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A novel Sm doped Cr_2O_3 sesquioxide-decorated MWCNTs heterostructured Fenton-like with sonophotocatalytic activities under visible light irradiation

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Abstract

Novel Sm doped Cr_2O_3 decorated MWCNTs nanocomposite photocatalyst was successfully prepared by a facile hydrothermal method for metoprolol (MET) degradation. A heterogeneous photo -Fenton like system was formed with the addition of H_2O_2 for ultrasonic irradiation (US), visible light irradiation (Vis) and dual irradiation (US/Vis) systems. The intrinsic characteristics of Sm doped Cr_2O_3 decorated MWCNTs nanocomposite was comprehensively performed using state-of-art characterization tools. Optical studies confirmed that Sm doping shifted the absorbance of Cr_2O_3 towards the visible-light region, further enhanced by MWCNTs incorporation. In this study, degradation of metoprolol (MET) was investigated in the presence of Cr_2O_3 nanoparticles, Sm doped Cr_2O_3 and Sm doped Cr_2O_3 decorated MWCNTs nanocomposites using sonocatalysis and photocatalysis and simultaneously. Several different experimental parameters, including irradiation time, H_2O_2 concentration, catalyst amount, initial concentration, and pH value, were optimized. The remarkably enhanced sonophotocatalytic

activity of Sm doped Cr_2O_3 decorated MWCNTs could be attributed to the more formation of reactive radicals and the excellent electronical property of Sm doping and MWCNTs. The rate constant of degradation using sonophotocatalytic system was even higher than the sum of rates of individual systems due to its synergistic performance based on the kinetic data. A plausible mechanism for the degradation of MET over Sm-Cr_2O_3/MWCNTs is also demonstrated by using active species scavenger studies and EPR spectroscopy. Our findings imply that ($^{\bullet}OH$), (h^+) and ($^{\bullet}O_2^-$) were the reactive species responsible for the degradation of MET based on the special three-way Fenton-like mechanism and the dissociation of H_2O_2. The durability and stability of the nanocomposite were also performed, and the obtained results revealed that the catalysts can endure the harsh sonophotocatalytic conditions even after fifth cycles. Mineralization experiments using the optimized parameters were evaluated as well. The kinetics and the reaction mechanism with the possible reasons for the synergistic effect were presented. Identification of degraded intermediates also investigated.

Keywords: Heterogeneous photocatalyst; Synergistic effect; Sm doped; Rare earth; β-blockers.

1. Introduction

Early in 1980s the presence of active pharmaceutical ingredients (APIs) was reported in the aquatic environments (Richardson et al., 1985). Currently, a large number of different APIs with varied concentrations have been detected in the aqueous environment, and even in drinking water resources (Verlicchi et al., 2012; Martínez et al., 2011). Generally, these APIs are discharged from pharmaceutical industries, hospitals, and domestic waters via improperly disposed pharmaceuticals or by human excretions. These APIs are partially metabolized by the body and secreted (Santos et al., 2011) and could be hazardous to human health and aquatic life (Simazaki et al., 2015). Thus, contamination of water with prescribed drugs traces and their metabolites is

of great concern. In addition, these recalcitrant organic pollutants turn in municipal sewage system and ultimately enter wastewater treatment plants (WWTP) (Isidori et al., 2009). The conventional treatment plants are ineffective in removing these hazardous compounds. Eventually, they will arrive in aqueous environment and water resources posing potential health threats to living organisms (Chakraborty et al., 2017). Recently, the occurrence of β-blockers has been repeatedly reported in the effluents of many (WWTP) around the world (Marothu et al., 2019). The database of APIs in the Environment of the German Federal Environment Agency records over 1750 entries about the presence of metoprolol in different water bodies worldwide in the year 2018. Also, the highest metoprolol concentrations in surface water and in (WWTP) were detected, amounting to several micrograms per liter in Asia and in Western Europe respectively (Eike, D 2019). Among the most important class of pharmaceutical compounds and from the top prescribed medications worldwide, β-blocker drugs is frequently detected in the environment, and also known as beta-adrenergic blocking agents. Due to blocking the action of epinephrine and norepinephrine on the β-adrenergic receptors of the sympathetic nervous system of the human body, primarily in the heart (Verlicchi et al., 2012; Isidori et al., 2009; Yang et al., 2010). They are used to treat a variety of cardiovascular diseases, like, coronary artery disease, chronic heart failure, arrhythmias, and hypertension (Abramovi´ et al., 2011). There per capita use in countries such as United Kingdom, Switzerland, and Finland, has increased to 3.2, 1.1 and 0.1 g per year, respectively (Alder et al., 2010). As β-blockers are extensively used in households and hospitals, several measurements have been constantly carried out in hospital wastewater (HWW), surface water and (WWTP) (Gabet-Giraud et al., 2010). Moreover, β-blockers are considered as pseudo-persistent compounds with inconspicuous adverse effects even at low concentration appearing from long-term exposure (Xu et al., 2011). The most commonly

77 prescribed β-blockers medications are, metoprolol (MET), propranolol (PRO) and atenolol
78 (ATE) (Wilde et al., 2014). In recent years, MET is represented by the excessive use, with usage
79 increased by a factor of 4 and as a result, its appearance is expected to increase in aqueous
80 effluents as well (Alder et al., 2010). In Finland, MET is consumed in higher amount per person
81 compared to other European countries. Furthermore, it has been reported that the presence of
82 eight pharmaceutical compounds including β-blockers in twelve Finnish sewage treatment plants
83 (STPs) effluents up to µg/L concentrations of the raw and STPs effluents. Also, in the rivers
84 receiving STPs effluents and MET was the prevailing compound in the effluent samples (Vieno
85 et al., 2007). It should be pointed out that MET has slow in direct hydrolysis and/or photo
86 transformation (Piram et al., 2008). In this context, the most powerful techniques for the
87 treatment of wastewater effluents are advanced oxidation processes (AOPs) and should include
88 in all wastewater treatment plant. AOPs are capable to achieve high destruction with complete
89 decomposition of persistent organic contaminants into CO_2, H_2O, and inorganic salts. Based on
90 the generation of hydroxyl radicals ($^{\bullet}OH$), which are highly reactive species that mitigate the
91 deterioration of environment (Molinari et al., 2006; Song et al., 2008). Photocatalytic treatment
92 is proved to be an effective for the degradation of MET and PRO (Romero et al., 2011). An
93 overview on the degradation of β-blockers in the aquatic environment with different
94 photocatalytic procedures found in the literature has been reported by Marothu et al 2019. More
95 recently, the application of graphite-PVC composite as anode (Mussa 2020) and through bio-
96 electro-Fenton (BEF) (Yang et al., 2021) was investigated for the electrochemical degradation of
97 (MET). Moreover, photocatalytic degradation of (MET) using a TiO_2/natural zeolite composite,
98 UV/chlorine, UV/H_2O_2 and using AOPs— Quantitative Structure Activity Relationship (QSAR)
99 analysis to predict Eco-toxicity has been studied (Jessica 2021; Gao et al., 2020; Melanie et al.,

