

POLYANILINE-BISMUTH FERRITE NANOCOMPOSITE PHOTOCATALYST IMMOBILIZED ON LIQUID NATURAL RUBBER AS INTEGRATED ADSORBENTS-PHOTOCATALYST FOR REMOVAL OF CIPROFLOXACIN ANTIBIOTIC

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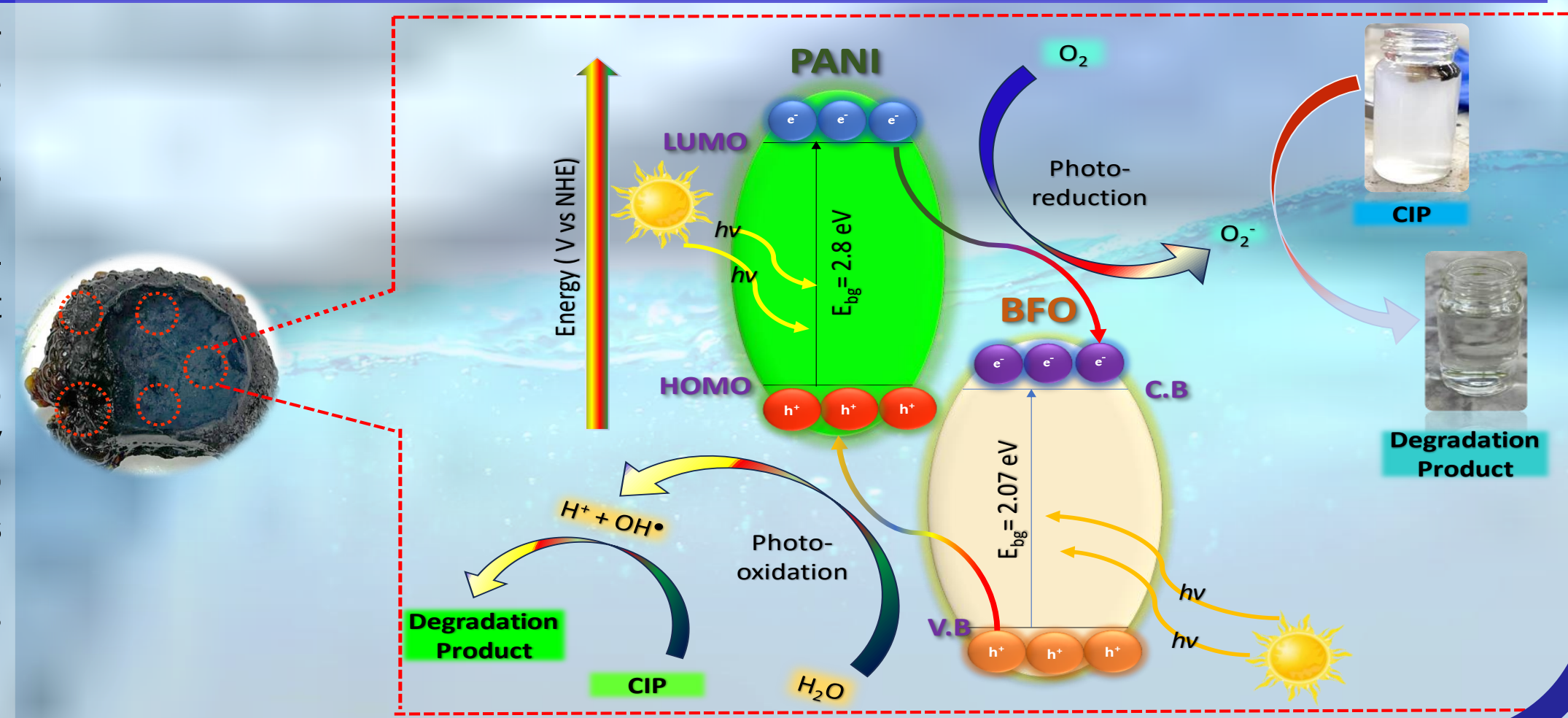
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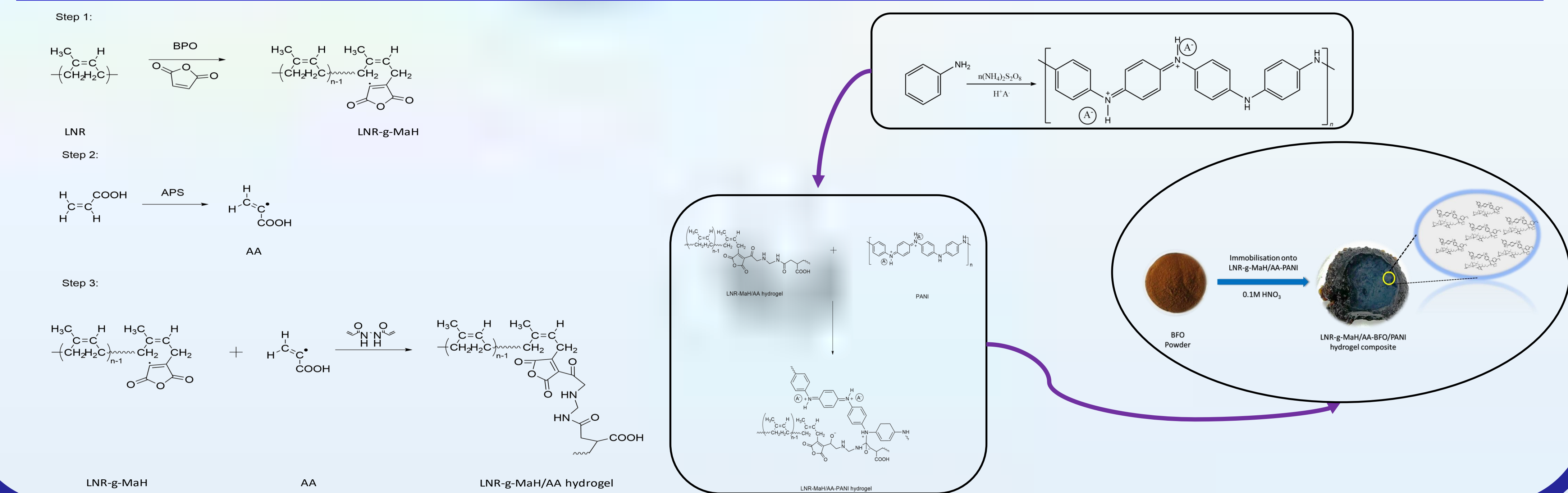


