

Glean Investigation of the Photocatalytic Degradation of Anew Designed MWCNT/PANI/Zr(IV)W

Yashfeen Khan^{1*}, Anees Ahmad² and Jassim Hosny Hamed Al Daleen³

^{1,2,3}Department of Chemistry, Faculty of Science, Aligarh Muslim University
E-mail: ¹ykhanalig@gmail.com, ²aneesahmad@yahoo.com

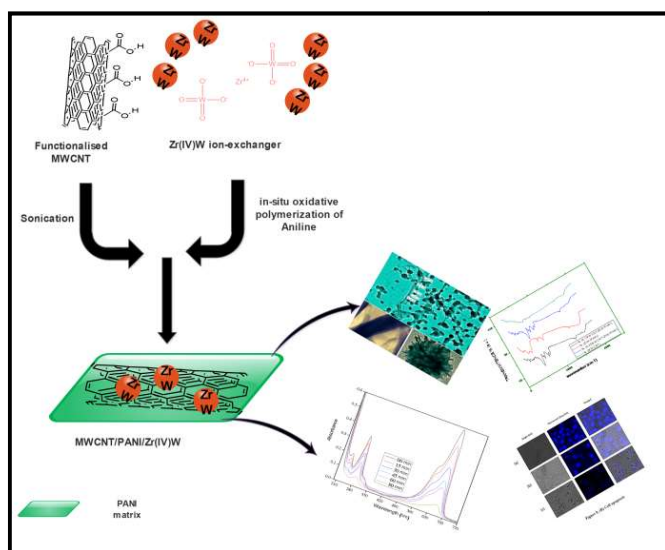
Abstract—In the last few decades, nano-composites have been the topic of interest. Carbon-nanotubes are of significant scientific importance due to their remarkable properties in almost every field, be it electronic, mechanical, thermoplastic, optical, electrical, biological, and environmental. The area of material science is currently undergoing a shift from developing traditional materials such as metals, ceramics, polymers, and composites to a more revolutionary trend of developing nanostructures, which are functionalized, self-assisting and occasionally even self-healing. Albeit, these advances are potentially game-changing, the excitement must be tempered somewhat as several bottlenecks exist. The functionalized ternary nanostructure MWCNT-PANI/Zr(IV)tungstate, i.e.(MWCNT/PANI/Zr(IV)W) was successfully developed via in situ oxidative polymerization of aniline monomer. The microstructure and morphology of the prepared composites were characterized by using Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and high-resolution transmission electron microscopy (HRTEM). The higher photo catalytic degradation rate has been reported by the composite when tested on Rhoda mine B (an industrial dye).

1. INTRODUCTION

Modern era enlightens the synthesis of hybrid nano-composites over their counterparts because of higher application potentials in hybrids[1]. So far, the studies showed that polymeric nano-composites consist of nano-particles embedded in organic polymers, making a new class of materials. The combination of conducting nano-particles (here, MWCNTs) and conducting polymer (here, PANI), described as hybrid electrically conducting nano-composites, is a newly emerging field. In the present paper, we are incorporating an ion exchanger for the first time in CNT based composite. These materials may exhibit unprecedented properties, attractive for both the industrial and academia purposes. There is a variety of applications for conductive nano-composites, i.e., sensors, actuators, touch screens, etc. We are going to revolve around conducting and relative environmental and biological properties. The combination of conductive polymers with conductive carbon nanotubes has already shown some synergistic properties. Ternary PANI/CNT/inorganic exchanger composites are also comprehensively reviewed from an application point of view. The three components of the current paper, which makes the base of ternary composite synthesized in this paper are:

Carbon-Nanotubes (CNTs). Iijima, in 1991, discovered the dark forest of the strongest material known i.e.CNT, the allotropes of Carbon.[2] Nanotubes are membranes of fullerene family in terms of structure and are categorized as **SWCNT**, **MWCNT**. Individual nanotubes align themselves into ropes led together by van der Waals forces, i.e., pi-stacking. C-bonding possesses sp² bonds similar to graphite. These provide unique strength to CNTs.[1], [3], [4] The nanotube structures are represented with various parameters in the published papers.[3], [4]

