Environmentally benign fabrication of SnO$_2$-CNT nanohybrids and their multifunctional efficiency as an adsorbent, catalyst and antimicrobial agent for water decontamination

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Herein, we described a biogenic, additive free, eco-friendly synthesized SnO$_2$-CNT nanohybrid as an efficient, re-collectable and reusable material for onsite water remediation. We demonstrated that the SnO$_2$-CNTs can provide a one stop solution for water remediation as it effectively accomplished the major treatment tasks like adsorption, catalytic transformation/degradation and disinfection. The structural, morphological, surface chemical compositions of the nanocomposite and the adsorption, catalytic and antimicrobial properties were investigated using common characterization and instrumental techniques. The results revealed the brilliant efficiency of SnO$_2$-CNT nanoadsorbent towards As (III) and a maximum Langmuir adsorption capacity of 106.95 mg/g was observed at high arsenite concentration ($c_0 = 1$ mg/L). The nanoadsorbent was also found to be equally efficient in low arsenite concentration ranges ($c_0 = 100 \mu$g/L) as it could bring down the arsenic concentration below maximum permissible limit. Moreover, using model pollutants like p-nitrophenol, Alizarin red S, Metronidazole, bacterial strains (Bacillus subtilis, Escherichia coli, Streptococcus pneumoniae etc.), and fungal strains (Aspergillus niger and Candida albicans), the multifunctional capability of SnO$_2$-CNT towards water decontamination has been established. Our results suggested the promising potential of hierarchical nano-heterojunctions for engineering efficient water treatment processes.

The well-being of mankind is being alarmingly threatened by the increasing environmental crisis and the cardinal being the scarcity of clean drinking water. Rapid urbanization and illimitable human interventions have led to contamination of natural water sources leading to ecological disarray and jeopardizing both aquatic and humanoid biomes. Activated carbons from various natural feed stocks have been extensively utilized for water decontamination because of their low cost, easy synthesis, highly porous nature and good adsorption capacity. However, the microscopic pores of activated carbon often get blocked after several runs of adsorption-desorption process, thereby, decreasing adsorption efficiency. Carbon nanotubes (CNTs) have immense potential to substitute activated carbons and have been believed to revolutionize water treatment technologies in near future. The open structure of CNTs offers high surface area, faster kinetics and higher adsorption capacity due to the easy and undisrupted access of the contaminants to the reactive sites. Moreover, introduction of surface functionalities such as -OH, -COOH etc., and hybridization with various metal oxide nanoparticles like Fe$_2$O$_3$, ZrO$_2$, CeO$_2$, MnO$_2$ etc., can dramatically improve the adsorption behavior.

However, development of cost effective and environment friendly fabrication methodologies is one of the biggest challenges to the widespread applicability of CNT based nanoadsorbents. Chemical vapor deposition (CVD) is probably among the most effective methods available for the low cost and large scale synthesis of CNTs.

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Recently, various natural carbon feedstocks such as palm oil, turpentine oil, clarified butter, chicken fat etc. have been successfully utilized for the synthesis of CNTs by CVD process. Moreover, various bio resources like plants extract, bacterial proteins, biomolecules etc. have been utilized to control the size and aggregation of nanoparticles. This enabled the green and mass production of CNT-metal oxide composite feasible.

Herein, SnO₂-CNTs were fabricated employing a biosynthetic procedure, utilizing, sunflower oil as a carbon source and Coccinia grandis extracts as complexing and stabilizing agent. The as synthesized SnO₂-CNT nanocomposites were exploited to perform multidimensional functions in water treatment including adsorption of arsenic, disinfecting pathogenic microorganisms and catalytic transformation/degradation of organic pollutants. Arsenic is one of the most toxic contaminants found in natural water and is widespread in many regions around the world. In India, north-eastern states and some parts of west Bengal are at high risk with ground water contamination. According to World Health Organization (WHO) guidelines, the arsenic content in drinking water should be less than 10 μg/L. However, millions of peoples worldwide drink water with a higher arsenic concentration, thereby suffering from long term health issues like cancers of the skin, liver, lung, and bladder, cardiovascular diseases, neurotoxicity and etc. As (III) is the dominant species in ground water and because of its nonionic existence (H₃AsO₃), it has little affinity towards the most of the adsorents. Therefore, pre-treatment oxidation of As (III) to As (V) thus enhances arsenic removal efficacy by many water treatment processes. The photocatalytic oxidation of As (III) to As (V) over semiconducting nanoparticles offers an environmentally benign method for such preoxidation. TiO₂ assisted photocatalytic oxidation of As (III) has been widely reported. Various hybrid materials like TiO₂ coated CNTs, CeO₂-CNTs, Fe₂O₃-CNTs etc. have also been utilized for rapid and effective arsenic sorption. However, reports on oxidative adsorption of As (III) over composite nanomaterials are very scant. Therefore, it is desirable to develop low cost photocatalytic adsorbent capable of oxidizing As (III) to As (V) under UV irradiation followed by simultaneous adsorption of arsenic.