Introduction

A hydrogel-based photocatalyst was employed to remove ciprofloxacin (CIP) from wastewater using a liquid natural rubber (LNR) /bismuth ferrite (BFO) hydrogel composite with the incorporation of the chromophore, polyaniline (PANI), as a conductive polymer. Maleic anhydride (MaH) was added as the crosslinking agent while acrylic acid (AA) enhanced the gelation process of the hydrogel composite. Response surface methodology (RSM) was used to optimize several parameters for the synthesis of the hydrogel composite and to monitor the adsorptive-photodegradation process. By monitoring the UV absorbance of CIP, without a post-treatment separation phase, the synthesized LNR-g-MaH/AA-PANI/BFO hydrogel composite showed astounding performance with up to 95% removal efficiency. The hydrogel composite was able to maintain extraction for up to ten cycles, indicating stability. Furthermore, CIP was adsorbed very rapidly under sunlight irradiation compared to removal under dark conditions, indicating that BFO and PANI caused photodegradation. Electron paramagnetic resonance (EPR) spectroscopy was used to monitor intrinsic paramagnetic centres during photocatalysis. Further EPR-spin trapping experiments were used to identify reactive oxygen species generated during photolysis as evidence of the mechanism of action. The results show potential for the new hydrogel nanohybrid to improve the performance of wastewater treatment systems.