The surface of CNT is the most useful part for any incorporation or deposition to occur. But the surface is non-reactive because of the intrinsic van der Waals forces among the tubes and hence, hinders the proper dispersion of CNTs



into any polymeric matrix. To make the surface reactive, functionalization of the CNTs is done through different means like noncovalent functionalization, covalent functionalization, endohedral functionalization, external decoration with any inorganic material or maybe direct use of HNO_3 . Functionalization provides sites of co-ordination on the sidewalls and tube tips so that different materials may get attached with the CNTs yielding a well-dispersed composite with extravagant properties in comparison to its counterparts. [3]

Polyaniline(PANI). Among conducting plastics, polyaniline has become a particular focus of interest because of its environmental stability, feasible conductivity by changing protonation state or Oxidation Sate.[5] Polyaniline compounds can be designed to achieve the particular conductivity required for a given application. The resulting blends can be as conductive as silicon or germanium and as insulating as glass. PANI exists in emeraldine form in our synthesized composite. It is the most attractive state due to tunable form, partially oxidized ($n=0.5$, **Green** for the emeraldine salt, **Blue** for the emeraldine base).[2], [6], [7]

Zirconium tungstate. Zirconium tungstate (ZrW_2O_8) is a ceramic material that exhibits potent, isotropic negative thermal expansion(NTP) over a wide temperature range from 0.3 to 1050 K. The configuration and transition of three phases ZrW_2O_8 can be achieved under certain temperatures and pressures. ZrW_2O_8 nanoparticles can be synthesized at lower temperatures by hydrothermal reaction followed by subsequent heat treatment by converting the precursor $\text{ZrW}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ to ZrW_2O_8 . [8]

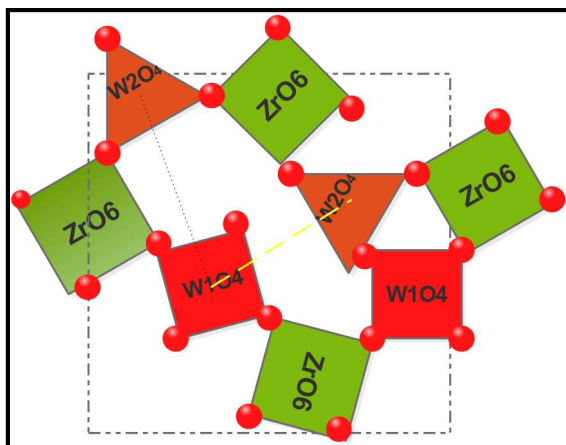


Figure 1: Polyhedral representation of cubic crystal structure of ZrW_2O_8 .

Fig.1 shows a cubic ZrW_2O_8 structure that consists of corner-sharing ZrO_6 octahedra (in green) and WO_4 tetrahedra (in red). Each WO_4 tetrahedron only shares three of its four oxygen atoms and leaves an oxygen atom in a free position. Due to the uniquely flexible metal-oxygen-metal linkage, the transverse vibration of the oxygen atom, connected between the Zr and

W atoms, excited at a low thermal energy results in small counter-rotation of WO_4 and ZrO_2 polyhedra. This is the origin of the negative thermal expansion properties of ZrW_2O_8 , and is also termed as a “quasi-rigid unit mode.” [8]

2. EXPERIMENTAL

Acid functionalization of MWCNTs:

1gram of MWCNT is treated with a 200mL solution of 1M H_2SO_4 and 1M HNO_3 in the ratio 3:1 respectively and kept in Ultra-sonicator for 15 mins at 50° Celsius.

After 15 minutes, the sample is washed with DMW until the pH was neutralized. The washed sample is filtered using a centrifuge and then dried under vacuum for 24 hours at 60° giving a black powdered functionalized MWCNT.

Preparation of Zirconium tungstate ion exchanger:

The solution of 0.1M Zirconium oxychloride and 0.2M Sodium tungstate in 250mL each are prepared in DMW. Zirconium solution was stirred on a non-heated stirrer; pH is checked using pH meter. If pH found was 0.5 or 0.6 tungstate solution is added. Tungstate added it makes the mixed solution basic. The mixture is stirred for about 2 hours on the non-heated magnetic stirrer and then kept for drying at 60° . After drying a white colored powder, inorganic Zirconium tungstate ion-exchanger was obtained.

Composite formation:

Three samples are taken into consideration depending upon the presence and absence of MWCNT in the composite as follows:

Table 1: Description of samples composition.