2021). The metoprolol removal is about ten times faster with the photo Fenton like process than with the photocatalytic or photolytic processes (Avil´es-García et al., 2021). Moreover, the integration between the different AOPs has been found to be promising and highly efficient process. Furthermore, it increases the generation of $^{\bullet}OH$, within a short time span, speeding up the oxidation process and consequently rising mineralization degree of organic pollutants (Madhavan et al., 2010). Moreover, several recent studies have addressed the possibility of simultaneously using sonolysis (US) and photocatalysis called as sonophotocatalysis (US/UV). This represents an attractive strategy for eco-friendly remediation. Also, it can significantly accelerate the degradation performance and achieve a complete mineralization of recalcitrant organic pollutants synergistically. This combination process increase the generation of $^{\bullet}OH$ and eliminate the drawbacks associated with the un-combines process (Eshaq et al., 2020). Transition metal ions (Fe(II), Fe(III), Cu (II)) induced decomposition of H_2O_2 and generates different types of reactive oxygen species (ROS) including highly efficient $^{\bullet}OH$ and $^{\bullet}O_2^-$ through a redox cycle. These transition metals have been extensively used in classical Fenton and Fenton-like reactions for efficient removal of recalcitrant organic pollutants via oxidation reactions (Collins and TAML, 2002; Shah et al., 2003). As Fe, Cu, and Cr presences in multiple oxidation states from -2 to +6, but only Cr(III) and Cr(VI) species are usually detected in water. Cr(III) and Cr(VI) have been reacted with H_2O_2 to generate $^{\bullet}OH$ constantly based on Cr(III)/Cr(VI) redox cycle through Fenton-like reactions (Bokare et al., 2014; Pettine et al., 2002). However, Cr(VI), is a human carcinogen Group ‘A’ with the high potential risks for human health and environmental, causes allergic dermatitis, and pulmonary congestion mutagenic liver damage (Codd et al., 2001). Thus, any addition of Cr (VI) into wastewaters as a reagent is not reasonable, due to its carcinogenicity and higher toxicity. On the other hand, Cr(III) is essential micronutrient for both

plants and animals necessary in sugar metabolism (Levina et al., 2005). Furthermore, Cr(III) at pH>5 is precipitated as insoluble chromium hydroxide, while Cr(VI) is completely soluble in water at the same pH. This contrasting toxicity profile for both Cr species is essentially depending on the solubility behaviour of both Cr species (Bokare et al., 2014). Cr is a transition metal-oxide material with potential applicability in optical and electronic devices. Sesquioxide (Cr_2O_3) or Cr(III) is one of the most important p-type semiconductor (Anjum et al., 2018), having a wide band gap of ($Eg \approx 3.4$ eV) (Rajesh kumar et al., 2019), heterogeneous catalysts (He et al., 2002), gas sensor (Stănoiu et al., 2012), and solar energy collector (Teixeira et al., 2001). Cr(III) is kinetically inert and it has the most thermodynamically stable oxidation state of Cr (Gunnewiek et al., 2014). Doping in metal oxide within certain limit of metal ions, serves to increase stability, absorption of light and increase the charge carrier lifetime. Among metal ions, rare earth (RE) metals have high conductivity and high thermal stability due to their incompletely occupied 4f and empty 5d orbitals (Peng et al., 2017). Doping of RE ions, with the metal oxide semiconductor materials is an effective method to enhance their photocatalytic activities because RE ions can act as an electron trap. That, suppressed the electron-hole pairs (e^-/h^+) recombination which in turn enhanced the destruction of recalcitrant organic pollutant in wastewater (Xiao et al., 2008). Among the most widely used RE metals, samarium (Sm) is an excellent candidate as dopants. Due to its nontoxicity, low price, good stability, ability to control the chelation of Sm intermediate in the transition state and high efficiency in improving photocatalytic activity (De la Cruza et al., 2011). It has been observed that the photocatalytic activity enhanced with the increased of Sm concentration in the Sm doped ZnO due to the existence of Sm(III)/Sm(II) sites. That, can act as an electron-hole trap canters, thus, retarded the recombination rate (Sin et al., 2013). It has been found that the doping of ZnO nanoparticles with

Sm significantly improved its photocatalytic activity by 6.98 times compared to undoped ZnO and increased absorption in the visible area for methylene blue degradation (Sukriti et al., 2020). More recently, multi-walled carbon nanotubes (MWCNTs) have attracted great attention as promising nanoparticles, and they have been seriously taken into consideration in fundamental research and technological development. MWCNTs have been widely used in semiconductor photocatalysts application. They possess unique nanostructures and significant properties, such as novel electrical and mechanical properties, optical properties, high surface area, with favourable thermal stability (Milne et al., 2014). In addition, it has excellent electron-carrying capability leding to the enhanced the photocatalytic performance (Iijima, 1991; Jitianu, 2004). The presence of MWCNTs in $BiVO_4/Bi_2WO_6$/MWCNTs composite, narrowed the band gap, improved the specific surface area, and avoided the agglomeration of nanocomposites. Furthermore, increase the lifetime of charge carriers by suppressed the rate of recombination of (e^-/h^+) pairs resulting in enhanced photocatalytic efficiency in wastewater treatment (Lin et al., 2019). However, to the best of our knowledge, there is no article that has been published yet on the study MWCNTs decorated doping of rare earth ions particularly Sm(III) in Cr_2O_3 and their sonophotocatalytic performance under visible light irradiation. Herein, Sm-Cr_2O_3/MWCNTs was successfully fabricated with uniform morphology via a simple hydrothermal route and characterized by XRD, Raman, FTIR, SAED, SEM, EDS, TEM, HRTEM, DRS, BET and XPS for the first time. The efficacy as a heterogeneous Fenton-like catalyst for (MET) abatement in the presence of ultrasonic, visible light, and dual irradiation with H_2O_2 was tested. Moreover, the effect of different lumped parameters was optimized for instance; irradiation time, catalyst dose, H_2O_2 initial concentration pH, the mineralization and reusability were investigated. Furthermore, experimental with addition of specific scavengers to understand contributions of the different

reactive species and reaction pathway were carried out. In addition, the possible mechanism with pathways of MWCNTs supported Sm doped Cr_2O_3, the synergistic effect with reaction kinetics was evaluated and identification of degraded intermediates was discussed.

2. Experimental

2.1. Materials

The drug (±)-Metoprolol(+)-tartrate salt, ≥99%, ammonia solution (25%), chromium (III) nitrate nonahydrate $Cr(NO_3)_3.9H_2O$, nitric acid (70%), samarium(III) nitrate hexahydrate $Sm(NO_3)_3.6H_2O$, sodium hydroxide, multi-walled carbon nanotubes (MWCNTs) >90% carbon basis, with D x L (110–170 nm x 5–9 μm), hydrogen peroxide (30%, w/v) and ethanol were purchased from Sigma Aldrich. Milli-Q-highly purified water system prepared in the laboratory and was used throughout all experiments.

2.2. Synthesis of catalysts

2.2.1. Synthesis of chromium sesquioxide (Cr_2O_3) nanoparticles

$Cr(NO_3)_3.9H_2O$ (0.1M) was dissolved in 100 mL of deionized water (D.I) for 30 min under constant stirring. After that, ammonia solution was added drop wise under continuous stirring until pH reached to 10.5. The reaction mixture was then transferred to a Teflon- sealed autoclave and hydrothermally aged at 150°C for 17 h (Abdullah et al., 2014). A green flocculent precipitate was recovered through centrifugation, washed repeatedly using D.I water, finally with ethanol and subsequently dried at 70°C for 4 h. Finally, the Cr_2O_3 nanoparticles were formed after calcination in air with the heating rate of 5°C/min at 800°C for 2h.

