Enhanced visible light driven Photocatalytic activity of MnO₂ nanomaterials and their hybrid structure with carbon nanotubes

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Keywords: nanocomposites, MnO₂, carbon nanotubes, scavengers, visible light, photocatalysis

Abstract
MnO₂ nanomaterials were synthesized using a simple wet redox method. Crystal structure of as prepared pure and Al doped MnO₂ nanomaterials was investigated using X-ray diffraction (XRD) technique. Crystal structure was further confirmed by FTIR analysis. Morphology of pure MnO₂, Al doped MnO₂, MnO₂/CNT hybrid structure and Al doped MnO₂/CNT hybrid structure was studied using scanning electron microscopy (SEM). Energy dispersive X-ray spectroscopy confirmed the presence of all the constituent atoms in the crystal structure of all the samples. Bandgap value was found to decrease with the modification (doping and hybrid structure). Photocatalytic efficiency of all the MnO₂ samples was studied using the photodegradation of methylene blue (MB) under the visible light (solar radiation). Effect of different intermediates on the photodegradation efficiency was studied using different scavengers.

1. Introduction
Extensive use of organic dyes in ever growing textile industry is causing environmental peril. Almost 20% of total dye production vanishes during the process of dying and leads to industrial effluents. By-products of these organic dyes produced through oxidation or other reactions are harmful and cause eutrophication. Environmental Remediation is essential to sustain good quality of health for human beings. Semiconductor nanomaterials are potential aspirants for environmental remediation, since they can produce charge carriers to breakdown organic dyes when exposed to the light of some suitable frequency. Several processes are in practice for wastewater remediation such as ion exchange, membrane process, biodegradation and photocatalysis etc. Out of these technologies photocatalysis is considered the best because it is economical and the photocatalyst is regenerated for repeated use.

Capability of semiconducting materials to generate electrons and holes, when exposed to light, makes them budding materials for photocatalysis. Heterogeneous photocatalysis involving the use of semiconductor nanostructures has become a promising technique for the degradation of inorganic and organic pollutants [1]. The semiconductors are categorized as direct bandgap semiconductors or indirect bandgap semiconductors. The semiconductors in which electronic excitation involves no change in momentum are called direct bandgap semiconductors. The semiconductors in which electronic excitation involves a change in momentum are termed as indirect bandgap semiconductors. This change in momentum is atoned by transferring heat to vibrating particles (Phonon) [2]. The materials that show direct bandgap usually emit light during deexcitation and the materials with indirect bandgap emit heat first to conserve the total energy of the system and then get deexcited [3].

The semiconducting material which can generate electron-hole pairs in the presence of light is known as photocatalyst. For a photocatalytic system, the important features of a photocatalyst are surface area, morphology, bandgap as well as band edge and charge carriers [4].
Transition metal oxides owing to their characteristics mentioned above are recognized as good materials for photocatalysis. Oxides of transition metals like Ni, Cu, Fe and Mn etc. have been studied a lot as a catalyst [5]. Out of these metal oxides manganese oxides have great potential towards wastewater remediation. Moreover, manganese dioxide has good catalytic potential even at low temperature [6]. MnO₂ is found in different phases and α-MnO₂ is supposed to be the best. The reason is that it has large tunnel (2 × 2) structure with 4.62 Å size. Consequently, it can lodge ions in these tunnels, which will act as free charge carriers.

Khan et al reported that MnO₂/activated carbon composite showed an excellent photocatalytic reduction of Congo red as compared to MnO₂ nanoparticles [7]. Photocatalytic competency of MnO₂ doped with Al³⁺ and Ag⁺ was found to increase [8]. This increase was the consequence of doping ions electron trapping capability to reduce recombination. Indirect bandgap of in-situ Al doped MnO₂ was found to decrease from 2.57 eV to 2.41 eV [9]. Oxygen vacancies produced in Al doped MnO₂ microspheres resulted the fermi level up [10]. Consequently, bandgap is narrowed down. MnO₂ ternary nanocomposite with graphene nanosheets and carbon nanotubes degraded 71% MB only within one hour [11].

Here in this manuscript undoped MnO₂, Al doped MnO₂, MnO₂/CNT hybrid structure and Al doped MnO₂/CNT hybrid structure were prepared using a simple wet redox method. Inherent conductivity of MnO₂ is increased by doping [12] while the composite can only enhance the superficial conductivity [8]. To enhance the inherent and superficial conductivity, hybrid structure of nanomaterials with carbon nanotubes and Al doping in MnO₂ were made. The effect of doping and hybrid structure on structure and morphology of MnO₂ nanomaterials was studied. The role of different intermediates using scavengers was investigated. Photocatalytic activity comparison of all these samples towards methylene blue (MB) was investigated using Agilent cary-60 UV-visible spectrophotometer.