Besides heavy metals, various organic contaminants like dyes, pharmaceuticals, pesticides etc. are environmentally redundant materials and are serious threat to biosphere. Catalytic transformation and photocatalytic degradation of these hazardous contaminants to mineralized products is an efficient method of decontamination of water. The catalytic reduction of nitroarenes is being widely used as a touchstone reaction to testify the catalytic transformation and photocatalytic degradation of these hazardous contaminants to mineralized products is an efficient method of decontamination of water. The catalytic reduction of nitroarenes is being widely used as a touchstone reaction to testify the catalytic efficiency of a catalyst. Also, 4-nitrophenols are considered as toxic, carcinogenic and teratogenic elements, cause impairment to liver, central nervous system, kidney etc. Moreover, textile dyes like Alizarin red S and pharmaceutical compounds like Metronidazole were potentially carcinogenic and prone to mount up in aquatic biome, thereby leading to water pollution. Therefore, complete remediation of these organic contaminants from water is indeed compulsory.

Additionally, development of multidrug-resistant microorganisms, especially the pathogenic bacteria and fungi at an alarming rate is a matter of global health concern. Hence, new substitute and safe antimicrobial agents to treat drinking water against human microbial pathogens is of pressing demand. Due to the advancement of antimicrobial nanotherapy, new bioengineered nanoparticles have emerged which showed antimicrobial activity due to degradation of cell membranes, alteration/destruction of cell walls, and nucleic acids. In that regard, Addae et al. and Sinha et al. reported destruction of cell walls of Bacillus species by Au/CuS and Ag-SnO₂ NPs. Recently, the broad spectrum antimicrobial activities of CNTs have also been established against E. coli, S. aureus, Klebsiella pneumonia, S. agalactiae, Salmonella typhimurium, and S. dysgalactiae. In addition, CNTs composites for example Graphene-CNT-Iron oxide, ZnO-MWCNTs, MWCNTs-CdS, MWCNTs-AgS have also been found to enhance broad spectrum antimicrobial activities may be due to synergism. The high potency of nanomaterials as antiviral, antibacterial, antifungal and antiprototzoal agents has thus revolutionized the pharmacological therapy.

Hence, in this work, we present a facile, bio-mediated, and economically viable fabrication of SnO₂-CNT nanocomposite and their multifunctional capabilities such as oxidative adsorption of As (III), catalytic transformation of nitroarenes, photocatalytic degradation of Alizarin red S dye, Metronidazole and antimicrobial competence. The structure-property relationship of the surface decorated CNTs with SnO₂ nanopartcles have been thoroughly investigated and are efficiently utilized in eradication of water contaminants.

Experimental Section

Materials and instruments. Fresh sunflower oil and Coccinia grandis leaves were obtained from local farmers market. Stannic chloride pentahydrate (SnCl₄·5H₂O) was obtained from Sigma Aldrich and used without further purification.