2.2.2. Synthesis of Sm doped Cr_2O_3 nanoparticles

$Cr(NO_3)_3.9H_2O$ (5.0 mmol) and $Sm(NO_3)_3.6H_2O$ (2.0 mmol) were added in 80 mL of D.I water. Next, NaOH (30 mmol) was slowly added drop wise under strenuous stirring to this solution.

Then, the obtained slurry was kept under sonicated treatment for 30 min, followed by continuous stirring for 3 h under ambient temperature conditions. After stirring, the resultant precipitate was accumulated with centrifugation, repeatedly washed with D.I water and ethanol, to remove the impurities, and subsequently dried at 70°C for 12 h. Calcination was performed at 800°C for 2 h for the dried powder.

2.2.3. Synthesis of MWCNTs/Sm -Cr_2O_3 nanocomposite catalyst

Due to the MWCNTs stability, it should be oxidized before preparing the MWCNTs/ Sm -Cr_2O_3 composites, with strong acids to introduce active function groups on their surface. MWCNTs were oxidized by refluxing with 70 wt% HNO_3 at 180°C under stirring conditions. Followed by several times rinsing with D.I water on a sintered glass filter. Finally, vacuum-dried at 100°C for 5 h to obtain oxidized MWCNTs.

The MWCNTs/Sm-Cr_2O_3 nanocomposite catalyst was prepared by dispersed a certain amount of oxidized MWCNTs and Sm/Cr_2O_3 in 25 mL ethanol and sonicated at 60 °C for 50 min followed by vacuum drying at 70°C for 12 h.

2.3. Characterizations of the catalyst

X ray diffraction (XRD) analysis were carried out to assess the purity and the crystallite structure of the prepared catalysts on a PANalytical diffractometer with Cu Kα radiation (λ = 1.54 Å) in the 2θ range of 20−80° with scanning speed 2ºθ min-1 at 40 kV and 40 mA. Infrared (IR) spectra were recorded on a Bruker Platinum ATR VERTEX 70v FT-IR Spectrometer. Raman analysis was conducted at room temperature using a Horiba, LabRam HR Evolution with a 514.5 nm green laser. TEM images, HRTEM and SAED were analysed using TEM on A JEOL, JEM-2010 (HT) at 200 kV. Morphology of the prepared catalysts were measured by SEM using a Hitachi S-4800, equipped with (EDS) for further structural and elemental mapping of catalysts. The mass

titration method (Franca et al., 2009) was performed for the prepared catalysts to determine the point of zero charge (pH_{PZC}) values. The presence of reactive oxygen species (ROS) were recorded by radicals trapping agent 5,5-dimethyl-pyroline-N-oxide (DMPO) and 2,2,6,6-tetramethylpiperidine (TEMP) on EPR spectroscopy, using EPR, Adani CMS 8400 with 9.5 GHz frequency. The absorption profiles and energy band gap (Eg) of the prepared catalysts were measured by DRS on Agilent Cary 5000 UV-Vis spectrometer equipped with a DRA 2500 integrating sphere, using $BaSO_4$ as a reflectance standard. Compositions, chemical state, and valence band position of the samples were measured by X-ray photoelectron spectroscopy (XPS), using an ESCALAB 250Xi with Al-Kα monochromatized radiation at1486.6 eV.

2.4. Sonophotocatalytic performance

Ultrasonic irradiation, were emitted from a commercial sonicator, attached with a titanium alloy probe with a tip diameter of 13 mm. Operated at fixed frequency (20 kHz) with a variable output power of 125 W (Sonics& Materials, Model: VCX 750). During all the sonocatalytic run, a thermocouple placed inside the reactor was used to monitor the temperature. The ultrasonic tip of the probe was immersed below the surface of the MET solution about 2 cm during the irradiation. All the experiments were performed in a double jacket quartz reactor of 110 mL capacity attached with a circulating cooling water system to keep the temperature at 25 ± 2˚C. For light irradiation a xenon lamp (MAX-350, Asahi Spectra Co., Ltd.) equipped with a VIS mirror module (385–470 nm; Asahi Spectra Co. Ltd.) was placed in position above the quartz double jacket reactor. During the sonocatalysis experiments, the light source was turned off, while, during the photocatalysis experiments, sonicator was turned off. During the photocatalytic runs a magnetic stirrer at 500 rpm was used to ensure adequate mixing of the suspension. In addition, both the US/UV irradiation sources were simultaneously performed during the

sonophotocatalytic experiments. The suspension was circulated for 30 min in dark before irradiation, to establish the adsorption–desorption equilibrium. For each catalytic run, a certain amount of the prepared catalyst was dispersed into 110 mL MET solution. The reaction was initiated after the rapid addition of H_2O_2 to MET solution and the US, Vis or US/Vis immediately turned on. 1 mL of sample was collected from the reaction solution at regular time interval filtered through regenerated cellulose (RC) membrane-syringe filters of 0.2 μm pore size. HPLC, SHIMADZU® with a UV detector at wavelength of 220 nm attached with Phenomenex® C18 column (5 μm, 150 mm × 4.6 mm) was used to measure the concentration of samples. A mixture of 10 mM monobasic potassium phosphate solution and methanol (60:40 by v/v) as the mobile phase was filtered through 0.22 Millipore membrane filter with 1 mL/min flow rate before being used during the analysis. TOC analysis for the mineralization was carried out using (TOC-VCPH Shimadzu) attached with (ASI-V-Shimadzu) auto sampler with TOC-V series analyzer. All the experiments were performed triplicates to ensure system's reproducibility and the error was calculated as standard deviation average ±.

3. Results and discussion

3.1. Characterization of the catalyst samples

3.1.1. X ray diffraction pattern analysis

Phase purity and crystal structure of the synthesized catalysts viz, Cr_2O_3, Sm- Cr_2O_3/ MWCNTs and oxidized MWCNTs were displayed in XRD patterns, Fig.1. The XRD pattern of oxidized MWCNTs revealed the appearance of the diffraction peaks at 2θ=25.83, 43.00, 44.99, 55.0 and 77.44, respectively that correspond to reflections of (002), (100), (101) (004) and (110) planes of MWCNTs of the hexagonal graphite structure (JCPDS Card No.75-1621) (Chamssedine et al.,

2007). The XRD pattern of Cr_2O_3 shows all the diffraction peaks that confirm the rhombohedral crystal structure, (Eskolaite) phase of Cr_2O_3 in accordance with (JCPDS Card No.38-1479). No impurity peaks were detected in in Cr_2O_3 pattern, confirming the synthesis of highly pure Cr_2O_3 with well crystalline structure. The XRD pattern of Sm(III) doped Cr_2O_3 reveals that no diffraction peaks of Sm were detected. Which indicates that Sm(III) ions are equally replacing the Cr(III) sites of Cr_2O_3 crystal lattice or inserts and disperses homogenously into the crystal lattice of Cr_2O_3. Thus, the decrease in the diffraction peaks intensities were observed because of Sm doping Cr_2O_3 lattice. Since Sm(III) ions have a larger radius 0.0959 nm than Cr(III) ions 0.0615 nm. The XRD pattern of Sm-Cr_2O_3/MWCNTs exhibits all characteristic peaks of both MWCNTs and Sm-Cr_2O_3, with slight decrease in peaks intensities and slight shift in peak positions due to contraction of the lattice which suggests the formation of composites nanoparticles. The average crystallite sizes of Cr_2O_3, Sm(III) doped Cr_2O_3 and Sm-Cr_2O_3/MWCNTs were 27, 43 and 83 nm, respectively were calculated based on the Scherrer's equation. Decrease in the crystal size of doped materials than Cr_2O_3 attributed to the formation of Sm-Cr_2O_3 on the surface of the doped materials and the segregation of Sm ions at the grain boundary of Cr_2O_3, which retards the growth of crystal grains with controlling direct contact of crystal grains (Anandan et al., 2007; El-Bahy et al., 2009).