2. Experimental work

2.1. Materials

Potassium permanganate (KMnO₄ 98% Merck); fumaric acid (C₄H₆O₄ 99% Sigma Aldrich), sulphuric acid (H₂SO₄ 98% Merck), ammonia (NH₃ 35% Merck), and aluminum nitrate (Al(NO₃)₃ 98% Merck) were precursor salts for the synthesis of undoped and doped MnO₂ nanomaterials. All the analytical grade reagents were used as received.

2.2. Synthesis of MnO₂ nanomaterials

Undoped MnO₂ nanomaterials were synthesized using the method described in our previous article [8, 13, 14]. Figure 1 displays the synthesis scheme. Briefly, KMnO₄ and C₄H₆O₄ were taken in the stoichiometric ratio. Distilled water was added in it and homogeneous mixture was made using hot plate stirrer. To this sulphuric acid was added to acidify the solution. Composition of all the samples is given in table 1. The mixture was kept for stirring until the pink color of KMnO₄ turned to brown. After the completion of the reaction, the product was washed several times and was kept for drying at 100 °C for 24 h and then grounded.. This grounded powder was calcinated to develop the phases and to diminish the stress in the crystal structure. This ground powder was then packed in airtight bags for further characterization. Doping was done simply by adding the stoichiometric amount of dopant.

2.3. Synthesis of MnO₂ nanomaterials/CNT hybrid structure

MnO₂ nanomaterials/CNT hybrid structure was prepared by simply placing a mixture of carbon nanotubes and MnO₂ nanomaterials in ultra sonicator figure 1. Typically, 90 mg of MnO₂ nanomaterials along with 10 ml of 100 ppm carbon nanotubes (CNT) were taken and 100 ml of distilled water was added. This solution was then ultra-sonicated for 2 h to make it homogenous. After that the product was isolated and dried at 100 °C in oven for 5 h. The product was grounded to yield fine powder and was packed in airtight bags for further characterization.

2.4. Characterizations

Crystal structure characterization was done by Bruker D8 A25 model using Cu kα, radiations having wavelength (0.154 nm). Morphological and elemental characterizations were assessed using ZEISS LEO SUPRA 55 FESEM and JEOL JCM-6000 Plus SEM. Functional groups presence was confirmed with the help of Jasco FTIR spectrometer model 6000. Optical characterizations were performed using dual beam UV-visible NIR spectrophotometer Agilent cary 60.

2.5. Photocatalytic activity

Photocatalytic activity of pure MnO₂ nanomaterials, Al doped MnO₂ nanomaterials, MnO₂ nanomaterials/CNT hybrid structure and Al doped MnO₂ nanomaterials/CNT hybrid structure was assessed using methylene
blue (MB) dye as a typical organic compound under visible light (solar radiation). Initially, 20 mg of the photocatalyst was added in 50 ml of 20 ppm methylene blue (MB) solution. This solution was then stirred for an hour in dark to attain equilibrium (when the rate of adsorption and desorption of MB on catalyst become equal). After attaining an equilibrium, the solution was then exposed to light. Before exposed to light 5 ml of this solution was taken and centrifuged to remove photocatalyst and then absorbance was taken. This was the absorbance at zero time. After exposure to light the solution was taken every 15 min and absorbance was taken. This was the absorbance at time $t'$. After the completion of the reaction, percentage degradation was calculated using the following equation;

$$\text{% degradation} = \frac{1 - A/A_0}{100}$$  \hspace{1cm} (1)

3. Results and discussion

3.1. X-ray diffraction (XRD)
Crystal structure of pure and Al doped MnO$_2$ nanomaterials was investigated using X-ray diffraction technique. All the diffraction peaks of pure and doped MnO$_2$ nanomaterials matched well with the tetragonal crystal
structure of α-MnO$_2$ (ICDD # 44-0141). All the diffraction peaks corresponded well to the lattice planes described in [15] figure 2(a).