Fourier transform infrared (FTIR) spectrum was taken by a 3000 Hyperion Microscope with Vertex 80 FTIR System (Bruker, Ettlingen, Germany) spectrometer. Transmission electron microscopy (TEM) was carried out on JEOL, 9JSM-100CX equipment with an accelerating voltage of 60–200 kV. Energy dispersive X-ray (EDX) analysis was performed using the same instrument. Scanning electron microscopic (SEM) images were obtained on a JEOL, JEM-6360 equipment, LEO, 1430vpequipment and on Quanta 150 equipment with an accelerating voltage of 1K-30KV. Powder X-ray diffraction (XRD) patterns were obtained using Philips X’PERT powder X-ray diffractometer with Cu-Kα radiation (λ = 1.54056 Å) with a scan speed 2°/min at room temperature. Raman Spectra were recorded on a Renishaw RM1000B LRM using a 514.5 nm (λexc = 2.41 eV) Ar⁺ laser excitation source. Nitrogen adsorption-desorption measurements were performed using a Quanta Chrome Nova 1000 gas adsorption analyzer. X-ray photoelectron spectroscopy (XPS) of the material was performed by PHI 5000 Versa Prob II spectrometer. pH measurement of solutions was carried out on a pH meter (Macro Scientific Works (Regd). New Delhi). The arsenic adsorption process was monitored using graphite furnace atomic absorption spectrometer (ANALYTIKJENA AG VARIO 6). The absorbance spectra of the samples were recorded using GENESYS 10S UV–visible spectrophotometer. HRLCMS was recorded using 1290 Infinity UHPLC System, Agilent Technologies, USA. Elementar Liqi TOC analyzer was used to perform TOC analysis. Electron spin
resonance (ESR) spectra were recorded using JEOL JES-FA200, Japan. The Photo Luminescence (PL) spectra were taken using Hitachi F4600 instrument.

The in vitro antimicrobial screening incorporated the fungal strains, viz., Candida albicans and Aspergillus niger and bacterial strains, viz., Escherichia coli, Bacillus subtilis, Staphylococcus aureus susp. Aureus, Streptococcus pneumonia and Pseudomonas aeruginosa. The stains were sub-cultured by Muller Hinton Broth (MHB) and maintain at 5 °C.

Synthesis. Catalyst free synthesis of MWCNT (Multiwalled carbon nanotube). The MWCNTs were prepared by chemical vapor deposition (CVD) method without using any external catalyst. A quartz boat loaded with sunflower oil (~10 g) was kept in a lower-temperature zone (300 °C) and an empty quartz boat was kept at a higher temperature zone (700 °C) in a horizontal quartz tube10. Argon gas was then purged at a rate of 6 cm3/min. The furnace was heated to 700 °C at a rate of 7 °C/min for 2 hours and then allowed to cool to ambient temperature whereupon the CNTs were obtained as black powder (yield ~3.0 g).

Synthesis of SnO2-MWCNT nanohybrids. Coccinia grandis leaf extract was prepared by boiling small pieces (wt. 2.5 g) of it in 100 mL of distilled water and filtering it through Whatman 40. A transparent sol was prepared by dissolving 3.0 g of SnCl4·5H2O in a minimum volume of distilled water. A calculated amount of MWCNT was added to it to get 1:1 weight ratio of the components and sonicated for about 30 minutes in order to obtain the homogeneously dispersed mixture. It was then added drop wise to the Coccinia grandis extract with constant stirring and maintaining a constant temperature of 70 °C for 2 h. The as obtained opal solution was then kept in a microwave oven and irradiated with thirty 10 s shots. This resulted in the precipitation of grayish mass which was centrifuged, washed several times with distilled water and air dried (yield ~4.5 g). No surfactants or stabilizing agents were used during the synthesis. The various phytochemicals present in plant extract acted as a complexing and stabilizing agent which can control the growth of the SnO2 nanoparticles in the reaction mixture (Fig. 1)10,13.

Oxidative adsorption of As (III) on SnO2-CNT nanoadsorbent. All the adsorption studies were done in batch mode on a rotary shaker fitted within UV chamber. Three Philips HZ147 11W UV Lamp of wavelength 260 nm with surface irradiance of 34.72 W/m² was utilized for photocatalytic oxidation of As (III). Calculated amounts sodium arsenite (NaAsO2) were dissolved in 1 L of distilled water to have 100 μg/L and 1 mg/L As (III) stock solutions. The arsenic adsorption was studied with 50 mL of the stock solution at pH 7.0 ± 0.1 under room temperature. The optimum amount of adsorbent for different concentrations was determined by dispersing varied amounts of adsorbent in 50 mL of As (III) solution for 300 minutes under constant mechanical stirring (50 rpm). For kinetics studies, optimum doses of adsorbent (0.1 g/L for 100 μg/L and 1.0 g/L for 1 mg/L) were dispersed in 50 mL of As (III) solutions and samples were collected in different times ranging from 0–240 min (in 15 min intervals), filtered and analyzed for arsenic using atomic adsorption spectrometer. The effect of change

Figure 1. Schematic representation of the bio-mediated synthesis of SnO2-CNT nanocomposite.
in concentration on adsorption behavior was examined by varying concentration in the range 40–100 µg/L and 0.4–1.0 mg/L respectively. Effects of competing ions and initial pH on arsenic removal were tested by varying interfering ions and pH respectively. The regeneration potential of the adsorbent was also investigated by five consecutive adsorption-desorption cycles. All batch experiments were performed in triplicate and the average values were reported.

