



PANI encapsulated α -MnO₂ nanocomposites as photocatalytic, antibacterial and anticorrosive agents: Sustainable experimental and theoretical studies

Harish Kumar^{a,*}, Manisha Luthra^b, Manisha Punia^b, Ankita Yadav^a, Rajni Kumari^a,
Rahul Sharma^a, Aarti Tundwal^a, Gaman Kumar^a, Pawanvir Kaur^c

^a Dept. of Chemistry, Central University Haryana, Mahendergarh, 123 031, India

^b Dept. of Chemistry, CDLU, Sirsa (Haryana), 125 055, India

^c Dept. of Chemistry, Govt. National PG College, Sirsa (Haryana), 125 055, India

ARTICLE INFO

Keywords:

Manganese oxide nanoparticles
Polyaniline
Anticorrosive
Antibacterial
Photocatalytic
Nanocomposites

ABSTRACT

Metal nanoparticles and conducting polymers have applications in the fields like purification, separation, adsorption, photocatalytic, antibacterial, sensors, electrical conductivity, etc. The α -MnO₂ nanoparticles, and polyaniline (PANI) were synthesized by the reverse micelle and chemical oxidative techniques, respectively. An *in-situ* technique was used for the synthesis of α -MnO₂/PANI nanocomposites (NCs). The characterization of α -MnO₂ nanoparticles and NCs was carried out by XRD, TEM, FTIR, and UV-visible techniques. The experimental data was supported by a theoretical (computational) study. Corrosion inhibition, antibacterial, and photocatalytic activity of α -MnO₂/PANI NCs were explored. The NCs show a maximum of $87 \pm 0.1\%$ corrosion inhibition efficiency. The NCs (100 ppm concentration) degrade $89.15 \pm 1.1\%$ of methyl orange dye after 3 h of UV exposure. The photodegradation of dye follows pseudo-first order kinetics with a rate constant of 0.0657 min^{-1} . The mechanism of photodegradation is supported by potentiostatic photocurrent measurement, impedance spectroscopy, pH variation, and chemical oxygen demand. The antibacterial property of NCs was compared to standard Hexa disk against Gram-positive and Gram-negative bacterial strains. The NCs show 18.5 mm and 15.3 mm Zone of Inhibition (1000 ppm) for *S. epidermis* and *E. coli*, respectively. The α -MnO₂/PANI NCs show very good anti-corrosive, antibacterial, and photocatalytic properties.

Credit author statement

Harish Kumar: Writing, Methodology, Conceptualization, Theoretical, Supervision, Investigation. **Manisha Luthra:** Experimental, Visualization, Analysis. **Manisha Punia:** Formal analysis, Experimental, Investigation. **Ankita Yadav:** Experimental, Investigation. **Rajni Kumari:** Writing, Investigation. **Rahul Sharma:** Formal analysis, Investigation. **Aarti Tundwal:** Formal analysis, Investigation. **Gaman Kumar:** Formal analysis, Investigation. **Pawanvir Kaur:** Formal analysis, Investigation.

1. Introduction

Metal nanoparticles (NPs), conducting polymers (CPs), and nanocomposites (NCs) have the potential to change the world through applications like sensors, energy storage devices, memory storage, super magnet, semiconductor, micro-electronic device, photocatalytic

degradation, protection of material by composite coating, antibacterial property, etc. [1–5]. The electrical, magnetic, mechanical, optoelectronic, and photocatalytic properties of NPs, CPs, and their NCs vary a lot depending on their size and surface area [6–9]. The size of metal nanoparticles depends upon synthetic conditions like reaction and annealing temperature, seeding time, nucleation length, concentration, separation and drying process (temperature, time, and conditions), etc. [5–7].

Polyaniline (PANI) like CPs are very unique materials because of the high order of unsaturation, conjugation, organic nature, fibrous and porous structure making them ideal for high-performing synthetic materials having numerous applications. The PANI in combination with metal NPs leads to synergistic electrical, optical, photocatalytic, anti-corrosive, antibacterial, adsorption, purification, separation, and energy and memory storage properties [7–12].

The metal NPs and PANI NCs can be designed for specific applications depending on their size and surface area. Metal NPs can be suitably

* Corresponding author.

E-mail address: harishkumar@cuh.ac.in (H. Kumar).

<https://doi.org/10.1016/j.rineng.2023.101250>

Received 16 February 2023; Received in revised form 13 June 2023; Accepted 18 June 2023

Available online 30 June 2023

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entrapped physically or chemically in the cavities of CPs resulting in unique Metal/PANI NCs. The photocatalytic process of NPs and NCs involves the complete removal of organic products from polluted water. It involves the breakdown of large-size complex organic molecules into simpler small molecules. The process involves an advanced oxidation method for the decomposition of organic pollutants by the generation of reactive oxygen species [10]. In comparison to other conventional methods of water purification, the purification of impure water by metal NPs and NCs is an easy and affordable process. Metal NPs when mixed with CPs like PANI form either n-p or p-n heterojunction. MnO_2/PANI forms an n-p type of heterojunction by decreasing the optical band gap ($E_g = 2.1$ eV) of pure MnO_2 NPs. Different researchers have tried different metal oxide NCs as photocatalytic agents for degrading organic compounds [1–5]. Zhang et al. have reported photocatalytic properties of PANI/Au NCs for the degradation of organic dye Rhodamine B under 12 h of UV exposure. A significant color change was observed after 12 h [1]. Rhazi et al. investigated the CPs-based NCs as an electrode material for electrochemical sensors. Graphene and carbon-based NPs were described as electrode materials for rechargeable batteries [2]. Sharma et al. reported the magnetic properties of PANI/ Fe_2O_3 -based NCs super magnetic material to be used in super magnets or memory storage magnetic tapes or quantum dots in micro secure digital (SD) cards [3]. Sivakumar and his coworkers reported the photocatalytic activity of Copolymer/ ZnO NCs for the purification of wastewater. The copolymer used was poly(aniline-co-aminophenol) along with ZnO NPs for the degradation of methylene blue dye (MBD). The NCs degrade 88% of the dye under UV exposure [4]. Want et al. have reported $\text{Zn}@ \text{ZnWO}_4/\text{WO}_4$ NCs heterojunction as photocatalyst material. It was observed that the NCs with 50 wt percent WO_3 have higher photocatalytic activity than other investigated NCs [5]. Jiang et al. have investigated the photocatalytic and photoluminescence properties of $\text{ZnO}@ \text{ZnWO}_4$ NCs. The NCs show a blue-green emission band in the wavelength range of 400–540 nm. The photocatalytic performance of NCs was observed twice in ZnO NPs [6]. Yeseffi and Haghighi have investigated photocatalytic properties of p-NiO/ BiOI heterojunction as NCs for the photodegradation of acid orange-7 dye in visible light. BiOI shows 90% and NiO shows 10% photocatalytic activity in visible light [7]. Anitha et al. have reported photoconductive and antibacterial properties of NiO/ CdO NCs and compared their antibacterial properties with standard antibiotics [8]. Kumar et al. $\text{CuO}/\text{ZnO}/\text{NiO}/\text{rGO}$ based NCs as optoelectronic, heat resistive, and anti-corrosive material. They found that NCs are far better anticorrosive agents than individual metal NPs and rGO [9]. Kumar et al. have reported the heat-resistive and anticorrosive properties of $\text{Cu}/\text{Ni}/\text{Zn}/\text{PANI}$ NCs. They observed that Metal oxide/PANI NCs are far better heat-resistive and anticorrosive materials than CPs PANI and provide a synergistic effect in their property when used in combination [10]. Zhang et al. have investigated $\text{Co}/\text{Co}_3\text{O}_4$ NCs as hybrid supercapacitors [11]. Ren et al. have explored $\text{Co}_3\text{O}_4/\text{PANI}$ NCs as super-capacitor [12]. Ma et al. investigated $\text{Co}_3\text{O}_4/\text{polypyrrole}$ NCs as electrode material for super-capacitor [13]. Monfared and Jamshidi investigated the photocatalytic properties of TiO_2/PANI NCs for the elimination of benzene from polluted water [14]. Zhang's research group has reported the photocatalytic activity of PANI/ TiO_2 NCs under UV illumination [15]. Sarmah and Kumar examined the degradation of Malachite Green dye under UV light by PANI/ TiO_2 NCs [16]. Nerkar et al. have explored the photolytic properties of PANI/ ZnO NCs for the degradation of Methyl Orange dye [17]. Bahl and Bagha have investigated the fiber-reinforced metal matrix NCs for push-out tests [18]. Bagha and Bahl have synthesized vapor-grown carbon fiber embedded in a polypropylene matrix for numerically integrated element analysis devices [19]. Bahl has published a review article on fiber-reinforced metal matrix NCs with high wear resistance, specific strength, and thermal stability [20]. In another paper, Bahl reported stainless steel wire reinforced with aluminum matrix gives rise to a composite of high mechanical and tensile strength [21]. Chandrasekar et al. have investigated the photocatalytic activity of Sn-doped MgO NPs

