetics of AR27 dye degradation.

| Reaction parameters                                                                                                                 | R <sup>2</sup> for 0th order | R <sup>2</sup> for 1st order | R <sup>2</sup> for 2nd order |
|-------------------------------------------------------------------------------------------------------------------------------------|------------------------------|------------------------------|------------------------------|
| <b>Effect of NiFe<sub>2</sub>O<sub>4</sub>/WRB catalyst load (g/L): 10 ppm AR27, 1 mM H<sub>2</sub>O<sub>2</sub>, pH 7</b>          |                              |                              |                              |
| 0.05 g/L                                                                                                                            | 0.94954                      | 0.99636                      | 0.95426                      |
| 0.10 g/L                                                                                                                            | 0.94974                      | 0.99723                      | 0.94398                      |
| 0.15 g/L                                                                                                                            | 0.95978                      | 0.99854                      | 0.9401                       |
| <b>Effect of change in pH: 0.1 g/L NiFe<sub>2</sub>O<sub>4</sub>/WRB, 1 mM H<sub>2</sub>O<sub>2</sub>, 10 ppm AR27</b>              |                              |                              |                              |
| pH 4                                                                                                                                | 0.98111                      | 0.97492                      | 0.96512                      |
| pH 7                                                                                                                                | 0.98271                      | 0.99723                      | 0.9773                       |
| pH 9                                                                                                                                | 0.98922                      | 0.98746                      | 0.98521                      |
| <b>Effect of AR27 dye concentration (in ppm): 0.1 g/L, NiFe<sub>2</sub>O<sub>4</sub>/WRB, 1 mM H<sub>2</sub>O<sub>2</sub>, pH 7</b> |                              |                              |                              |
| 5 ppm                                                                                                                               | 0.97199                      | 0.97399                      | 0.99447                      |
| 10 ppm                                                                                                                              | 0.96471                      | 0.99723                      | 0.92118                      |
| 15 ppm                                                                                                                              | 0.91473                      | 0.99671                      | 0.96272                      |
| <b>Effect of H<sub>2</sub>O<sub>2</sub> concentration: 0.1 g/L NiFe<sub>2</sub>O<sub>4</sub>/WRB, 10 ppm AR27, pH 7</b>             |                              |                              |                              |
| 0.5 mM                                                                                                                              | 0.99554                      | 0.99207                      | 0.95302                      |
| 1.0 mM                                                                                                                              | 0.95037                      | 0.99723                      | 0.93878                      |
| 1.5 mM                                                                                                                              | 0.95003                      | 0.99555                      | 0.95584                      |

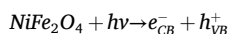
respectively. These results revealed that •OH prominently responsible for degradation of MB followed by •O<sub>2</sub><sup>-</sup> and e<sup>-</sup> whereas h<sup>+</sup> does not affect the degradation at all. In case of AR27, the highest decline in degradation to 19.21% was observed on addition of IPA while 19.87% on adding KI. The minimal decline in degradation to 90.75% and

**Table 7**Rate constants 'k<sub>1</sub>' and half-life times 't<sub>1/2</sub>' values calculated using first-order kinetic model for degradation of AR27 dye in various reaction conditions.

