



Metal oxide decorated polyaniline based multifunctional nanocomposites: An experimental and theoretical approach

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ABSTRACT

When combined with metal oxide nanoparticles, conducting polymers may result in unique or synergistic effects in their properties. Fe/Mn/CuO/PANI (FMC/PANI) based nanocomposites (NCs) were explored for five different novel applications. FTIR, UV-visible, XRD, Raman, and FESEM methods were used to identify the NCs. The anti-corrosive, photocatalytic, magnetic, antibacterial, and electrical properties were investigated by experimental and theoretical (DFT) methods. The computational technique was used for frequency, geometry optimization, and energy study. Different thermodynamic, kinetic, and molecular orbital parameters were investigated by the DFT study for the NCs. The anti-corrosive, photocatalytic, antibacterial, electrical, and magnetic properties of NCs were investigated at different concentrations. The FMC/PANI NCs show a maximum of $85 \pm 0.2\%$ CIE for MS in 1.0 M HCl solution. The magnetic study proves the paramagnetic nature of NCs. The photocatalytic activity of FMC/PANI NCs was investigated against MO dye under UV light. The antibacterial property of FMC nanoparticles (NPs) was investigated against gram-positive and gram-negative bacterial strains, that is, *B. subtilis* and *E. coli*, respectively. The ZOI was compared with six standard antibiotics and found to be comparable with common antibiotics. The FMC/PANI-based NCs were proven to be perfect photocatalytic, magnetic, antibacterial, electrical conductors, and anti-corrosive agents.

1. Introduction

The polymeric materials were referred to as electrical insulators before Shirakawa's groundbreaking discovery (1977) of Polyacetylene's conductivity via iodine chemical doping [1]. This discovery spurred further investigation to create other electrically conducting polymers (CPs), including polyacetylene, polyaniline, polypyrrole, polyphenylene, poly(*p*-phenylenevinylene), and polythiophene in place of metal, semiconductor, and insulator [2–6]. Since 1836, Polyaniline (PANI) has been a popular kind of polymer composed of aniline black monomeric units among many CPs because of its simplicity in synthesis, stability, capacity to manage size, and ability to generate hybrid structures. Due to the stability of doped and undoped states, simplicity in structural alteration, and process-ability of the solution, it is very interesting for different electronic device fabrications [7–11]. In contrast, PANI NCs coated with metal oxide NPs exhibit superior catalytic, sensing, photocatalytic, and electrical capabilities [12–18]. PANI

is widely used in electro-catalysis [19], rechargeable batteries [20,21], super capacitors [22], membrane separation [23–25], optoelectronic [26], extraction [27–29], solar cells [30], and electrochemical biosensors [31], among others. PANI/Silver/Zinc sulfide (PANI-Ag/ZnS) based NCs were investigated for photocatalytic properties for degrading methylene blue (MB) dye by Mazhar et al. [32]. They looked into the MB dye's photocatalytic degradation in presence of NCs. PANI doped with NPs offers a significant surface area for the interchange of electrons and holes and increases photocatalytic activity [33]. Transition metal NPs of the 3 d transition series were tried with different Carbon Nanotubes (CNTs), reduced graphene oxide (rGO), conducting polymers (CPs), Metal-Organic Frameworks (MOFs), Covalent Organic Frameworks (COFs), Black Phosphorous (BP), Transition metal dichalcogenides, MXenes, etc. [19–31]. Sivakumar et al. have investigated ZnO@copolymer NCs as photocatalytic material for the degradation of organic dyes [34]. Yadav et al. have investigated the anticorrosive and photocatalytic activity of the ACZ/PANI NCs [35]. S. Pandey et al. have investigated

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PANI/Fe₃O₄ doped with Cerium metal as NCs electrode material for supercapacitors (SCs) [36]. Singh et al. looked at the electrical conductivity of PANI doped with CdS [37]. Singh and Singh have reported the Silver/PANI NCs for detecting Hg²⁺ ions by chemo probe technique [38]. Singh and Shukla have investigated advancements made in the field of PANI-based NCs [39]. Modak et al. have looked into PANI-/Graphene NCs as EMI shielding material [40]. They noticed that as graphene concentration in NCs rises, EMI shielding also shoots up. Kumar et al. have synthesized Cu, Ni and Zn metal oxide/PANI based NCs as optoelectronic, thermal and anticorrosive NCs material for advanced functional applications [41]. Payam et al. have reported multifunctional application of mixed metal/PANI based NCs [42]. Ehsan et al. have reported different metal oxide/CPs based NCs for different applications like optical, electrical, mechanical and photocatalytic [43]. Ehsan et al. have investigated PANI based multifunctional NCs for antimicrobial, drug delivery, biosensors, regeneration of nerve, tissue engineering applications [44]. Islam et al. have reported graphene/Au NPs/PANI NCs as electronically conducting and electrochemical active material [45]. Alam et al. have reported AgO/PANI based NCs as electrical, optical and structural material of construction [46].

The first time, we are presenting the synthesis, characterization, and application investigation of Fe/Mn/CuO@PANI-based NCs using experimental and theoretical (DFT) methods. The interaction between PANI and Fe/Mn/CuO NPs was investigated in detail by the DFT technique. The characterization of FMC NPs and FMC@PANI NCs was done by XRD, SEM, Raman, FTIR, and UV-visible spectra. Experimental UV-visible, FTIR, and Raman spectra were compared with computational (DFT) spectra. The thermodynamic, kinetic, HOMO/LUMO molecular orbitals and chemical interaction parameters were investigated by computational techniques. FMC@PANI NCs were explored as having anti-corrosive, photocatalytic, magnetic, electrical conductivity, and antibacterial properties.

2. Experimental

2.1. Modified sol-gel technique

0.5 M acidic solution of the metal nitrates that is, Iron, Manganese, and Copper were selected for modified sol-gel synthesis. HNO₃ was used to bring the pH to 1–2 (Sol A). Instead of silica gel, we have used oxalic acid as organic precursor in ethanol to form gel. The advantage of oxalic acid over silica gel is that it is easy to remove from the products simply by annealing the products obtained. Oxalic acid and ethanolic mixture were prepared in the ratio of 1:4 (Sol B). At 70 °C, the Sol B and Sol A were mixed slowly dropwise at a constant revolution (600 rpm). A brown hue emerged after 6 h. The precipitates were cleaned using distilled water, followed by acetone. The precipitates were stored in a glass vial after drying at 70 °C for 6 h.

2.2. Chemical-oxidative polymerization of aniline

Aniline monomer (1.0 M) was combined with 0.1 M mixed metal NPs (FMC) in 1.0 M HCl. Drop by drop, the AlCl₃ oxidant (1.0 M) was added. The four-degree temperature was maintained using a crushed ice bath. 1.0 M of ammonium persulfate (APS) was added. The gelation process was continuously monitored for 7 h. Distilled water, dilute HCl, and ethanol were used for filtering and rinsing the products. Vacuum drying of the products was carried out for 12 h at 70 °C. The product was solid with a green-black hue.

2.3. Anti-corrosive study

The gravimetric method (ASTM-G-31) was used to find anti-corrosive properties of Fe/Mn/CuO@PANI NCs for Mild Steel (MS) in a 1.0 M H₂SO₄ as a corroding medium. The anti-corrosive properties of FMC@PANI NCs were investigated at different concentrations. With

sandpaper of various grades, the MS sheets were mechanically polished, starting from the lowest grade, 100 μ to 600 μ. A single pan analytical balance was used to precisely weigh the starting and final weights of MS specimens.