for degrading Methyl blue (MB) dye in the presence of UV light [22]. They observed that degradation of MB dye and phenol removal from impure water depends upon the concentration of Sn doped in MgO NPs. Perumal et al. have investigated the photocatalytic activity of surface-modified SnO_2 nanorods for degrading MB dye in sunlight [23]. They also performed recyclability experiments and SnO_2 nanorods and shows good recyclability behavior. In another research, Perumal et al. investigated the photocatalytic performance and energy conversion application of graphene oxide decorated SnO_2 NCs [24]. They observed that a 2% weight of graphene oxide in SnO_2 leads to 96% photocatalytic efficiency for MB dye under visible light. Panimalar et al. have investigated the long-term stability and reusability of Sn/MnO_2 NCs for photo-degradation and wastewater treatment [25]. A maximum of 98.5% degradation efficiency was observed for methyl orange dye. In another research group, Panimalar et al. have investigated the impact of silver NPs concentration on MnO_2 NCs for wastewater purification and photodegradation of dye [26]. The photo-degradation of methyl orange dye and phenol solution was investigated under visible light.

Till now, no researchers have reported the four applications of $\alpha\text{-MnO}_2/\text{PANI}$ NCs by theoretical (DFT) and experimental techniques. An extension to our study on NCs [9,10,27,28], here we are reporting the four novel applications of PANI encapsulated $\alpha\text{-MnO}_2$ NCs i.e., anticorrosive, photocatalytic, conductive, and antibacterial activity by theoretical and experimental techniques. $\alpha\text{-MnO}_2$ NPs, PANI, and $\alpha\text{-MnO}_2/\text{PANI}$ NCs were synthesized by reverse micelle, chemical oxidative, and *in-situ* techniques, respectively. Weightage has been given to understand the mechanism of corrosion inhibition and photocatalytic property of $\alpha\text{-MnO}_2/\text{PANI}$ NCs. The experimental and theoretical studies support each other results.

2. Experimental

The Manganese (II) chloride anhydrous (percentage purity 99%, CAS No.: 7773-01-5) was obtained from Sigma-Aldrich. The hydrochloric acid (37% pure) was obtained from Merck Scientific. The antibiotic Hexa disk (Hexa G-Minus 1) containing: TE-25 (Tetracycline 25 mcg), C-25 (Chloramphenicol 25 mcg), P-1 (Penicillin-G), AMP-10 (Ampicillin 10 mcg), S-10 (Streptomycin 10 mcg) and S3-300 (Sulphatrid 300 mcg) was procured from HiMedia. The mild steel (MS) of IS-2062 Fe-350 commercial grade was used for the corrosion experiments. The composition of MS was: C = 0.19, Ni = 0.09, Si = 0.17, Cr = 0.14, Cu = 0.06, Mo = 0.02, V < 0.02, Mn = 0.51, P = 0.044, S = 0.057, Fe = Rest.

2.1. Synthesis of MnO_2 NPs

0.5 M MnCl_2 solution was prepared. A solution of cyclohexane and water was made in a 1:9 ratio. 1% polyvinyl pyrrolidone (PVP) and TritonX/100 surfactant solution were prepared. The resulting solution was stirred at 600 rpm for 30 min. Hydrazine hydrate was added dropwise till the color changed. Tetrahydrofuran (THF) was used for the release of metal NPs from the micelle. The precipitates were filtered, washed, and dried.

2.1. Synthesis of Conducting Polymer, PANI

30 ml aniline monomeric solution was used for polymerization. The Sodium Lauryl-sulphate (SLS) and ferric chloride solution were taken. The crushed ice bath was used to maintain the temperature below 4 °C. The solution was stirred continuously until dark-colored precipitates were not obtained. The precipitates were filtered, washed, and dried.

The gravimetric study was carried out in 0.1 M hydrochloric acid solution as a corroding medium. The concentration of $\alpha\text{-MnO}_2/\text{PANI}$ NCs used was 100–1000 mg/ml. The mechanical polishing of MS specimens was carried out with 200–800 grades of sandpaper [29,30]. The ASTM (standard D-2688) was used to study the corrosion rate in the presence and absence of NCs [31]. The inhibition efficiency of NCs were

found from the Corrosion Rate of blank (CR_{blank}) and Corrosion Rate in the presence of an inhibitor ($CR_{Inhibitor}$) [32,33]. An impedance spectroscopic study was carried out with the help of an Autolab 128 N Metrohm instrument by using three electrodes-based cell. First Open Circuit Potential (OCP) was established and the variable frequency that is 0–10,000 Hz was imposed at OCP in the cell containing NCs and MBD.

The bactericidal activity of NCs was performed on two bacteria that is *S. epidermis* and *E. coli* by agar-agar well technique [34–36]. The two bacteria are selected that is Gram-positive and the Gram-negative. The concentration of α -MnO₂/PANI NCs used was 100, 200, 600, 800, and 1000 ppm. The average Zone of Inhibition in mm (ZOI) was observed for both of these test microorganisms. The average ZOI was compared with six standard antibiotics of hexa disk. The Hexa disk was composed of both broad-spectrum and narrow-spectrum antibiotics that are TE-25 (Tetracycline 25 mcg), C-25 (Chloramphenicol 25 mcg), P-1 (Penicillin-G), AMP-10 (Ampicillin 10 mcg), S-10 (Streptomycin 10 mcg) and S3-300 (Sulphatrid 300 mcg).

The photocatalytic study of α -MnO₂/PANI NCs was carried out on Methyl Orange Dye (MOD). A 0.1×10^{-3} M solution of dye was used for the photocatalytic study. The α -MnO₂/PANI NCs (100 ppm) were selected for the photocatalytic study. The NCs-treated dye solution was irradiated with UV light for 3 h. The absorbance of a portion of the solution was taken at regular intervals of 30 min. Eq. (1) was used to find the %age degradation of dye [37–39].

$$\text{Degradation} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

The kinetics of photo-degradation of organic dye was followed by Eq. (2).

$$\ln \frac{C_0}{C} = k t \quad (2)$$

The k gives the rate constant for the degradation of dye by the NCs.

The mechanism of photocatalytic activity was supported by the measurement of photocurrent generated during the photocatalysis process, impedance spectroscopy, pH variation, and chemical oxygen demand (COD) measurement.

The theoretical study was performed on α -MnO₂/PANI NCs by

Gaussian09W. Figs. 1 and 2 show the chemical interaction parameters data obtained from the theoretical study. Fig. 3 depicts the data of the corrosion study of NCs. Table S1 (ESI) depicts 3-dimensional atomic coordinates, single-point energy, and Mulliken charge. Table S2 (ESI) depicts MO coefficients of α -MnO₂/PANI NCs. Table 1 depicts the different theoretical parameters for α -MnO₂/PANI NCs observed from the Gaussian-09W program. The standard basis set and functional used are B3LYP, and 6-31G (d, p), respectively. Table 2 depicts the thermodynamic parameters of NCs. Fig. 4 shows the molecular structure (A), Electron Density Distribution (EDD) per atom (B), and van der Waal's surface per atom (C) of NCs. Fig. 5 depicts the lowest unoccupied MO (B), and highest occupied MO (C) of NCs. The different DFT parameters were obtained by Eqns. (3)–(14) [40–44].

$$\text{Electrochemical potential, } \kappa = \frac{(I + A)}{2} \quad (3)$$

$$\text{Hardness, } \eta = \frac{(I - A)}{2} \quad (4)$$

$$\text{Softness, } \sigma = \frac{1}{\eta} = \frac{2}{(I - A)} \quad (5)$$

$$\text{Fraction of electron shifted, } \Delta N = \frac{(\chi_{Fe} - \chi_{Inh})}{2 \times (\eta_{Fe} - \eta_{Inh})} \quad (6)$$

$$\text{Electrophilicity, } \omega = \frac{\mu^2}{2\eta} \quad (7)$$

$$\text{Charge transfer max., } \Delta N_{Max.} = \frac{I + A}{2(I - A)} \quad (8)$$

$$\text{Adsorption energy, } E_{Ad} = \frac{E_{s-x} - (E_s + E_x)}{n} \quad (9)$$

$$\text{Electron releasing, } \omega^+ = \frac{(I + 3A^2)}{16(I - A)} \quad (10)$$