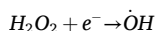
| Reaction parameters                                                                                                              | R <sup>2</sup> | k <sub>1</sub> (min <sup>-1</sup> ) | t <sub>1/2</sub> (min) | % degradation, time (in minutes) |
|----------------------------------------------------------------------------------------------------------------------------------|----------------|-------------------------------------|------------------------|----------------------------------|
| <b>Effect of NiFe<sub>2</sub>O<sub>4</sub>/WRB catalyst load (g/L): 10 ppm AR27, 1 mM H<sub>2</sub>O<sub>2</sub>, pH 7</b>       |                |                                     |                        |                                  |
| 0.05 g/L                                                                                                                         | 0.99636        | 0.0120                              | 57.75                  | 90.54%, 90                       |
| 0.10 g/L                                                                                                                         | 0.99723        | 0.012                               | 57.75                  | 91.33%, 90                       |
| 0.15 g/L                                                                                                                         | 0.99854        | 0.010                               | 69.3                   | 87.90%, 90                       |
| <b>Effect of change in pH: 0.1 g/L NiFe<sub>2</sub>O<sub>4</sub>/WRB, 1 mM H<sub>2</sub>O<sub>2</sub>, 10 ppm AR27</b>           |                |                                     |                        |                                  |
| pH 4                                                                                                                             | 0.97492        | 0.001                               | 693                    | 34.48%, 90                       |
| pH 7                                                                                                                             | 0.99723        | 0.012                               | 57.75                  | 91.33%, 90                       |
| pH 9                                                                                                                             | 0.98746        | 0.0067                              | 103.4                  | 13.35%, 90                       |
| <b>Effect of MB dye concentration (in ppm): 0.1 g/L NiFe<sub>2</sub>O<sub>4</sub>/WRB, 1 mM H<sub>2</sub>O<sub>2</sub>, pH 7</b> |                |                                     |                        |                                  |
| 5 ppm                                                                                                                            | 0.97399        | 0.013                               | 53.3                   | 87.26%, 90                       |
| 10 ppm                                                                                                                           | 0.99723        | 0.012                               | 57.75                  | 91.33%, 90                       |
| 15 ppm                                                                                                                           | 0.99671        | 0.009                               | 77                     | 80.85%, 90                       |
| <b>Effect of H<sub>2</sub>O<sub>2</sub> concentration: 0.1 g/L NiFe<sub>2</sub>O<sub>4</sub>/WRB, 10 ppm AR27, pH 7</b>          |                |                                     |                        |                                  |
| 0.5 mM                                                                                                                           | 0.99207        | 0.005                               | 138.6                  | 69.20%, 90                       |
| 1.0 mM                                                                                                                           | 0.99723        | 0.012                               | 57.75                  | 91.33%, 90                       |
| 1.5 mM                                                                                                                           | 0.99555        | 0.011                               | 63                     | 90.07%, 90                       |

67.13% were observed in case of AgNO<sub>3</sub> and p-BQ. Hence, the scavenger study for AR27 also shows that •OH was mainly responsible for degradation followed by h<sup>+</sup> and •O<sub>2</sub><sup>-</sup> while e<sup>-</sup> does not participate in degradation of AR27 dye pollutants.

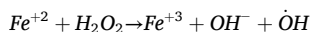
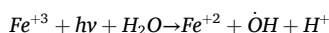
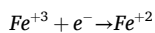
The photo-Fenton degradation can be proposed by the possible chemical interactions of MB and AR27 dyes with ROS and surface functional groups as represented in Fig. 20. The photocatalytic activity of NiFe<sub>2</sub>O<sub>4</sub>/WRB nanocomposite originated by the interaction of NiFe<sub>2</sub>O<sub>4</sub> and WRB. The porous structure of WRB supports NiFe<sub>2</sub>O<sub>4</sub> and acts as an electron acceptor that enhances the charge separation and prevents the rapid recombination of photogenerated electron-hole pairs. Upon incident of photon from visible irradiation, the absorption of visible light by NiFe<sub>2</sub>O<sub>4</sub> due to narrow band gap of 1.62 eV, the electrons (e<sup>-</sup>) in the valence band (VB) of NiFe<sub>2</sub>O<sub>4</sub> gets excited and migrated to the conduction band (CB) leaving holes (h<sup>+</sup>) in valence band.



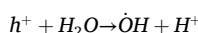
The photogenerated electrons from CB of NiFe<sub>2</sub>O<sub>4</sub> migrated to the biochar (WRB). WRB acts as an electron reservoir and therefore prevent the rapid recombination of electrons-holes while also increases the charge separation and enhances photodegradation. These electrons in WRB reacts with H<sub>2</sub>O<sub>2</sub> to generate hydroxyl (•OH) radicals.