When MnO$_2$ was doped with Al$^{3+}$ ions, peak shifting towards lower angle was perceived figure 2(b). This peak shifting is an indication of successful doping of dopant ions (Al$^{3+}$ ions) into the tetragonal crystal structure of MnO$_2$ nanomaterials. The peak shifting towards lower angle also indicated the expansion [16, 17], which is also confirmed by an increase in crystallite size and microstrain. The absence of peak (420) for doped sample is possibly due to reduction in crystallinity with doping [18, 19]. It can be perceived from XRD pattern that pure MnO$_2$ nanomaterials were well crystalline and this crystallinity was reduced with doping due to crystal structure distortion [20]. This reduction in intensity also confirmed the successful doping.

The average crystallite size was calculated by the Scherrer formula using XRD data [21–23].

$$D = \frac{K\lambda}{\beta \cos \theta}$$

Here ‘$D$’ is the crystallite size, $\lambda$ is the wavelength (Cu K$_\alpha$ = 1.54 Å), ‘$K$’ is a shape factor, ‘$\beta$’ is the full width half maximum (FWHM) and ‘$\theta$’ is the scattering angle. Average crystallite size was found to be 24 nm for pure MnO$_2$ nanomaterials. It was found to increase with aluminum doping and found to be 25 nm. This increase with doping is possibly due to somewhat bigger ionic radii of Al$^{3+}$ as compared to Mn$^{4+}$ [24]. This somewhat bigger ionic radii of Al$^{3+}$ also caused distortion which is indicated by the Williamson Hall plot.

Dislocation density tells about the irregularity in the crystal structure and is calculated by the formula;

$$\delta = \frac{1}{D^2}$$

Dislocation density is given in table 2.

Strain in the crystal structure of pure and doped MnO$_2$ nanomaterials was calculated using Williamson Hall plot by drawing $4\sin \theta$ on abscissa and $\beta \cos \theta$ on ordinate. Williamson Hall plots of pure and doped MnO$_2$ nanomaterials are shown in figure 3. Strain can either be compressive or tensile depending upon the slope of Williamson-Hall plot. Strain will be compressive if the slope is negative [25] and it will be tensile if the slope is positive [26]. From figure 3 and table 2 it is clear that pure MnO$_2$ nanomaterials had tensile strain [26, 27]. This strain was further expanded when MnO$_2$ nanomaterials were doped with aluminum ions, as a consequence of ionic radii difference between aluminum and manganese. Average crystallite size and microstrain are shown in table 2.

### 3.2. Fourier transform infrared spectroscopy (FTIR)

FTIR analysis of pure and Al doped MnO$_2$ was carried out to identify the functional groups present in the as-prepared MnO$_2$ nanomaterials. FTIR analysis was performed in the range (1000–390 cm$^{-1}$) figure 4. FTIR
spectrum of pure MnO₂ nanomaterials disclosed three bands below 1000 cm⁻¹. These bands were detected at 451 cm⁻¹, 530 cm⁻¹ and 705 cm⁻¹. All these bands are characteristics of metal-oxygen bond (Mn-O or Mn-O-Mn) vibrations in MnO₆ octahedron. All these bands are in good consistency with the previously reported results [8, 28, 29]. When MnO₂ nanomaterials were doped with aluminum ions a shift in absorption bands was experienced towards lower wavenumber. This shift in bands confirmed the doping of aluminum ions into MnO₂ nanomaterials [12]. This shift in bands towards lower wavenumber was ascribed to larger ionic radii of Al³⁺ ions (0.535 Å) as compared to ionic radii of Mn⁴⁺ ions (0.53 Å). Due to relatively larger ionic radii of dopant ions lattice parameters were increased. Consequently, bond strength was decreased, which in turn shifted the bands towards lower wavenumber [30]. When MnO₂ was doped with aluminum, oxygen vacancies were produced as a consequence of charge imbalance between Mn⁴⁺ and Al³⁺ ions. As a result MnO₆ octahedron was distorted which lowered the lattice vibration energy [30].

3.3. Field emission scanning electron microscopy (FESEM)

Field emission scanning electron microscopy was used to investigate the morphology of as prepared pure and Al doped MnO₂ figures 5(a)–(d). FESEM images revealed that the as prepared nano MnO₂ has capsule like morphology. FESEM images also showed the presence of carbon nanotubes (CNTs) on the surface of MnO₂ nanomaterials. This presence of CNTs on the surface of MnO₂ nanomaterials confirmed the hybrid structure formation. Aggregation was observed as a consequence of van der walls forces among MnO₂ nanomaterials.
increase in aggregation was observed with doping. This increase is possibly the result of higher surface energy. Average particle size was calculated by intercept technique from FESEM micrographs. A random line was drawn through the micrographs and the total no. of grain boundaries was calculated. Actual line length divided by the no. of grain boundaries give the value of average particle size.

\[
\text{Average particle size} = \frac{\text{actual length of line}}{\text{no. of grain boundaries}}
\]

Length of the pure MnO₂ nanomaterials was found to be 200 nm with 55 nm diameter. This length and diameter were found to decrease with aluminum doping. For Al doped MnO₂ nanomaterials the length was found to be 130 nm and diameter was found to be 40 nm. This decrease in particle size with doping was possibly the consequence of crystal growth inhibition [31, 32].