3.1.2. Infrared spectral analysis

To gain an understanding the functional group of the prepared samples, FTIR spectroscopy was performed. The FTIR spectra of the oxidized MWCNTs, Cr_2O_3 and Sm-Cr_2O_3/MWCNTs are displayed in Fig.2. The FTIR spectra show broad bands appear at 1620 and 3425 cm^{-1} corresponding to the OH stretching vibration of the absorbed water molecules. A band at 1740 cm^{-1} is assigned to the carboxylic (C=O) group attached to MWCNTs due to oxidation. The

respective bands appeared at 1428 and 2362 cm^{-1} are ascribed to C–H bending vibration and C–O bonds. The absorption bands at 2855 and 2922 cm^{-1} are attributed to C−H stretching vibration of methylene group generated from defects sites on the surface of MWCNTs by the acid oxidation treatment (Singh et al., 2015). The FTIR spectrum of Cr_2O_3 shows bands that appeared at 620 and 510 cm^{-1} are assigned to the rhombohedral Cr_2O_3 structure (Anandan et al., 2014). The spectrum of the Sm doped Cr_2O_3 and Sm-Cr_2O_3/MWCNTs clearly show that a slight shift in the intensity of the absorption band position, towards the lower wave number after Sm doping, assigned to the change in the bond length (Taylor, 1988; Faraz et al., 20018) and the formation of Sm-Cr_2O_3. However, the characteristic absorption bands of the MWCNTs are obviously disappearance which suggests that the surface of MWCNTs has been covered by Sm-Cr_2O_3.

3.1.3. Raman analysis

To probe the phase composition in the treated MWCNTs, Cr_2O_3 and Sm-Cr_2O_3/MWCNTs; further investigations using Raman analysis were performed, as presented in Fig.3. The Raman spectrum of MWCNTs exhibits two strong peaks in the regions 1336 cm^{-1} called (D-band) and 1576 cm^{-1} called (G-band), are attributed to the disordered in the carbon nanotubes wall and the in-plane vibration of the C–C bonded carbon atoms in graphene-like structures, respectively (Pourfayaz et al., 2014). This result indicates that the graphitic structure of CNTs was not destroyed during oxidation. Raman spectrum of Cr_2O_3 exhibits five Raman modes at about 307, 350, 386, 549 and 602 cm^{-1}, respectively corresponding to Raman modes of Cr_2O_3 (Yu et al., 2003). A sharp and strong vibrational peak intensity of Raman band at 549 cm^{-1} is assigned to the A1g mode, belonging to the Cr–O stretching vibration of Cr^{3+} ions in octahedral coordination. Thus, confirming the rhombohedral Cr_2O_3 structure with a high degree of crystallinity (Mougina et al., 2001). However, the broad peaks at 307 cm^{-1} and 349 cm^{-1} are

assigned to the E_g vibration mode. These results are in accord with the previous reports (Larbi et al., 2017). The Raman spectrum of Sm-Cr_2O_3/MWCNTs displays all the characteristic bands of Cr_2O_3 and MWCNTs. Moreover, the peaks are broadened with a slightly shift of Raman band to lower wave numbers, and the intensity of the Sm-Cr_2O_3 peaks is slightly increased, due to the formation of the composites. While the MWCNTs peaks is disappeared after covering with the Sm-Cr_2O_3, according to the formation of Sm-Cr_2O_3/MWCNTs composite. This is consistence with FTIR results.

3.1.4. SEM - EDS Analysis

To analyze surface morphologies of the oxidized Cr_2O_3, MWCNTs, and Sm-Cr_2O_3/MWCNTs were studied by SEM analysis as shown in Fig.4(a-d). The SEM image of Cr_2O_3 displays a uniform near rhombohedral shapes with smooth surfaces Fig.4(a). While the SEM image of the oxidized MWCNTs exhibits smooth, straight, and uniform tube walls 4(b). It is worth mentioning that acid treatment did not deteriorate the structural integrity of MWCNTs. The SEM image of Sm-Cr_2O_3/MWCNTs shows that the Sm-Cr_2O_3 nanoparticles are well dispersed along the sidewall of the MWCNTs Fig.4(c,d). The chemical compositions and the distribution of the elements in the Sm-Cr_2O_3/MWCNTs were scanned by EDS analysis and EDS elemental mapping of the selected area in Fig. 4(e-j). The presence of Cr, O, Sm and C confirmed the existence of Sm-Cr_2O_3 on the MWCNTs.

3.1.5. TEM, HRTEM and SAED analysis

To obtain more persuasive proof in shape, size and crystal structure of the prepared catalysts TEM, HRTEM and SAED were performed. The TEM micrographs of the treated MWCNTs, Cr_2O_3 and Sm-Cr_2O_3/MWCNTs were manifested at Fig.5(a-c). TEM image of oxidized MWCNTs shows tubular structural morphology with average diameter of 70-85 nm and the

329 nanotubes length of 100 nm to several micrometers Fig.5(a). Whereas, Cr_2O_3 shows a uniform
330 near rhombohedral shapes with average particle size of 25-35 nm, which agree with crystallite
331 sizes data calculated by Scherrer's equation Fig.5(b). TEM image of Sm-Cr_2O_3/MWCNTs
332 clearly shows that the homogenous Sm-Cr_2O_3 nanoparticles are dispersed uniformly and
333 homogenously over the surface of MWCNTs Fig.5(c). In addition, a strong attachment of Sm
334 doped Cr_2O_3 nanoparticles on MWCNTs surface enhances the photocatalytic activity due to
335 increases the number of active sites. The HRTEM image shows typical MWCNTs decorated
336 with Sm-Cr_2O_3 nanocrystal is illustrated in Fig.5(d). The lattice fringe spacing of Cr_2O_3 is 0.26
337 and 0.36 nm, which match to (104) and (012) the interplanar spacing for crystal plane of Cr_2O_3-
338 eskolaite.Whilst, the lattice fringes of 0.344 nm correspond to the (002) crystalline plane of the
339 MWCNTs wall. The corresponding SAED pattern of Sm-Cr_2O_3/MWCNTs shows the existence
340 of single crystalline phase of Cr_2O_3 as presented in Fig.5(e). The presence of spotty ring pattern
341 endorses the crystalline nature of Sm-Cr_2O_3/MWCNTs nanocomposites. Thus, TEM HRTEM
342 and SAED analysis explicitly validates the formation of Sm-Cr_2O_3/MWCNTs nanocomposite.