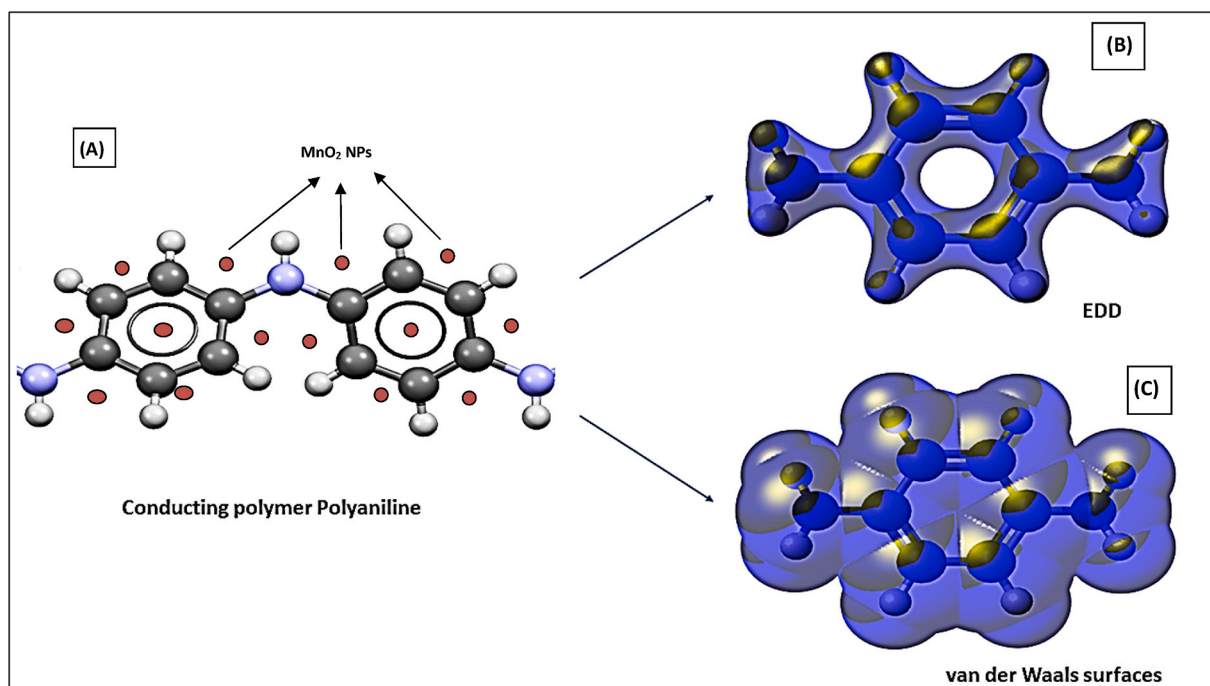


Fig. 1. Polyaniline (PANI) and α -MnO₂ nanoparticles (A), EDD per atoms of PANI (B), and van der Waal surfaces (C).

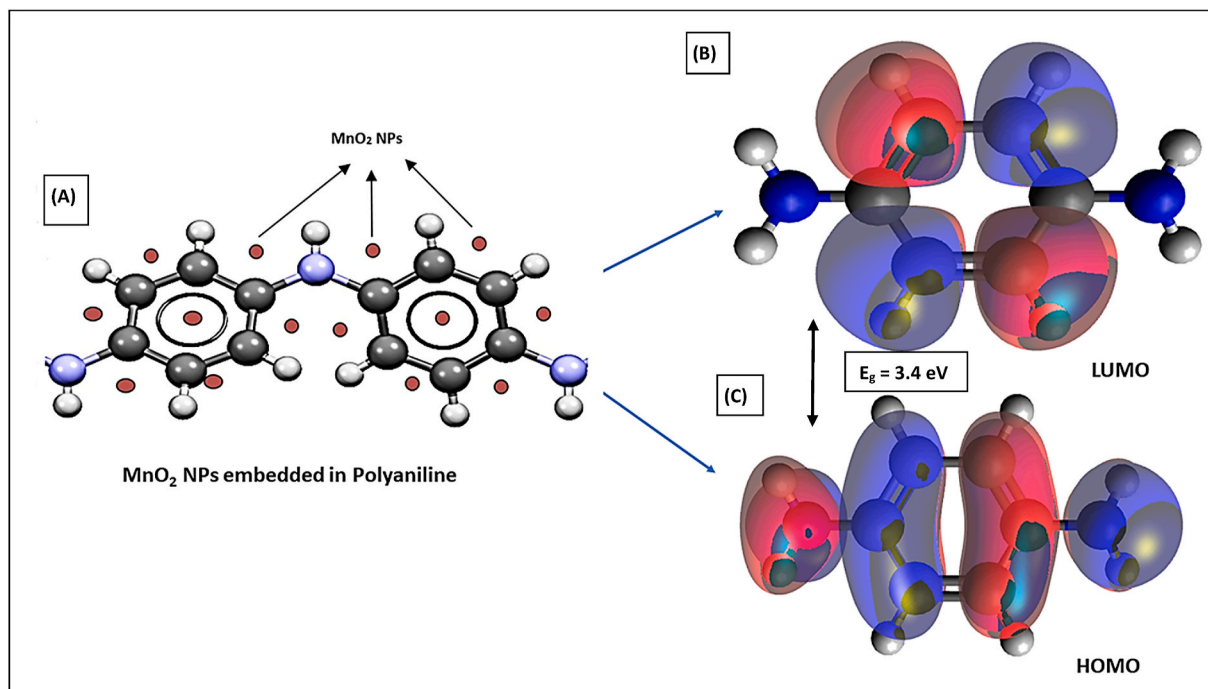


Fig. 2. α -MnO₂ nanoparticles embedded in PANI (A), LUMO of PANI (B), and HOMO of PANI (C).

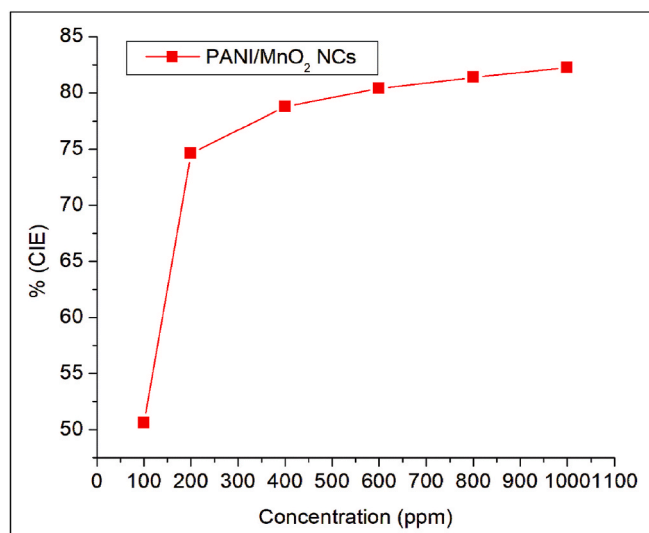


Fig. 3. Corrosion inhibition efficiency of α -MnO₂/PANI nanocomposites at 0–1000 ppm concentrations for mild steel exposed to 0.1 M hydrochloric acid for 3 h.

Table 1

Chemical reactivity parameters for α -MnO₂/PANI NCs at room temperature were obtained from Gaussian09W software, Standard basis set and exchange functional used are: B3LYP 6-31G (d,p).

E_{HUMO} (-eV)	E_{LUMO} (-eV)	ΔE (eV)	I (eV)	A (eV)	χ (eV)	η (eV)	σ (eV ⁻¹)
5.87	2.41	3.46	5.87	2.41	4.14	1.73	0.578
ΔN (eV)	E_{Ad} (kJ/mol)	ω (au)	ω^+ (au)	ω^- (au)	$\Delta\Psi$ (-eV)	PA (eV)	
1.196	7.12	6.5 $\times 10^{-6}$	0.1747	0.1767	0.424	-0.113	

Abbreviations; ΔE : Energy difference, I : Ionization energy, A : Electron affinity, χ : Electrochemical potential, η : Global hardness, ΔN : Maximum charge transfer index, E_{Ad} : Adsorption energy, ω : Electrophilicity, ω^+ : Electron accepting power, ω^- : Electron donating power, $\Delta\Psi$: Metal inhibitor interaction energy, PA: Proton affinity of the inhibitor molecule.

$$\text{Electron accepting power, } \omega^- = \frac{(3I + A^2)}{(16(I - A))} \quad (11)$$

$$\text{The work function, } \Delta\phi = -\frac{(\phi_{Fe} - \chi_{Inhib})^2}{4(\eta_{Fe} + \eta_{Inhib})} \quad (12)$$

$$\text{Back - donation energy, } \Delta\epsilon_{BD} = -\frac{\eta}{4} \quad (13)$$

$$\text{Proton affinity, } PA = E_{pro} - (E_{non\ pro} + E_{H^+}) \quad (14)$$

3. Results and discussion

The structural and optical information of α -MnO₂ NPs, CPs PANI, and α -MnO₂/PANI NCs were obtained from UV-visible spectroscopy. Fig. S1 (ESI) depicts UV visible spectra of α -MnO₂ NPs, CPs PANI, and α -MnO₂/PANI NCs. Fig. S2(ESI) shows the direct and indirect bandgap of PANI and MnO₂/PANI NCs, respectively. The α -MnO₂ NPs show an absorption

Table 2

Theoretical parameters for α -MnO₂/PANI NCs at room temperature obtained from Gaussian calculation, Standard basis set and exchange functional used are: B3LYP 6-31G (d, p).