Research Methodology



Conclusions/ Outlook

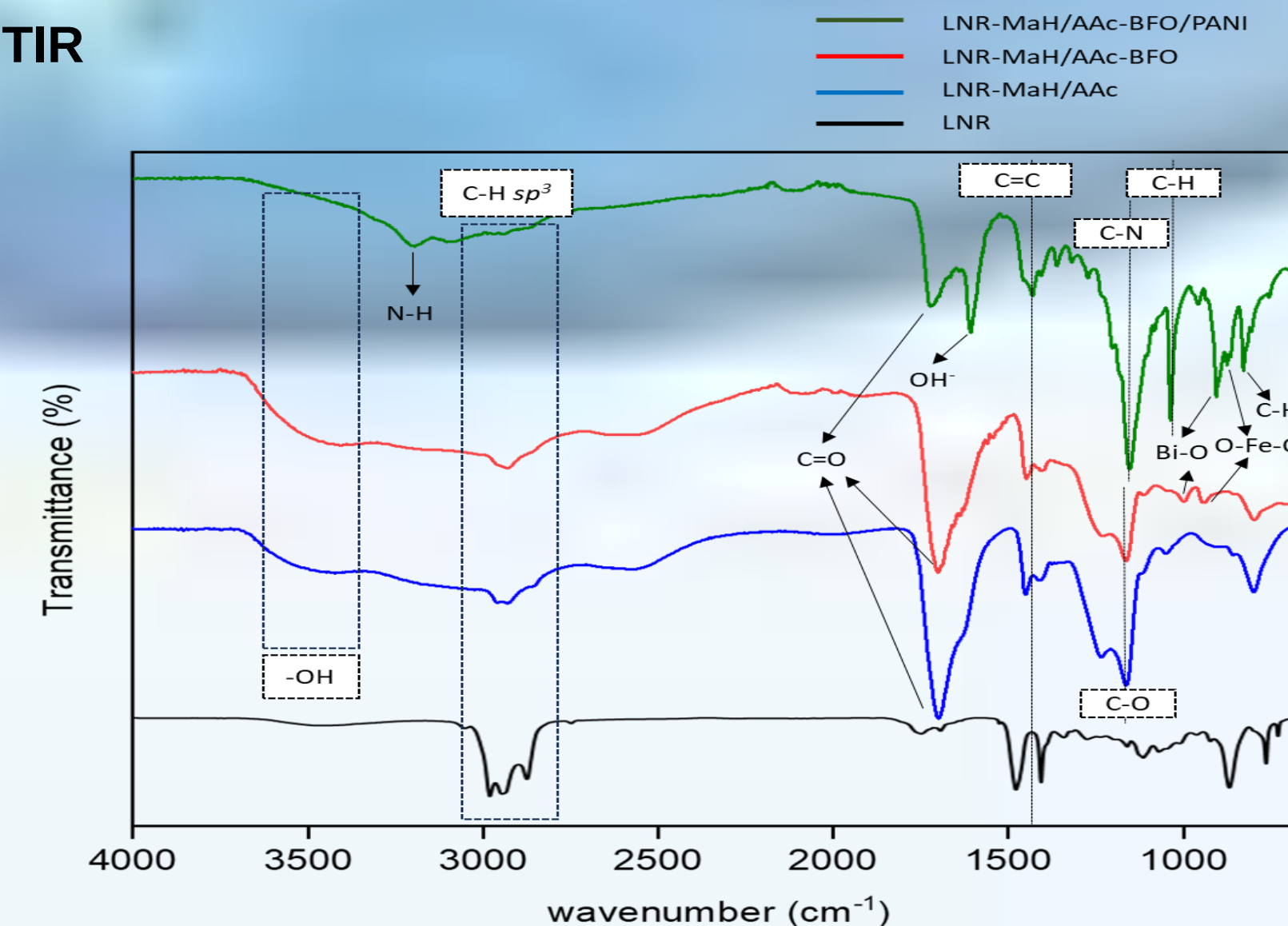
- Pristine BFO has magnetic anisotropy based on the asymmetric line shape of the EPR signal with g value of 2.11.
- The hydrogel composite exhibits a sharp EPR signal with a g value of 1.94, which may be indicative of pristine BFO stabilized through immobilization within liquid natural rubber.
- TEM and SEM images showed the presence of pores that aid in the adsorption process while the agglomeration proved the immobilization of BFO by comparison of studies from various authors.
- Reusability studies showed stability of the hydrogel composite with a great percentage of antibiotic removal.
- Future work will focus on the efficiency of the hydrogel composite by performing kinetic, isotherm, and thermodynamics studies. Cyclic voltammetry tests will be performed to understand the conductivity of the hydrogel composite due to the inclusion of PANI as the conducting polymer.