S. No.	MWCNT (g)	ZrW/PANI (g)	Composite
1.	0	0.25	ZrW/PANI
2.	0.15	0.25	ZrW/PANI/MWCNT(0.25)
3.	0.75	0.25	ZrW/PANI/MWCNT(0.75)

Firstly, MWCNT (various amounts) are dispersed in 50mL of 0.2M CTAB by ultrasonication for 30 minutes. Now, ZrW prepared earlier is added to the different quantities of MWCNT.

Polymerization: 1ml of Aniline is added dropwise to the three variable MWCNT suspensions which are further sonicated for 20 minutes — 50ml of Potassium persulphate (KPS) solution prepared in 1M aq. HCl is added dropwise to the 3suspension solutions.

All three suspensions are stirred at 10° C to -5° C in an ice bath for 2 hours then filtered using a centrifuge and washed several times with DMW and double-distilled Ethanol. Three filtered samples are dried for 24 hours at 60° C leading to the required product, i.e., Ternary nano-composite. Initially, the

inorganic part, i.e., Zirconium tungstate ion-exchanger, is prepared by combining Ammonium tungstate with Zirconium oxychloride. Secondly, MWCNTs bought from the market is functionalized with sulphuric acid and nitric acid in 3:1 ratio through ultrasonicator. The acid-functionalized MWCNT are much more dispersible in common organic, inorganic solvents like N-methyl-2-pyrrolidone, (NMP), Methyl ethyl ketone (MEK), N, N-dimethylacetamide (DMA), N, N-dimethyl formamide(DMF) and many more.

In the third step, which is the step towards the composite formation, we prepared three samples; one is ZrW/PANI, the second one is ZrW/PANI/(.15g)MWCNT and the third one ZrW/PANI/(.25g)MWCNT.

3. CHARACTERIZATION TECHNIQUES

FTIR

The IR spectra were recorded on Perkin Elmer Spectrum2 Version 10.4.00 with KBr pellets in the range 400-4000 cm^{-1} to identify and ensure the functional groups present in the synthesized nanocomposite.

SEM

The surface morphology of the synthesized no composite was studied using SEM model no. JSM, 6510, LV.

TEM

TEM was employed to observe the morphology of the synthesized material using model no; JEM2100

4. RESULTS AND DISCUSSION

In Fig. 2 FTIR spectrum clearly shows the presence of C=C stretch of the benzenoid ring at 1483 cm^{-1} and the C=N stretch of quinoid ring unit of PANI vibration at 1576.47 cm^{-1} . The strong band around 1147.33 cm^{-1} is the measure of the degree of electron delocalization and hence, considered as the characteristic peak of PANI conductivity.[9]

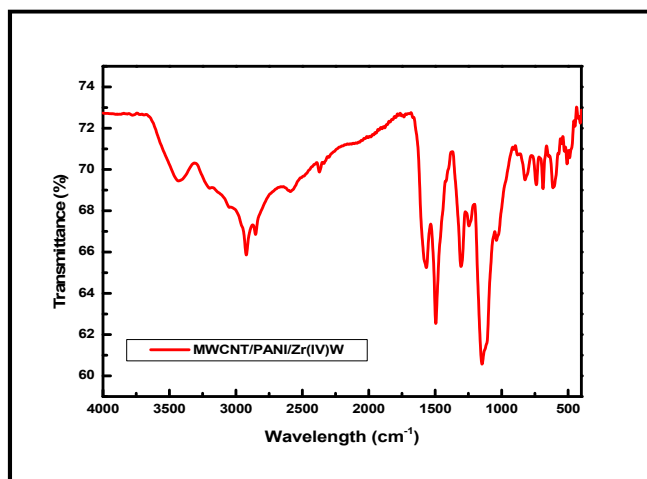


Fig. 2: FTIR of MWCNT/PANI/Zr(IV)W nanocomposites

Peaks at 2851.90 cm^{-1} and 2351.85 cm^{-1} are assigned to the N-H stretching of a secondary amine and NH^+ stretching of amine in PANI respectively. Substitution at benzene rings peak appears at around 738.60 cm^{-1} . Also, a very sharp and strong band at 3433.12 cm^{-1} is assigned to hydrogen OH stretching, a broad and strong peak at 2921.59 cm^{-1} implies aqua (OH) symmetric stretching. The sharp and medium peak at 1566.53 cm^{-1} is assigned to aqua H-O-H bending. Rest others are for superposition of metal-oxygen stretching and wagging, twisting and rocking modes.

