$MoSe_2$ Modified ZIF-8 Novel Nanocomposite for Photocatalytic Remediation of Textile Dye and Antibiotics Contaminated Wastewater

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Abstract

COVID-19-led antibiotic waste generated from hospitals and health centers may cause serious health issues and significantly impact the environment. In the coming decades, antibiotic resistance will be one of the most significant threats to global human health. Photocatalytic water remediation is an effective and promising environmental solution that can be utilized to address this issue to convert antibiotic waste into non-toxic products by utilizing renewable and abundant solar energy. In the present study, a novel nanocomposite of Zeolitic imidazolate frameworks (ZIF-8) and molybdenum diselenide ($MoSe_2$) were efficiently synthesized by the solvothermal method for the complete degradation of the antibiotics and textile waste from water. The morphology, crystallinity and band gap of the samples were characterized by field emission scanning electron microscopy (SEM), X-ray diffraction (XRD) and UV-Visible Spectroscopy. Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) provides the binding information of the sample. The photocatalytic activity was tested for degradation of the antibiotics: Tetracycline Hydrochloride (TC) and Metronidazole (MNZ)) used in COVID-19 treatment and textile dye: malachite green. Time-resolved photoluminescence spectroscopy confirmed the enhanced charge separation in $MoSe_2$@ZIF-8 nanocomposite with an average lifetime of 4.72 ns as compared to pristine samples. The nanocomposite showed ~100% removal efficiency with rate constant of $63x10^{-3}$, $49x10^{-3}$ and $42x10^{-3}$ min^{-1} for TC, MNZ and Malachite green, respectively. The photocatalytic degradation of TC was carried out under different pH conditions (4,7 and 9) and the degradation mechanism was explained on the basis of Zeta potential measurements and active species trapping experiment. The byproducts of the photocatalytic treatment of TC antibiotics were tested using Liquid Chromatography-Mass Spectroscopy (LC-MS) and they were found to be non-toxic for aquatic and human life. The regeneration property of the nanocomposite was confirmed by FESEM with regeneration efficiency of 88.7% in the 4^{th} cycle. Thus,

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$MoSe_2$@ZIF-8-based photocatalysts have potential application in water remediation, especially in making the antibiotic waste less toxic.

Keywords: TCSPC, Photocatalysis, Zeta Potential, Antibiotics, COVID-19

1. Introduction

COVID-19 has resulted in an increased pharmaceutical waste in the environment, rivers and coastal waters (Chen et al. 2021) (Dharmaraj et al. 2021). Antibiotic waste management is a critical problem because of its high environmental and human health hazards (Tsai 2021, Wang et al. 2020a). Antibiotics are not easily metabolized resulting in the expulsion of their residues through feces and urine to the aquatic ecosystem leading to serious environmental problems (Li et al. 2020). Moreover, these antibiotics cannot be removed by traditional procedures such as biological processes, filtration, coagulation and sedimentation (Adams et al. 2002, Barhoumi et al. 2017, Stackelberg et al. 2007). Tetracycline Hydrochloric (TC) and Metronidazole (MNZ) have been explored as potential therapeutic drugs in treating COVID-19 patients because of their potential antiviral properties (Gharebaghi et al. 2020, Sodhi &Etminan 2020). Tetracycline Hydrochloric antibiotics are primary antibiotic groups found in the different ecosystems that is used for human therapy (viral infections and inflammatory disorders) and agricultural purposes (Daghrir &Drogui 2013, Sodhi &Etminan 2020). Recently, a computational study has shown that TC plays a key role in treating SARS-CoV-2 main proteases and COVID-19-related lung disease (Gironi et al. 2020). Metronidazole (MNZ) is the most widely used of the second-generation quinolones and is used to treat joints, gastroenteritis, respiratory tract and cellulitis. MNZ is a redox-active prodrug that acts as a biocidal agent and studies have revealed that it decreases the COVID-19 infection (Gharebaghi et al. 2020). However, MNZ induces an acute and sub-lethal effect on most species of aquatic life. One serious water pollution concern involving the discharge of antibiotic waste into the water bodies is the possibility of the development of antibiotic-resistant bacteria in the wastewater (Dharmaraj et al. 2021). Dyes are primary constituents of textile wastewater and, constitute a group of toxic and carcinogenic contaminants.

For the treatment of antibiotic and textile wastewater, photocatalysis is a facile, highly efficient environmental-friendly and straightforward technology as compared to other conventional techniques (Adams et al. 2002, Ashraf et al. 2020, Kumar et al. 2022, Kumar et al. 2020, Mittal et al. 2019, Qin et al. 2021). ZIF-8 has been considered a potential photocatalyst for CO_2 reduction, water-splitting and photocatalytic degradation due to its large surface areas, well-defined porous structures and superior photocatalytic performance (Chin et al. 2018, Li et al. 2019b, Peng et al. 2020, Shinde et al. 2021). However, ZIF-8-based photocatalysts are limited due to the low electron discharge ability and high recombination rate of photogenerated electron-hole pairs (Fu &Ren 2020, Qiu et al. 2018). Therefore, to overcome the issues related to ZIF-8 and improve its catalytic performance, the nanocomposite of ZIF-8 with $MoSe_2$ was constructed. Molybdenum diselenide ($MoSe_2$) has been proven to be a potential co-catalyst for photocatalysis due to more active sites and reduced recombination rate of charge carriers (Mittal &Khanuja 2020a, Siddiqui et al. 2018). Therefore, it is advantageous to construct a nanocomposite by combining the photocatalytic properties of $MoSe_2$ with the strong adsorbing properties of ZIF-8 to generate a potential photocatalyst to degrade antibiotic wastes.

In this study, we have synthesized a novel photocatalyst by a two-step method: The Hydrothermal method for $MoSe_2$ and the solvothermal method for the synthesis of $MoSe_2$@ZIF-8 nanocomposite. A series of pollutants (antibiotics: TC, MNZ and dye: Malachite green) are used to evaluate the degradation efficiency of the synthesized samples. $MoSe_2$@ZIF-8 nanocomposite showed enhanced degradation efficiency, ~3 times higher than pristine $MoSe_2$. The degradation efficiency obtained at different pH (4, 7 and 9) was explained using zeta potential measurements. The highest degradation efficiency for TC was observed in the alkaline medium due to the effect of electrostatic attraction between TC^{2-} and the positive charge on the surface of the nanocomposite. The proposed photocatalysis mechanism was supported by a scavenger experiment that confirms the role of active species in the degradation of pollutants. Repeated experiments confirmed the reusability and regeneration ability of the nanocomposite. To the best of our knowledge, the $MoSe_2$@ZIF-8 nanocomposite has not been reported before for wastewater treatment.

2. Experimental Section

2.1. Materials

Sodium molybdate (Na_2MoO_4) with 99.99% purity and hydrochloric acid ($HCl.H_2O$) with 99.96% purity was bought from Thermo Fisher Scientific India Pvt. Ltd. Selenium (Se, 99.99%) and hydrazine hydrate ($N_2H_4.H_2O$) with 98% purity was bought from Central Drug House Pvt. Ltd. To prepare ZIF-8, 2-methylimidazole (98%) and zinc nitrate (Zn $(NO_3)_2$) were obtained from Loba Chemie Pvt. Ltd. Milli-Q water was used for all the experimental work.