References

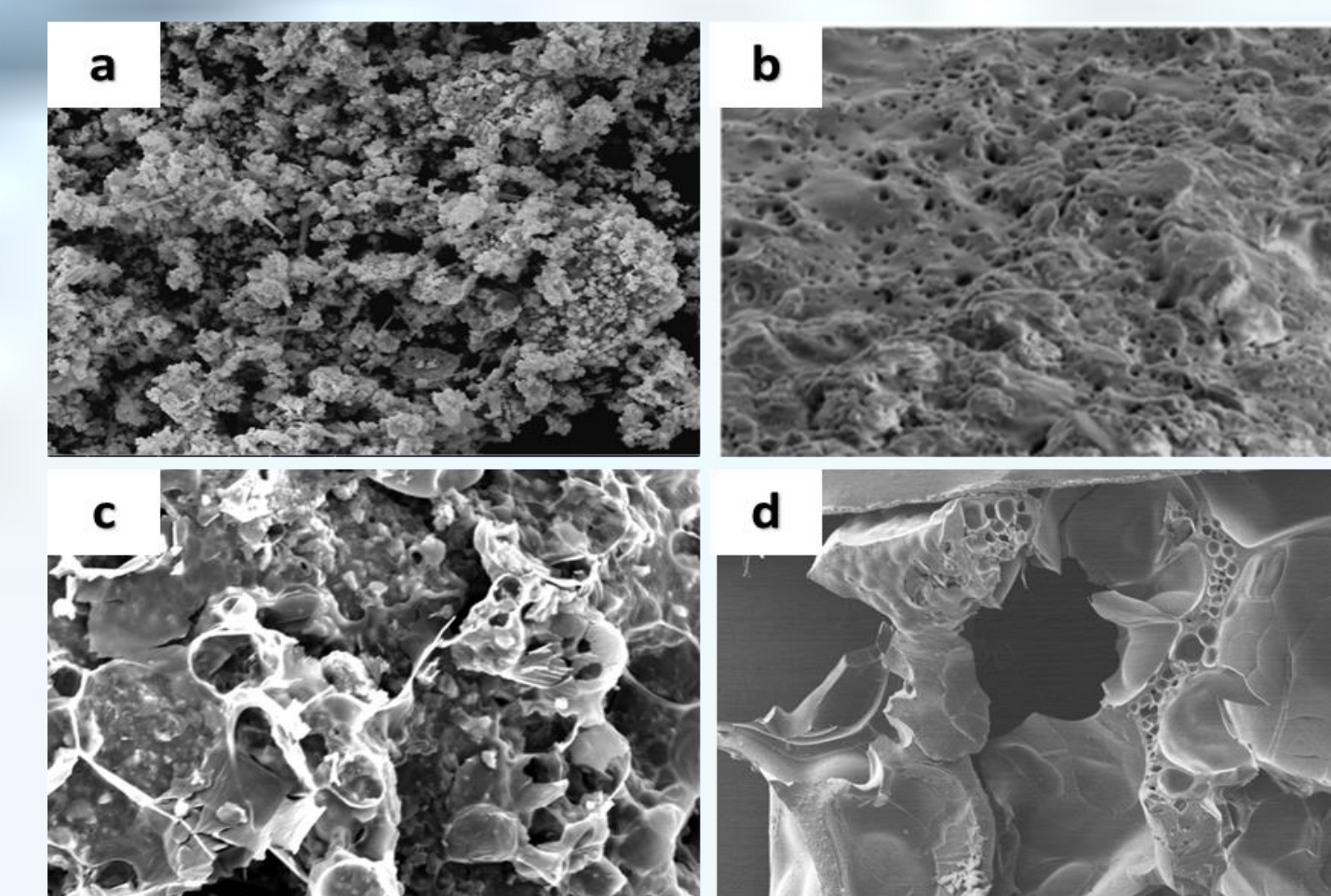
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Results