343 *3.1.6. XPS analysis*

344 To obtain further investigate of the oxidation states sensitivity and surface composition of the
345 prepared Sm-Cr_2O_3/MWCNTs, XPS analysis before and after the dual irradiation system was
346 performed in Fig.6 (a,b). The presence of the peaks of Cr, O, Sm, and C has been shown in the
347 XPS survey spectrum of Sm-Cr_2O_3/MWCNTs before dual irradiation performance was presented
348 in Fig.6(a). The Cr peaks located at 586.4 and 577.4 eV are assigned to the Cr $2p_{1/2}$ and Cr $2p_{3/2}$
349 respectively, which is consistent with that of Cr^{3+} (Rahman et al., 1995). The observed peak
350 located at 530.43 eV is attributed to O 1s. The peaks are appeared at 1083.7 and 1109.7 eV, is
351 attributed to Sm $3d_{5/2}$ and Sm $3d_{3/2}$ signals of Sm^{3+} state, which is in accordance with the binding

352 energy in Sm_2O_3 (Lixi et al., 2015). The C 1s binding energy of the MWCNTs at 284.7 eV (Yan
353 et al., 2006), is assigned to the peak of graphitic carbon from MWCNTs. The results endorse that
354 the Sm-Cr_2O_3/MWCNTs is stable and can catalyze oxidation- reduction cycles in the presence of
355 H_2O_2 to produce $^{\bullet}OH$ under visible light irradiation. XPS spectra of the Sm-Cr_2O_3/MWCNTs
356 nanocomposite after dual irradiation performance are displayed in Fig.6(b).The XPS spectra
357 before and after dual irradiation performances display that, there are some of evident changes in
358 the intensity and in the shape of the peaks with a slight shift in the peak position. This finding
359 suggests to the presence of Cr^{3+}/Cr^{6+}, Sm^{3+}/Sm^{2+} cycles in Sm-Cr_2O_3/MWCNTs composite,
360 without obvious change in the composition and valance states in the XPS results. These changes
361 reveal that through heterogeneous Fenton like mechanism, ($^{\bullet}OH$) are generated. Based on the
362 above XPS results are consistent with EDS results.

363 *3.1.7. DRS analysis*

364 The light absorption properties of the Cr_2O_3, Sm-Cr_2O_3 and Sm-Cr_2O_3/MWCNTs, UV-visible
365 diffuse reflectance spectroscopy (DRS) was performed in the range of 250–800 nm to investigate
366 the optical properties, shown in Fig.7(a). Cr_2O_3 shows strong absorption of UV with an
367 absorbance edge of 360 nm, but weak absorption of visible light. While the absorption spectrum
368 of Sm doped Cr_2O_3 exhibit strong absorption in the visible-light range with a shift of the
369 absorption edge around 650 nm. This shift can be attributed to the charge transfer transition
370 between Sm ion 4f level electrons and Cr_2O_3 conduction band or valence band. Compared with
371 Sm-Cr_2O_3 the light absorption ability of the Sm-Cr_2O_3/MWCNTs nanocomposite is significantly
372 enhanced with a slight shift in the visible range due to incorporation of MWCNTs (Lin et al.,
373 2016). The band gap energy (Eg) can be calculated from the intercept of the straight-line portion
374 of the plot of the modified Kubelka−Munk function [F(R∞)hν]1/2 versus (hν) the energy of the

absorbed light (Zhou et al., 2016). A plot of the modified Kubelka−Munk function versus the energy of photon energy as displayed in Fig.7(b) affords the estimated value of band gap energies (Eg) for Cr_2O_3, Sm-Cr_2O_3 and Sm-Cr_2O_3/MWCNTs were evaluated to be 3.30, 2.40, and 2.10 eV, respectively. It is worth mentioning that, the narrower the band gap, higher photocatalyst activity. These results indicate that the Sm-Cr_2O_3/MWCNTs nanocomposite can absorb the visible light in the UV as well as the visible regions and narrow the band gap. These results suggested that the Sm-Cr_2O_3/MWCNTs nanocomposite can be applied for the removal of recalcitrant pollutant as a visible light photocatalyst. Thus, we univocally conclude the successful formation of the Sm-Cr_2O_3/MWCNTs nanocomposite, because of the XRD, FTIR, Raman, SEM, EDS, elemental mapping TEM, HRTEM, SAED, XPS and DRS studies.

3.2. Screening of US or Vis-light irradiation capabilities in MET degradation

3.2.1. MET degradation using sonolysis or photolysis catalytic system

The effect of either US or Vis-light irradiation alone was screened in absence of any catalyst or any promoter to estimate the effectiveness of the capability of the US or Vis-light irradiation for the extent of MET degradation. As shown in Fig. S1. the obtained data reveal that the extent of degradation after 60 min. was only 17 and 10%, for US and Vis respectively. The low efficiency of US or Vis-light irradiation is attributed to the generation of different reactive radicals generated during the sonolysis (within both extreme pressure and temperature) or photolysis (attributed to the photolysis of water). Induces the generation of a considerable amounts of free radicals such as $^{\bullet}OH$ and $H^{\bullet}$, which can generate other reactive oxygen species (ROS) (Petrier et al., 1994). The hydroxylation reaction undergoes through the reaction of organic compounds by the generated radicals and moreover through oxidation reaction in presence of air or oxygen (Henglein, 1995; Tauber et al., 1999). However, the rate constant (K) value for the reaction of

oxygen and hydrated electrons (e_{aq}-) and that between e_{aq}- and MET and the tartrate ion is 1.9×10^{10} M^{-1} s^{-1}, 6.8×10^{7} M^{-1} s^{-1} and 1.7×10^{7} M^{-1} s^{-1}, respectively. While the rate constants for two hydroxyl radicals combination and for the reaction of •OH react with MET and the tartrate ion is 5.2–6.2 × 10^{9} M^{-1} s^{-1}, 5.2×10^{9} M^{-1} s^{-1} and 5.5×10^{8} M^{-1} s^{-1}, respectively (Slegers et al., 2003). Although, (K) value for combination of two •OH's is lower than that for the reaction between MET and the tartrate ion with •OH, there exists a considerable loss of the generated •OH and e_{aq}- which takes place before participation in MET degradation process. That interprets limited the efficiency of sonolysis alone under the used conditions. Also, the obtained data reveal that the extent of degradation after 60 min with photolysis alone was insignificant and the produced amounts of •OH's were not enough for complete degradation of MET. The effect of different H_2O_2 concentration using sonolysis and photolysis irradiation in the range of 10–80mM was investigated, in Fig. S2. The degradation extent at 40mM H_2O_2 reached 33% and 50% under US and Vis-light irradiation respectively, while the degradation extent at 60mM H_2O_2 reached 11% and 23% under US and Vis-light irradiation respectively. Thus, the degradation extent decreased with more increase in H_2O_2 amount further on this concentration. The enhancement for the degradation efficiency upon the addition of H_2O_2 is due to enrichment in the production of hydrogen peroxide radicals (Beltran, 2003; Voigt et al., 2021) .Furthermore, the bond energy between O–O (139 kJ mol−1) in H_2O_2 cleavage much easier than that of the bond energy between O-H (463 kJ mol−1) of water (Mehrdad and Hashemzadeh, 2010). While, the free radicals generated were scavenging instead of producing additional radicals upon the addition of the extra amount of hydrogen peroxide. Recognized as the scavenging phenomenon of •OH, ultimately the degradation efficiency decreases (Panda and Manickam, 2017; Abbasi and Asl, 2008).