On the other hand, the migrated electrons and visible light enhances the regeneration of Fe<sup>+2</sup> in catalytic redox cycle of Fe<sup>+2</sup>/Fe<sup>+3</sup> that activates H<sub>2</sub>O<sub>2</sub> and continuously produces •OH radicals,

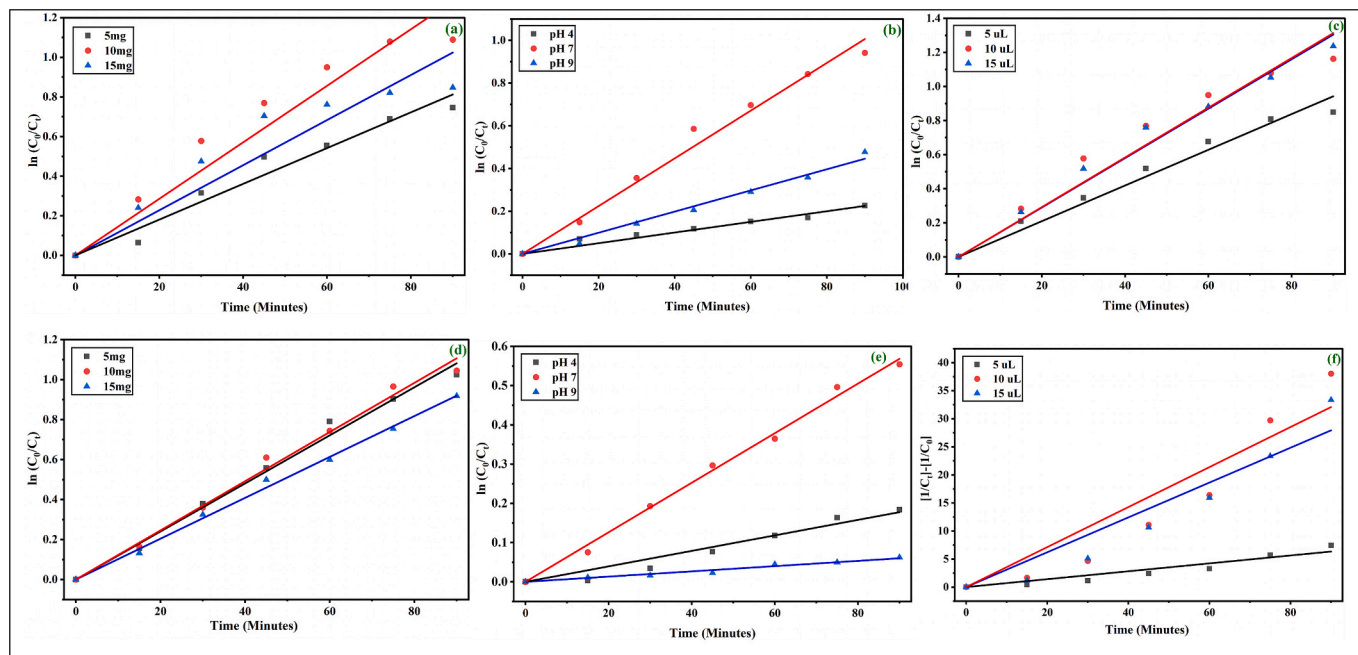


while the h<sup>+</sup> in valence band also oxidizes H<sub>2</sub>O or surface hydroxyl group to generate •OH radicals.



These hydroxyl (•OH) attack MB and AR27 dye molecules and initiate the azo bond cleavage to breakdown in smaller intermediates and mineralizes to produce harmless H<sub>2</sub>O and CO<sub>2</sub>.