2.4. Antibacterial study

The antibacterial activity of both NCs and NPs was investigated against bacterial test organisms and was compared with standard antibiotics. The Agar well diffusion assay was used to find the Zone of Inhibition (ZOI). Two bacterial strains were used to test the antibacterial effect, that is *B. subtilis* and *E. coli*. The FMC NPs show antibacterial activity for both Gram-positive and gram-negative bacterial strains reported in terms of average ZOI in millimeters.

2.5. Photocatalytic study

The photocatalytic activity of Fe/Mn/CuO@PANI NCs was investigated against methyl orange dye (MOD) using the UV-visible absorption technique. MOD was exposed to UV light in the presence of NCs and continuously monitored for 150 min. The photocatalytic performance of FMC/PANI NCs (100 mg/ml) on MRD was reported in terms of maximum absorbance (λ_{max}) and C_t/C_0 .

2.6. Magnetic properties of NCs

Calculations of the magnetic characteristics and susceptibility of NCs were performed using a Gouy's balance. Since our NCs contain Fe and Mn which shows paramagnetic properties. We are interested to see whether these magnetic properties of Fe and Mn were masked or not in the presence of Cu and CPs PANI. The variation in weight (mg) of NCs was investigated against a magnetic field (H^2).

2.7. DFT study

The theoretical investigations were made using Gauss View 5.0 and Gaussian09 programs. Energy, frequency, and optimization studies were carried out using a B3LYP basis set having functional 6-311G + (d, p). The DFT study was performed in solvent free system. LUMO, HOMO, atomic charges, van der Waal and contour surfaces, chemical potential, LUMO and HOMO energy difference, electron affinity, global hardness, Max. charge transfer index, electrochemical potential, adsorption energy, electrophilicity, electron-donating power, etc., were observed to find adsorption sites and interaction energy of FMC@PANI NCs.

3. Results and discussion

3.1. FTIR spectra of NCs

Fourier Transform-Infrared was employed to assess the NCs and NPs to identify any functional groups and pollutants. The FTIR spectra of FMC NPs and FMC assembled PANI NCs are displayed in Fig. 1. FTIR spectrum of FMC NPs showed absorption peaks at 620, 508, and 520 cm⁻¹ due to iron oxide, manganese oxide, and copper oxide, respectively. At 3383, 1625.75, 1488, and 1358 cm⁻¹, the PANI NCs quinonoid and benzenoid rings were found due to bending and stretched vibrational states. A broad peak around 3400 cm⁻¹ was due to moisture present in the NCs. A shift in absorption peaks at 3383, 1625.75 and 520 cm⁻¹ were observed due to variety of factors, like change in the chemical environment, interactions between the FMC NPs and the PANI matrix.

FMC NPs have distinctive vibrational modes detected by FTIR spectroscopy. When FMC NPs were embedded within a CPs PANI matrix, the interactions between the NPs and the PANI leads to change in the local chemical environment. This causes the vibrational modes of the FMC NPs to shift to different frequencies [47]. The interactions between

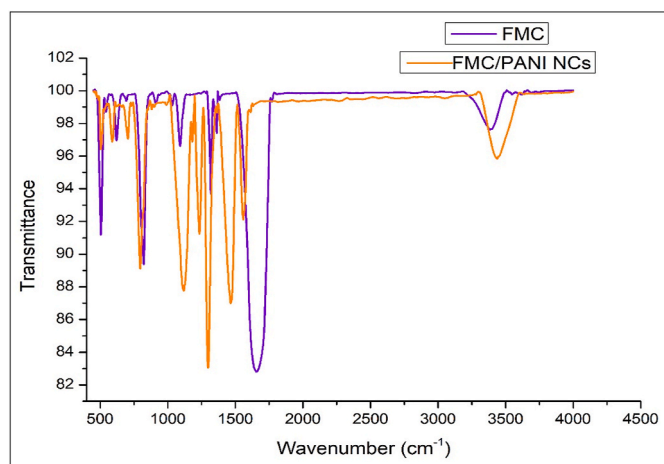


Fig. 1. FTIR spectra of FMC nanoparticles (violet) and FMC/PANI nanocomposites (yellow). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

the FMC NPs and the CPs PANI matrix also lead to changes in the bonding between the atoms. This causes the vibrational modes of the FMC NPs to shift in absorption frequency. The presence of the CPs PANI matrix also influences the overall electromagnetic field around the FMC NPs, which affects the vibrational modes and lead to peak shifting.

3.2. UV spectra of NCs

The FMC NPs as well as FMC/PANI NC absorbance spectrum are shown in Fig. 2 (A). Fig. 1S (ESI) shows theoretical UV–visible spectra of PANI CPs obtained from Time Dependent Hartree-Fock DFT (TD-SCF)

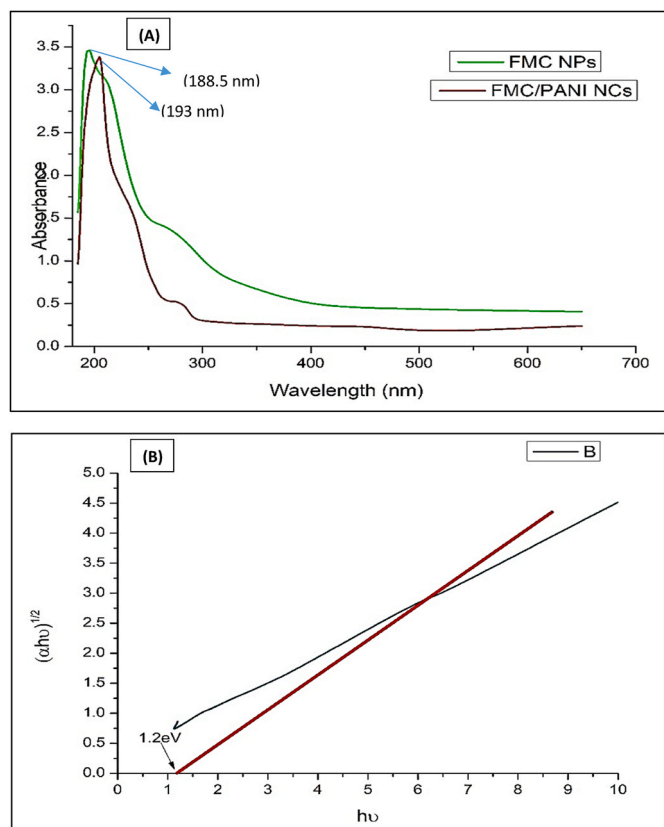


Fig. 2. (A) UV–visible spectra of FMC NPs and FMC/PANI NCs. (B) Indirect band gap of FMC/PANI NCs obtained from Tauc plot.

method. The NCs indirect bandgap determined from Tauc plots is illustrated in Fig. 2B. The highest absorbance of FMC NPs and FMC/PANI NCs was 3.4 at 196.5 nm and 3.2 at 204 nm, respectively. This shifting of peaks can be attributed to factors, like change in the size, shape, and chemical environment of the FMC NPs, and also interactions between the FMC NPs and the PANI matrix. FMC NPs exhibit Localized Surface Plasmon Resonance (LSPR), which is a collective oscillation of electrons on the surface of the NPs in response to incident UV or visible light [48]. The LSPR is highly dependent on the size, shape, and chemical environment of the NPs, which influences the frequency and intensity of the absorbance peak in the UV–visible spectrum.

When FMC NPs are embedded within a PANI matrix, the interactions between the FMC NPs and the PANI leads to changes in the size, shape, and chemical environment of the FMC NPs. The PANI matrix can induce a deformation in the shape of the FMC NPs, leading to changes in the LSPR peak frequency. The PANI matrix can also modify the chemical environment around the FMC NPs, which alter the electronic structure of the FMC NPs and affect the LSPR peak intensity [49].

The optical band gap of FMC/PANI NCs.