3.2.2. Effect of ultrasonic or photo-heterogeneous Fenton

The degradation efficiency of MET, in silent mode without US or Vis-light irradiation were performed, to probe the capability of Sm-Cr_2O_3/MWCNTs. It can be seen that the degradation efficiency reached 15% using 80mM of H_2O_2, 0.1 g L^{-1} of the catalyst, MET (10 mgL^{-1}) at pH 7 and after 60 min of stirring. Thus, the degradation efficiency decreases as the result of the turbulence of the solution.

3.2.2.1. Effect of sonocatalytic or photocatalytic irradiation time.

The sonocatalytic and/or photocatalytic degradation of MET (10 mgL^{-1}) at 80mM of H_2O_2 in presence of 0.3 g L^{-1} of Sm-Cr_2O_3/MWCNTs nanocomposite and pH = 7 at room temperature, the effect of irradiation time was investigated after 60 min time for irradiation. The results showed that the degradation efficiency has been increased remarkably to 77 and 84% for US and Vis-light, respectively as displayed in Fig. S3.The higher degradation performance resulted on adding H_2O_2 to US can be attributed to excessive generation of $^{\bullet}OH$ due to the metal -induced H_2O_2 decomposition at the solid liquid interface wherein highly reactive oxygen species are generated through a redox cycle. Based on the heterogeneous Fenton-like reaction using chromium oxide, the reaction between Cr(III) and H_2O_2 generates chromium species Cr(IV) as a synchronous intermediate (Tsou and Yang, 1996). Instantly, Cr(IV) species are able to generates Cr(V) species as reactive chromium intermediates (Shi and Dalal, 1990). Which are able to generate a considerable numbers of $^{\bullet}OH$ due to a series of reactions with H_2O_2 (Shi et al., 1993) follows a sequential Fenton-like pathway as is illustrated in the following equations (Bokare and Choi, 2011):

$$Cr(III) + H_2O_2 \rightarrow Cr(IV) + {}^{\bullet}OH + OH^{-} \quad (1)$$

443 $Cr(IV) + H_2O_2 \rightarrow Cr(V) + {}^{\bullet}OH + OH^-$ (2)

444 $2Cr(IV) \rightarrow Cr(V) + Cr(III)$ (3)

445 $Cr(V) + H_2O_2 \rightarrow Cr(VI) + {}^{\bullet}OH + OH^-$ (4)

446 According to the above equations, the transformation of Cr(III) into Cr(VI) via redox cycle in the
447 Cr(III)/Cr(VI)-H_2O_2 system generates ${}^{\bullet}OH$, Cr(IV) and Cr(V) species, as active intermediate
448 through Fenton-like reactions.

449 On the other hand, the addition of MWCNTs in Sm-Cr_2O_3/MWCNTs increased the adsorption
450 ability of the catalysts due to the dispersion of the catalyst on the nanotubes. In addition,
451 MWCNTs increased particle fragmentation, cavitation bubbles and consequently increased
452 induction of hot spots, through the heterogeneous nucleation of bubbles, which can cause
453 pyrolysis of water molecules to produce hydroxyl radicals under US irradiation (Zhang et al.,
454 2011). The higher catalytic activity of Sm-Cr_2O_3/MWCNTs under Vis-light irradiation can be
455 attributed to accelerate the charge transfer due to doping of Sm on Cr_2O_3 which resulted in the
456 increase in ${}^{\bullet}OH$ formation. When the catalyst is irradiated with Vis-light, the electron e^- is
457 excited from the valance (VB) band to the conduction band (CB), leaving holes (h^+) in the VB of
458 Cr_2O_3. The (e^-) in the CB reacts with the Sm^{3+} in order to that it is a strong lewis acid that has
459 partially filled 4f orbital which can trap the e^- and suppress the recombination of charge carrier,
460 thus enhancement of their lifetime. Consequently, the unstable form of Sm^{+2} ions is formed, that
461 has the tendency to transfer the e^- to O_2, to form ${}^{\bullet}O_2^-$ which form ${}^{\bullet}OOH$ after protonation was
462 formed. Then it was converted to the ${}^{\bullet}OH$. Simultaneously, h^+ VB reacts with the water
463 molecules adsorbed on the catalyst surface and form hydroxyl radical. In addition, O_2 and H_2O
464 molecules act as scavengers to trap e^- and h^+ to generate ${}^{\bullet}OH$ species (Sin et al., 2013). Thus, the

generation of $^{\bullet}O_2^-$ and $^{\bullet}OH$ leads to the degradation of MET. The degradation mechanism for Sm-doped Cr_2O_3/MWCNTs is shown in the following equations:

$$Sm\text{-}Cr_2O_3/MWCNTs + Vis\text{-}light \rightarrow Cr_2O_3 \quad (e^-_{cb} + h^+_{vb}) \quad (5)$$

$$Sm^{3+} + e^-_{cb} \rightarrow Sm^{2+} \quad \text{(electron trapping)} \quad (6)$$

$$Sm^{2+} + O_2 \rightarrow Sm^{3+}\ {}^{\bullet}O_2^- \quad \text{(electron transfer)} \quad (7)$$

$$^{\bullet}O_2^- + H^+ \rightarrow {}^{\bullet}OOH \quad (8)$$

$$^{\bullet}OOH + H^+ + e^-_{cb} \rightarrow H_2O_2 \quad (9)$$

$$H_2O_2 + e^-_{cb} \rightarrow {}^{\bullet}OH + OH^- \quad (10)$$

$$h^+_{vb} + H_2O \rightarrow H^+ + {}^{\bullet}OH \quad (11)$$

$$h^+_{vb} + OH^- \rightarrow {}^{\bullet}OH \quad (12)$$

On the other hand, the addition of MWCNTs also, acts as an electron trap and is able to suppress the e-/h+ recombination (Zhao et al., 2017), with Sm because it can act as conductive to transferring and separation of exciting electrons as electron mediators. The e^- on the surface of Sm-Cr_2O_3 can be trapped and transferred quickly by the MWCNTs. The e^- on MWCNTs can react with O_2 to produce $^{\bullet}O_2^-$ and $^{\bullet}OH$ as displayed on the following equations.

$$Sm\text{-}Cr_2O_3/MWCNTs + Vis\text{-}light \rightarrow Cr_2O_3 \quad (e^-_{cb} + h^+_{vb}) \quad (13)$$

$$Sm^{3+} + e^-_{cb} \rightarrow Sm^{2+} \quad \text{(electron trapping)} \quad (14)$$

$$Sm^{2+} + MWCNTs \rightarrow Sm\text{-}MWCNTs\ (e^-) \quad \text{(electron transfer)} \quad (15)$$

$$Sm\text{-}MWCNTs\ (e^-) + O_2 \rightarrow Sm^{3+}/MWCNTs + {}^{\bullet}O_2^- \quad (16)$$

$$^{\bullet}O_2^- + H_2O \rightarrow {}^{\bullet}OH + OH^- + O_2 \quad (17)$$

$$h^+ + OH^- \rightarrow {}^{\bullet}OH \quad (18)$$

Thus, Sm and MWCNTs dopants in Cr_2O_3 improved the photocatalytic degradation of MET due to the separation of the charge carriers by trapping, resulted in increase in the generation of $^{\bullet}OH$, $^{\bullet}O_2^-$ and h^+ from the two postulated mechanism.