To understand the charge separation process, following equations have been used to calculate the E<sub>VB</sub> and E<sub>CB</sub> of NiFe<sub>2</sub>O<sub>4</sub>,

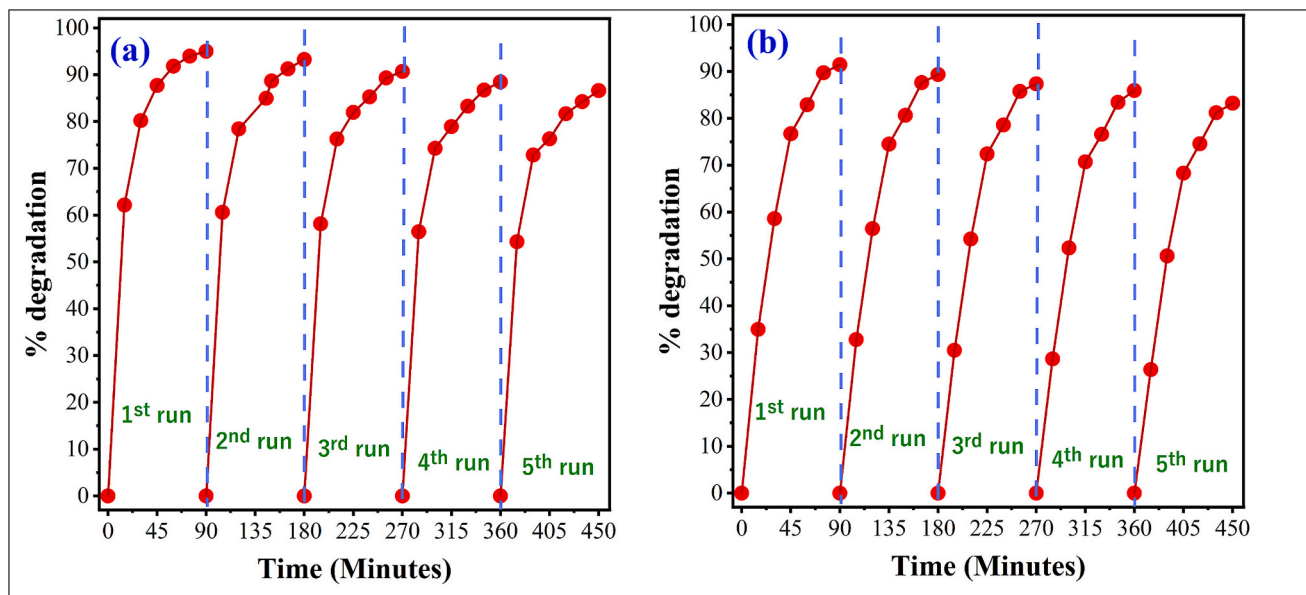


**Fig. 17.** First-order kinetic model applied to different reaction conditions: Variation in  $\text{NiFe}_2\text{O}_4/\text{WRB}$  dosage, pH conditions and  $\text{H}_2\text{O}_2$  concentration for (a–c) MB dye and (d–f) AR27 dye degradation.

**Table 8**

Comparison of dye removal efficiency of reported  $\text{NiFe}_2\text{O}_4/\text{Biochar}$  nanocomposites.

| Catalyst                                                   | Synthesis method   | Catalyst dosage (g/L) | Dye pollutant     | Initial dye conc. (ppm) | Irradiation source | pH | Reaction Time | %dye removal | Ref.      |
|------------------------------------------------------------|--------------------|-----------------------|-------------------|-------------------------|--------------------|----|---------------|--------------|-----------|
| $\text{NiFe}_2\text{O}_4/\text{Ag}_3\text{PO}_4/\text{BC}$ | Hydrothermal       | 2.6                   | MB                | 10                      | Vis                | 7  | 90            | 94           | [20]      |
| $\text{NiFe}_2\text{O}_4/\text{AC}$                        | Hydrothermal       | 1.0                   | RhB               | 10                      | Vis                | 7  | 90            | 99.7         | [21]      |
| $\text{NiFe}_2\text{O}_4/\text{BC}$                        | One-step pyrolysis | 2.0                   | RhB               | 4                       | UV                 | 3  | 30            | 99.9         | [22]      |
| $\text{NiFe}_2\text{O}_4@\text{AC}$                        | Hydrothermal       | 0.1                   | RhB               | 10                      | Dark               | 6  | 360           | 96.58        | [38]      |
|                                                            |                    |                       | MO                |                         |                    |    |               | 94.47        |           |
|                                                            |                    |                       | MR                |                         |                    |    |               | 96.45        |           |
| $\text{NiFe}_2\text{O}_4/\text{WRB}$                       | Hydrothermal       | 1.0                   | MB                | 5                       | Vis                | 7  | 90            | 95           | This Work |
|                                                            |                    |                       | AR27 <sup>a</sup> | 10                      |                    |    |               | 91.43        |           |