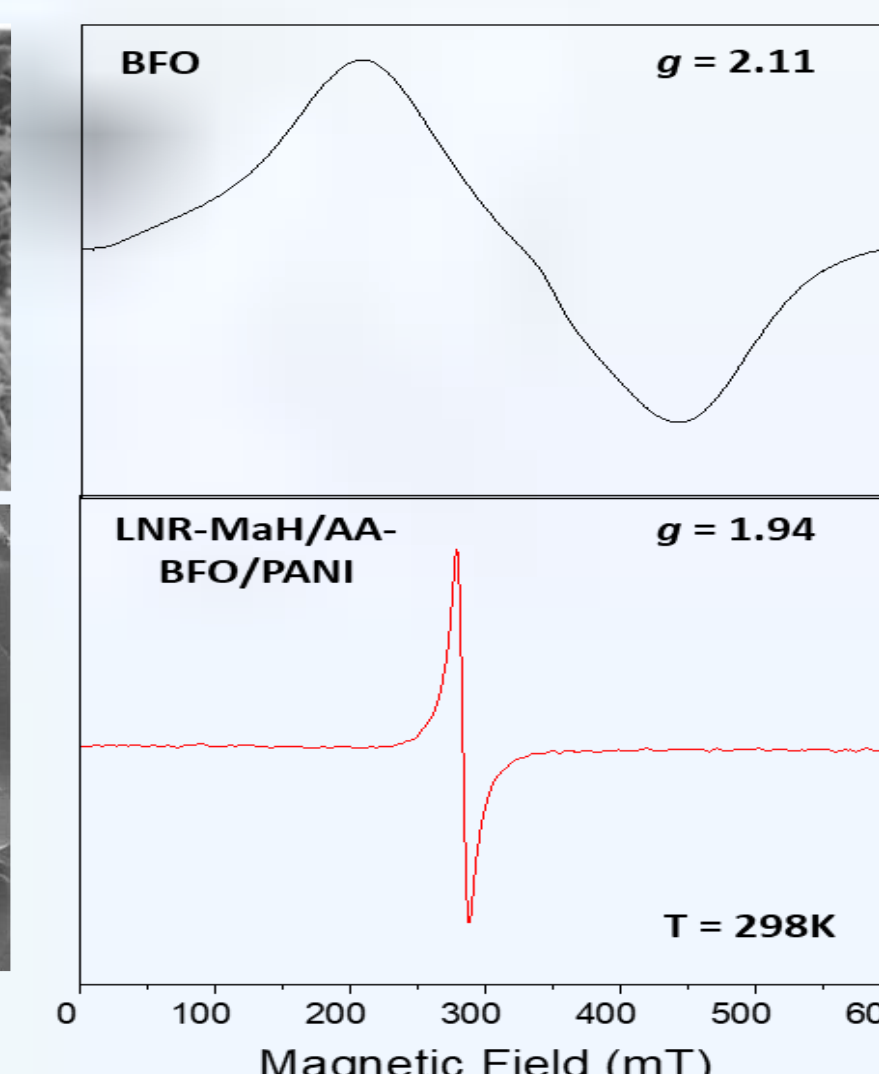
FTIR



SEM –EDX IMAGES



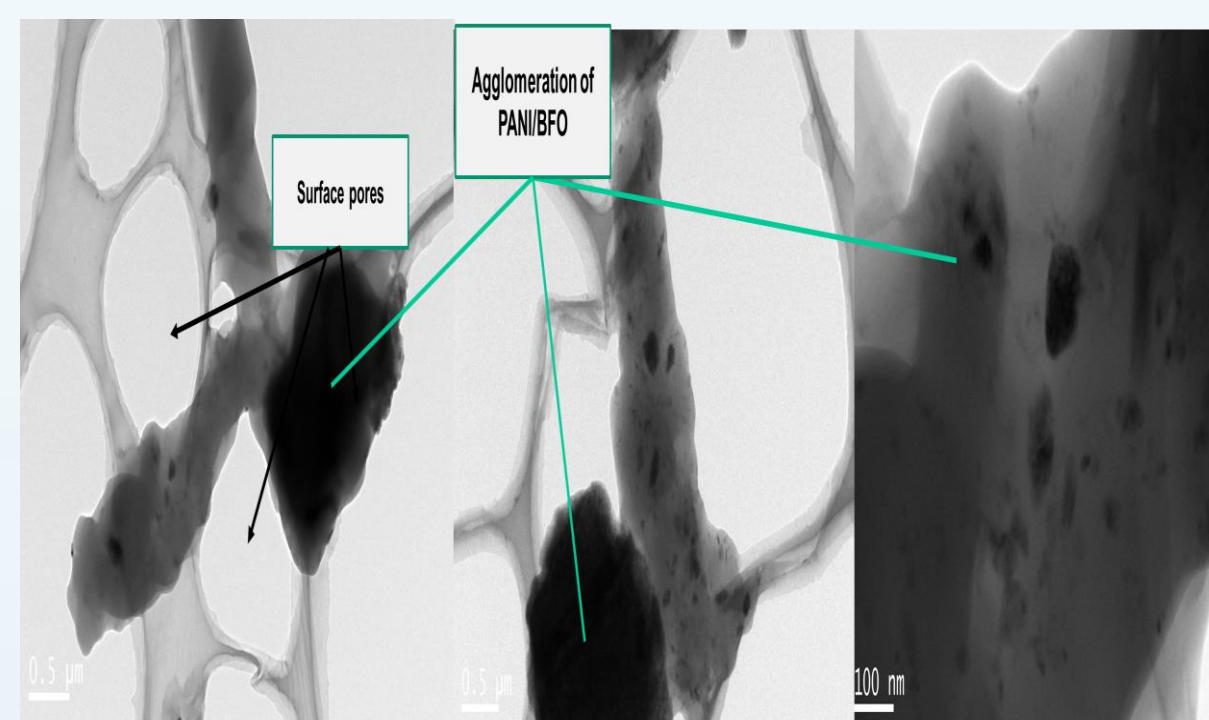
EPR SPECTROSCOPY



The pristine BFO exhibits an asymmetric line shape, characteristic of samples having magnetic anisotropy. The spectrum features a shoulder at ~350 mT. This indicates an anisotropy of the g value or anisotropy in the exchange fields. A possible explanation of the observed EPR spectrum involves unpaired electrons trapped by vacancies or defects, which is supported a g value slightly larger than 2 (2.11). It should also be noted that the existence of a Fe³⁺ defect complex generated at elevated temperatures during the synthesis, provides local 3d moments. These local magnetic moments may be involved in ferromagnetic behavior.

The EPR spectrum of the hydrogel composite at room temperature is strong, with $g = 1.94$, and can be well described with a single Lorentzian line. Our results show that the hydrogel composite holds a g value lower than 2, which is indicative of the electron configuration and requires further investigation.