2.2. Synthesis of $MoSe_2$@ZIF-8 Nanocomposite

For the synthesis of ZIF-8, solution A was prepared by dissolving 0.585 g of zinc nitrate in 4 mL of Milli Q water using a magnetic stirrer. Solution B was prepared by dissolving 2-methylimidazole in 40 mL of Milli Q water followed by the 6 mL of DMSO also known as linker solution. Solution A was then added to the Linker solution and magnetically stirred for 5 min, forming a milky white solution. The obtained solution was centrifuged at 15000 rpm for 15 min followed by washing and drying to yield ZIF-8 (Kaur et al. 2017). $MoSe_2$ was prepared by the hydrothermal method according to a previously reported study (Mittal &Khanuja 2020a). Fig. 1 showed the schematic for the synthesis of $MoSe_2$@ZIF-8 nanocomposite. $MoSe_2$@ZIF-8 nanocomposite was synthesized using a similar method as ZIF-8. In the above procedure, 0.1g of $MoSe_2$ was dissolved in 6 mL of DMSO before its addition to the linker solution and magnetically stirred for 5 min. All the further steps were similar to the synthesis of pristine ZIF-8 (Chen et al. 2019). Finally, obtained $MoSe_2$@ZIF-8 material was labeled as ZM.

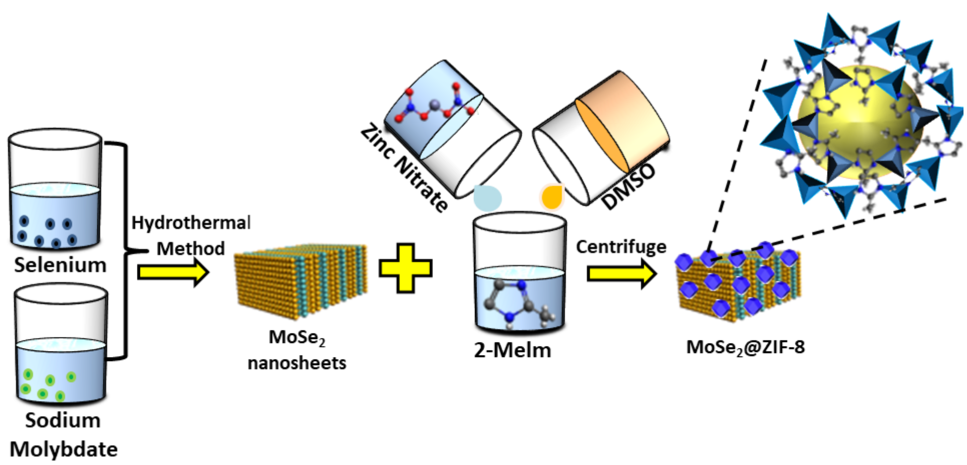


Fig. 1: Synthesis mechanism of $MoSe_2$@ZIF-8 Nanocomposite

2.3. Characterization

The morphology of the prepared samples was characterized using FESEM-Field Emission Scanning Electron Microscope (Quanta 3D FEG). X-ray diffraction (XRD) diffractograms were recorded using Rigaku Smart Lab XRD. Samples were characterized for optical study using a UV-

Vis spectrometer (Agilent technologies, Cary 100 series). Thin films of the samples were prepared by dissolving in ethanol for functional groups study and spectra were recorded by Fourier transform infra-red (FTIR) spectroscopy (Bruker Tensor 37 FTIR spectrometer). X-ray photoelectron spectroscopy (XPS) was collected on ESCA+ Omicron Nano Technology with a characteristic energy of 1486.7eV. Surface charge measurement of the samples was performed using Zeta potential (Malvern Zetasizer Nano ZS) using ethanol as dispersing solvent. Time Correlated-Single Photon Counting (TCSPC) measurement of the samples was recorded using a spectrometer (Horiba (DeltaFlex01-DD)). The intermediate and final degraded products of antibiotic degradation solution were examined by Liquid Chromatography-Mass Spectroscopy (LC-MS) from the Xevo TQD system.

3. Results and Discussion

3.1. Morphology and components

Fig. 2 (a-c) shows FESEM micrographs of ZIF-8, $MoSe_2$ and ZM nanocomposites. It is observable in Fig. 2(a), that pure ZIF-8 nanoparticles are polyhedrons with an average particle size of ~300 nm. Fig. 2(b) clearly shows the nanosheets of $MoSe_2$. As shown in Fig. 2(c), ZM nanocomposites consist of well-shaped polyhedrons of ZIF-8 nanoparticles with an average particle size of about 116 nm uniformly dispersed on the surface of $MoSe_2$ nanosheets.

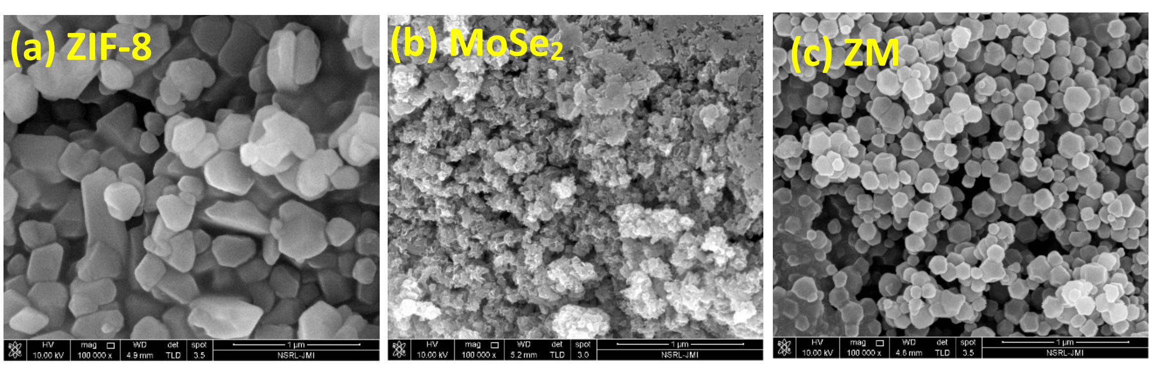
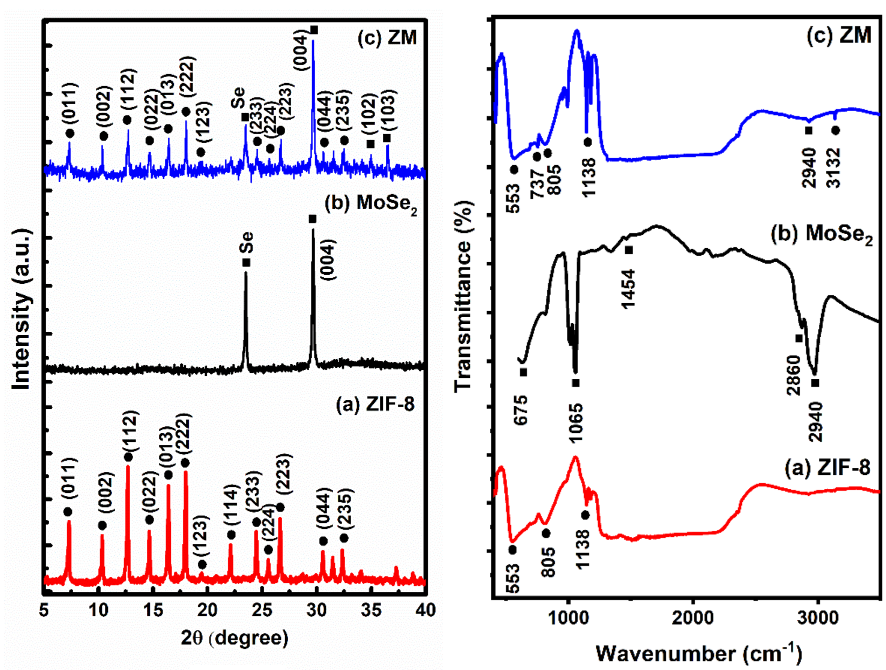


Fig. 2: FESEM images of (a) ZIF-8, (b) $MoSe_2$ and (c) ZM nanocomposite

The structural properties of $MoSe_2$, ZIF-8 and the ZM nanocomposite were investigated by XRD [Fig. 3 (a-c)]. The XRD pattern of the pristine ZIF-8 [Fig. 3(a)] showed diffraction peaks at 7.3°, 10.3°, 12.7°, 14.7°, 16.4°, 18.0°, 19.3°, 22.1°, 24.6°, 25.6°, 26.7°, 30.6° and 32.3° corresponds to (011), (002), (112), (022), (013), (222), (123), (114) (233), (224), (223), (044) and (235) planes of

ZIF-8, respectively (JCPDS Card No: JCPDS 00-062-1030) (Si et al. 2018). In $MoSe_2$ [Fig. 3(b)], the main peak at 29.6° corresponds to the (004) plane. Both ZIF-8 and $MoSe_2$ peaks were observed in the ZM nanocomposite, which implies that the ZIF-8 is in close contact with the $MoSe_2$ nanosheets.