**Fig. 18.** Reusability study of  $\text{NiFe}_2\text{O}_4/\text{WRB3}$  nanocomposite over five successive photo-Fenton cycle (a) 5 ppm MB (b) 10 ppm AR27.

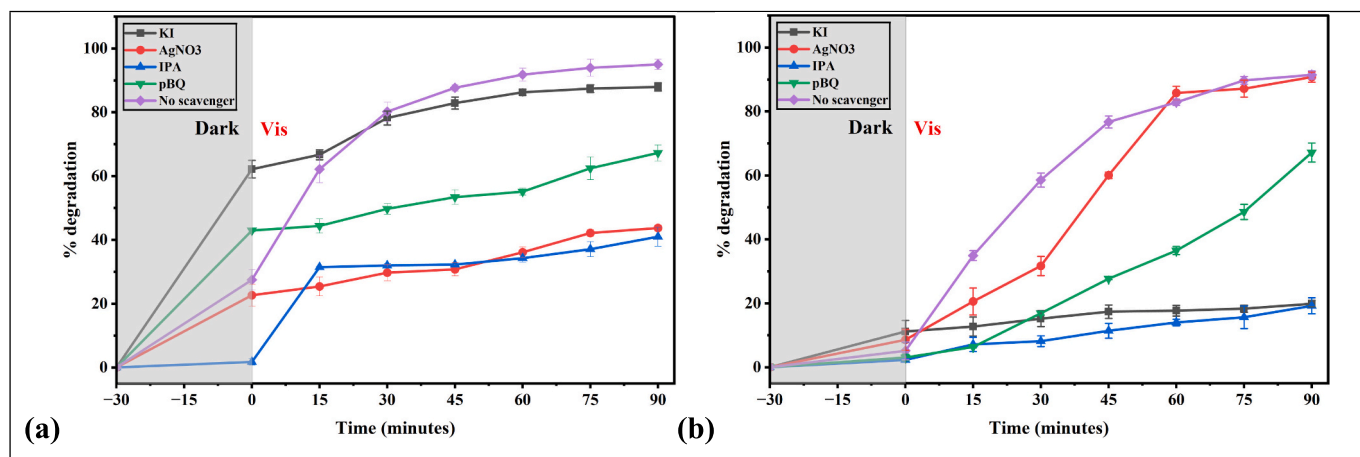


Fig. 19. Effect of different scavengers on degradation of (a) MB and (b) AR27 dye effluents in photo-Fenton process at reaction conditions: 0.1 g/L  $\text{NiFe}_2\text{O}_4/\text{WRB3}$ , 1 mM  $\text{H}_2\text{O}_2$  and pH = 7.