The indirect bandgap of NCs was identified by using Tauc Eq. (1) [47].

$$\alpha h\nu = B(h\nu - E_g)^n \quad (1)$$

The absorption coefficient was determined via Lambert's-Beer relation [48]. For the FMC/PANI NCs, a linear connection between $(\alpha h\nu)^{1/2}$ and $h\nu$ was found. Due to the π - π^* transition (VB to CB), the energy band gap (E_g) of NCs was only 1.2 eV as opposed to 3.2 eV for pure PANI and 2.7 eV for FMC NPs [49]. The indirect bandgap decreased from 3.2 eV (PANI) or 2.7 eV (FMC) to 1.2 eV when FMC NPs were added to PANI. The band gap obtained from the DFT study was 1.5 eV. A slight variation in optical band gap observed from DFT (theoretical) and UV visible (experimental) study was quite obvious as reactions conditions in two studies are quite different. The PANI NCs with FMC NPs thus had improved electrical conductivity.

3.3. SEM study of FMC NPs, CPs PANI and FMC/PANI NCs

Surface investigation of FMC NPs and FMC/PANI NCs was done by SEM technique. Fig. 3 shows FESEM images of Fe/Mn/CuO@PANI-based NCs (Fig. 3 A and B), SEM image of FMC NPs (Fig. 3C), SEM image of CPs PANI (Fig. 3D), and Energy Dispersive Spectra (EDS) (Fig. 3E). FMC NPs of size 120–130 nm were synthesized by the modified sol-gel technique. The NPs appeared spherical and agglomerated together (Fig. 3C). The CPs PANI were cylindrical in nature having large cavities for the entrapment of NPs (Fig. 3D). The NPs, when combined with PANI CPs, were get completely entrapped in the PANI framework (Fig. 3 A and B). Average size of FMC/PANI NCs range from 150 to 180 nm. Large cavities in PANI act as sites of entrapment of NPs and hence are not visible in the surface study. The surface of FMC/PANI NCs appears to somewhat porous in nature due to CPs PANI matrix (Fig. 3 A and B). This provides large surface area for catalytic activity and adsorption of different adsorbate on the surface of NCs. EDS elemental analysis of NCs shows peaks corresponding to Fe, Mn, and Cu NPs (Fig. 3C). A few other peaks corresponding to nitrogen and oxygen atoms of PANI CPs were also observed in EDS spectra.

3.4. XRD study of NCs

The structural information, morphology, crystal planes, miller indices, indexing pattern, and particle size of FMC NPs and FMC/PANI NCs was investigated by the XRD technique. Fig. 4 shows the X-ray diffraction pattern of FMC@PANI-based NCs. The average particle size obtained from the Scherer equation was 165 nm. There was a close agreement in average particle size of NCs obtained from FESEM and XRD techniques. The Rietveld refinement method was used for indexing the

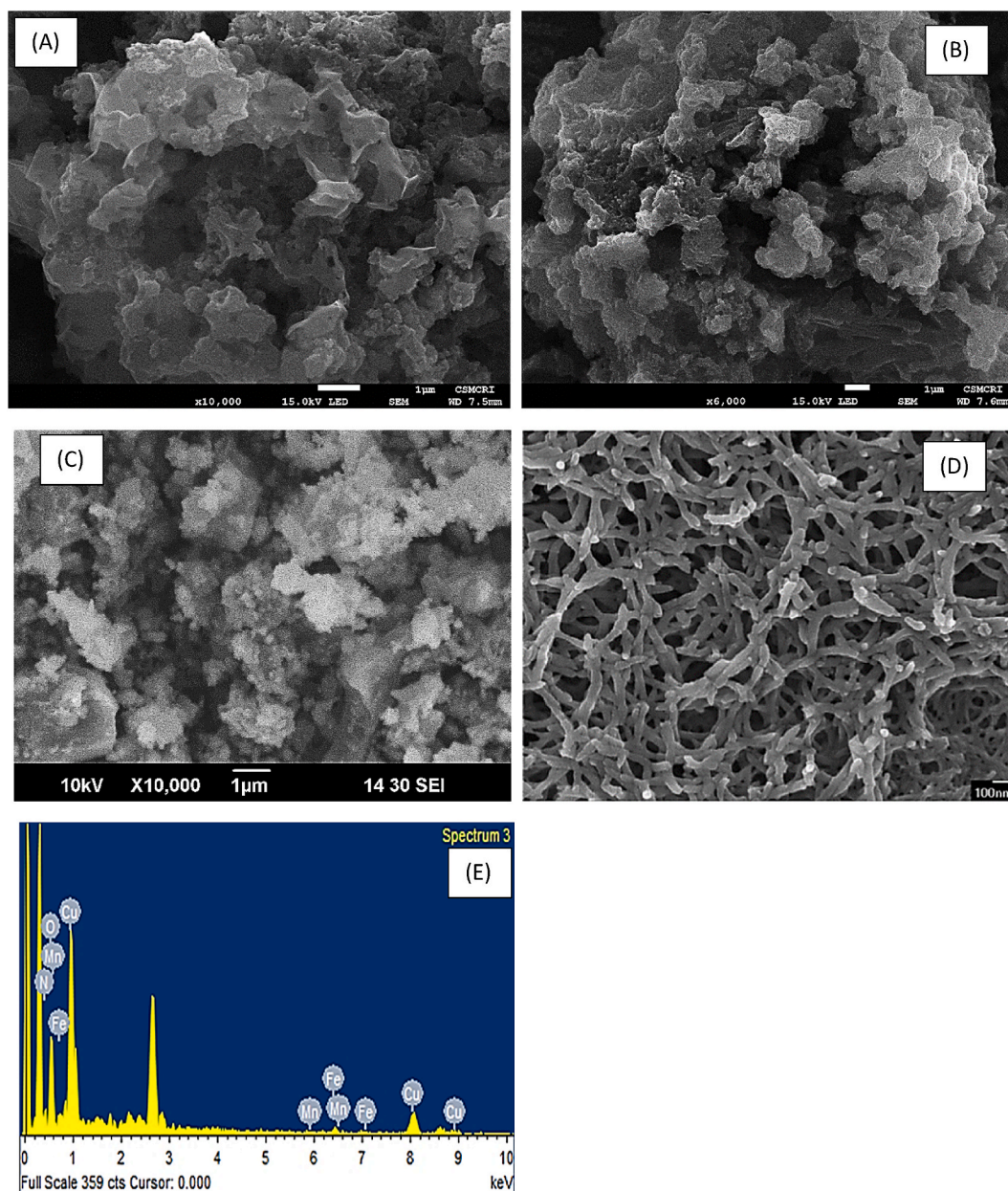


Fig. 3. FESEM images of FMC/PANI-based NCs (A and B), FMC NPs (C), CPs PANI (D) and EDS of FMC/PANI NCs (E).

peaks of the NCs. The XRD pattern of FMC NPs was indexed at 23 (110), 26 (102), 30 (111), 37 (201), 52 (221), 57 (202), and 63 (113). The peaks at 35 (101) correspond to Fe_2O_3 NPs. The peaks at 37 (201) and 50 (210) correspond to MnO NPs. The peaks at 32 (110), 35 (111), 47 (121), 53 (221), 57 (202), and 68 (113) correspond to CuO NPs. The indexing pattern of FMC NPs corresponds to JCPDS No. 39–1346, 089–4836, and 48–1548, respectively for Fe_3O_4 , Mn_2O_3 , and CuO NPs [50,51]. The XRD pattern of FMC@PANI-based NCs was observed at 26 (102), 35 (111), 47 (121), 53 (221), and 68 (113). The characteristic peaks of PANI appeared at 26 (102) [35].