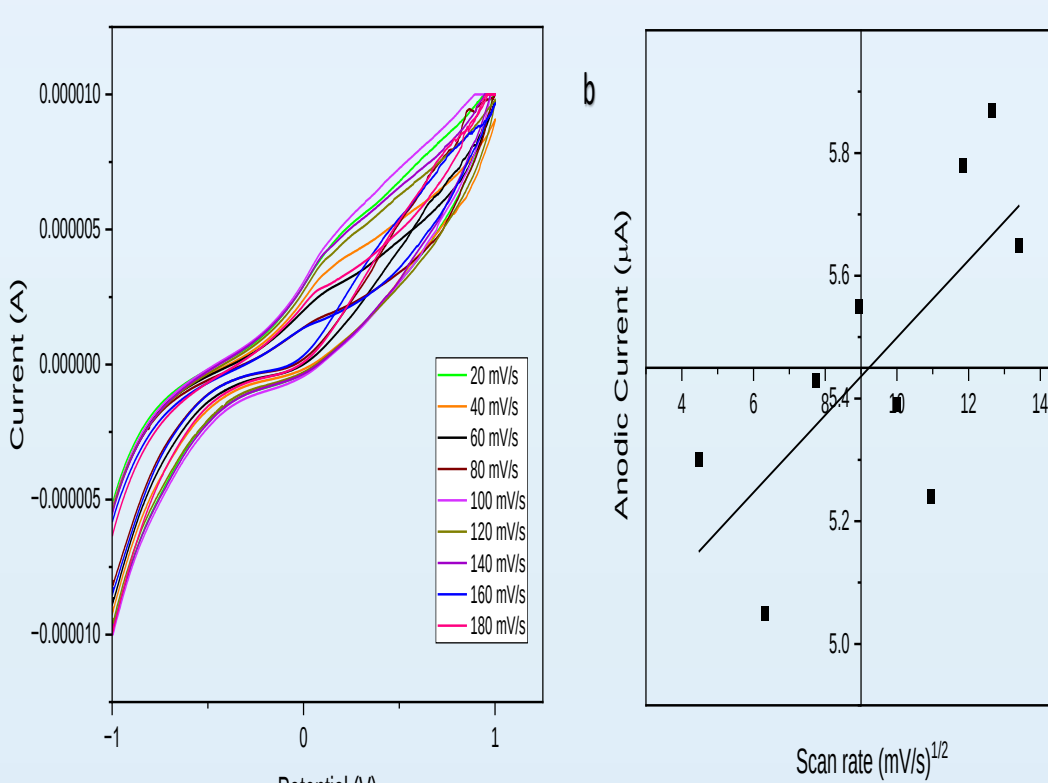
TEM IMAGES



- Transmission Electron Microscopy (TEM) images of the hydrogel composite are shown at 500x and 100x nm magnification.
- A certain agglomeration can be seen in the images that indicate the presence of PANI and BFO photocatalyst.

According to Cui *et al.*, (2018), PANI has the tendency to agglomerate, which is confirmed by the TEM images. Furthermore, the large pores that can be observed through the images further prove the presence of active sites for the adsorption of CIP antibiotics. SEM images support this finding.