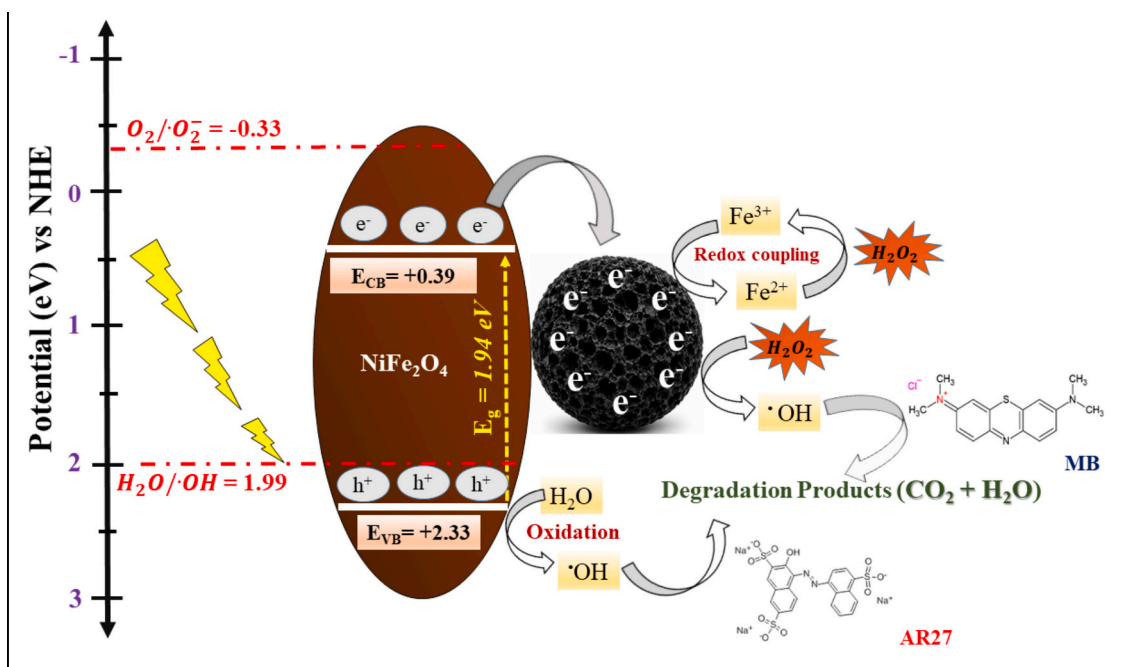


Fig. 20. Proposed photo-Fenton degradation mechanism for MB and AR27 dyes over  $\text{NiFe}_2\text{O}_4/\text{WRB}$  nanocomposite.

$$E_{VB} = X - E_e + 0.5 E_g$$

$$E_{CB} = E_{VB} - E_g$$

where  $X$  is the absolute electronegativity of  $\text{NiFe}_2\text{O}_4$  while  $E_e$  is the energy of free  $e^-$  on hydrogen scale (4.50 eV) and  $E_g$  is the band gap energy (eV) of  $\text{NiFe}_2\text{O}_4/\text{WRB3}$  photocatalyst. Absolute electronegativity of  $\text{NiFe}_2\text{O}_4$  ( $X = 5.86$  eV) and free electron energy on hydrogen scale ( $E_e = 4.50$  eV) has been considered for the calculation. The band gap of  $\text{NiFe}_2\text{O}_4/\text{WRB3}$  calculated as 1.94 eV while band gap of pure  $\text{NiFe}_2\text{O}_4$  was 1.62 eV. In general, Biochar does not possess fixed CB and VB positions like  $\text{NiFe}_2\text{O}_4$  as it is amorphous carbonaceous material with  $sp^2/sp^3$  hybridised carbon, surface defects and oxy-functional groups. The  $E_{CB}$  was calculated and found to be +0.39 eV for  $\text{NiFe}_2\text{O}_4/\text{WRB3}$  while it was +0.55 eV for  $\text{NiFe}_2\text{O}_4$  and hence shifted upward. Similarly, the  $E_{VB}$  was calculated as 2.33 eV for  $\text{NiFe}_2\text{O}_4/\text{WRB3}$  while it was +2.17 eV for pristine  $\text{NiFe}_2\text{O}_4$ . Since the oxidation potential for hydroxyl radical generation ( $\text{H}_2\text{O}/\cdot\text{OH}$ ) is 1.99 eV vs NHE and reduction potential for

$\text{O}_2/\cdot\text{O}_2^-$  is  $-0.33$  eV vs NHE but as  $E_{CB}$  (+0.39) was found to be greater than  $-0.33$ , so the  $e^-$  in CB was inefficient to convert dissolved  $\text{O}_2$  into radicals  $\cdot\text{O}_2^-$  while  $E_{VB}$  (+2.33) found to be greater than +1.99, hence the photogenerated holes could efficiently generate hydroxyl radicals. Therefore, among all the ROS, the hydroxyl radicals found to be primarily responsible for the degradation of MB and AR27 dye pollutants.