FTIR spectra of ZIF-8, $MoSe_2$ and ZM nanocomposite are shown in Fig. 3 ii(a-c). ZIF-8 and ZM have similar FTIR peaks, indicating that surface modification does not destroy the fundamental structural framework. In the FTIR spectra of ZIF-8 in Fig. 3 ii(a), the bands at 553 cm^{-1} and 805 cm^{-1} are assigned to the out-of-plane blending of 2- methyl imidazole rings (Ulu 2020). The peak located at 1138 cm^{-1} is assigned to the C-N vibration of the imidazole ring (Wu et al. 2017). In the FTIR spectra of $MoSe_2$ as shown in Fig. 3 ii(b), the peaks located at 1065 cm^{-1} and 1454 cm^{-1} are assigned to Se-O and carboxylate (COO^-) stretch (Liu et al. 2017). The peaks located at higher frequencies 2860 cm^{-1} and 2940 cm^{-1} are attributed to the presence of acyclic stretching of C-H (Harpeness et al. 2003, Liu et al. 2017). Compared with the FTIR analysis of pristine ZIF-8, the ZM nanocomposite [Fig. 3 ii(c)] showed the existence of an adsorption band at 3132 cm^{-1} corresponding to the methyl group present in the linker and imidazole ring (Kaur et al. 2017).



(i) (ii)

Fig. 3: (i) XRD diffractograms and (ii) FTIR spectra of (a) ZIF-8, (b) $MoSe_2$ and (c) ZM nanocomposite

UV-Vis absorption spectra of the ZIF-8, $MoSe_2$ and ZM nanocomposite are shown in figure 4 i(a-c), respectively. All the samples show absorbance in the wavelength range of 200 to 800 nm. The ZIF-8 had maximum absorbance at 305 and 350 nm, while the ZM nanocomposite at 340 and 365 nm.

The band gap of samples is calculated from the Tauc'c plot as shown in Fig. 4 ii(a-c). The energy band gap values were calculated using Eq. (i):

$$\alpha h\upsilon = (h\upsilon - E_g)^n \qquad \text{(i)}$$

where h is the Planck's constant, α is the absorption coefficient, ν is the frequency, E_g is the bandgap of the photocatalyst, n is the number that determines the transition property which is taken as 0.5 for direct bandgap and 2 for indirect bandgap semiconductor (Mittal &Khanuja 2021). In this case, $MoSe_2$ is an indirect bandgap semiconductor whereas ZIF-8 is a direct bandgap semiconductor, however, in the bandgap calculations of ZM nanocomposite, n is taken as 2 because ZIF-8 is the base material (Chen et al. 2019). The $MoSe_2$, ZIF-8 and ZM nanocomposite exhibited absorbance in the visible region with the band gap of 1.71 eV, 2.70 eV and 3.22 eV.

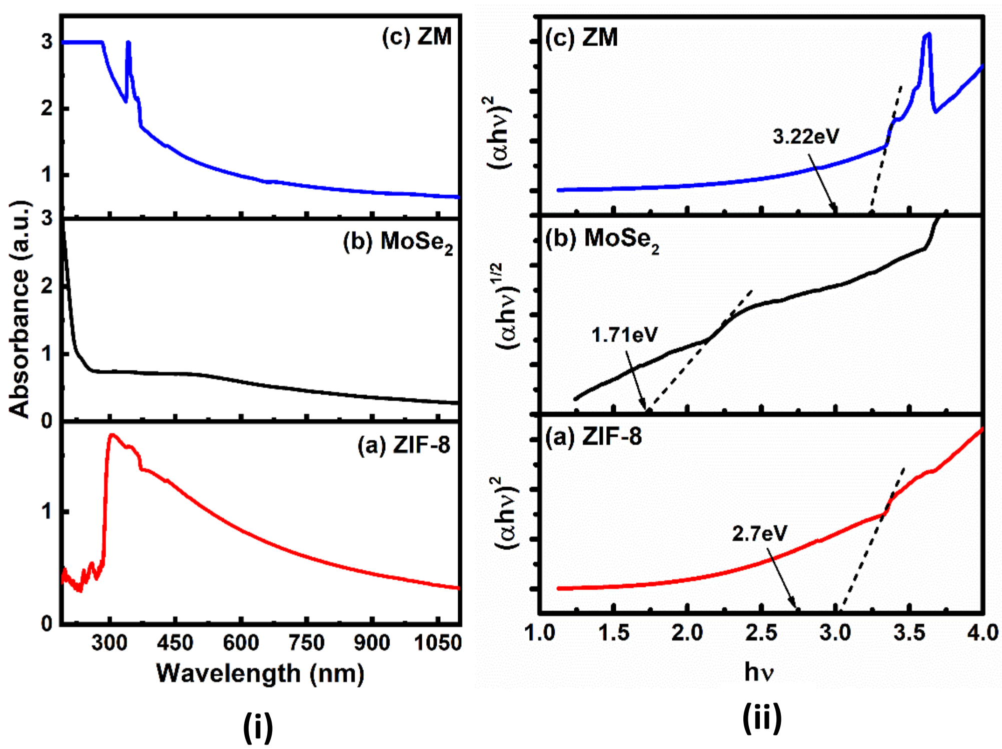


Fig. 4: (i) UV absorbance spectra and (ii) Tauc's plot of (a) ZIF-8, (b) $MoSe_2$ and (c) ZM nanocomposite

XPS spectra were used to investigate the elemental valence and bonding information of the ZM nanocomposite. The survey spectrum shown in Fig. 5 (a) confirms the presence of Zn, Mo, Se, C, O and N. The peaks located at 1021.6 eV and 1044.6 eV binding energies in Fig. 5 (b) are assigned to Zn $2p_{3/2}$ and Zn $2p_{1/2}$ of Zn^{2+}, respectively (Jia et al. 2018). As seen in Fig. 5 (c), peaks centered at 229.78 eV and 233.1 eV corresponds to the binding energies of Mo(V)($3d_{5/2}$) and Mo(V)($3d_{3/2}$) respectively, which indicates the formation of Mo-Se bonds, whereas peaks at 228.27 and 231.54 eV correspond to Mo^{4+} characteristics and peaks at 231.72 and 235.03 eV correspond to Mo^{6+}, respectively. The XPS results of Se 3d are displayed in Fig. 5 (d), the Se 3d core level demonstrates two peaks at 53.8 and 55.3 eV that can be attributed to Se $3d_{3/2}$ and Se $3d_{5/2}$, respectively, representing an oxidation state of -2 for Se in $MoSe_2$ (Bi et al. 2015, Ge et al. 2018). The high-resolution N 1s core level spectrum in Fig. 5 (e) can be deconvoluted into three prominent peaks at 398.3, 398.9 and 399.9 eV, which are attributed to the pyridinic, pyrrolic and graphitic nitrogen, respectively (Li et al. 2018). As shown in Fig. 5 (f), the C 1s core level spectrum can be deconvoluted into three peaks centered at 283.9, 285.1, and 286.1 eV, corresponding to C-C, C-N and C-O bindings, respectively (Luanwuthi et al. 2015). It is observed that the binding energies of the Zn 2p, Mo 3d and Se 3d peaks in ZM nanocomposite are shifted to lower binding energy by 1 eV, implying that the $MoSe_2$ and ZIF-8 are interacting with each other (Chen et al. 2019). Thus, the above detailed material characterizations confirm the successful synthesis of ZM nanocomposite.