3.5. Raman spectroscopic study of NCs

Raman spectroscopy is a quite useful technique to investigate the vibrational and rotational behavior of materials when exposed to electromagnetic radiation. The Stokes, anti-Stokes lines, metal-metal interactions, Longitudinal Optical Vibrations (LOV) in the fingerprint region, crystallinity and phase behavior, etc., are a few crucial pieces of

information that can be obtained from Raman spectra. Fig. 5 shows Raman spectra of FMC NPs and FMC/PANI-based NCs. Experimental Raman spectra were compared with theoretical (DFT) Raman spectra (Fig. S4, ESI). Fig. 4S (ESI) shows the theoretical Raman and Vibrational Circular Dichroism (VCD) spectra of PANI obtained from DFT study. LOV-1 of the Fingerprint region was significant in the Raman spectra of FMC NPs. The LOV-1 peaks are masked in FMC/PANI NCs due to the presence of a major fraction of PANI CPs in the NCs. LOV-2 (d band) proves the synthesis of defect-free FMC@PANI NCs. A high-intensity LOV-3 (g band) in Raman spectra of FMC NPs was due to metal-metal phonon interactions. These interactions are due to the structural resemblance between Iron and Manganese atoms and are further supported by the small size and quantum confinement phenomenon. The LOV-3 (g bands) did not appear in FMC/PANI NCs.

3.6. Anti-corrosive study of FMC/PANI NCs

The ability of NCs to resist corrosion was assessed using a Mild Sheet

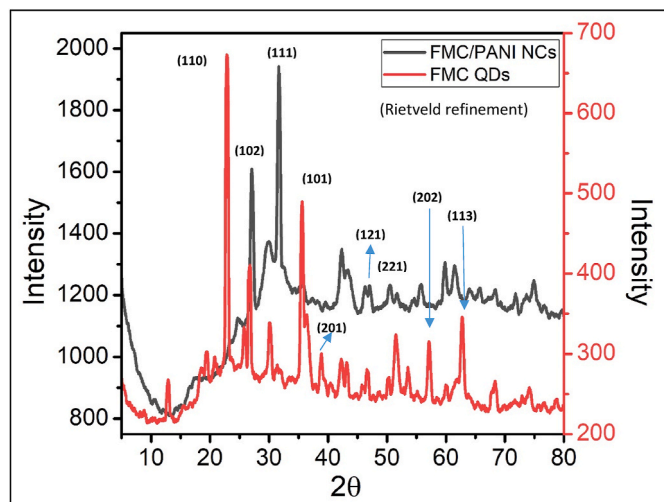


Fig. 4. X-ray diffraction pattern of Fe/Mn/CuO@PANI-based nanocomposites.

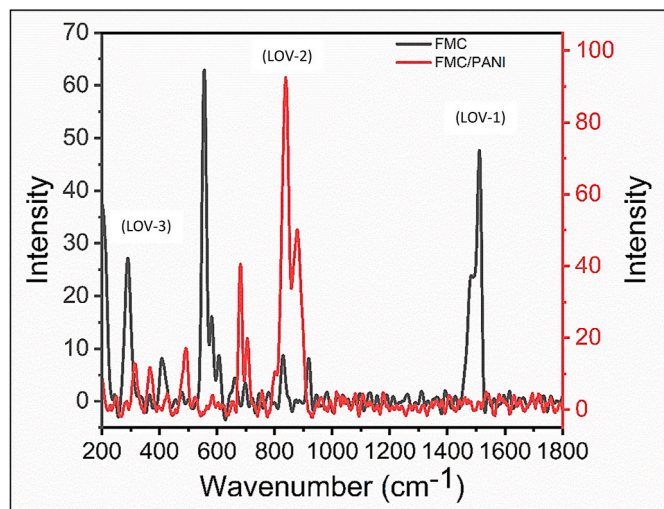


Fig. 5. Raman spectra of Fe/Mn/CuO (FMC) NPs and FMC@PANI-based nanocomposites.

(MS) in 1.0 M HCl. The 3-h immersion of MS in a 1.0 M HCl solution containing varying concentrations of NCs was performed. According to ASTM (G-31) recommendations, the corrosion rate (CR) in mpy, the corrosion inhibition efficiency (CIE), and the change in weight of the MS were determined [51]. As NCs concentration rises, weight loss and CR decline but CIE rises (Table 1). Fig. 6 illustrates the alteration in CIE with NCs concentration. With escalating FMC/PANI NCs concentrations, the CIE rises linearly. This may be due to small size and large surface area of

Table 1

Weight loss, corrosion rate, and CIE of Fe/Mn/CuO@PANI-based nanocomposites towards mild steel corrosion in HCl medium.

Sr. No.	Concentration (ppm)	Weight loss (mg)	Corrosion Rate (mpy)	% Corrosion Inhibition Efficiency	θ
1	100	34.1	1108.12	41.9	0.42
2	200	27.2	883.9	43.8	0.44
3	400	20.1	653.17	58.4	0.58
4	600	15.6	506.94	67.7	0.68
5	800	9.8	318.46	79.7	0.80
6	1000	7.1	230.72	85.3	0.85
7	Blank	48.4	1572.8	—	—

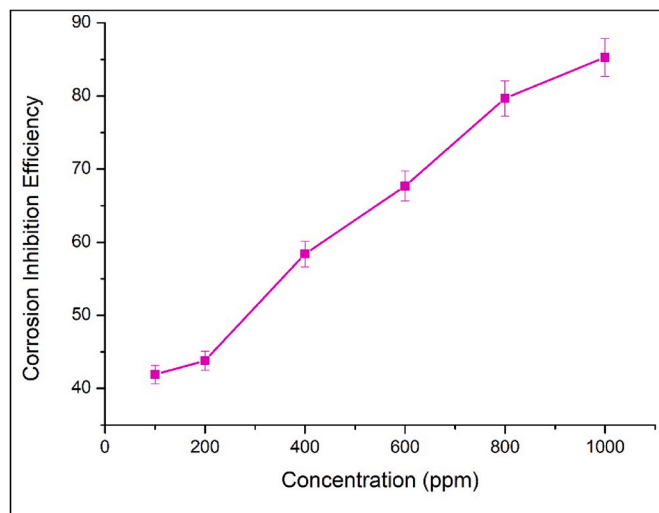


Fig. 6. Corrosion inhibition efficiency versus concentration (ppm) of Fe/Mn/CuO@PANI-based nanocomposites.

NCs which increases its penetration power in the fine pores of MS sheets and high surface energy increases its adsorption power on the surface of MS. The same fact was supported by the computational study proved by high adsorption energy, chemical potential, binding energy and global hardness and softness parameters. The CIE observed was 85% at 1000 ppm concentration of FMC/PANI NCs. Almost a linear response between CIE and concentration of NCs was observed. The fraction of surface covered (θ) by the FMC/PANI NCs increases with inhibitor concentration. In an acidic condition, the FMC@PANI NCs seem to be a viable anti-corrosive nanomaterial for MS.

Mechanism of anticorrosive properties of FMC/PANI NCs

FMC/PANI NCs has shown promising anticorrosive properties for MS in acidic medium due to their unique combination of electrical conductivity and mechanical properties. The mechanism by which these FMC/PANI NCs exhibit anticorrosive properties involves different factors, like: i) *Barrier Effect*: The FMC/PANI NCs act as a barrier against the corrosive attack of acid that may come in contact with the MS surface. This barrier effect helps to prevent the corrosive HCl from reaching the MS substrate and causing damage, ii) *Passivation Effect*: The FMC/PANI NCs also act as a passivation layer for the MS substrate. The passivation layer forms a protective film on the MS surface, which inhibits the electrochemical reactions that induces corrosion, iii) *Electrochemical Effect*: The FMC/PANI NCs also act as an electrochemical barrier against corrosion. The NCs can be designed to have a specific redox potential that is more positive than that of the MS substrate. This potential difference creates a thermodynamic barrier to the oxidation of the MS substrate, which helps to prevent corrosion, iv) *Self-healing Effect*: FMC/PANI NCs have the ability to self-heal, which means that they can repair any damage that occurs to the corrosive effect of HCl. This self-healing effect can help to prevent MS corrosion from spreading throughout the material.