The FTIR spectra of Zr(IV)W shows broad bands in the region $\sim 3400 \text{ cm}^{-1}$ attributed to asymmetric and symmetric hydroxo-OH and aqua-OH stretches. A sharp medium band at 1566 cm^{-1} is assigned to aqua (H-O-H) bending.[10], [11]

Here in SEM images of Fig. 3(a) shows functionalized CNTs are smooth, dense and hollow ropes of diameter 10-40 nm and length up to few micrometers.

And ZrW are oval granules which intermingle with PANI as observed in Fig. 3 (b)

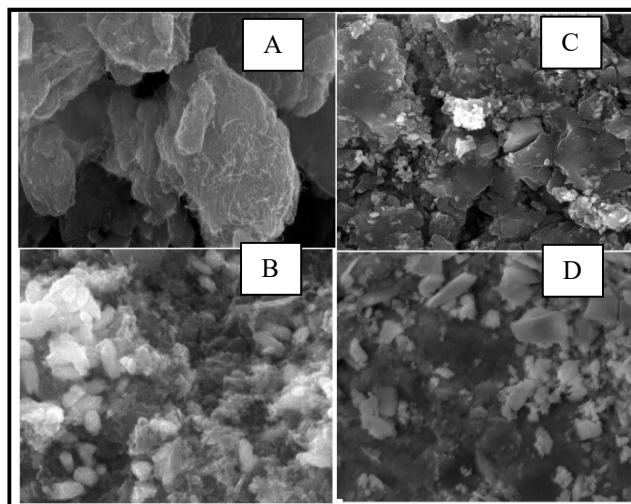


Fig. 3: SEM micrographs of a) MWCNT, b) ZrW/PANI

c) MWCNT(0.25g)/PANI/Zr(IV)W and d) MWCNT(0.75g)/PANI/Zr(IV)W

Fig. 3(c & d) shows that MWCNTs are introduced into the in-situ polymerized PANI ZrW system (through ultrasonication).[2], [12]

TEM micrographs in Fig. 4 (a) shows MWCNTs have untangled structures due to the chemical modifications that are functionalization. Functionalization untangled the tubular structure of MWCNT and made the C- sites available for interaction.[1]

Fig. 4(b) shows the TEM micrographs of inorganic ion exchanger ZrW in the PANI matrix. The hollow structures of MWCNTs are filled with ion exchanger ZrW.[9], [12]

Fig. 4(c and d) implies the filling of ZrW in the inner cavities of MWCNT has taken place. The outer walls of MWCNT are uniformly coated with PANI, as shown in figure c and d. PANI and ZrW are well dispersed on and into the multiwalled CNT respectively during the ultrasonication, PANI polymer chains are fetched and torn MWCNT-exchanger bundles into single MWCNT ZrW. Quinoid rings of PANI interact with MWCNT ZrW and leads to the adsorption of PANI on MWCNT surface forming a tubular core of PANI surrounding MWCNT ZrW.[2]

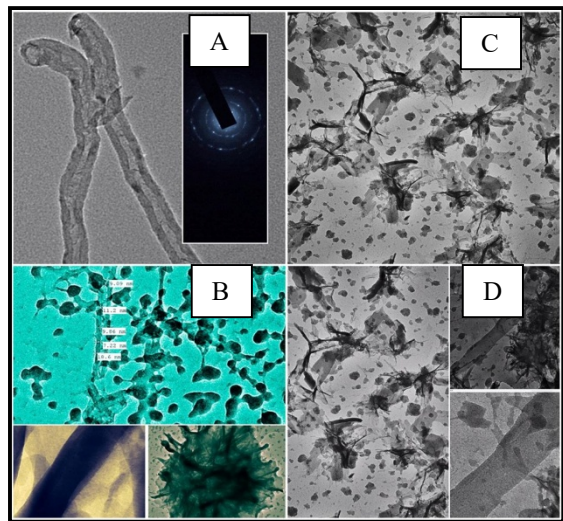


Fig. 4: TEM micrographs of a) MWCNT, b) ZrW/PANI

c) MWCNT(0.25g)/PANI/Zr(IV)W and d) MWCNT(0.75g)/PANI/Zr(IV)W

5. APPLICATIONS

Evaluation of photocatalytic degradation:

The photocatalytic performance of synthesized nanocomposite was investigated by the mineralization of RhB dye in aqueous solution and the presence of atmospheric air. As observed from the experimental studies, that there was no degradation of RhB under UV-light irradiation in the absence of photocatalyst. Although, some degradation of RhB could be seen in the presence of fabricated composites in the dark due to adsorption of dye on the surface of the catalyst. The RhB dye showed an excellent amount of adsorption on the surface of the synthesized composite in the presence of both light and photocatalyst. Thus, indicating that for the efficient degradation of joint dye function of both light and catalyst are required. In the experimental set-up, an aqueous solution of RhB (10 ppm, 180 mL) was irradiated in photoreactor with a UV lamp in the presence of the nanocomposite under constant stirring and bubbling of atmospheric oxygen. The mineralization of the dye was tested by measuring the change in the absorbance at their ($\lambda_{\max}=663$) as a function of irradiation time. Figure 5(A) showed that 97.69% degradation

of RhB dye takes place after 80 min of irradiation time in the presence of the composite material.

The result reveals that the main absorption peaks of RhB decrease gradually as well as color-fading was observed with the increase in irradiation time, and this may be due to the gradual decomposition of the chromophoric group present in the dyes.[13][14] Fig. 5(B) gives the change in percentage degradation of dyes with or without photocatalyst in the presence of composite material under UV-light.

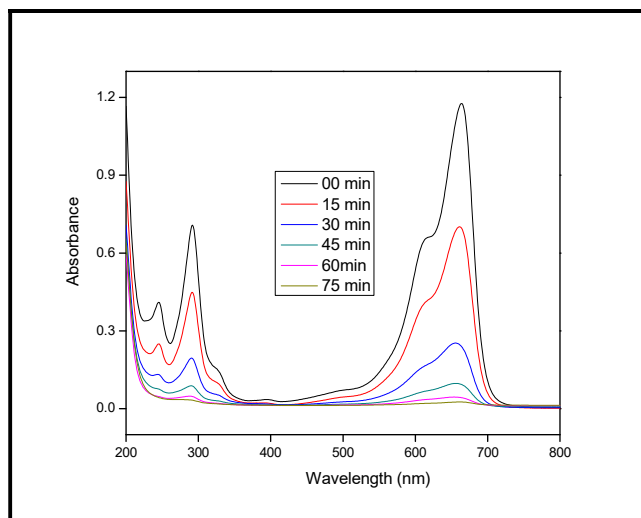


Fig. 5(A): Photocatalytic degradation RhB dye in the presence of ZrMo/MWCNT/PANI composite UV light illumination at different time intervals

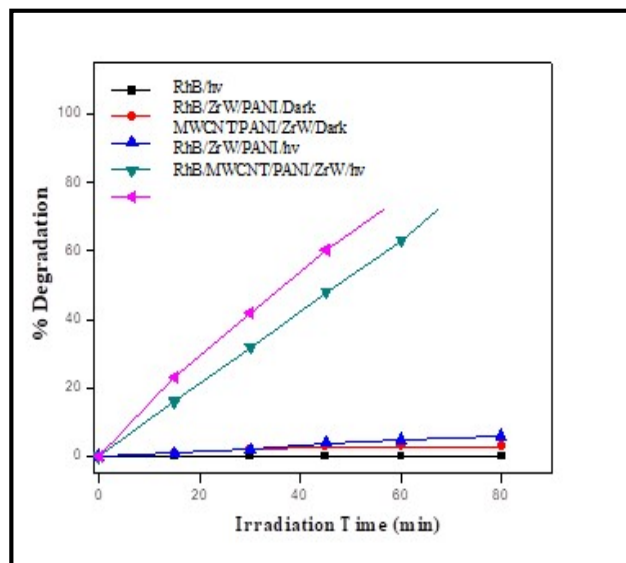


Fig. 5(B): Percentage photodegradation of RhB dye in aqueous solution over the nanocomposite in the presence and absence of UV light illumination

The maximum degradation of RhB dye in the presence of the composite is a result of their good interaction. Hence, good adsorption of RhB dye on the composite's surface was observed, which is considered as an eco-friendly method for removing dyes from wastewater and making it tender. The absorbing dye is then degraded by the active species. In addition to this, the higher mineralization of composite can be explained due to the formation of new trapping sites. These trapping sites affect the lifetime of the charge carriers by increasing the arrival time of photogenerated electron and the hole on the surface of the composite and thus, decrease the electron-hole recombination rate and increase the surface area of the composite that leads to the faster degradation of dye.