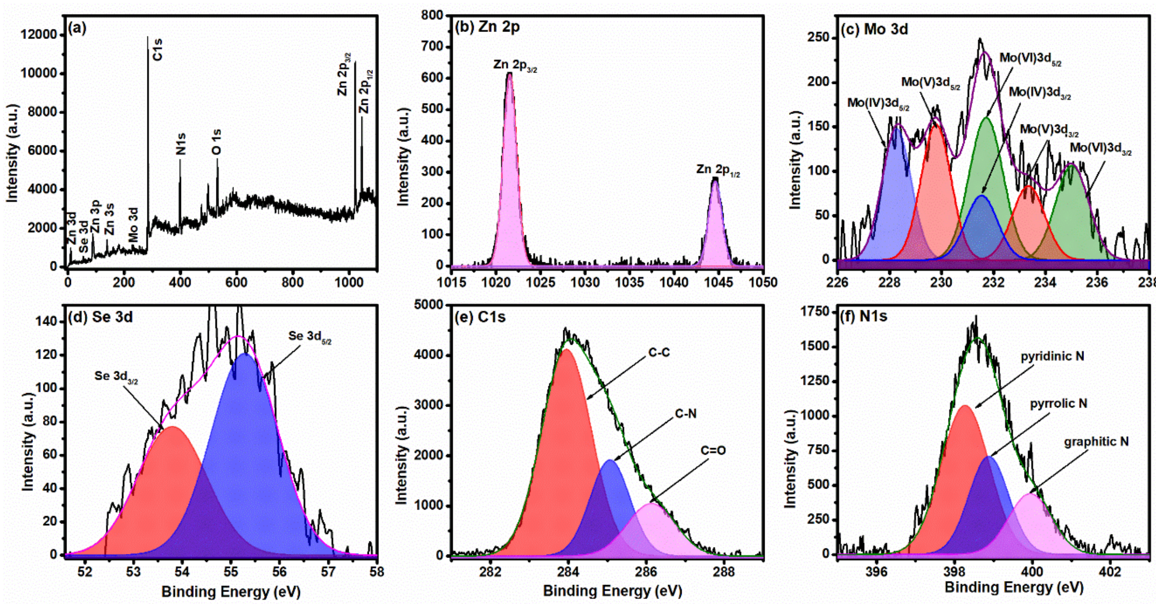


Fig. 5: (a) XPS survey spectra survey of ZM nanocomposite and high-resolution core spectra of (b) Zn 2p, (c) Mo 3d, (d) Se 3d, (e) N 1s and (f) C1s

3.2 Photocatalytic activity

The comparative photocatalytic degradation of Metronidazole (MNZ) and Tetracycline hydrochloride (TC) antibiotics and Malachite Green (MG) dye in aqueous solutions was performed using $MoSe_2$, ZIF-8 and ZM nanocomposites under light irradiation from Xenon arc lamp (AM 1.5G solar illumination 100 mW/cm^2). For each photocatalytic degradation test, 20 mg of photocatalyst and 1mg of the target pollutant were used in 100 mL of milli Q water. During light irradiation, 2 mL of the solution was taken out at a fixed interval for UV-Vis spectroscopy. The absorbance peaks for MNZ (318 nm), TC (357 nm) and MG (618 nm) were measured using UV-Visible spectroscopy and a decrease in intensity with irradiation time was measured (Huang et al. 2013, Medidi et al. 2018, Saghi &Mahanpoor 2017). The photocatalytic degradation efficiency (η) was calculated using $\eta = \left(1 - \frac{C}{C_0}\right)$ 100%, where, C_o and C represents degradation of pollutant before and after irradiation at time t, respectively.

The degradation and efficiency plots are shown in Fig. 6 (a-e). The photocatalytic degradation efficiency of TC [Fig. 6 (a)] by $MoSe_2$, ZIF-8 and ZM nanocomposite is 38.5%, 66.3% and 73.7%, respectively. The degradation of MNZ (Fig. 6b) by $MoSe_2$, ZIF-8 and ZM nanocomposite are 34.7%, 28.3% and 99.4%, respectively. The degradation of MG dye by $MoSe_2$, ZIF-8 and ZM nanocomposite is 63.3%, 91.6% and 99.4%, respectively. Malachite green dye was decolorized, as shown in the inset of Fig. 6(c). As observed from the results, the photocatalytic degradation efficiency of the ZM nanocomposite was enhanced as compared to pristine $MoSe_2$ and ZIF-8.