4.8. Magnetic study of NCs

NCs' magnetic properties may be assessed effectively by comparing the magnetization degree to the applied magnetic field (H^2). To determine magnetic susceptibility, a Gouy's balance was employed. The change in the weight fraction of NCs as a result of the applied magnetic field (H^2) is plotted in Fig. 7. As the magnetic field intensified, the weight of the NCs raised asymptotically. This demonstrates the paramagnetic properties of the FMC/PANI NCs by showing a rise in the

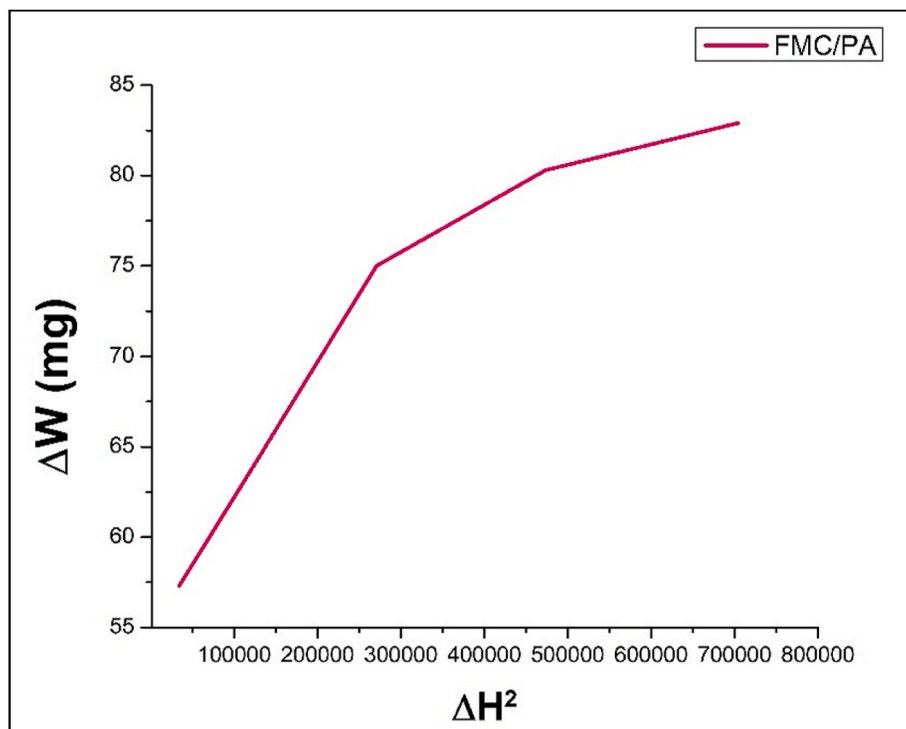


Fig. 7. Magnetic properties of Fe/Mn/CuO@PANI-based nanocomposites.

magnetic field around the sample [52]. Additionally, the magnetic susceptibility was measured by Eq. (2):

$$\chi = \frac{2g \times \Delta m}{A(\Delta H^2)} \quad (2)$$

Synthesized NCs exhibit paramagnetic properties because of their magnetic susceptibility $\chi = 0.0252$. As a result, PANI NCs decorated with FMC NPs can be employed to create super magnetism, magnetic recording tapes, and flash memory on a USB pen drive.

4.9. Photocatalytic activity of NCs

We investigated the photocatalytic properties of NCs on methyl orange dye (MOD) using UV–visible spectroscopy. MOD was subjected to a

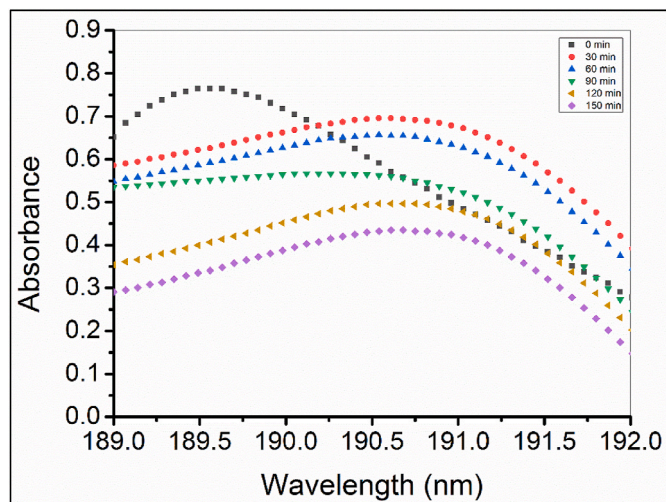


Fig. 8. Photocatalytic activity of Fe/Mn/CuO@PANI-based NCs against MR dye.

150-min irradiation at different NCs dosages. The photocatalytic performance of FMC/PANI NCs on MOD is depicted in Fig. 8 over time in UV–Visible light. As the time increases, the absorbance maxima decline (zero to 150 min).

Fig. 9 displays the change in C_t/C_0 over time (min.) for the photocatalytic activity of FMC/PANI NCs (100 mg/ml) on MOD under UV light. Maximum absorbance (λ_{max}) and C_t/C_0 decrease as dye exposure time increases. The C_t/C_0 ratio decreases from 2.228 to 1.76 after 150 min. The greatest absorbance of 1.892 was attained after 30 min and fall to 1.66 after 150 min of exposure to UV light. As a result, in UV light, FMC/PANI NCs exhibit good photocatalytic capabilities.

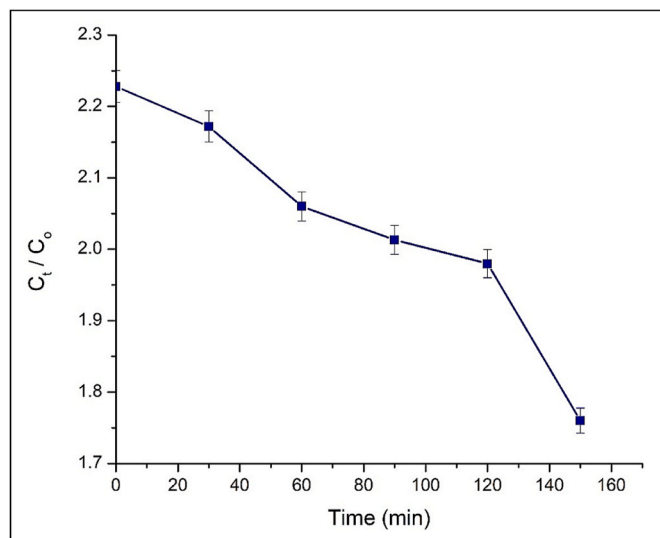


Fig. 9. The variation of C_t/C_0 with time (in minutes) for the photocatalytic activity of FMC/PANI NCs (100 mg/ml) on MRD under UV light.