3.2.2.2. Effect of H_2O_2 addition

The addition of H_2O_2 in the range of 10–80mM improves the degradation efficiency of MET up to a definite amount of H_2O_2, for US 40mM, and for Vis-light 50mM as display in Fig. S4. The decomposition of H_2O_2 under US or Vis-light irradiation to produce hydroxyl radicals causes a remarkable enhancement in degradation efficiency. Hydrogen peroxide dissociates to generate hydroxyl radicals under US or Vis-light irradiation. However, it also, has the scavenger effects of $^{\bullet}OH$ by H_2O_2 with extravagant amounts of H_2O_2.Which is capable to decrease the MET degradation slightly. Thus, H_2O_2 plays a vital role in the enhancement or decline degradation extent and is considered as highly relevant in the catalytic degradation domain (Pham et al., 2018). Moreover, the addition of H_2O_2 also acts as an e^- trap and can increase separation ability of (e^-/h^+) pairs (Malato et al., 2000). The result showed that the Vis-light irradiation improves the generation of $^{\bullet}OH$ more than US that endure the scavenging effect of H_2O_2 added up to 50mM.

3.2.2.3. Effect of catalyst loading

The amount of catalyst is considered as one of the main parameters for the degradation studies from economical point of view. Therefore, it is necessary to avoid the use of excess catalyst and

find out the optimum loading for efficient degradation performance of MET. Various amounts of the catalyst in the range of (0.1-1) g $L^{-1}$of Sm-Cr_2O_3/MWCNTs were tested for US and Vis-light irradiation on the degradation of MET as display in Fig.S5 .The results indicates that the 0.3 g L^{-1} is the optimum catalyst amount for the degradation of MET. Further increase in the catalyst amount, the degradation efficiency begins to decrease slowly. The aggregation of Sm-Cr_2O_3/MWCNTs particles causing decrease in the surface active sites number and increase in the opacity and light scattering of the particles at high concentration. Which in turn, decrease in the irradiation path through the sample at high concentrations (Kaur and Singh, 2007).

3.3. Optimization condition of sonophotocatalysis-Fenton system for the degradation of MET using Sm-Cr_2O_3/MWCNTs nanocomposite.

To identify the optimum parameters for the mineralization of MET; all the different conditions of the sonocatalytic and photocatalytic processes were optimized and performed in the dual irradiation system for the degradation of MET as illustrated in Fig.8. The results manifest that the sonophotocatalytic system was capable to achieve total degradation of MET (10 mg/L) after 50 min of dual irradiation US/UV using 0.3 g L^{-1} of the Sm-Cr_2O_3/MWCNTs in the exitance of 50 mM H_2O_2 and pH = 7. The sonophotocatalytic degradation efficiency was higher compared to the individual sono or photocatalytic degradation or even their sum, which a synergistic effect proved. The sonophotocatalytic degradation efficiency was higher than that of the sonocatalytic or photocatalytic system by 26% and 20%, respectively with the extent of degradation ordered sonophotocatalysis > photocatalysis > sonocatalysis. This remarkable degradation performance can be ascribed to the simultaneous use of US and Vis-light irradiation. Moreover, the presence of two sources of irradiations enhances the generation of hydroxyl radicals, which eventually enhances sonophotocatalytic performance. However, the two major

factor induced synergy that contributes to the US were the deactivation of the catalyst and de-agglomeration. This causes removing adsorbed moieties from the surface via microstreaming and microbubbles eruptions (Anju et al., 2012). The synergy index was calculated from the rate constant of each systems under the identical conditions using the following Eq. (19) (Verma et al., 2013).

$$\textbf{Synergy}\ (S\%) = \frac{(\mathbf{k}_{\textbf{sonophotocatalysis}} - (\mathbf{k}_{\textbf{sonocatalysis}} + \mathbf{k}_{\textbf{photocatalysis}}))}{\mathbf{k}_{\textbf{sonophotocatalysis}}}\ \mathbf{X\ 100} \quad (19)$$

The synergetic effect of sonophotocatalytic degradation was faster than the sole systems as depicted in Table 1 and in Fig.S6. Moreover, the results indicate that the dual irradiation system has a value greater than 1, indicating a positive synergistic effect on MET degradation performance.

3.3.1. Effect of initial pH

To investigate the effect of pH on the sonophotocatalytic system, a wide pH range of 3–11 was used to determine the applicability of the Sm-Cr_2O_3/MWCNTs for MET degradation in Fig.S7. The result indicates that MET degrade completely after 50 min in the presence of the Sm-Cr_2O_3/MWCNTs with US/Vis system through the extended pH range, even under acidic at pH= 3 and basic (pH =11) conditions, attributed to the surface charge of the material (Romero et al., 2013). The pH_{ZPC} values determined for MWCNTs, Cr_2O_3, and Sm-Cr_2O_3/MWCNTs were 4, 7.6 and 6.8, respectively. The catalyst surface was positively charged, when the values of pH lower than pH_{PZC}, become negatively charge at pH higher than pH_{PZC}. Thus, under acidic conditions the catalyst surface was positively charged and the recombination rate of e^-/h^+ pairs was decreased providing a higher degradation rate of MET. Meanwhile, the surface was

552 negatively charged under basic conditions with the repulsive electrostatic effect between catalyst
553 surface and deprotonated MET (Ye et al., 2018). The pKa values of MET have been reported to
554 be 9.7 (Benitez et al., 2011; Jessica et al., 2021). This suggests that it can lose a proton from the
555 –OH group on the side chain and transformed into negatively charged anion form. The presence
556 of negative charges on the catalyst surface inhibits the sorption of $^{-}$OH ions and water molecules,
557 and consequently decreases the amount of $^{\bullet}$OH radicals formed and increasing the recombination
558 rate of the electrons generated in the CB with VB of the catalyst (Huerta Aguilar et al., 2015).
559 The same effect of alkaline pH in MET degradation has been reported and discussed by (Ye et
560 al., 2018; Habibi et al., 2005), where, the major MTP degradation occurred in the (bulk liquid
561 phase) and secondary occurred on catalyst surface (liquid interface). Which, involving either
562 direct oxidation by $^{\bullet}$OH adsorbed on the catalyst surface or photo generated h^{+}. The high pH
563 induced repulsive effect of the catalyst surface towards deprotonated MTP molecules resulted in
564 inhibition of the secondary MTP degradation route. However, using the Sm-Cr_2O_3/MWCNTs
565 showed a remarkable achievement through the extended alkaline pH range and can be cover all
566 the alkaline pH range attributed to the relation between pH and Cr(VI)/Cr(III) and O_2/H_2O_2
567 couples. This demonstrate that H_2O_2 can oxidize Cr(III) at pH > 8 and reduce Cr(VI) at lower
568 pH. Since the reducing strength of H_2O_2 strongly increases with decreasing pH, the H_2O_2-
569 induced reduction of Cr(VI) to Cr(III) at pH < 3 is used for removing chromate from wastewaters
570 (Bokare and Choi, 2011).

571 *3.4. Trapping experiments of reactive species*

572 To investigate the sonophotocatalytic pathway with full understanding of the MET degradation
573 process over Sm-Cr_2O_3/MWCNTs, it is imperative to identify the leading active species using
574 the trapping experiments as display in Fig.9. In this study, a series of different concentration of

scavengers were selected to identify the major active species involved in the dual irradiation system for MET degradation. We insert potassium dichromate to trap e^-, ethylene diaminetetraacetic acid (EDTA) to trap (h^+), benzoquinone (BQ) to trap ($^{\bullet}O_2^-$) and isopropanol (IPA) to trap ($^{\bullet}OH$). From the results manifested in Fig.9, it is apparent that the introduction of (IPA), (EDTA) and (BQ), unveil a considerable decline in the sonophotocatalytic performance of Sm-Cr_2O_3/MWCNTs for the degradation of MET. Nonetheless, the degradation extent of MET slightly enhances with the addition of (e-) trappers because trapping of the generated electrons owing to increase the number of surviving h+. Thus, it can be deduced that the active species and function major roles follow the order $^{\bullet}OH > h^+ > {}^{\bullet}O_2^-$ in the MET degradation with dual irradiation system.