Nuclear Repulsive energy (Hartrees)	Rotational constants (GHz)	Dipole moment (D)	Quadrupole moment (xy axis)	KE of Symmetry A'	KE of Symmetry A''	Molecular mass (amu)
341.47	5.531	0.0015	-36.394	1.047×10^3	4.662×10^1	108.068
Internal Energy, E (Thermal) kCal/mol	Heat capacity, C _v (Cal mol ⁻¹ K ⁻¹)	Entropy, S (Cal mol ⁻¹ K ⁻¹)	Zero-point vibrational energy (kCal/mol)	Thermal correction to E (Hartree/Particle)	Thermal correction to Enthalpy, H (Hartree/Particle)	Thermal correction to G (Hartree/Particle)
88.43	27.87	81.41	143.17	0.238	0.219	0.184

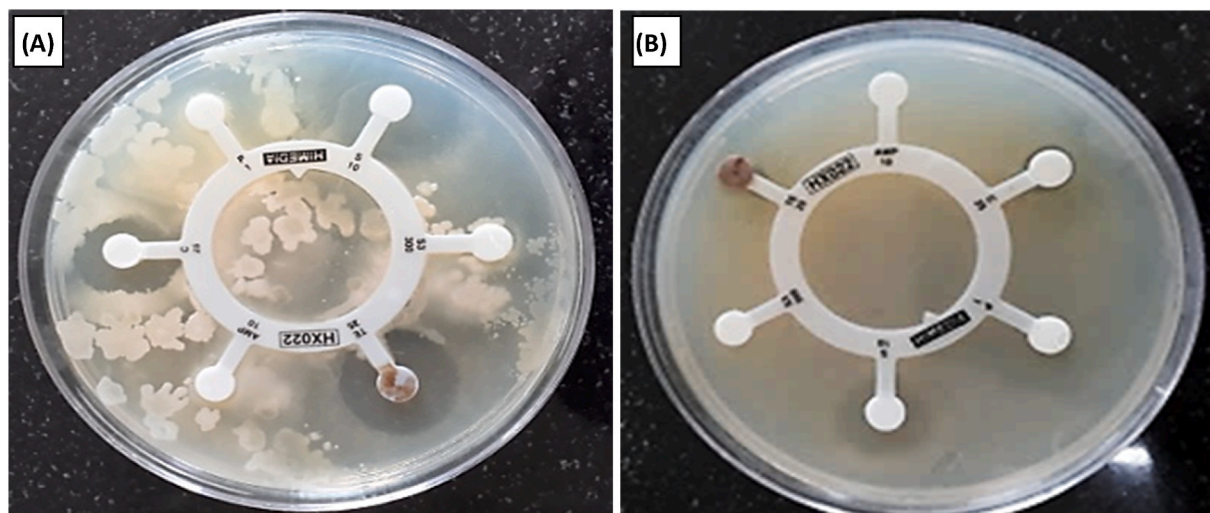


Fig. 4. Zone-of-Inhibition (ZOI) shown by different standard antibiotics (hexa disk) with *S. epidermidis* (A) and *E. coli* (B). The composition of Hexa disk is: TE-25: Tetracycline 25 mcg; C-25: Chloramphenicol 25 mcg; P-1: Penicillin-G; AMP-10: Ampicillin 10 mcg; S-10: Streptomycin 10 mcg; and S3-300: Sulphatrid 300 mcg.

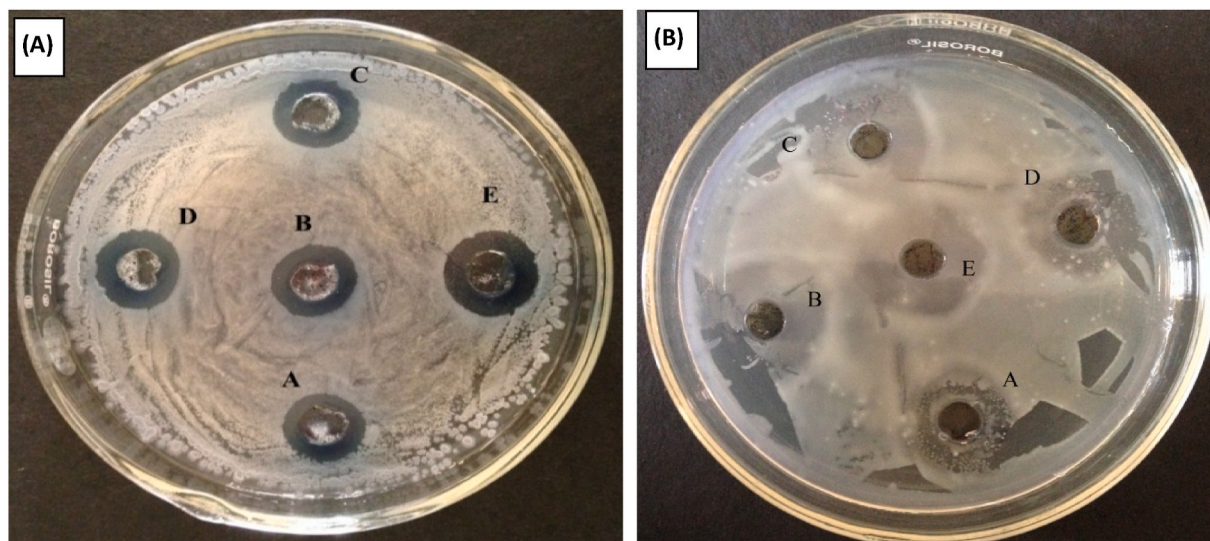


Fig. 5. ZOI revealed by α -MnO₂/PANI NCs against *S. epidermidis* (A) and *E. coli* (B). ZOI at 100 (a, a), 200 (b, b), 600 (c, c), 800 (d, d) and 1000 ppm (e, e) shown by α -MnO₂/PANI NCs against *S. epidermidis* and *E. coli*, respectively.

band at 320 nm. The PANI shows an absorption band at 330 nm. The α -MnO₂/PANI NCs shows two absorption band at 265 and 333 nm. The direct and indirect bandgap observed from Tauc plots of PANI were 3.45 eV and 3.47 eV, respectively. The direct and indirect bandgap observed for α -MnO₂/PANI NCs was 2.56 eV and 2.63 eV, respectively Fig. S2 (ESI). It was observed that both direct and indirect bandgap decreases as we move from CPs PANI to α -MnO₂/PANI NCs. This was due to the

entrapment of MnO₂ NPs between the cavities of CPs PANI thus creating a Fermi level between the valence and conduction band of PANI.

The identification of the optical band in CPs and metal oxide-based NCs contributes to the fundamental understanding of their electronic and optical properties. It provides insights into the mechanisms governing charge transfer, exciton formation, and light-matter interactions in these materials. The observation of the optical band in CPs and metal

oxide-based NCs is significant due to its implications in optoelectronic devices, tunable optical properties, energy conversion and storage, sensor applications, and fundamental research.

Fig. 3S illustrates the FT-IR spectra of α -MnO₂ NPs, PANI, and α -MnO₂/PANI NCs. Fig. 3S(A) shows FTIR spectra of α -MnO₂ NPs. The majority of peaks appeared in the fingerprint region i.e., 450 to 750 cm⁻¹. The α -Mn-O stretching peak was observed at 573 and 561 cm⁻¹ [45]. The peaks at 565 and 630.21 cm⁻¹ were assigned to Mn-O and O-Mn-O, respectively.