4.10. Mechanism of photocatalytic activity

Fig. 10 shows the detailed mechanism of photocatalytic activity shown by FMC/PANI NCs for the degradation of MOD in UV light. The mechanism of photo-catalysis by the NCs starts with the absorption of photochemical radiation by the NCs followed by the formation of charge carrier species, i.e., oxygen and hydroxyl free radicals [53–58]. This is followed by the combination of charge carrier and then entrapping of conduction band electrons from FMC NPs and finally oxidation of MOD dye. The mechanism of photocatalytic activity of FMC/PANI NCs involves the generation of electron-hole pairs upon exposure to UV light, which then participate in redox reactions that lead to the degradation of MOD. The photocatalytic activity of FMC/PANI NCs is attributed to the presence of a semiconductor photocatalyst, such as FMC NPs, which is embedded within a PANI matrix. The semiconductor photocatalyst has a band gap ($E_g = 2.7$ eV) that corresponds to the energy of the UV light, allowing it to absorb photons and generate electron-hole pairs. The generated electron-hole pairs then participate in redox reactions with MOD in the surrounding environment. In FMC NPs, the holes (h^+) can react with H_2O molecules to produce $\bullet OH$ radicals, which are highly reactive species that oxidizes and degrade MOD. The electrons (e^-) can reduce dissolved O_2 molecules in water to produce $\bullet O_2^-$ radicals, which participate in redox reactions with MOD [54,55]. The PANI matrix in the NCs material serves many important functions. It acts as a scaffold to support the photocatalyst and prevent aggregation of NPs, thereby increasing the overall surface area available for photocatalysis. It also facilitates the transfer of electrons and holes between the photocatalyst and the MOD, which is important for efficient redox reactions [56,57].

In addition to these, the CPs PANI matrix also serve as a sensitizer, absorbing light energy and transferring it to the photocatalyst. This increases the overall photocatalytic activity of the FMC/PANI NCs and increase the range of wavelengths of UV light for absorption [58].

4.10.1. Antibacterial study of FMC NPs

Employing the Agar well diffusion assay, the antibacterial action of FMC NPs was examined towards two types of bacteria, *B. subtilis* (Gram + ve) and *E. coli* (Gram -ve). The Zone of Inhibition (ZOI) for Gram-negative and Gram-positive bacteria was measured in mm [59]. Concerning the Gram + ve bacterium (*B. subtilis*), there was no ZOI observed. Table 2 lists the ZOI (mm) of six well-known antibiotics for *E. coli*. The ZOI of FMC NPs towards Gram-negative bacterial strains (*E. coli*) at various dosages is shown in Table 3. It was observed that ZOI rises as FMC NPs concentration rises. At 1500 mg/ml, our NPs displayed a maximal ZOI of 10.5 mm for *E. coli*. Fig. 11 (a, b) shows various FMC

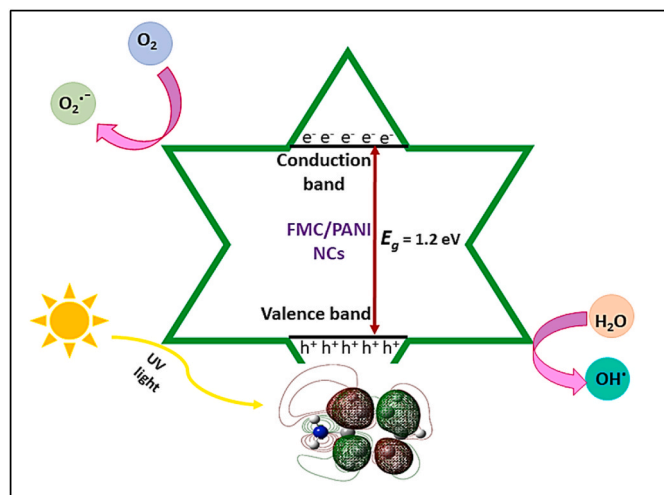


Fig. 10. Mechanism of photocatalytic activity shown by FMC/PANI NCs for degrading MOD in UV light.

Table 2

Zone of Inhibition in mm (ZOI) against *E. coli* bacterial strain as indicated by Hexa disc.

Six standard antibiotics present in Hexa disc						
Bacteria	TE (25)	C (25)	P1	AMP 10	S (10)	S3 (300)
<i>E. coli</i>	18.22	15.13	22.60	10.29	15.24	25.21

Table 3

Zone of Inhibition in mm (ZOI) displayed by FMC NPs at different concentrations against *E. coli* bacterial strain.

Bacterial test organism	FMC NPs Concentration (ppm)				
	200 ppm	500 ppm	800 ppm	1000 ppm	1500 ppm
<i>E. coli</i>	No zone	1.2 mm	1.9 mm	3 mm	10.5 mm

NPs concentrations. ZOI was observed to be effective against *E. coli* at 200, 500, 800, 1000, and 1500 parts per million (Fig. 11 c). Various common antibiotics (Hexa disc) were also tested as a reference for *E. coli*. Fig. 12 shows ZOI (mm) by FMC NPs at different concentrations against *E. coli*. Corresponding to six antibacterial drugs, the ZOI produced by the NPs is better. The entry of iron, manganese, and copper oxide NPs via microbial protein receptors through the cell wall due to small size and large surface energy (in nm range) is the plausible mechanism of FMC NPs' antibacterial effect. These NPs damage hereditary material and hence inhibit binary fission. To cure several illnesses, our FMC NPs might be employed in the field of antibiotics.

4.10.2. Computational (DFT) study

The DFT study was carried out on FMC@PANI NCs to find attacking sites, internal energy, free energy, work function, electrochemical affinity, LUMO and HOMO molecular orbitals energies, binding energy, kinetic energy, entropy, repulsive nuclear energy, dipole moment, electron affinity, global hardness, electron-donating power, atomic charges per atom, etc. [60–65]. Table 4 shows Mulliken's atomic charges per atom of PANI NCs observed from the DFT calculation of energy. Table 5 shows the thermochemical parameters of FMC@PANI NCs obtained from the DFT study, standard basis set: 311G + (d, p) and Functional: B3LYP. The different DFT parameters used in computational study are: Iso-surface: colored; density → SCF (Self-consistent field); Potential → Coulomb potential SCF; iso-value = 0.05, iso-value range = −0.1 to 0.1; spin = α . Table 6 shows the computational parameters of FMC@PANI NCs, Standard basis set: 311G + (d, p) and Functional: B3LYP. Fig. 13 shows the PANI geometry optimized structure, atomic charges (non-colored), atomic charges (colored), and Contour Surfaces per atom. Fig. 14 shows PANI HOMO (A), LUMO (B), HOMO + Contour (C), and LUMO + Contour surfaces (D). The Mulliken atomic charge was found to be a maximum of 5th Carbon, and a minimum of 6th Carbon of FMC/PANI NCs (Table 4 and Fig. 13). The adsorption energy of FMC/PANI NCs was found to be 4.32 kJ/mol, which is greater than room temperature thermal energy (Table 6). This will help in stronger adsorption of NCs on MS electrodes and bacterial strains. The internal energy of FMC/PANI NCs was also found appreciable, i.e., 74.89 kcal/mol, which makes this composite suitable for photocatalytic and adsorption study. The ionization energy, electron affinity, and global hardness parameters suggest that FMC/PANI NCs bind strongly with the MS surface, thus protecting it from corrosion [66–68].