6. CONCLUSION

The successfully fabricated f-MWCNT-PANI/Zr(IV)W nanocomposite synthesized by *insitu* polymerization of PANI and characterized by various instrumental techniques. The composite material exhibited good photocatalytic performance by effectively degrading the RhB dye (97.69%) within 80 min of irradiation time. The superior photocatalytic effect of the composite is attributed to the electron-sink function of MWCNT, which may facilitate the separation of charge carrier by suppressing the recombination rate of the photo-generated electron and hole pairs, as well as the higher surface area of the composite.

Compliance with ethical standards

The authors declare that they have no competing interest.

7. ACKNOWLEDGEMENT

The authors are humbly thankful to the Instrumental facilities provided by the Chairman, Department of Chemistry, A.M.U. and USIF (University Sophisticated Instruments Facility), A.M.U., Aligarh. One of the authors (Yashfeen Khan) is thankful to the University Grand Commission (UGC), Government of India for the financial aid.

REFERENCES

- [1] C. N. R. Rao and A. Govindaraj, 'Carbon Nanotubes', in *RSC Nanoscience and Nanotechnology No. 18 Nanotubes and Nanowires, 2nd Edition*, 2011, pp. 1–189.
- [2] C. Oueiny and S. Berlioz, 'Carbon nanotube – polyaniline composites', *Prog. Polym. Sci. Elsevier*, vol. 39, pp. 707–748, 2014.
- [3] L. Chen, H. Xie, and W. Yu, 'Functionalization Methods of Carbon Nanotubes and its Applications', in *Carbon Nanotubes Applications on Electron Devices*, L. Chen, Ed. Shanghai, 2008, pp. 213–232.
- [4] E. N. Ganesh, 'Single Walled and Multi Walled Carbon Nanotube Structure, Synthesis and Applications', *Int. J. Innov. Technol. Explor. Eng.*, vol. 2, pp. 2278–3075, 2013.
- [5] H. Wang, J. Lin, and Z. Xiang, 'Journal of Science: Advanced Materials and Devices Polyaniline (PANi) based electrode materials for energy storage and conversion', *J. Sci. Adv. Mater. Devices*, vol. 1, pp. 225–255, 2016.
- [6] S. S. Shinde and J. A. Kher, 'A Review on Polyaniline and Its Noble Metal Composites', *Int. J. Innov. Res. Sci. Eng. Technol.*, vol. 3, pp. 16570–16576, 2014.
- [7] § Raquel Sainz,† William R. Small,‡ Nigel A. Young,‡ Cristina Valle's,† Ana M. Benito,† Wolfgang K. Maser*,† and Marc in het Panhuis*,‡, 'Synthesis and Properties of Optically Active Polyaniline Carbon Nanotube Composites', *Macromolecules*, vol. 39, pp. 7324–7332, 2006.
- [8] H. Wu, 'Physical and Thermal Properties of Zirconium Tungstate Nanoparticles with Different Morphologies from Hydrothermal Synthesis', 2012.
- [9] T. S. Najim and A. J. Salim, 'Polyaniline nanofibers and nanocomposites: Preparation, characterization, and application for Cr(VI) and phosphate ions removal from aqueous solution', *Arab. J. Chem.*, 2014.
- [10] H. Patel, A. Parikh, and U. Chudasama, 'A comparative study of proton transport properties of metal (IV) tungstates and their organic derivatives', *Bull. Mater. Sci.*, vol. 28, no. 2, pp. 137–144, 2005.
- [11] I. M. Arzelán and B. Salta, '3, 2, 3', vol. 3, p. 2005, 2011.
- [12] P. Taylor, S. A. Nabi, R. Bushra, and M. Shahadat, 'Toxicological & Environmental Chemistry Application of Zr (IV) tungstate for removal of metal ions from aqueous solutions', no. February 2012, pp. 37–41.
- [13] W. Raza, M. M. Haque, and M. Muneer, 'Synthesis of visible light driven ZnO: Characterization and photocatalytic performance', *Appl. Surf. Sci.*, vol. 322, pp. 215–224, 2014.
- [14] W. Raza, M. M. Haque, M. Muneer, M. Fleisch, A. Hakki, and D. Bahnemann, 'Photocatalytic degradation of different chromophoric dyes in aqueous phase using la and Mo doped TiO₂ hybrid carbon spheres', *J. Alloys Compd.*, vol. 632, pp. 837–844, 2015.