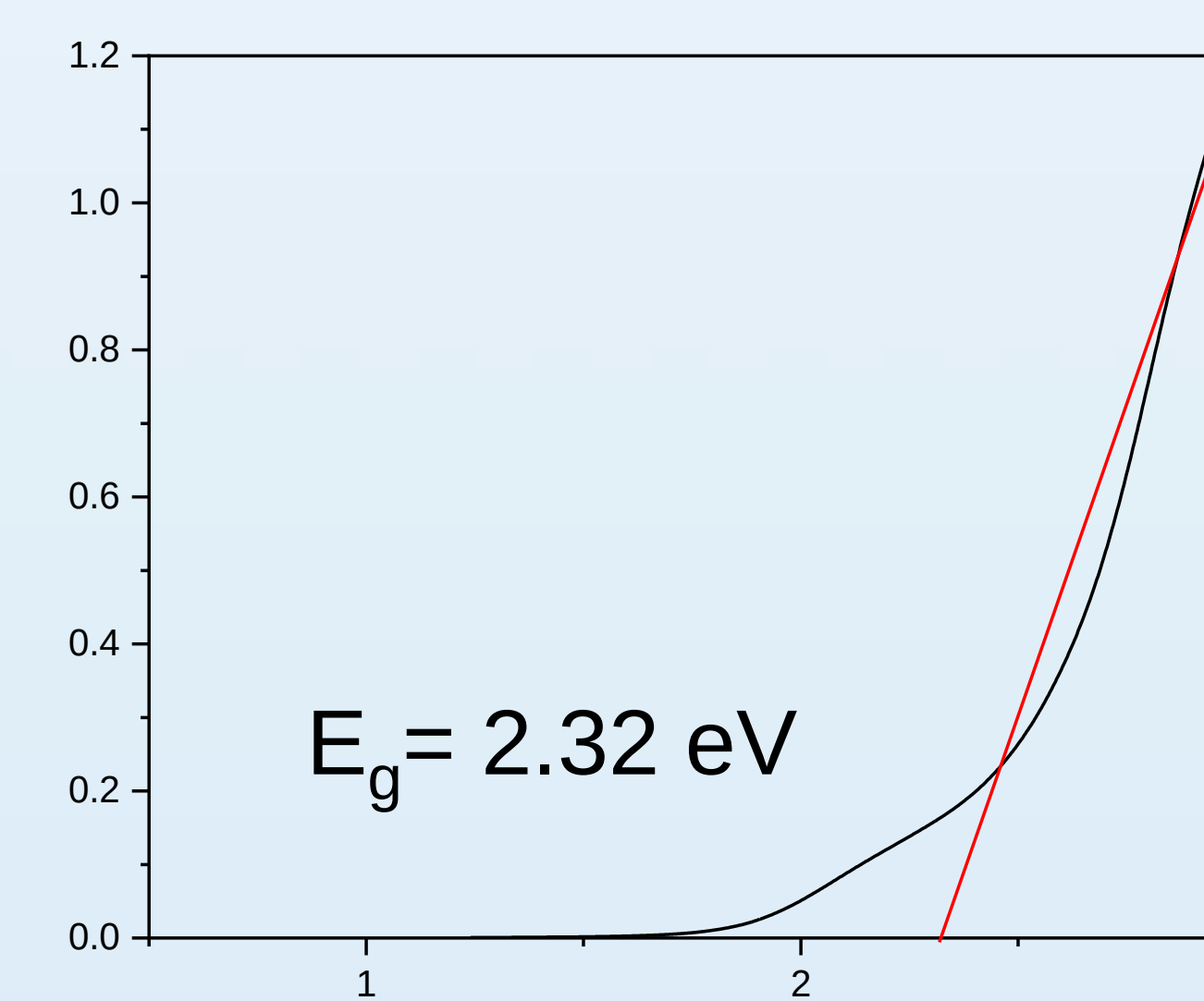
ELECTROCHEMISTRY ANALYSIS



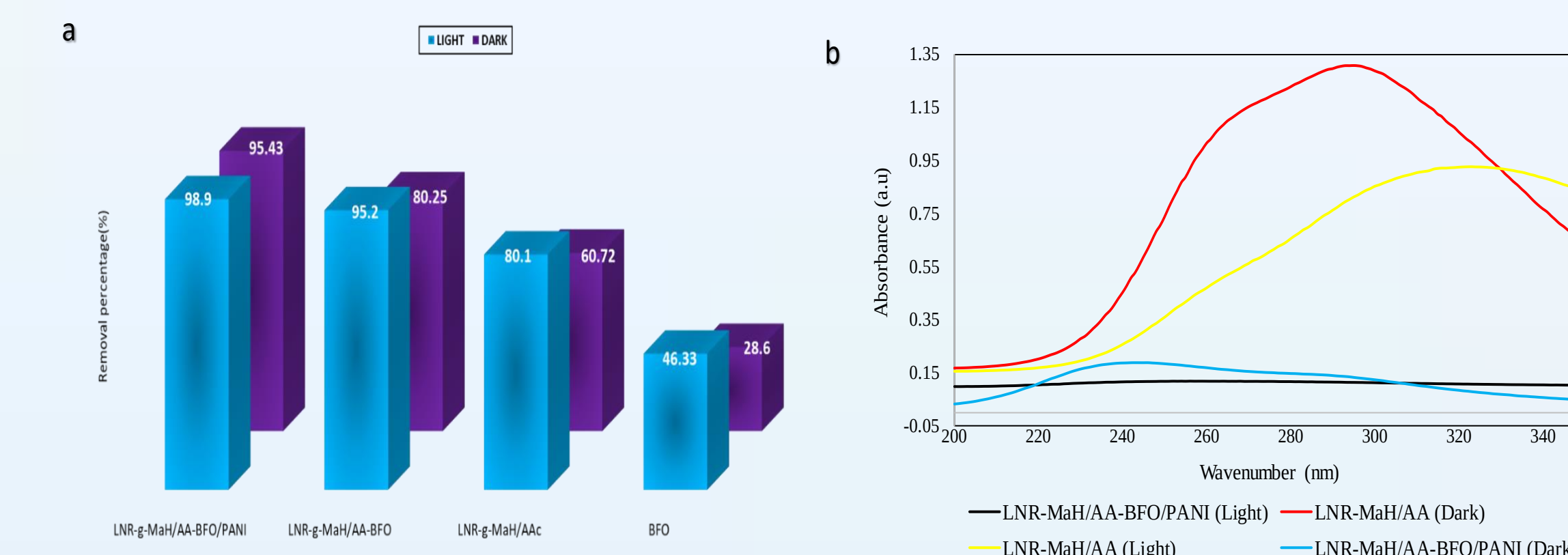
- The reduction peak exhibited a lesser magnitude compared to the oxidation peak, so providing evidence for the presence of polyaniline (PANI) in the LNR-MaH/AA-BFO/PANI hydrogel composite, which demonstrates its electrostatic conductivity.
- The anodic waves as shown in figure, exhibited a shift towards more positive potentials, suggesting the occurrence of an irreversible process.