Fig. 3S(B) shows the FT-IR of PANI. The peaks at 2853.54 cm⁻¹ and 2278.35 cm⁻¹ were assigned to -C-H and = CH stretching. The two characteristic peaks at 1517 cm⁻¹ (Quinoid) and 1583 cm⁻¹ (Benzene) also appeared. The characteristic N = Q = N peak appears at 1115 cm⁻¹. The peak at 807 cm⁻¹ was assigned to the para-substituted benzene ring [46,47].

Fig. 3S(C) depicts FT-IR of α -MnO₂/PANI NCs. The majority of sharp peaks were observed in the fingerprint region of the spectrum. The peak at 803.65 cm⁻¹ was due to a para-distributed benzene ring. C-H in the plane (1208.50 cm⁻¹) and out of the plane (891.50 cm⁻¹) bending vibrations were also seen. C-N stretching (aromatic) peak appeared at 1347.76 cm⁻¹. The two peaks at 1517 and 1583 cm⁻¹ are due to the Benzene and Quinoid ring, respectively. The N-H stretching peak appeared at 3340.24 cm⁻¹ [48].

Fig. 4(A) depicts the X-ray diffraction pattern of the α -MnO₂ NPs. The peaks are indexed at 2θ angles of 13 (110), 18.1 (200), 28.42 (110), 30.21 (101), 44.54 (111), 55.16 (211), and 64.64 (002) [49–51]. The indexing pattern corresponds to α -MnO₂ tetragonal phase having cell parameters $L = B = H$: 6.143 Å having space group Fd₃m (JCPDS card no. 44-0141). Peaks corresponding to the β -phase of MnO₂ were absent in the XRD pattern of MnO₂. The average particle size of the α -MnO₂ NPs obtained using the Scherrer equation was 22 nm. The X-ray diffraction pattern reveals the crystalline phase of α -MnO₂ NPs [52,53].

It is only in the late 90s, the crystalline form of PANI was discovered by the chemical oxidative and XRD technique [54,55]. The crystalline form of PANI (emeraldine salt) is soluble in most inorganic acids and the majority of organic solvents [56–58]. Figs. 4(B) and (C) depicts the X-ray diffraction pattern of PANI, α -MnO₂/PANI NCs. The XRD pattern of PANI was indexed at 2θ of 4° (100), 18° (220), 20° (310), and 21.5° (311). A shift towards a lower angle was due to the scattering of X-rays from PANI to an interstitial position. XRD pattern shows that during the synthesis of α -MnO₂/PANI NCs, there is a chemical interaction between PANI and MnO₂ which results in some structural modifications in the α -MnO₂ NPs [59].

Fig. 5S(A) depicts the TEM image of α -MnO₂ NPs. TEM image gives useful information about the structure and morphology of NPs. The α -MnO₂ NPs were agglomerated together because of the very small size of the micellar cavity formed during the reverse micellar technique. The different sizes of α -MnO₂ NPs can be seen in the TEM image i.e., 17.41 nm, 25.21 nm, 15.32 nm, and 20.65 nm with an average particle size of 19.64 nm which is very close to the XRD.

Fig. 5S(B) depicts a cylindrical-shaped PANI. We have used oxalic acid as an organic precursor and get converted it into conductive carbon at high temperatures in pyrolysis processes [60]. There is a probability that carbon atoms were generated during the co-pyrolysis process, which increases the conductivity of PANI. The TEM image of PANI shows the different sizes of PANI formed i.e., 38.55 nm, 29.47 nm, 32.23, and 35 nm with an average size of 33.89 nm.

Fig. 5S(C) represents cylindrical-like structures of α -MnO₂/PANI NCs. The α -MnO₂ NPs get perfectly entrapped in the molecular cavities of PANI and the same is verified from the TEM image of PANI NCs. The cavities/hole present in PANI provides a suitable surface for the adsorption of α -MnO₂ NPs in the PANI NCs [58,59]. The globular shape of α -MnO₂ NPs promotes this process of entrapment of NPs in the cavities of PANI. The TEM image of NCs shows an average size of 35–40 nm.

3.1. Theoretical study

Tables S1 (ESI), S2 (ESI), Tables 1 and 2, Figs. 1 and 2 depict the data obtained from the computational study. Table S1 (ESI) depicts 3-D coordinates and Mulliken charges of α -MnO₂/PANI NCs. The charge was high on the N atom which signifies that N is the suitable site for adsorption. Table S2 (ESI) depicts alpha-occupied and alpha-unoccupied molecular orbitals. “The eigenvalue of HOMO and LUMO helps in finding the energy gap between the two and is an important criterion in deciding the adsorption power of an inhibitor molecule” [40–42]. The energy of HOMO was greater than LUMO which makes it favorable for physio-sorption. Table 1 depicts different DFT parameters of the NCs. The parameters like adsorption energy, global softness, and chemical potential prove the high affinity of NCs towards adsorption on the MS surface. The electron-releasing tendency (ω^-) also proves the strong ligand behavior of PANI NCs. Table 2 depicts different theoretical parameters observed for PANI NCs by using Gaussian09W software. High E , C_v , S signifies that PANI NCs are in a high state of energy and thus have a strong tendency of adsorption on the MS surface. A high percentage of electronic charge distribution of two N atoms (Fig. 1) and greater van der Waal surfaces around carbon atoms of benzene also make PANI NCs favorable for the adsorption of the MS surface [43]. Fig. 2 depicts the LUMO and HOMO of PANI NCs. A small energy difference between LUMO and HOMO suggests the presence of Fermi level which reduced the gap between valance and conduction band due to the presence of α -phase MnO₂ NPs in the interstitial sites of PANI. The same information was obtained from the XRD study of PANI NCs. Hence, experimental and theoretical studies reinforce each other results.

3.2. Corrosion inhibition properties

To find different applications of PANI NCs, we have tested the anti-corrosive properties of α -MnO₂/PANI NCs for MS in 0.1 M hydrochloric acid. Six concentrations of PANI NCs were tested i.e., 100, 200, 400, 600, 800, and 1000 ppm. Table 3 displays the data from the corrosion experiments. Fig. 3 displays variation in inhibition efficiency against the concentration. An almost linear increase in inhibition efficiency was observed w.r.t. concentration of PANI NCs [13]. An $87 \pm 0.1\%$ inhibition efficiency was achieved at a 1000 ppm concentration of NCs. The inhibition efficiency of PANI NCs was comparable to other chemical and organic corrosion inhibitors reported in the literature [9,10,42–44]. The surface study of MS coupons was performed with the metallurgical microscope. Fig. 5S6 displays a metallurgical image of MS coupons treated with 0.1 M HCl after the gravimetric study. The size and depth of the pit and crack decrease with the concentration of NCs. Table 4 depicts the pore length (μ m), porosity (percentage), and film thickness (μ m) measured by Meta-Plus software provided with the metallurgical microscope. The porosity (percentage) and length of the pores decreases and the thickness of the barrier film increases with the concentration of PANI NCs. The same information of an increase in film thickness with the concentration of NCs was obtained from the computational study. Hence, PANI NCs form a continuous surface-blocking film that protects the surface of MS from the attack of hydrochloric acid [35–38].

3.3. Antibacterial study

The antibacterial activity of α -MnO₂/PANI NCs was explored against *E. coli* and *S. epidermis* by the Agar-Agar well-diffusion technique. The ZOI was investigated for both these Gram-negative and Gram-positive bacterial strains. Table 5 shows the ZOI in mm of Hexa disk: TE-25 (Tetracycline 25 mcg), C-25 (Chloramphenicol 25 mcg), P-1 (Penicillin-G), AMP-10 (Ampicillin 10 mcg), S-10 (Streptomycin 10 mcg) and S3-300 (Sulphatrid 300 mcg) against the two bacterial strains. Table 6 depicts ZOI shown by α -MnO₂/PANI NCs against *E. coli* and *S. epidermis*. Fig. 4 displays the images of culture grown and antibacterial activity shown by standard Hexa disk against *S. epidermis* (A) and *E. coli* (B).

Table 3

Weight loss, corrosion rate, and corrosion inhibition efficiency (CIE) of α -MnO₂/PANI NCs at different concentrations by gravimetric method at 25 °C in 0.1 M hydrochloric acid.