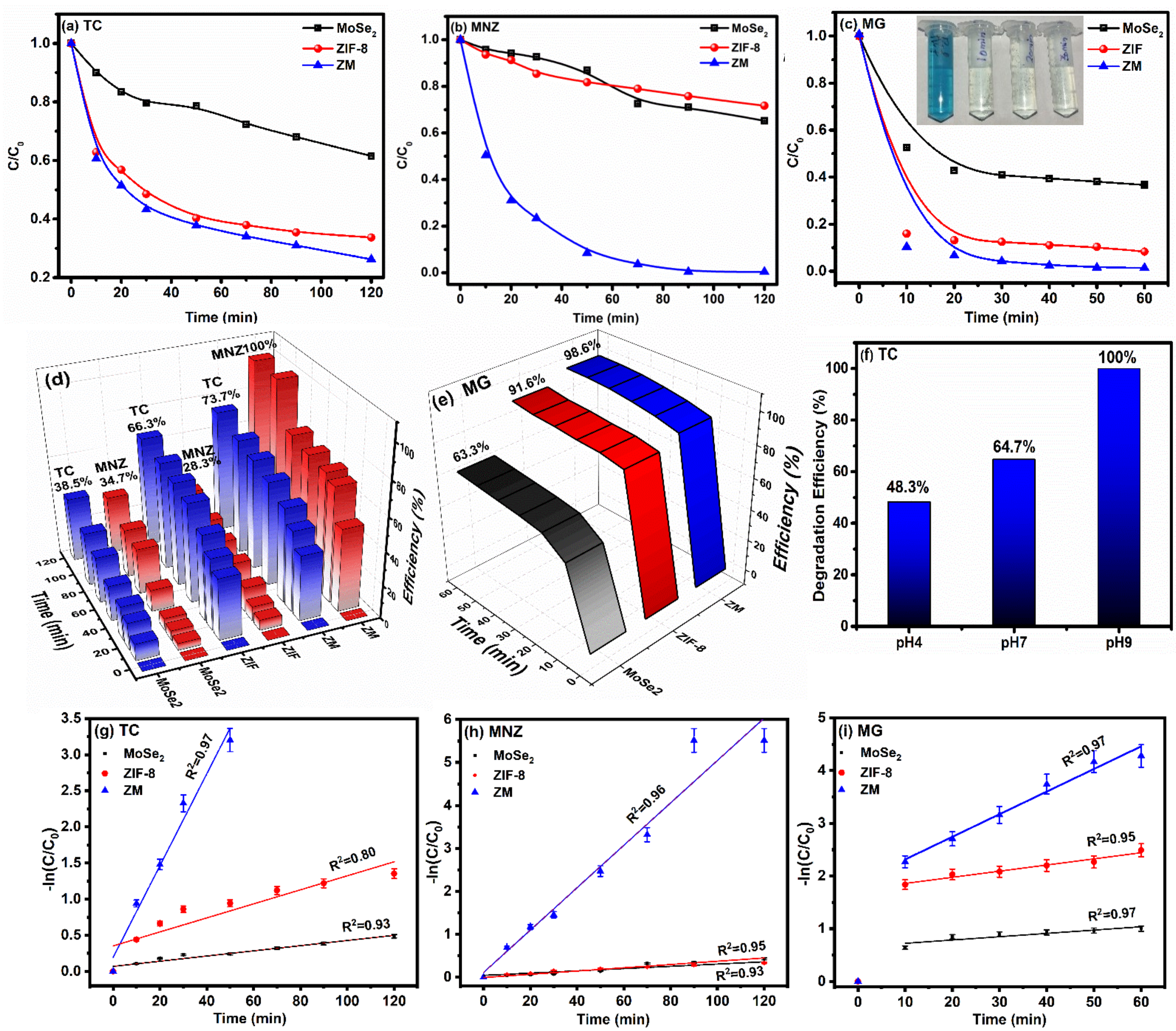


Fig. 6: Photocatalytic degradation of $MoSe_2$, ZIF-8 and ZM nanocomposite, C/C_0 plot for (a) TC (b) MNZ antibiotics and (c) MG dye; efficiency (η) vs time (min) plot for (d) TC, MNZ antibiotic and (e) MG dye; (f) degradation plot of TC under different pH conditions using ZM nanocomposite; First order kinetics plot of (g) TC, (h) MNZ and (i) MG

3.3 Photocatalytic Properties

3.3.1 Effect of pH

The pH of the solution highly influences the photocatalytic degradation activity because it can affect both catalyst and pollutant. In this study, the photocatalytic degradation of TC by ZM nanocomposite was studied under different pH conditions (acidic pH 4, basic pH 9 and neutral pH

7) as shown in Fig. 6 (f). When the pH of the solution was 4, 7 and 9, the photocatalytic degradation efficiency of TC was 48%, 64.7% and 99.4%, respectively. The pH value of the solution affects not only the surface charge and physical-chemical properties of the pollutant and photocatalyst but also the generation of hydroxyl radicals. At lower pH, the primarily responsible oxidation species is photogenerated positive holes, however, at neutral pH or higher pH, it is hydroxyl radicals. According to the experiment, the pollutant degradation efficiency increases with the increasing pH of the solution.

3.3.2 Rate Kinetics Study

To further evaluate the photocatalytic process of the system, the kinetics of photocatalytic activity was studied using the pseudo-first-order kinetic eq. that was used as follows:

$$-\ln\left(\frac{C_t}{C_o}\right) = kt \qquad \text{(ii)}$$

Where, 'k' denotes the rate constant of the reaction.

The kinetic studies implies that degradation of TC, MNZ and MG by ZM nanocomposite follows pseudo-first-order kinetics as shown in figure 6 (g-i) with R^2 (linear correlation coefficient) value of 0.97, 0.96 and 0.97, respectively. The k (rate constant) linear correlation coefficient value for degradation of TC, MNZ and MG by ZM is 0.06 min^{-1}, 0.05 min^{-1} and 0.04 min^{-1}, respectively. Rate constant and linear coefficient values for photocatalytic performance of $MoSe_2$, ZIF-8 and ZM nanocomposite are summarized in Table 1. The modified surface charge and improved charge transfer and separation in the ZM nanocomposite makes it more favourable for photocatalytic activity.

Table 1: Photodegradation efficiency, Rate constant (k) and R^2 values of prepared photocatalysts

Pollutant	**TC**			**MNZ**			**MG**		
Photocatalyst	**$MoSe_2$**	**ZIF-8**	**ZM**	**$MoSe_2$**	**ZIF-8**	**ZM**	**$MoSe_2$**	**ZIF-8**	**ZM**
Efficiency (%)	38.5	66.3	100 (pH 9)	34.7	28.3	100	63.3	91.6	98.6
k x (10^{-3}) (min^{-1})	3.5	9.7	63	2.6	3.8	49	6.2	11	42
R^2	0.80	0.93	0.97	0.93	0.95	0.96	0.97	0.95	0.97

Till date, several illustrations of semiconductor-MOFs nanocomposites have been reported to shown potential improvement in the photocatalytic activity, some of them have been listed in Table 2 along with the results of the present study. These findings imply that ZIF-8 and $MoSe_2$ nanocomposite is a promising photocatalyst for effective degradation of dye and antibiotics.

Table 2: The results of Photocatalytic performance of ZIF-8, $MoSe_2$ and their nanocomposites reported in literature

Photocatalyst	Morphology	Pollutant	Efficiency (η)-Light Conditions	Reference
g-C_3N_4@ZIF-8	Rhombic dodecahedron	TC[1], RhB[2] & Cr (VI)[3]	TC (87.6%), Rh B (99.3%) & Cr (VI) (96.6%) in 60 min under the full spectrum irradiation	(Yuan et al. 2021)
ZnCDs/ZnO@ZIF-8	Polyhedrons	TC[1]	85% in 200 min under visible-light illumination	(Cheng et al. 2021)
Pt doped TiO_2-ZnO@ZIF-8	Polyhedral nano structure	Phenol	86.9% in 24h under UV light irradiation	(Jing et al. 2022)
ZIF-8-derived ZnO@In_2O_3	Hollow microtubes	TC[1], MG[4], MB[5] & RhB[2]	TC (93.2%), MG (80.6%), MB (25.9%) and RhB (8.6%) in 200 min under AM 1.5G sunlight simulator	(Li et al. 2021)

MoS_2-ZIF-8	Petal nanosheets	CIP[6] & TC[1]	CIP (93.2% in 180 min) & TC (75.6% in 180 min) -visible light irradiation	(Chen et al. 2019)
Porous ZIF-8	-	MeB[7] & Flu[8]	MeB (99%) & Flu (25%) in 250 min under 450 W medium pressure mercury vapor lamp	(Soliman et al. 2022)
Ag/AgCl@ZIF-8 modified g-C_3N_4	Rhombic dodecahedron	Levofloxacin	87.3% in 60 min-visible light irradiations	(Zhou et al. 2019)
CdS/MOF-derived porous carbon	Polyhedral crystals	Cephalexin	93.1% in 50 min-300W Xe lamp	(Yang et al. 2017)
ZIF-8@PTA@AuNP	Rhombic dodecahedron	TC[1]	~86%-UV light exposure	(Beni et al. 2020)
Carbon nitride/porous zeolite	Globular tablet like	RhB[2], SuB[9], TC[1] and CIP[6]	98% (RhB), 96% (SuB), 95% (TC), and 92% (CIP)- light irradiation	(Kumar et al. 2018)
MPg-C_3N_4-ZIF8	Spherical	TC[1]	74.8% in 180 min-visible light irradiations	(Li et al. 2019a)
C_3N_4-ZIF8		TC[1]	96% in 60 min-sunlight	(Panneri et al. 2017)
C-ZnS/$ZnMoO_4$ and C-ZnS/MoS_2 using ZIF8	Sphere like	TC[1] & RhB[2]	100% of TCH in 80 min and 100% of RhB in 120 min-300 W Xenon lamp	(Cui et al. 2019)