3.4. Elemental analysis

Presence of various elements in pure and doped samples along with their hybrid structures was confirmed using energy dispersive X-ray spectroscopy (EDX). EDX spectra of all the samples are exhibited in figures 6(a)–(d). EDX analysis of pure MnO₂ nanomaterials clearly demonstrated that they only contain Manganese and oxygen ions. Two unlabeled Peaks between 3 and 4 KeV might be because of the presence of potassium ions [33, 34]. Potassium ions came from KMnO₄ and residue in large tunnel structure of MnO₂. Al doped MnO₂ nanomaterials showed the presence of Al along with Mn and O. Hybrid structure of pure and Al doped MnO₂ nanomaterials with carbon nanotubes also indicated the presence of C along with other elements. EDX spectra confirmed the successful hybrid structure formation of MnO₂ nanomaterials with carbon nanotubes and aluminum doping.

3.5. UV-visible analysis

Optical properties of pure and Al doped MnO₂ nanomaterials and their hybrid structure with carbon nanotube were investigated using UV-visible NIR spectroscopy. UV-visible spectra of all the prepared samples are shown in figure 7. Pure MnO₂ nanomaterials showed the absorption maximum at a wavelength of 400 nm approximately. It can be predicted that when MnO₂ nanomaterials were modified through doping or hybrid
structure formation red shift was observed. The possible reason for this red shift is the defects in the crystal structure as a consequence of dopant ions [35]. Al doped MnO₂ nanomaterials and Al doped MnO₂ nanomaterials/CNT hybrid structure showed a greater absorption potential in the wavelength region near 550 nm, which proved both of these potential contestants to harvest visible light more efficiently than pure MnO₂ nanomaterials.

Figure 6. EDX spectra of (a) pure MnO₂ nanomaterials (b) Al doped MnO₂ nanomaterials (c) MnO₂/CNT hybrid structure (d) Al doped MnO₂/CNT hybrid structure.

Figure 7. UV-visible spectra of MnO₂ nanomaterials, Al doped MnO₂ nanomaterials, MnO₂ nanomaterials/CNT hybrid structure and Al doped MnO₂ nanomaterials/CNT hybrid structure.
Using UV-visible data bandgap values of pure MnO₂ nanomaterials, Al doped MnO₂ nanomaterials, MnO₂ nanomaterials/CNT hybrid structure and Al doped MnO₂ nanomaterials/CNT hybrid structure were calculated. Bandgap value of all the prepared samples was calculated by drawing Tauc plot. Tauc plot was drawn by taking energy on abscissa and \((\alpha h\nu)^2\) on ordinate. The equation that provides base for the calculation of bandgap value is given below \[36\] :

\[
(\alpha h\nu)^2/n = A(h\nu - E_g)
\]

Here ‘n’ represents the indirect or direct bandgap and \(h\nu\) represents the energy. If the value of ‘n’ is 2 then there is indirect bandgap, while the bandgap is direct for the \(n = 1/2\). Direct bandgap is when the electronic excitation involves no change in momentum, while indirect bandgap involves the change in momentum. In order to keep the law of conservation this change in momentum is compensated by coupling energy with phonon (lattice vibration).

When the graph between energy \((h\nu)\) and \((\alpha h\nu)^2\) was drawn, the value of bandgap from this Tauc plot was calculated when the straight line was extra plotted. The point where this extra plot intersected abscissa (slope) is the bandgap value by equation \(3\). Energy is simply calculated by the following equation;

\[
\text{Energy}(h\nu) = 1240/\text{wavelength}
\]

Tauc plots of all the samples are given in figures 8(a)–(d). Bandgap value of all the samples is given in table 3. Direct and indirect band gap value of pure MnO₂ nanomaterials was found to be 4.53 eV and 1.74 eV respectively and corresponded well to previously reported values \[37\]. Existence of two types of bandgap for a material is also evident from the already reported literature \[38\]. From figures 8(a)–(d) it can be assessed easily that bandgap value for doped and hybrid structures showed redshift \[39\]. This reduction in bandgap is attributed to high carrier concentration \[39\]. The bandgap reduction with Al doping is also associated with the introduction of impurity level. This doping alienated the molecular orbital into two orbitals (bonding orbital and antibonding orbitals). The antibonding orbitals presented vacant orbitals which provided space for electrons to be accommodated. Thus it led towards the band narrowing \[9\]. Consequently, the bandgap value decreased.