Concentration (mg/ml)	Average weight loss (mg)	Absolute deviation	Standard deviation (σ_d)	Precision in weight measurement	Corrosion rate (mpy)	CIE
Blank	50.75	0.05	0.02	50.75 $\pm$ 0.02	1688.5	–
100	23.2	0.02	0.01	23.2 $\pm$ 0.01	771.8	54.29
200	11.5	0.03	0.02	11.5 $\pm$ 0.02	382.6	77.34
400	10.3	0.05	0.01	10.3 $\pm$ 0.01	342.7	79.70
600	9.6	0.04	0.02	9.6 $\pm$ 0.02	319.4	81.08
800	9.1	0.03	0.01	9.1 $\pm$ 0.01	302.7	82.07
1000	6.6	0.02	0.02	6.6 $\pm$ 0.02	219.5	87.00

Table 4

Coating Thickness, Percentage Porosity, and Pore Length (PL) of blank and α -MnO₂/PANI NCs treated MS samples observed from Meta Plus Software.

Concentration (ppm)	Coating Thickness (μ m)	Percentage porosity	Pore Length (μ m)
Blank	48.76	77.27	174.21
100	61.74	57.23	121.4
200	144.65	41.23	112.4
400	191.67	31.24	77.5
600	210.13	19.01	56.1
800	218.15	16.4	41.2
1000	227.21	13.1	19.3

Table 5

Zone of Inhibition (mm) shown by different standard antibiotics with *S. epidermidis* and *E. coli*.

	Six standard antibiotics present in Hexa disc					
	TE (25)	C (25)	P ₁	AMP 10	S (10)	S3 (300)
<i>S. epidermidis</i>	19	17	15	NS	23	NS
<i>E. coli</i>	11	9	NS	NS	13	NS

Note: NS: Not shown; **TE-25:** Tetracycline 25 mcg; **C-25:** Chloramphenicol 25 mcg; **P-1:** Penicillin-G; **AMP-10:** Ampicillin 10 mcg; **S-10:** Streptomycin 10 mcg; **S3-300:** Sulphatrid 300 mcg.

Table 6

Zone of Inhibition in mm (ZOI) shown by α -MnO₂/PANI NCs against *S. epidermidis* and *E. coli* bacterial strain at different concentrations.

Bacterial test organism	α -MnO ₂ /PANI NCs				
	Concentration (ppm)				
	100	200	600	800	1000
<i>S. epidermidis</i> (ZOI in mm)	8.3	10.2	12.3	15.1	18.5
<i>E. coli</i> (ZOI in mm)	8.7	10.8	11.4	13.2	15.3

Fig. 5 displays the images of culture grown and ZOI shown by α -MnO₂/PANI NCs at different concentrations against two microorganisms. ZOI was found to increase with the NCs concentration. The standard antibiotic S(10) shows 23 and 13 mm ZOI and the NCs show 18.5 and 15.3 mm ZOI (1000 ppm) for *S. epidermidis* and *E. coli*, respectively. ZOI shown by PANI NCs was almost similar to six antibiotics present in the Hexa disk. α -MnO₂/PANI NCs were explored for their antibacterial activity and have shown promising results in inhibiting the growth of two bacteria. The probable mechanism of antibacterial activity exhibited by these NCs can be attributed to factors like (i) *Damaging the bacteria*: The NCs physically interact with the bacterial cell membrane, leading to its structural disruption. This can occur through direct contact between the NCs and the *E. coli* and *S. epidermidis* cells, causing structural changes and permeability alterations in the cell membrane. The physical damage will results in leakage of cellular contents, impaired nutrient uptake, and ultimately cell death, (ii) *Reactive Oxygen Species (ROS) generation*: α -MnO₂/PANI NCs have the ability to generate reactive oxygen species

such as hydrogen peroxide (H₂O₂) and superoxide radicals (O₂⁻) when exposed to light. These ROS are highly reactive and induce oxidative stress within bacterial cells. The ROS can damage various cellular components, including proteins, lipids, and DNA, leading to cellular dysfunction and bacterial death, (iii) *Electrostatic interactions*: The CPs PANI component of the NCs carries negative charges (electron-rich centers). Bacterial cells, on the other hand, have a positively charged surface due to the presence of lipopolysaccharides. The electrostatic interaction between the CPs and the bacterial cell surface can disrupt the membrane integrity and disrupt essential cellular processes, and (iv) *Ion release*: MnO₂ NPs within the NCs can release metal ions, particularly manganese ions (Mn²⁺), into the surrounding environment. These manganese ions will exhibit antibacterial activity by interfering with bacterial metabolic processes. They disrupt the enzymatic reactions, inhibit cellular respiration, and impair DNA replication and repair mechanisms, leading to bacterial cell death. However, the exact mechanism of antibacterial activity of NCs may vary depending on the specific composition and properties of the CPs and MnO₂ NCs, as well as the target bacterial species.

3.4. Photocatalytic study

The photocatalytic activity of α -MnO₂/PANI NCs was observed against MOD by UV-visible technique for a continuous 3 h. Fig. 6 displays the results of the UV study of NCs (100 ppm) for MOD w.r.t. time. Fig. 7 depicts absorbance (A) w.r.t. λ at different times. The α -MnO₂/PANI NCs show 19.67, 31.43, 46.75, 61.45, 77.94, and 89.15% degradation of methyl orange dye (MOD) after every 30 min. The advantage of MOD over other dyes in photocatalytic activity studies by NCs includes, (i) *Sensitive to visible light*: MOD is sensitive to visible light, particularly in the range of 400–600 nm [61,62]. This characteristic makes it well-suited for photocatalytic activity studies, as many

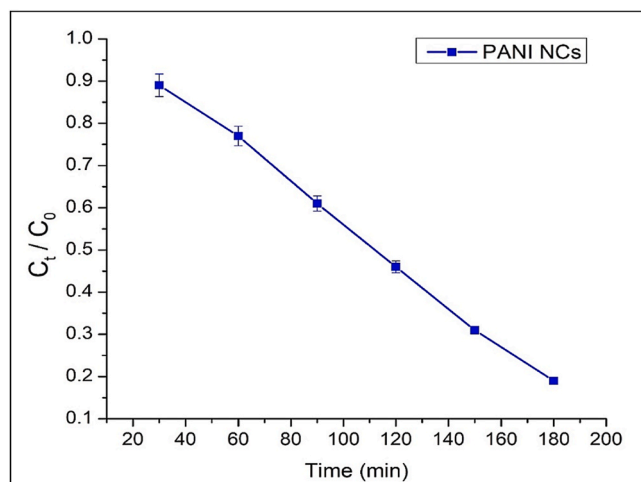


Fig. 6. Photocatalytic activity of α -MnO₂/PANI NCs (100 mg/l) for degrading MRD w.r.t. time in UV light.

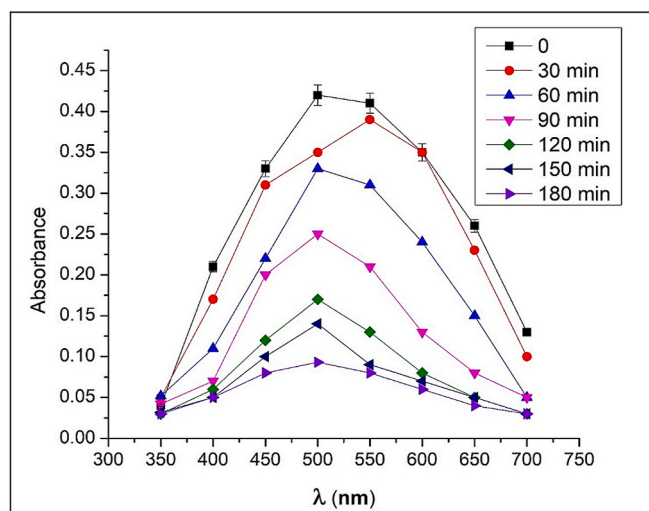


Fig. 7. UV visible absorbance shown by α -MnO₂/PANI NCs (100 ppm) w.r.t. wavelength (nm) at different time interval (min).

photocatalysts exhibit optimum performance under visible light irradiation, (ii) *Easy detection and quantification*: MOD has a distinct color change from orange to pink/red upon reduction or degradation. This feature enables easy visual detection and quantification of the photocatalytic activity, (iii) *Stability and compatibility*: MOD is relatively stable and compatible with various NCs used in photocatalysis research, (iii) *Cost-effective*: MOD is a commercially available and relatively inexpensive dye compared to some other organic dyes used in photocatalytic studies, (iv) *Established research benchmark*: MOD has been widely utilized as a model dye in various photocatalytic studies due to its well-established photophysical and photochemical properties, (v) *Environmental relevance*: MOD is often used as a model compound to simulate the degradation of organic pollutants, particularly azo dyes, which are

commonly found in wastewater. The choice of dye ultimately depends on the specific research objectives, target applications, and compatibility with the NCs being investigated [63].