ZIF-8	Nanoparticles	MB[5]	82.3%-visible light irradiation	(Jing et al. 2014)
$MoSe_2$	Nanoflower	RhB[2]	99% within 5 mins- visible light irradiation	(Jiang et al. 2017)
$MoSe_2$-PANI	Nanosheets	RhB[2] & CR[10]	99.1% CR in 120 min and 83.2% RhB in 150 min- xenon arc lamp	(Mittal et al. 2019)
$MoSe_2$-PPy	Nanoparticles	RhB[2] & CR[10]	98.6% CR in 15 min and 84.4% RhB in 15 min- xenon arc lamp	(Mittal &Khanuja 2021)
TiO_2@ZIF-8	Spherical	MB[5]	99.1%- UV light irradiation for 180 min	(Fu &Ren 2020)
TiO_2 NPs-ZIF8	Hexagonal	MB[5] & RhB[2]	93% of MB and 57% of RhB in 120 min- UV-Visible light irradiation	(Chandra &Nath 2017)
$BiMoO_6$-ZIF8	Flower like structure	MB[5]	66.88% in 100 min- 300W Xe lamp with 420nm cut-off filters	(Xia et al. 2019)
$MoSe_2$@ZIF-8	Rhombic dodecahedron	TC[1], MNZ[11] & MG[4]	~100% of TC, MNZ in 120 min and 98.6% of MG in 60 min- Xenon arc lamp	Present Study

[1]Tetracycline, [2]Rhodamine B, [3]Chromium Hexavalent, [4]Malachite green, [5]Methylene Blue, [6]Ciprofloxacin, [7]Methyl Blue, [8]fluorescein, [9]Sulforhodamine B, [10]Congo Red, [11]Metronidazole

3.3.3. Surface charge

The surface charge of the photocatalyst plays an important role in the adsorption of the pollutant onto its surface. As observed in Fig. 7(a), the surface charge of $MoSe_2$, ZIF-8 and ZM nanocomposite are found to be -5.6, 14.3 and 10.1 mV, respectively. The surface charge of TC at $4 < pH < 7$ is positive whereas at $9 < pH < 12$ the surface charge is negative (Li et al. 2019a). The surface charge of MNZ is neutral in the range of $4 < pH < 10$ so it is not affected by the pH conditions (Carrales-Alvarado et al. 2014). As observed in Fig. 6(f), ZM has high photocatalytic degradation efficiency for TC at pH 9 because of the competitive electrostatic attraction between the active species of TC (TC^{2-}) and the positive surface of ZM nanocomposite. However, when pH is 4 or 7, the dominant species of TC are TCH_2 and TCH^- and the adsorption capacity of ZM decreases because of the electrostatic repulsion (Li et al. 2019a). The higher degradation efficiency at basic conditions is in agreement with the zeta potential results.

3.3.4 Photogenerated charge carrier lifetime study

The photogenerated charge carrier dynamics have been studied with time correlated single- photon counting system (TCSPC) for ZIF-8 and ZM nanocomposite and the decay spectra are fitted with exponential function as shown in Fig. 7(b)(Mittal &Khanuja 2020b). The magnified portion of the spectra is as shown in the inset of Fig. 7(b). The average lifetime of photogenerated charge carriers in ZIF-8 and ZM nanocomposite were obtained to be 2.70 ns and 4.72 ns, respectively. The TCSPC results confirm that the construction of ZM nanocomposite is advantageous for efficient charge-carrier separation, which results in high photocatalytic activity for nanocomposite.

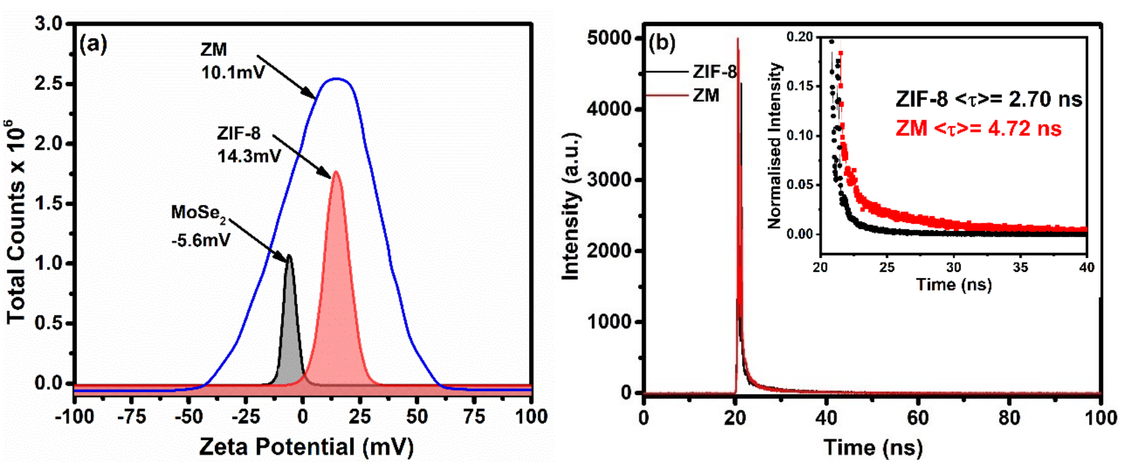


Fig. 7: (a) Zeta Potential of $MoSe_2$, ZIF-8 and ZM nanocomposite and (b) TCSPC spectra of ZIF-8 and ZM nanocomposite upon excitation at 375 nm and emission at 425 nm, (inset) magnified image of TCSPC spectra

3.4. Photocatalysis mechanism

The photocatalytic degradation mechanism of ZM nanocomposite was proposed and the schematic is as shown in Fig. 8. The heterojunction created by ZIF-8 and $MoSe_2$ is advantageous in enhancing photocatalytic activity by improving the photogenerated charge carrier generation, transfer and separation. The $MoSe_2$ and ZIF-8 could be excited by the light irradiation of energy larger than that of their forbidden band and photoinduced electrons transferred from valence band to conduction band in both ZIF-8 and $MoSe_2$. The photoinduced holes can be transferred from the VB of ZIF-8 (1.68 V) to VB of $MoSe_2$ (1.2 V), which helps in reducing the recombination rate (Mittal &Khanuja 2021, Wang et al. 2020b). However, due to the CB position of ZIF-8 (-3.41 V), the photogenerated electrons cannot move to the CB of $MoSe_2$ (-0.21 V) (Mittal &Khanuja 2021, Wang et al. 2020b). The electrons in CB can react with the dissolved O_2 to generate superoxide radicals ($O_2^{\bullet-}$) and holes in the VB react with water to form hydroxyl radicals ($OH^{\bullet}$). These radicals can react with the adsorbed pollutant and decompose it into simple and non-toxic molecules.