5. Future scope of metal oxide decorated PANI based NCs

Mixed metal oxide and PANI based multifunctional NCs have a promising future and a wide scope in advanced functional applications. These PANI based NCs have unique properties such as high electrical conductivity, high surface area, excellent mechanical strength, and

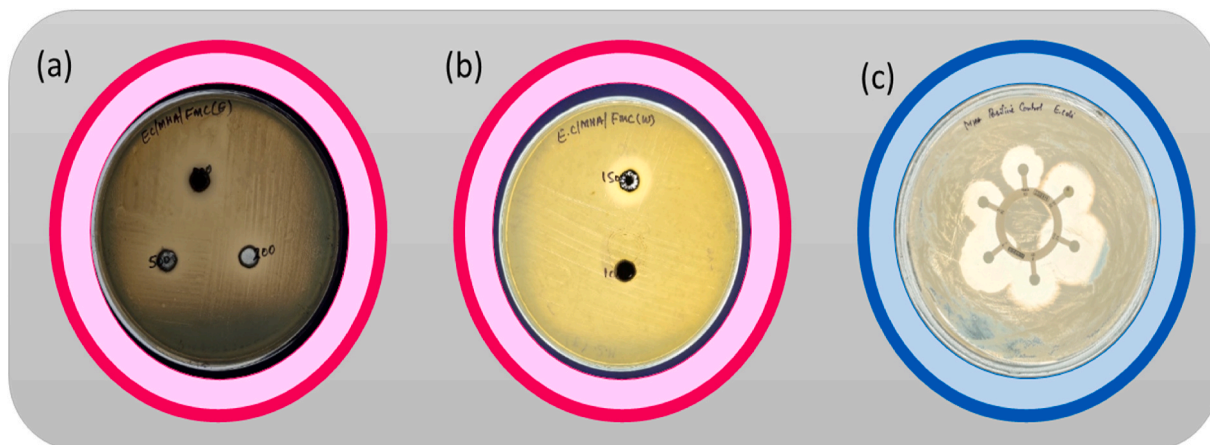


Fig. 11. (a, b) Zone of inhibition (ZOI) shown at different concentration of FMC NPs against *E. coli* at 200, 500, 800, 1000 and 1500 ppm (c) Zone of inhibition (ZOI) produced by different standard antibiotics (hexa disk) with *E. coli*.

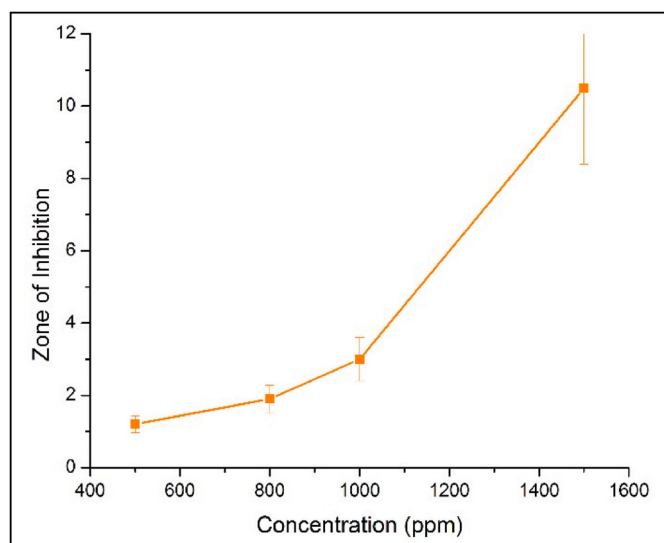


Fig. 12. ZOI (mm) shown by FMC NPs at different concentration against *E. coli*.

Table 4

Mullikan atomic charges per atom of PANI observed from DFT calculation of Energy.

Element	Number	Mullikan Atomic Charges
C	1	0.287
C	2	-0.253
C	3	-0.144
C	4	-0.035
C	5	0.949
C	6	-0.932
H	7	0.148
H	8	0.167
H	9	0.142
C	10	-0.128
O	11	-0.261
H	12	0.128
O	13	-0.212
C	14	-0.270
H	15	0.144
H	16	0.156
H	17	0.147
O	18	-0.314
H	19	0.280

biocompatibility, which makes them suitable for a variety of applications.

The metal oxide and PANI based NCs can be used for the development of high-performance batteries, supercapacitors, and solar cells. The high electrical conductivity and large surface area of these NCs increases the efficiency of energy conversion and storage devices. The metal oxide and PANI based multifunctional NCs can be used as conductive materials in electronic devices, such as sensors, transistors, and optoelectronics. They can also be used for the development of flexible electronics due to their excellent mechanical properties. These multifunctional NCs can be used as efficient catalysts for various chemical reactions, including water splitting and CO₂ reduction. These NCs can enhance the catalytic activity and stability of the catalysts due to their high surface area and excellent conductivity. These NCs can be used for drug delivery, imaging, and tissue engineering. These NCs can improve the bioavailability and targeted delivery of drugs, as well as the imaging contrast due to their unique optical properties. They can also enhance the mechanical properties of tissue engineering scaffolds due to their excellent mechanical strength. Overall, the future scope of mixed metal oxide and PANI based NCs is broad and includes various fields, such as energy, electronics, catalysis, and biomedicine.

6. Conclusions

Fe/Mn/CuO NPs were synthesized by the modified sol-gel method. CPs PANI was prepared by the chemical oxidation method. *In situ* technique was used for the preparation of FMC/PANI NCs. The characterization of FMC NPs and FMC/PANI NCs was done by Raman, XRD, SEM, UV-visible, and FTIR techniques. The computational (DFT) technique was used for frequency, geometry optimization, and energy study. Different thermodynamic, kinetic, and molecular orbital parameters were investigated by the DFT study for the NCs. The anti-corrosive, photocatalytic, antibacterial, electrical conductivity and magnetic properties of NCs were investigated at different concentrations. The FMC@PANI NCs show a maximum of 85% CIE for MS in 1.0 M HCl solution. The magnetic study proves the paramagnetic nature of NCs. An increase in weight was observed with an increase in the strength of magnetization. The photocatalytic activity of FMC@PANI NCs was investigated against MOD under UV light. The ratio of C_t/C_0 decreases from 2.228 to 1.76 after 150 min of exposure to FMC@PANI NCs under UV light. The λ_{max} decreases from 1.82 to 1.66 after 150 min of exposure. The antibacterial property of FMC NPs was investigated against Gram-positive and Gram-negative bacterial strains that are *B. subtilis* and *E. coli*, respectively. The ZOI was compared with six standard antibiotics and found to be comparable with standard antibiotics. The FMC@PANI NCs were proven very good anti-corrosive, antibacterial, photocatalytic,

Table 5
Thermochemical parameters of FMC@PANI NCs obtained from DFT study, Functional: B3LYP, Basis set: 6-311G + (d, p).

Nuclear Repulsive energy (Hartrees)	Rotational constants (GHz)	Dipole moment (D)	Quadrupole moment (xy axis)	Binding energy (–Ha)	Binding energy (–Kcal/mol)	Kinetic Energy (Kcal/mol)	Molecular mass (amu)	Internal Energy, E (Thermal) kCal/mol	Heat capacity (Cal/mol-Kelvin)	Entropy, S (Cal/mol-Kelvin)
263.78	5.2391	1.4093	–37.4646	4.32	2.71	98.1	93.057	74.899	23.828	75.495

Table 6
Computational parameters of FMC@PANI NCs obtained from DFT study, Functional: B3LYP, Basis set: 6-311G + (d, p).

E_{HUMO} (–eV)	E_{LUMO} (–eV)	ΔE (eV)	I (eV)	A (eV)	χ (eV)	η (eV)	σ (eV ^{–1})
2.21 <1- ΔN (eV)	0.23 E_{Ad} (kJ/mol)	1.98 ω (au)	2.21 ω^+ (au)	0.23 ω^- (au)	1.22 Mol. Mass	0.99	1.01
0.61	4.32	271	0.075	0.211	93.057		

Abbreviations; *I*: ionization energy, *A*: electron affinity, η : Global hardness, ΔE : Energy difference, χ : electrochemical potential, ΔN : max. Charge transfer index, ω : electrophilicity, ω^- : electron donating power, ω^+ : electron accepting power, E_{Ad} : adsorption energy.

electrical conductors, and magnetic nanomaterials.

Credit author statement

Ankita Yadav: Methodology; Formal Analysis; Validation; and Writing – original draft, **Harish Kumar:** Conceptualization;

Supervision; Formal Analysis; Data curation; Validation; Software; Investigation; Resources; Experimental design; and Writing –, review & editing., **Rahul Sharma:** Formal Analysis; and Validation., **Rajni Kumari:** Data curation; and Validation, **Devender Singh:** Formal Analysis; and Validation, **Osama A. Hamed:** Formal Analysis; and Validation.