Figure 8. Direct bandgap of (a) pure MnO₂ nanomaterials (inset: indirect bandgap) (b) Al doped MnO₂ nanomaterials (inset: indirect bandgap) (c) MnO₂ nanomaterials/CNT hybrid structure (inset: indirect bandgap) (d) Al doped MnO₂ nanomaterials/CNT hybrid structure (inset: indirect bandgap).
Bandgap value also found to decrease for hybrid structures. This decrease in bandgap value is attributed to enhanced surface contact between pure and Al doped MnO$_2$ nanomaterials and carbon nanotubes. Actually, hybrid structure with CNT provided larger surface area for adsorption. As a result of this increase in surface area adsorption capability enhancement provided more light to be absorbed towards the visible region of light spectra [40].

### 3.6. Photocatalytic activity

Photocatalysis is a technique that is based on the amputation of organic content from industrial effluents using solar radiation. It involves the degradation of organic matter from industrial effluents using a catalyst. The catalyst accelerates the removal process in the presence of light of some suitable wavelength.

The effectiveness of all four samples towards methylene blue degradation was assessed by taking 10 mg of photocatalyst in 50 ml of 20 ppm methylene blue solution. The mixture of photocatalyst and methylene blue solution was exposed to solar radiation for 75 min. Photodegradation spectra of methylene blue degradation are shown in figures (a)–(d). It can be assessed from the spectra that doped and hybrid structures displayed much better photodegradation as compared to pure MnO$_2$ catalyst. % degradation using all the samples is shown in table 3. Kinetic plot for the photodegradation of methylene blue (MB) using different photocatalysts is shown in figure 10(a). $-\ln A/A_0$ versus time graph is shown in figure 10(b).

The enhanced photocatalytic competency of Al doped MnO$_2$ nanomaterials was attributed to the electron trapping capability of dopant ions, which reduce the recombination of electron-hole pairs. This increase is also attributed to rough and enhanced surface area of Al doped MnO$_2$ nanomaterials [38, 41]. Al doped MnO$_2$ nanomaterials/CNT hybrid structure and MnO$_2$ nanomaterials/CNT hybrid structure also displayed much better photodegradation competency towards methylene blue (MB) degradation. The photocatalytic degradation competency of both the hybrid structures is attributed to their enhanced surface contact. The enhancement in photodegradation is also attributed to lower bandgap value as a consequence of sample functionalization [40]. Furthermore, carbon nanotubes trapped the excited electrons and hindered the recombination. This hindrance provided more electrons to generate superoxide radicals [42]. Figures 5(b), (d) and 6(c), (d) confirmed the presence of CNTs and carbon as well as oxygen. There are evidences of photocatalysis enhancement by CNTs functionalization [43, 44]. Comparison of this catalyst with the already reported literature is given in table S1 is available online at stacks.iop.org/MRX/7/105015/mmedia. It can be assessed from table S1 that this catalyst possesses better photocatalytic efficiency in relatively shorter time.

Photodegradation of methylene blue (MB) using pure MnO$_2$ nanomaterials, doped MnO$_2$ nanomaterials and their hybrid structure with carbon nanotubes can be explained by an adsorption-oxidation-desorption Fenton like mechanism. When a semiconductor photocatalyst is exposed to photon of light having energy equal to or greater than bandgap energy of semiconductor, electrons are excited to higher energy levels leaving behind holes. The excited electrons are captured by oxygen to generate superoxide radical (O$_2^\cdot$), leaving behind a hole (h$^+$). Holes are captured by water molecules to convert them into very reactive hydroxyl radicals. Mechanism of the whole reaction is given below.

$$\text{MnO}_2 + h\nu \rightarrow e_{vb}^- + h^+_{cb}$$
$$e_{vb}^- + O_2 \rightarrow O_2^-$$
$$h^+ + H_2O \rightarrow OH$$
$$\text{MB} + O_2^- + OH \rightarrow \text{Photodegradation products}$$