3.5. EPR spectroscopy

To determine the radicals produced while using Sm-Cr_2O_3/MWCNTs, photocatalyst under the (US/Vis) irradiation system, EPR spectroscopic analysis was executed as shown in Fig.10(a,b). DMPO and TEMP were used as spin trap for radical species. The EPR spectrum taken with DMPO in the absence of Sm-Cr_2O_3/MWCNTs did not show any peaks in EPR spectra. Whereas, four typical peaks were detected when Sm-Cr_2O_3/MWCNTs was added and their intensity increases with irradiation time. Which indicates the formation of DMPO-OH adduct suggest the generation of more $^{\bullet}OH$ as shown in Fig.10(a). Thus, more free radicals would be generated as a result of a good separation effect on photo-generated e^-/h^+ pairs (Wang et al., 2019) performed by Sm-Cr_2O_3/MWCNTs. While, by adding the TEMP trapping agent, a triplet pattern of equal intensity was indexed in Fig.10(b), indicates the presence of TEMP-$^1O_2$ adduct in EPR spectra and confirms the formation of the singlet oxygen. Moreover, these characteristic peaks decreased with time irradiation. It suggested that $^1O_2$ radical generation was gradually exhausted through

direct participation in the degradation reaction under dual US/Vis irradiation systems with fast reaction rate. EPR analysis clearly confirmed the production of $^{\bullet}OH$ and $^{1}O_2$ radicals in MET degradation by using Sm-Cr_2O_3/MWCNTs under US/UV system.

3.6. Reusability

The stability and recyclability of Sm-Cr_2O_3/MWCNTs is of supreme importance to explore as it could reduce the cost of the catalytic process appreciably, thus, produce a promising catalyst for the destruction of virulent organic pollutant. The sonophotocatalytic stability and reusability of Sm-Cr_2O_3/MWCNTs throughout six successive runs under the same operating conditions is presented in Fig.11. The sonophotocatalytic performance slightly decreased after six cycles. The enhanced stability of Sm-Cr_2O_3/ MWCNTs toward MET degradation is attributed to the synergic effect between Sm-Cr_2O_3 and MWCNTs. Furthermore, the sonophotocatalytic stability of the Sm-Cr_2O_3/MWCNTs is also indicated by its XRD and SEM analyses data. There was no obvious change in XRD patterns and morphology after the six successive runs of sonophotocatalytic degradation of MET as illustrated in Fig. S8(a,b). Thus, the recycling results reflect the superior stability and recyclability of the Sm-Cr_2O_3/MWCNTs nanocomposite with their applicable potential for environmental applications.

3.7. TOC and mineralization

TOC measurements after complete MET removal, about 10% of organic compounds remained in the system with the Sm-Cr_2O_3/MWCNTs as TOC measurements displayed. However, the percentage of remaining organic compounds decreased to 4% after 120 min of dual US/Vis irradiation systems, as shown in Fig.S9. The formed intermediates need longer time to be completely mineralized, due to their slower rate of reaction with attacking $^{\bullet}OH$ (Wang et al.,

1998). It is worth mentioning that, higher generation rate of $^{\bullet}OH$ and $^{\bullet}O_2^-$ and enhanced performance of e^-/h^+ pairs is the remarkable effect in the sonophotocatalytic performance of the Sm-Cr_2O_3/MWCNTs.

3.8. Determination of intermediates and mechanism of photodegradation, determination of intermediate degradation products by GC-MS

To characterize all the degradation products formed under various stress conditions, Gas chromatography – mass spectrometry GC–MS analysis was performed. Analyzing reaction mixtures by GC-MS analysis, several intermediate aromatic compounds were identified. GC–MS analysis of MET revealed the presence of three unique fragments (267, 107and 71) (m/z) Fig S10 (a). While, the analysis of mixtures obtained after dual irradiation system US/Vis irradiation (50 min) allowed the identification of several new intermediate organic compounds as displayed in Fig. S10 (b). Each peak was analyzed in each chromatogram to determine the molecular ion (M), the characteristic fragmentation pattern and the retention time (min). The product was identified by comparing the molecular ion and mass fragmentation pattern with those reported in the GC-MS library. The MET has a molecular weight [M+] = 267.1.The identified intermediates allowed for the proposal of a possible mechanism for MET degradation. Thus, the reaction pathway for the degradation of (MET) includes the transformation of metoprolol to hydroquinone via the cleavage of the C-O in the aryl ether to form 4-(2-methoxy ethyl) phenol. Then it is transformed to form 2-(4-hydroxylphenyl) ethanol with consecutive hydroxylation. After that, it is oxidized to form the 4-hydroxybenzaldehyde followed by transformed to hydroquinone (Pinedo et al., 2016). Metoprolol is also degraded directly to hydroquinone. Then, this aromatic compound is oxidized with further oxidation to 1,2,4-benzenetriol, which is rapidly oxidized to low molecular weight organic acids before being completely mineralized to CO_2 and H_2O (Moctezum et al., 2013). The

photocatalytic degradation using a xenon lamp as irradiation source of ß-blockers and MET as model compound in an aqueous suspension of TiO_2 (Leyva et al., 2019) had the similar mechanism (Romero et al., 2013). In this study two intermediates were detected at m/z 300, 332, and 108 respectively, corresponding to 4-(2-methoxyethyl) phenyl and 4-[2-hydroxy-3-(propan2-ylamino) propoxy] benzaldehyde (Abramović et al., 2011). Which regarding to the binding of hydroxyl radicals in the aromatic ring and one for the hydrogen abstraction with elimination of water to generate a carbonyl, followed by the loss of ammonia. Then after breaking of c-c bond in the aliphatic part, amino-diol and the ethanolamine side are formed due to the loss of isopropyl moiety and the hydroxyl group. Thus, the proposed mechanism of MET degradation demonstrated that the same mechanism as previously studied (Song et al., 2008).

Conclusion

A successful synthesis via a facial hydrothermal route for Sm doped Cr_2O_3 decorated MWCNTs. Optimum parameters for the degradation of MET with dual irradiation system were identified in terms of H_2O_2 concentration, irradiation time, catalyst dosing and pH. Furthermore, the photocatalytic performance enhancing by Sm doping which shifting the photogenerated carriers to surface of photocatalyst and suppressing photoinduced charge recombination. The absorption edge of the Sm-Cr_2O_3/MWCNTs shifted to longer wavelength as compared to Cr_2O_3 which generating e^- and h^+ under Vis-light irradiation as display in the diffuse reflectance spectra. A dual irradiation US/UV system for the degradation pathway of MET on the Sm-Cr_2O_3/MWCNTs were discussed based on the identified intermediates after 50 min. Hydroxylation of the aromatic ring, by addition of $^{\bullet}OH$ or cleavage of the amine lateral chain followed by shortening of methoxy group in the lateral chain, is the main pathway for the degradation process by dual irradiation system.

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