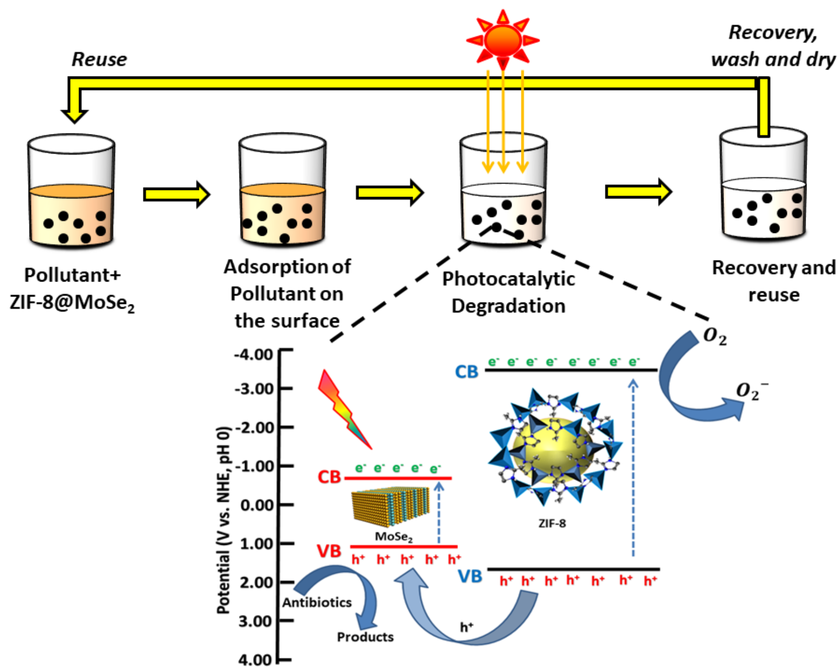


Fig. 8: Schematic illustration of photocatalytic mechanism, reusability and charge transfer in the ZM nanocomposite under visible light irradiation

3.4.1. Scavenger Test

To investigate the generation of active species and their role in the photocatalytic degradation process, tetra-butyl alcohol (t-BuOH), potassium iodide (KI) and para-benzoquonine (BQ) were used as $OH^{\cdot}$, $OH^{\cdot}$ & h^{+}, and $O_2^{\cdot-}$ quenchers, respectively (Mittal &Khanuja 2020c). The photocatalysis was performed in the presence of 20 mg of ZM nanocomposite in 100 mL of each TC and MNZ solution (1 mg/100 mL) and 1 mM of each scavenger under light irradiation for 60 min and efficiency results are shown in the Fig. 9(a) and 9(b), respectively. The photodegradation efficiency of ZM for TC and MNZ was ~100 % without any scavenger in the solution and the photocatalytic degradation performance was significantly reduced with the addition of quenchers, and the degradation efficiency for TC was 52.7% with addition of BQ, 84.5% with t-BuOH and 88.1% when KI was added. It can be concluded that the superoxide radicals are the main free radicals that are responsible for the degradation of TC (Qiang et al. 2019). In the scavenger test for the degradation of MNZ, the final degradation rate was 42.1% with addition of KI, 62.6% with t-BuOH and 86.7% when BQ was added. It can be concluded that the holes and hydroxyl radicals are mainly responsible for the degradation of MNZ (Ahmaruzzaman et al. 2019).

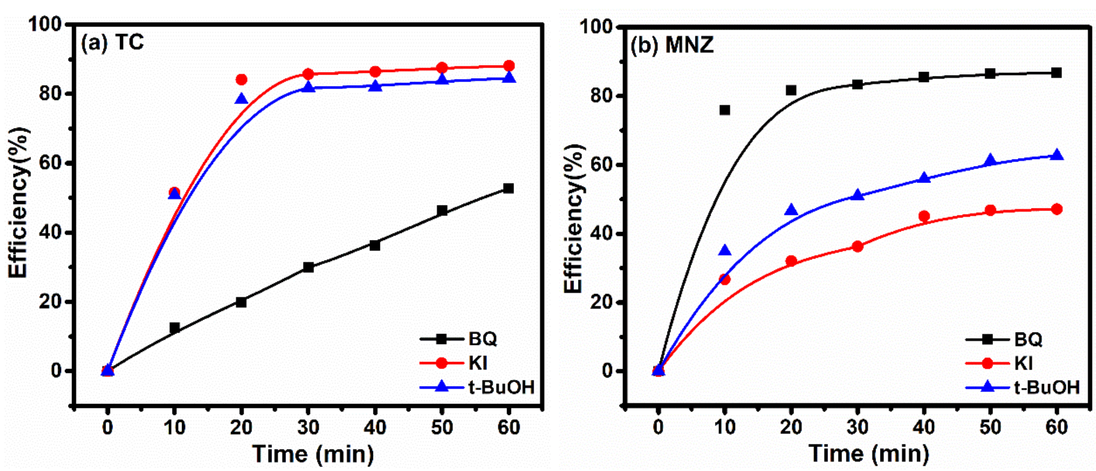


Fig. 9: Photocatalytic degradation efficiency of ZM nanocomposite in the presence of para-benzoquinone (BQ), potassium iodide (KI) and tert-butyl alcohol (t-BuOH) for (a) TC and (b) MNZ

3.4.2. Possible Photocatalytic Degradation Pathway of TC by LC-MS

The intermediate products generated during photocatalytic degradation of TC were investigated by LC-MS using the solution which were collected during photocatalytic reaction at 10 min and 120 min. Fig. 10(a and b) shows the chromatographs at 10 and 120 min, respectively. The chromatograph in Fig. 10(a) shows that the TC (m/z = 445) degraded into the product with m/z value of 460 due to the hydroxylation of aromatic ring((Jeong et al. 2010)) (Li et al. 2019c, Luo et al. 2020). Further the simultaneously demethylation and oxidation of the TC resulted in the formation of product with m/z value of 432 (Wang et al. 2018). The chromatograph shows that TC was further oxidized by radicals, resulting in formation of ketone and a methyl group, forming a new product after 120 min with m/z value of 433 and 415 (Zhang et al. 2020). The stepwise attack of reactive oxygen species resulting in the simultaneously destruction of the 4-ring structure by deamination and dihydroxylation resulting into products with m/z value of 244, 222 and 175. The resulted product is further degraded into the product with m/z value of 143 via adding hydroxyl groups, which in turn leads to the generation of product with m/z value of 122 via dihydroxylation (Niu et al. 2013). The simpler ring-opened products, with m/z value of 85, 73 and 57 are the final products formed after the photocatalytic degradation for 120 min (Li et al. 2019c). The degradation pathway was proposed using these identified intermediate products and the structural identification and m/z of these intermediate is shown in Fig. 10 (c). The intermediate products of m/z 460, 433 and 432 (labelled with red color in fig. 10(c)) are as toxic as TC but the finally degraded products (labelled with green color in fig. 10(c)) are not harmful to the aquatic life (Wang et al. 2018). After 120 min of photocatalytic reaction, 99.4% of TC was degraded using ZM nanocomposite. Hence, ZM nanocomposite exhibited a desirable degradation efficiency and a promising application potential for antibiotics waste contaminated water treatment.