Ethical approval

Not applicable.

Consent to publish

All the authors of the manuscript give their consent to publish this paper in its present form.

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Declaration of competing interest

There is no Conflict of Interest with anybody or any agency in

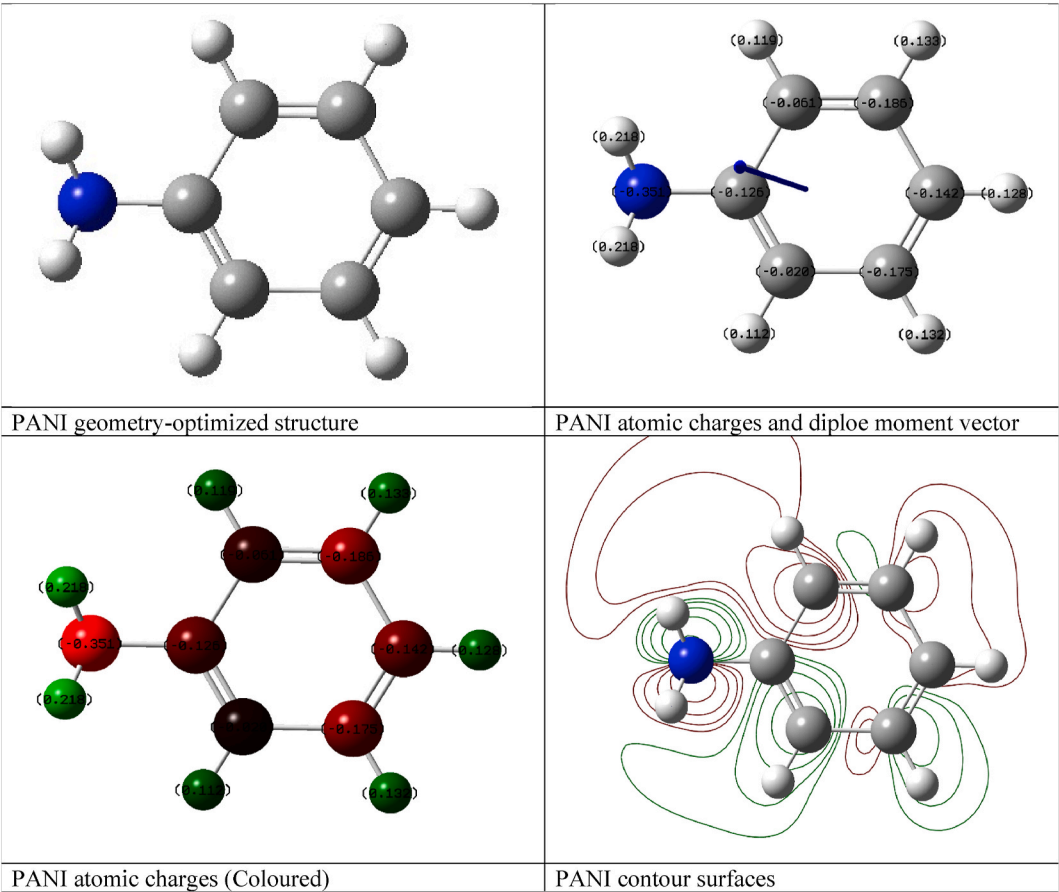


Fig. 13. PANI geometry optimized structure, atomic charges (non-colored), atomic charges (colored), Contour surfaces per atom.

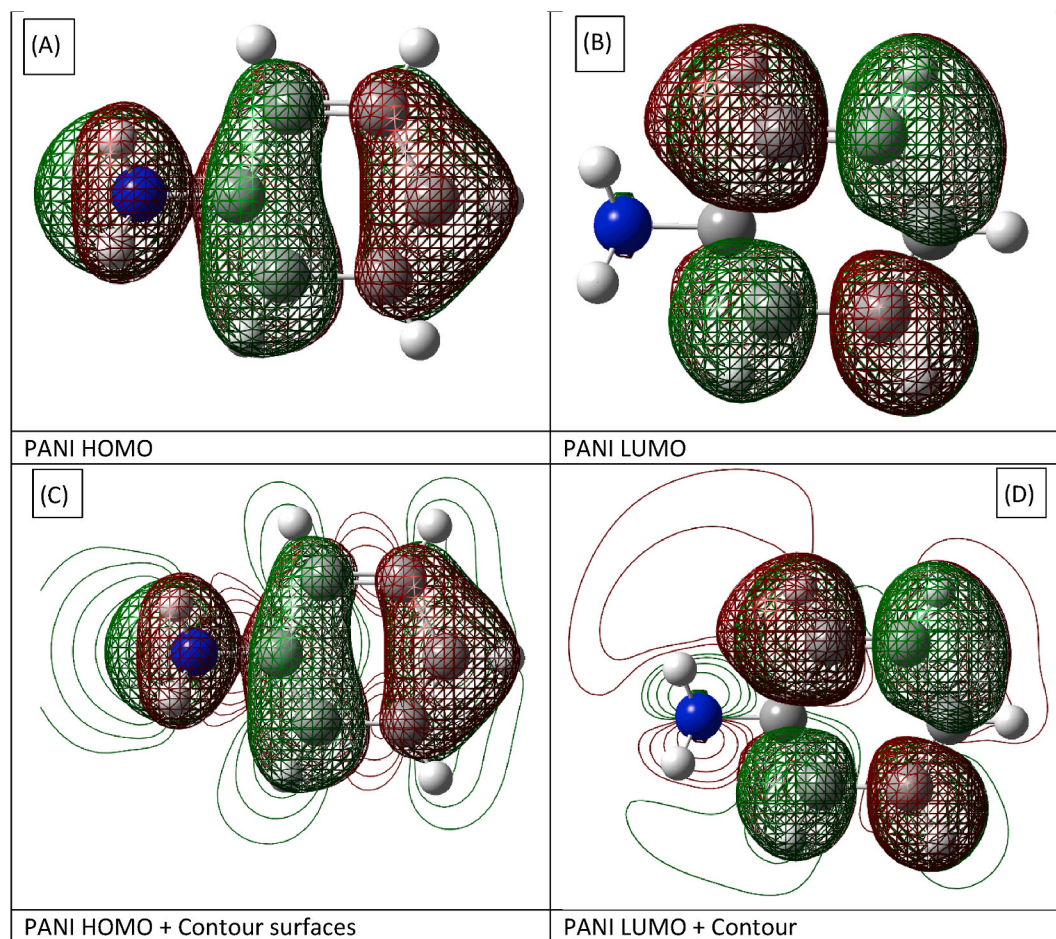


Fig. 14. PANI HOMO (A), LUMO (B), HOMO + contour (C), and LUMO + Contour surfaces (D).

publishing this research article entitled “Metal oxide decorated Polyaniline based multifunctional nanocomposites: An experimental and theoretical approach”. We author of this publication take the whole responsibility if any Conflict of Interest arises in near future.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.rineng.2023.101161>.

Abbreviations used

FMC	Fe/Mn/CuO
NCs	Nanocomposites
PANI	Polyaniline
DFT	Density Functional Theory
CIE	Corrosion Inhibition Efficiency
CR	Corrosion rate
MS	Mild Steel

MO	Methyl Orange
ZOI	Zone of Inhibition
FTIR	Fourier Transform Infrared Spectroscopy
CPs	Conducting Polymers
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
APS	Ammonium Per Sulfate
ASTM	American Society for Testing and Materials
MOD	Methyl Orange Dye
B3LYP	Becke, 3-parameter, Lee–Yang–Parr

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