3.5. Top of form

The performance of α -MnO₂/PANI NCs was found to be higher than ZnO/ZnWO₄ NCs [6], ZnO/PANI NCs [4], MO/PANI NCs [27,28], Graphene/V₂O₅ NCs [37]. The absorbance maxima were found to decrease with time (Fig. 7). The absorbance ratio (C_t/C_0) also decreases with time. The order of photocatalytic action and rate constant of photodegradation of MOD was calculated from Eqs. (1) and (2). The photodegradation of MOD by the NCs follows a pseudo-first-order reaction with a rate constant of 0.0657 min⁻¹.

3.6. Study of mechanism of photocatalytic activity of the α -MnO₂/PANI NCs

The direct and indirect bandgap (E_g) of α -MnO₂/PANI NCs was found to be smaller than CPs PANI and MnO₂ NPs. The high photocatalytic activity shown by α -MnO₂/PANI NCs was attributed to the synergistic effect of PANI and α -MnO₂ NPs [64]. The electron in the CB of α -MnO₂ NPs combines with the oxygen-free radicals ($O_2^{\cdot-}$) of α -MnO₂/PANI NCs. The oxygen-free radicals then react with H₂O vapor leading to the formation of OH[•] that degrade MOD. The products of degradation of MOD are N₂C₆H₄NH₂, H₂O, and SO₂ [65]. Fig. 8 depicts the probable mechanism of the photocatalytic activity shown by the NCs.

The probable mechanism of photodegradation of organic dye by the NCs.

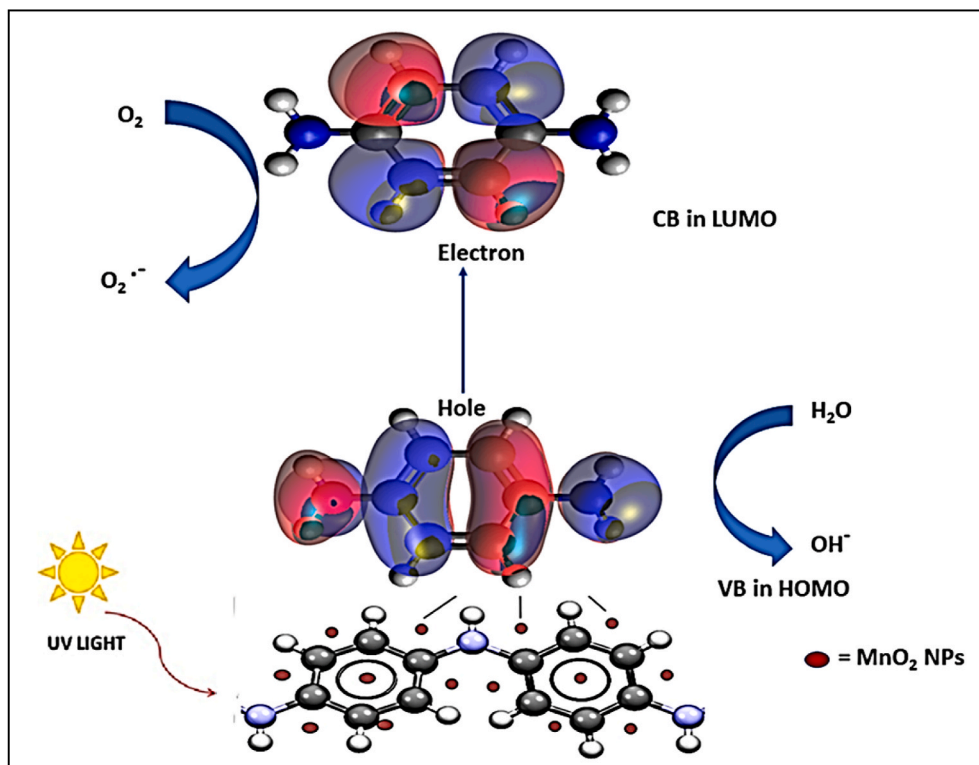
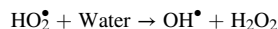
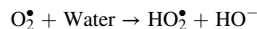
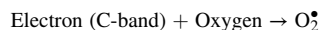
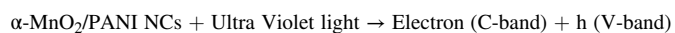
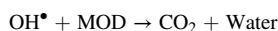
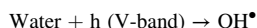
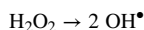


Fig. 8. The probable mechanism of degradation of MOD by the α -MnO₂/PANI NCs under UV light.



The combination of an electron in the conduction band (CB) and oxygen in the air gives rise to $\text{HO}_2^\bullet$. Further, combination of $\text{HO}_2^\bullet$ and H_2O leads to $\text{OH}^\bullet$ radical. These two are the vital steps of photocatalytic activity of $\alpha\text{-MnO}_2/\text{PANI}$ NCs for degrading MOD [66–68]. Sonu et al. have investigated the photocatalytic activity of $\text{Ag}/\text{CoFe}_2\text{O}_4$ heterojunction as a photocatalytic agent for degrading MOD under UV light and degrading up to 89% of dye under visible light [67]. Singh et al. investigated $\text{Ag}/\text{BiOBr}/\text{Graphene}$ NCs as photocatalytic agents for the degradation of phenol. Up to 98% photodegradation of phenols was observed under visible light [68]. Table 7 shows a comparative study of Photocatalytic activity shown by different metal oxide NPs for degrading different organic dyes in comparison with our $\alpha\text{-MnO}_2/\text{PANI}$ NCs.

3.6.1. pH variation study to support the photocatalytic activity of NCs

This mechanism was further supported by observing changes in pH with the progress of the photocatalytic action of NCs. Fig. 9 shows the variation of pH of the solution containing $\alpha\text{-MnO}_2/\text{PANI}$ NCs and MO dye w.r.t. time. Before starting the photocatalytic process, the pH of the solution was 4.4. After 30 min of UV light exposure, the pH increases to 6.2. After 180 min of UV exposure, pH increases to 8.5. The increase in pH with an increase in photodegradation of dye was due to the production of hydroxyl ions which leads to an increase in the pH of the solution. The orange color of MOD in the basic medium (pH 7.2) was not observed after 90 min of UV exposure (Fig. 9). It means that $\alpha\text{-MnO}_2/\text{PANI}$ NCs have started degrading the MOD dye after 30 min of UV exposure as indicated by a color change from light red to slight grayish. After 180 min of UV exposure, the color of the solution was dark grey. The orange color of MOD was not seen in the basic medium. This confirms that the NCs have completely degraded the MOD.

3.6.2. Photocatalytic study to support the photocatalytic activity of NCs

The photocurrent produced due to exposure to UV light in the solution containing $\alpha\text{-MnO}_2/\text{PANI}$ NCs and MOD was continuously monitored using Autolab potentiostat/Galvanostat Model-M204 [69–71]. The UV lamp was kept on for 50 s and then off for 50 s and the cycle goes on and the photocurrent generated during UV exposure was continuously monitored using a three electrodes-based electrochemical cell supplied with the instrument. Fig. 10 shows the variation of photocurrent with time while switching on and off processes of the UV lamp. It was observed that the magnitude of the photocurrent rises sharply when the UV lamp was switched on and falls sharply on switching off the lamp. When the UV lamp was on for a continuous 50 s there is a slight decrease in photocurrent (Fig. 10). This experiment proves the photocatalytic action of $\alpha\text{-MnO}_2/\text{PANI}$ NCs for MOD.

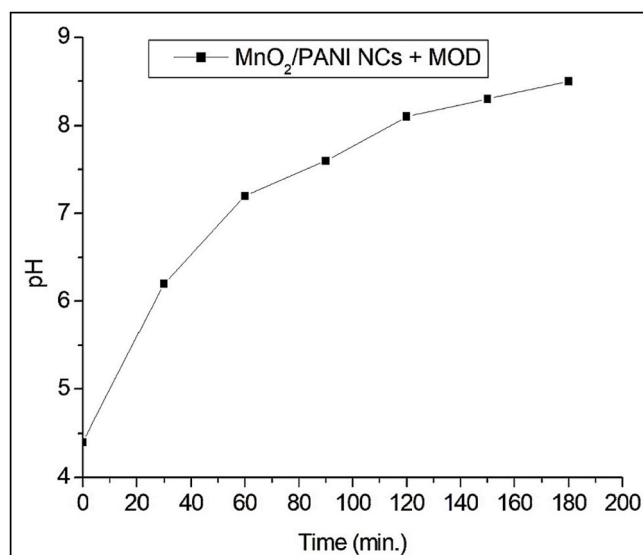


Fig. 9. Variation of pH of $\alpha\text{-MnO}_2/\text{PANI}$ NCs + MOD solution with respect to the progress of photocatalytic reaction.