The presence of a poorly defined anodic wave at elevated scan rates in the LNR-MaH/AA-BFO/PANI system implies that the oxidation process was likely governed by diffusion (Pollap *et al.*, 2020).

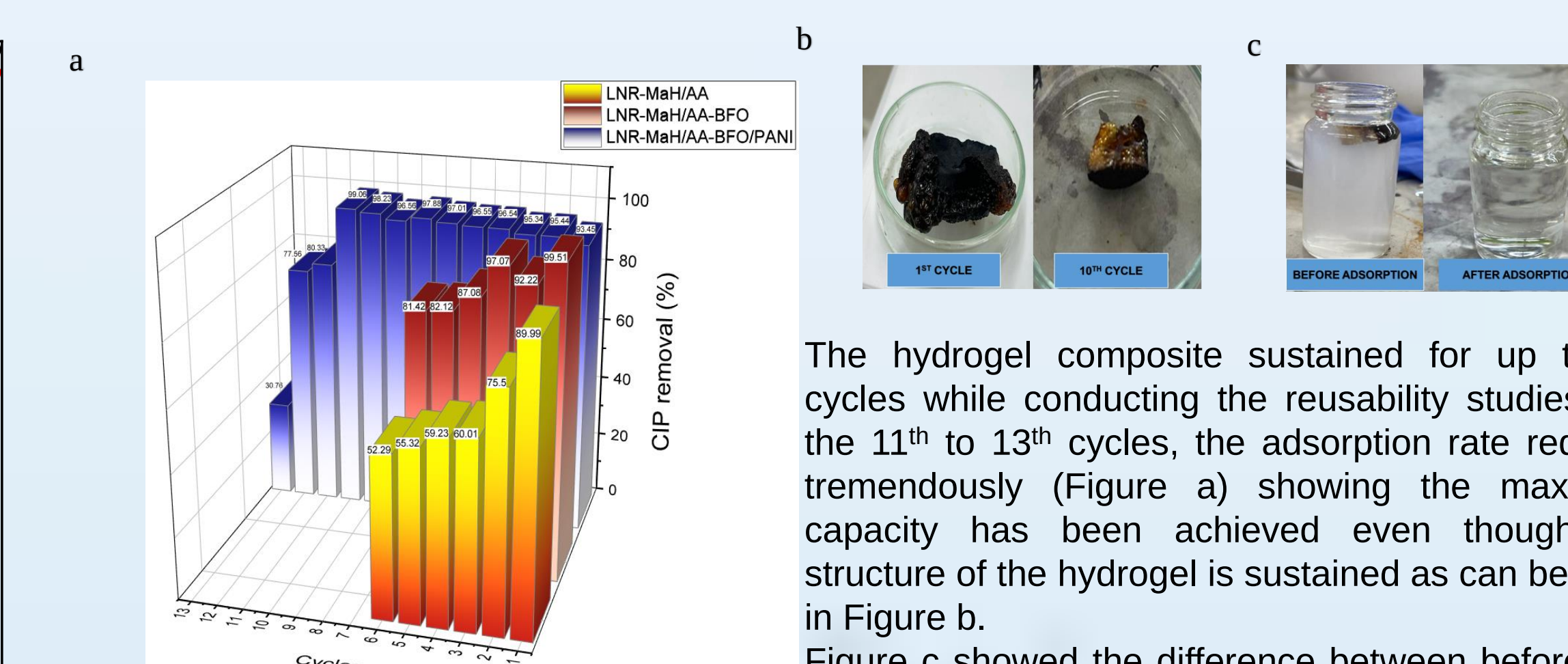
UV-DRS



ADSORPTION AND PHOTODEGRADATION STUDIES



REUSABILITY STUDIES



The hydrogel composite sustained for up to 10 cycles while conducting the reusability studies. On the 11th to 13th cycles, the adsorption rate reduced tremendously (Figure a) showing the maximum capacity has been achieved even though the structure of the hydrogel is sustained as can be seen in Figure b.

Figure c showed the difference between before and after adsorption of CIP antibiotic by the hydrogel composite.