Kinetic plot of all the MnO$_2$ samples was drawn in figure 10(a) and rate constant was determined using the following pseudo first order equation;

$$-\ln A/A_0 = Kt$$

(6)

Here ‘$A_0$’ is the initial absorption value of methylene blue (MB), $A$ is the absorption value of methylene blue (MB) at a given time, ‘K’ is the rate constant and ‘t’ is the time when the absorbance was taken. Kinetic plot

| S. No | Sample name                          | Bandgap value (eV) Direct/Indirect | % degradation | Rate constant (min$^{-1}$) |
|-------|-------------------------------------|-----------------------------------|---------------|---------------------------|
| 1     | MnO$_2$                             | 4.53/1.74                         | 24            | 0.0061                    |
| 2     | Al doped MnO$_2$                    | 4.35/1.58                         | 48            | 0.0112                    |
| 3     | MnO$_2$/CNT hybrid structure        | 4.40/1.63                         | 70            | 0.0165                    |
| 4     | Al doped MnO$_2$/CNT hybrid structure | 4.31/1.35                       | 88            | 0.0213                    |

**Table 3.** Bandgap value, % degradation of MB and rate constant of all the samples.
displayed that the highest rate constant was observed for Al doped MnO2 nanomaterials/CNT hybrid structure ($K = 0.0213 \text{ min}^{-1}$). Rate constants for all the samples are shown in table 3.

3.7. Role of different active species towards MB removal
Role of different active species towards methylene blue (MB) degradation was studied using different scavengers for different active intermediates. Typically used scavengers were Ethylenediaminetetraacetic (EDTA), ascorbic
acid, silver nitrate and 2-propanol for hole, superoxide radical, electrons [45] and hydroxyl radicals respectively [38, 46].

Figure 11(b) shows the % photodegradation of Al doped MnO2 nanomaterials/CNT hybrid structure. Kinetic plot for the photodegradation of methylene blue by Al doped MnO2 nanomaterials/CNT hybrid structure using different scavengers is shown in figure 11(a). From figure 11(a) it can be predicted that photodegradation competency of Al doped MnO2 nanomaterials/CNT hybrid structure was significantly decreased using different scavengers except for ascorbic acid. It indicated that all the intermediates except superoxide radicals were involved in the photodegradation process of methylene blue (MB). When 10 mg of EDTA as a hole scavenger was added to the solution containing Al doped MnO2 nanomaterials/CNT hybrid structure and methylene blue, photodegradation was decreased to 9% only. This showed that hole has a great impact on the photodegradation of methylene blue (MB). Furthermore, the photodegradation was again found to decrease up to 15% when 10 mg of silver nitrate was added as an electron scavenger. This proved the significant role of electrons towards methylene blue (MB) degradation. When the same amount of 2-propanol as a scavenger of hydroxyl radical was added to the system the photodegradation efficiency was found to decrease once again up to 12%. However, when 10 mg of ascorbic acid was added to act as superoxide radical, the photodegradation was found to be 50%. This indicated that superoxide radicals have very little or no impact on the photodegradation of methylene blue (MB).

4. Conclusion

It was deduced that Crystal structure of MnO2 nanomaterials was modified with the doping and was found to expand with doping. FTIR peak shifting with doping towards lower wavenumber further confirmed the doping of Al ions into MnO2 basic structure. FESEM images displayed the decrease in particle size with doping as a result of growth rate inhibition. FESEM images also confirmed the hybrid structure formation of carbon nanotubes with MnO2 nanomaterials. UV-visible spectra of modified MnO2 nanomaterials showed red shift as a result of defects in crystal structure. Photocatalytic competency of the doped and hybrid structure samples was found to increase as a result of enhanced surface area and better contact between carbon nanotubes and MnO2 nanomaterials. Photodegradation efficiency of Al doped MnO2 nanomaterials/CNT hybrid structure was found to decrease when various scavengers for different intermediates were applied.

Acknowledgments

Authors are thankful to the Islamia University of Bahawalpur (Pakistan) and Higher Education Commission of Pakistan (6276/Punjab/NRPU/R&D/HEC/2016). Author from King Saud University (KSU) sincerely appreciates the KSU for their contribution through Researchers Supporting Project (RSP-2020/163). Dr Sonia Zulfiqar is highly grateful to American University in Cairo (AUC) for financial support through STRC mini-grant and research project No. SSE-CHEM-S.Z.-FY19-FY20-FY21-RG (1–19)-2018-Oct-01-17-53-22.
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