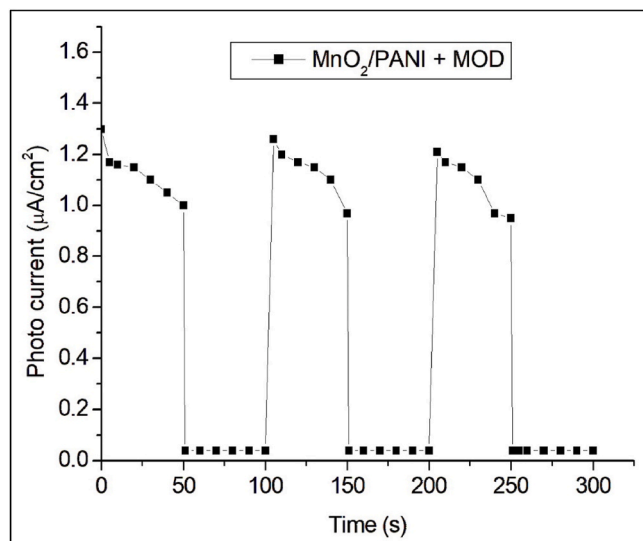


Fig. 10. Variation of photocurrent with time (s) while exposing the solution containing MnO_2/PANI NCs + MOD. The UV lamp was continuously switched on and off every 50 s.

3.6.3. Impedance spectroscopy study to support photocatalytic activity

The photocatalytic of $\alpha\text{-MnO}_2/\text{PANI}$ NCs for MOD was further supported by an impedance spectroscopy study. The impedance spectroscopy was carried out while irradiating the solution with UV light [72].

Table 7

Comparative study of photocatalytic activity shown by different metal oxide NCs. For degrading different organic dyes with $\alpha\text{-MnO}_2/\text{PANI}$ NCs (Sr. No. 9).

S. No.	Nanocomposites	Organic compound/Dye	UV or Visible light	%age of photocatalytic activity	Reference
1.	$\text{ZnO}/\text{ZnWO}_4/\text{WO}_3$	Methyl orange dye	UV light	80	[5]
2.	$\text{ZnO}-\text{ZnWO}_4$	Methylene blue dye	UV light	78	[6]
3.	PANI/Au	Rhodamine B	UV light	81	[1]
4.	$\text{Poly}(\text{aniline-co-o-aminophenol})/\text{ZnO}$	Methylene blue dye	UV light	88	[4]
5.	of $p\text{-NiO}/\text{BiOI}$ heterojunction	Acid orange 7 dye	Visible light	90	[7]
6.	PANI/TiO_2 NCs	Malachite Green dye	UV Light	84	[16]
7.	PANI/ZnO NCs	Methyl orange dye	UV light	78	[17]
8.	$\text{Graphene-V}_2\text{O}_5$ NCs	Methylene Blue Dye	Sunlight	85	[37]
9.	MnO_2/PANI NCs	Methyl orange dye	UV light	89	–

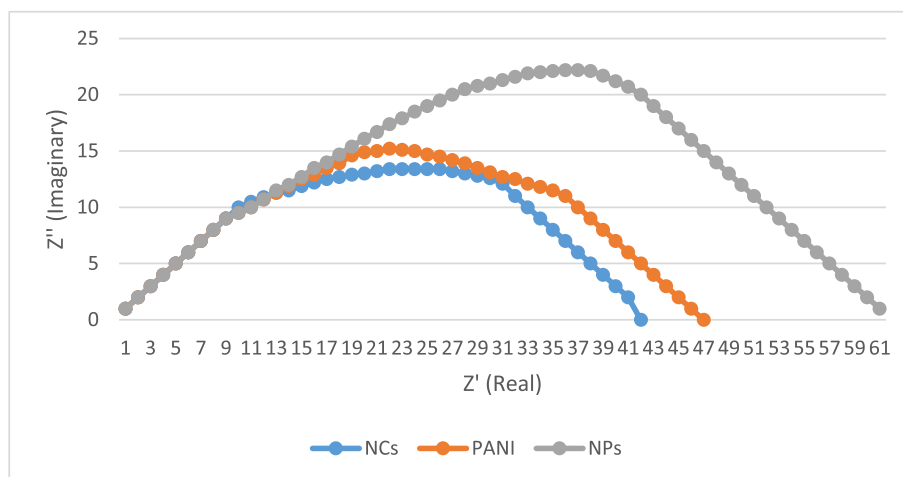


Fig. 11. Nyquist plots showing real (Z') versus imaginary impedance (Z'') for α -MnO₂ NPs, PANI and α -MnO₂/PANI NCs.

The impedance spectroscopy study was carried out in the presence of MnO₂ NPs, PANI CPs, and MnO₂/PANI NCs. Fig. 11 depicts Nyquist plots [real (Z') versus imaginary impedance (Z'')] of MnO₂ NPs, PANI, and MnO₂/PANI NCs. The rate of charge transfer and charge separation between electrons and holes increases in the presence of α -MnO₂/PANI NCs in comparison to MnO₂ NPs and PANI CPs (Fig. 11). This was proven by a decrease in charge transfer resistance (R_{ct}) in the presence of MnO₂/PANI NCs.

3.6.4. Chemical oxygen demand (COD) study to support photocatalytic activity

The photocatalytic activity of MnO₂/PANI NCs against MOD was further supported by the chemical oxygen demand (COD) of water [73, 74]. The COD of the solution containing MnO₂/PANI NCs + MOD was found using Eq. (15).

$$COD = \frac{8 \times 1000 \times DF_x M_x (V_B - V_s)}{\text{Volume of sample taken}} \quad (15)$$

Here, V_B and V_s represent the volume of blank and solution titration, M_x is molarity and DF is the dilution factor.

The COD of the solution decreases with an increase in the photodegradation of the dye [75–81]. Initially COD was higher (95.4 mg/l) before the start of UV exposure to the solution. After 180 min of UV exposure, the COD of the solution decreases (25.3 mg/l) appreciably. This indicates that almost 90% of MOD decomposed by the MnO₂/PANI NCs.

4. Limitations and future scope of the study

Although, the α -MnO₂/PANI NCs have shown good antibacterial, anticorrosive, and photocatalytic properties, other applications like the charge-storing capacity of electrode material used in rechargeable batteries, and supercapacitors need to be explored. Other applications of α -MnO₂/PANI NCs like adsorption power and purification of impure water may be explored. Further, NCs of MnO₂ with other conducting polymers like polypyrrole, polythiophene, and polyacetylene may be synthesized for different advanced functional applications. In the future, metal nanocomposites with reduced graphene oxide, and a metal-organic framework may be explored for different multidimensional applications.

5. Conclusions

α -MnO₂ NPs were synthesized by the inverse micelle method. CPs PANI was synthesized by the Chemical Oxidative method. α -MnO₂/PANI

NCs were produced by the *in-situ* method. α -MnO₂ NPs, PANI, and α -MnO₂/PANI NCs were characterized by X-ray diffraction, TEM, FT-IR, and UV-visible techniques. The experimental findings were compared with the different computational studies. Corrosion inhibition, antibacterial, and photocatalytic studies were explored at different concentrations of NCs. α -MnO₂/PANI NCs show $87 \pm 0.1\%$ corrosion inhibition efficiency for MS in 0.1 M hydrochloric acid. Computational study (DFT) proves the strong affinity of chemisorption on mild steel. The antibacterial property of PANI NCs was compared with 06 antibiotics (Hexa disk). α -MnO₂/PANI nanocomposites show almost comparable Zone of Inhibition to six standard antibiotics for *S. epidermis* and *E. coli*. α -MnO₂/PANI nanocomposites degrade $89.15 \pm 1.1\%$ of MOD after 3 h of UV light exposure. The mechanism of photodegradation is supported by Potentiostatic photocurrent measurement, impedance spectroscopy, pH variation, and COD demand. The COD of the solution decreases from 95.4 mg/l to 25.3 mg/l after 180 min of exposure to UV light. The charge transfer resistance decreases in the presence of α -MnO₂/PANI NCs in comparison to pure α -MnO₂ and CPs PANI. The magnitude of photocurrent increases in the presence of UV light. The α -MnO₂/PANI NCs can be successfully used in applications like corrosion inhibition, antibacterial, and photocatalytic degradation of organic compounds.

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.

Data availability

Data will be made available on request.

Acknowledgments

The authors of this article duly acknowledge the administrative and infrastructural support provided by the authorities of CDLU, Sirsa, and CUH, Mahendergarh.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.rineng.2023.101250>.

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