#### 4. Conclusion

In the present work, magnetic nanocomposites  $\text{NiFe}_2\text{O}_4/\text{WRB}$  were synthesized using hydrothermal method and utilized in the photo-Fenton degradation of MB, AR27 and RIE. The structural, optical and morphological properties were investigated for the synthesized  $\text{NiFe}_2\text{O}_4/\text{WRB}$  nanocomposites. Different amount of WRB was employed to support  $\text{NiFe}_2\text{O}_4$  and their corresponding band gap was measured by UV-DRS, which found the highest band gap of 1.94 eV for  $\text{NiFe}_2\text{O}_4/\text{WRB3}$  while the lowest band gap of 1.68 eV for  $\text{NiFe}_2\text{O}_4/\text{WRB1}$ . The crystallite size of 7.35 nm and high specific surface ( $187.63 \text{ m}^2/\text{g}$ ) as



well as the band gap (1.94 eV) of NiFe<sub>2</sub>O<sub>4</sub>/WRB3 nanocomposite accounted for enhanced charge separation efficiency and faster photo-degradation of MB and AR27 dye pollutants. From the synthesized NiFe<sub>2</sub>O<sub>4</sub>/WRB nanocomposites, NiFe<sub>2</sub>O<sub>4</sub>/WRB3 exhibited the better performance due to the fact that the increase of biochar amount in NiFe<sub>2</sub>O<sub>4</sub>/WRB prevents the agglomeration of NiFe<sub>2</sub>O<sub>4</sub> nanoparticles (NPs) by enhancing the interaction of NPs with the surface functional group of biochar. The photo-Fenton process revealed the excellent photocatalytic activity of NiFe<sub>2</sub>O<sub>4</sub>/WRB3, achieving maximum degradation of 95% of 5 ppm MB and 91.43% for 10 ppm AR27 while 64.52% of RIE and 87.6% for mixed dyes within 90 min of visible irradiation using 0.1 g/L catalyst dosage and 1 mM H<sub>2</sub>O<sub>2</sub> at pH 7.0 ± 0.01. The reaction kinetics revealed that under optimum photo-Fenton experimental conditions, all degradation reactions are described and best fitted in first-order model with R<sup>2</sup> > 0.95 compared to zero-order and second-order reaction kinetics. Additionally, the reusability studies demonstrated good chemical stability of NiFe<sub>2</sub>O<sub>4</sub>/WRB3 nanocomposite by retaining more than 80% degradation efficiency even after the fifth cycle for both MB and AR27 dyes. Radical scavenger studies further determine the dominant reactive species and found •OH radicals primarily responsible for the photo-Fenton degradation of both MB and AR27 dyes. Overall, the synthesized NiFe<sub>2</sub>O<sub>4</sub>/WRB nanocomposites exhibit outstanding photocatalytic degradation efficiency, chemical stability and recyclability as compared to pure NiFe<sub>2</sub>O<sub>4</sub>. Therefore, NiFe<sub>2</sub>O<sub>4</sub>/WRB nanocomposites can be utilized as an eco-friendly, cost-effective and sustainable materials for wastewater treatment. Future studies should focus on large scale implication of these materials for treatment of real industrial wastewater through optimized continuous-flow photocatalytic reactor. Furthermore, the life-cycle assessment (LCA) and economic analysis need to be performed for large-scale treatment of diversified pollutants including pharmaceutical waste and pesticides.

### CRedit authorship contribution statement

**Hozefa Dhila:** Writing – original draft, Investigation, Formal analysis, Data curation. **Abhishek Bhapkar:** Validation, Resources, Formal analysis, Data curation. **Shekhar Bhame:** Validation, Supervision, Project administration, Conceptualization.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.rechem.2026.103770>.

### Data availability

Data will be made available on request.

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