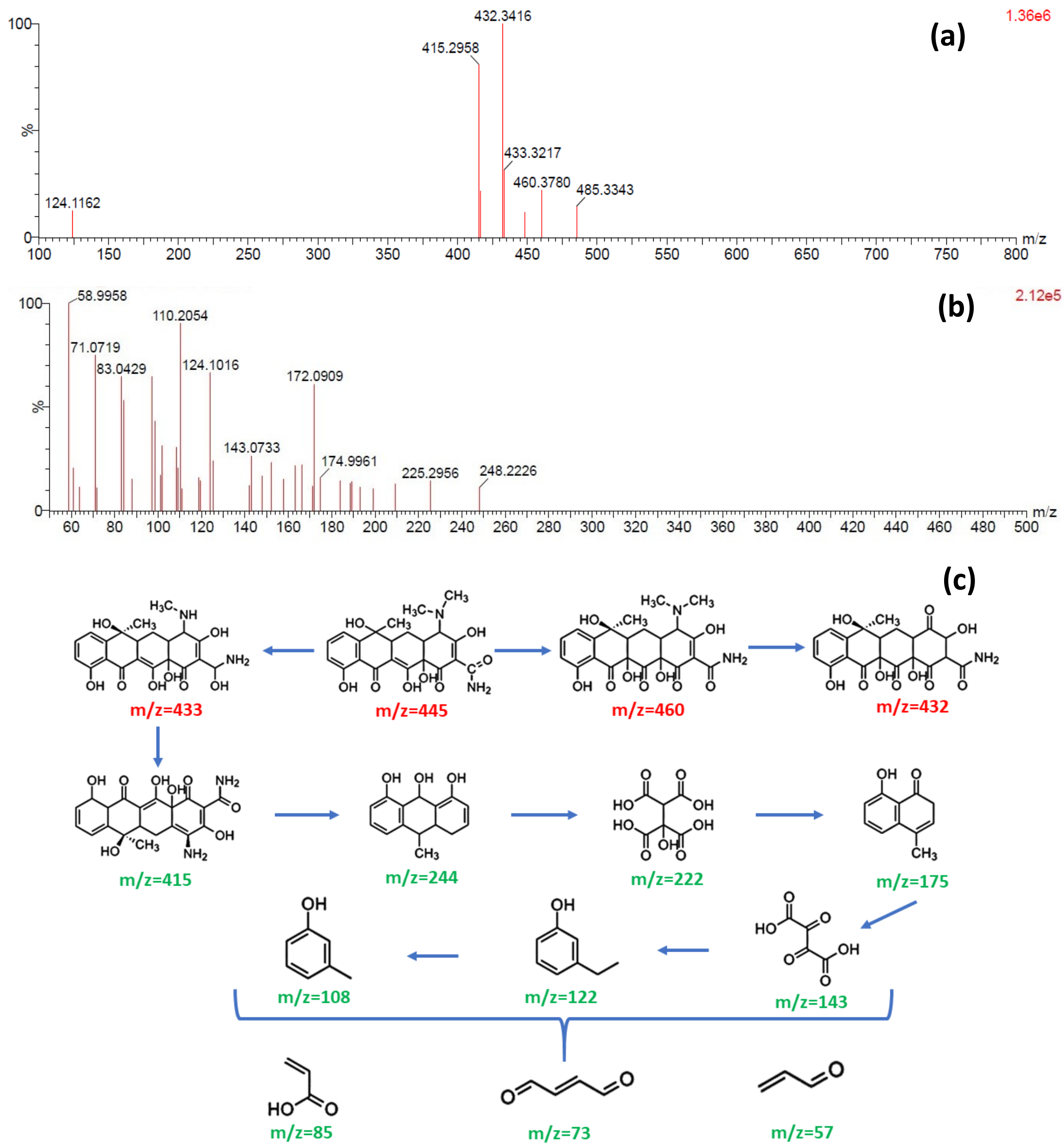


Fig. 10: LC-MS spectrum of degraded solution of TC at (a) 10 min, (b) 120 min and (c) possible photocatalytic degradation pathway for TC

3.5 Reusability of $MoSe_2$@ZIF-8 Nanocomposite

To determine the reusability and regeneration ability of the ZM nanocomposite, four cycles of the photocatalytic degradation of TC were performed under light irradiation using 50 mg of ZM for the degradation of TC with a concentration of 10 mgL^{-1}. After each cycle of the photocatalytic degradation, the ZM was extracted from the degradation solution by filtration and washed by milli Q water, followed by drying at 60 °C for 4 h. The ZM nanocomposite showed good photocatalytic degradation efficiencies, as shown in Fig. 11(a). The regeneration efficiency of the nanocomposite as calculated using eq. (iii) are 93.2%, 96.6% and 88.7% in 2, 3 and 4 cycles, respectively.

$$Regeneration\ efficiency\ (\%) = \frac{Degradation\ efficiency\ in\ nth\ cycle}{Degradation\ efficiency\ in\ (n-1)th\ cycle} \times 100 \qquad \text{(iii)}$$

Moreover, the FESEM images of the as-prepared ZM nanocomposite and after 4 cycles of photocatalytic degradation are shown in Fig. 11(b and c). There is no visible change in the morphology of the catalyst. This indicates that ZM nanocomposite is a suitable and potential candidate for practical applications as a photocatalyst.

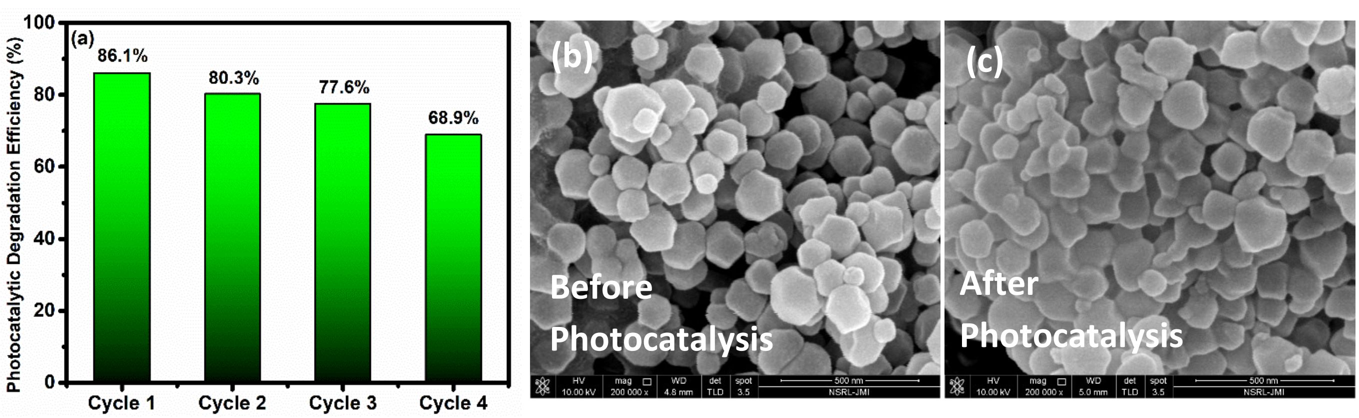


Fig. 11: Reusability and Regeneration of the ZM nanocomposite: (a) 4 cycles of the photocatalytic degradation of TC; FESEM image of the ZM nanocomposite (b) Before photocatalysis and (c) after 4 cycles of photocatalysis

4.0. Conclusion

This study provided a cost-effective and potential photocatalytic material, which has the capability to treat water contaminated with antibiotics waste used for COVID-19. The superior degradation efficiencies were achieved for Tetracycline Hydrochloride, Metronidazole antibiotics and Malachite Green dye. As observed from the results the photocatalytic degradation efficiency of ZM nanocomposite was enhanced as compared to pristine $MoSe_2$ and ZIF-8 and the enhancement could be attributed to the competitive absorption on the surface (as described through zeta potential) of nanocomposite as well as improved photogenerated charge transfer and separation efficiency (as explained through TCSPC results) resulting from the heterojunction between ZIF-8 and $MoSe_2$. The pH = 9 is optimal from the degradation rate of Tetracycline Hydrochloride antibiotic. In the photocatalytic degradation of antibiotics, the main active species for degrading Tetracycline Hydrochloride is superoxide radicals, while the main active species for the degradation of Metronidazole are holes and hydroxyl radicals. The finally degraded products of the antibiotic (TC) were not harmful to the aquatic organisms (as confirmed through LC-MS). The photocatalyst retained good regeneration ability after four consecutive cycles, thereby confirming reusability and regeneration ability of the ZM nanocomposite.

Statement and Declarations

Ethical Approval: We consciously assure that the manuscript is our own original work, which has not been previously published elsewhere.

Consent to Participate: All authors have been personally and actively involved in substantial work leading to the paper, and will take public responsibility for its content.

Consent to Publish: We have seen a version of the manuscript to be submitted/published (including any pictures) and we hereby give our consent for publication in the Environmental Science and Pollution Research.

Author Contribution: All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Honey Mittal, Aruna Ivaturi and Manika Khanuja. All authors read and approved the final manuscript.

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Competing Interest: There are no Conflicts of interests.

Availability of data and materials: No datasets were generated or analyzed during the current study

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