Evaluation of catalytic and photocatalytic properties of the nanocomposite. The catalytic hydrogenation of 4-nitrophenol to 4-aminophenol was used to investigate the catalytic efficiency of nanocatalysts. In a typical reaction, 1.5 mL of 3 × 10⁻⁴ M aqueous solution of 4-nitrophenol and 0.5 mL of 3 × 10⁻² M NaBH₄ solution were mixed in a quartz cuvette to have concentrations of 2.33 × 10⁻⁴ M and 7.5 × 10⁻³ M respectively. Then, 0.1 mg of the SnO₂-CNT nanocatalyst was introduced into the reaction mixture and the disappearance of the yellow color was monitored using UV-Visible spectrophotometer.

The photocatalytic properties of SnO₂-CNT were investigated by means of photodegradation of Alizarin red S and Metronidazole as water pollutants. The UV photo-reactor was consisted of three Philips HZ147 11W UV Lamp of wavelength 260 nm as a light source. The irradiance on the surface of the reaction mixture was calculated to be 34.72 W/m². The experiments were performed using 10 mg/L to 80 mg/L solutions Alizarin red S and Metronidazole separately with various quantities of catalyst. The solutions were sonicated for about 60 min in dark to establish the adsorption equilibrium and then exposed with UV radiation over different time under magnetic stirring condition. The progress of the degradation process was monitored using UV-Visible spectrophotometer.

All the experiments were carried out at room temperature. The reproducibility of the results has been verified by repeating the experiments three times and an average error of ±3 was observed for reduction and degradation process.

Evaluation of antimicrobial activity. Agar well diffusion technique was employed for antimicrobial activity of SnO₂-CNT nanohybrids. Freshly prepared Potato dextrose agar and Muller Hinton Agar media were utilized for fungal and bacterial culture respectively. Approximately 6 mm wells were made in the solidified media and samples (50 µL) of three different molar concentrations were filled in three such wells. Azithromycin, Ciprofloxacin, Metronidazole and Cephalexin were utilized as positive control for bacteria and Nystatin and Ketoconazole for fungi. DMSO was used as negative control. The dishes were incubated for 47 h at 24 °C for fungal culture and 24 h at 36 °C for bacterial culture. After incubation, the zone of inhibition (ZOI) was measured in millimeter (mm).

Results and Discussion

Role of Coccinia grandis leaf extract in deposition of SnO₂ nanoparticles over CNT surface. Phytosynthesis of nanoparticles utilizing plant resources is an emerging method to reduce toxicity of nanoparticles commonly associated with conventional synthesis. Plants are known to nurture a wide range of metabolites. The various phytochemicals present in plant play a crucial role in formulating and enhancing bioactivity of the nanoparticles. The aqueous extracts of Coccinia grandis leaves are reported to have flavonoids, proteins and amino acids, glycosides, polyphenolics, carbohydrates, alkaloids etc. These phytochemicals have polar functional groups such as hydroxyl, aldehydes, ketones, esters, amides along with the carbon backbone as evident from the FT-IR spectrum of the aqueous leaf extract (Fig. S1 ESI). The chelation effect of these functional groups may lead to the complexation or capping of the Sn⁴⁺ ion with the phytochemicals. The nucleation phase begins with hydrolysis-condensation reactions and on microwave irradiation, the sudden blast of energy breaks the complex to form SnO₂ nanoparticles. The SnO₂ nanoparticles then undergo growth and stabilization phase wherein certain phytochemicals prevent the self agglomeration to form extremely small spherical SnO₂ nanostructures (Fig. S2 ESI). The surface functionalities of CNTs may encourage the growth and stabilization phase of SnO₂ nanoparticles on its surface thereby leading to the formation of stable SnO₂-CNT nanohybrid. Also, a comparative account of TEM micrographs of SnO₂-CNT nanohybrid before and after the microwave irradiation has been represented in Fig. S3 ESI. It was evident that before microwave irradiation, SnO₂ nanoparticles were agglomerated and not evenly distributed over CNT surface. However, TEM micrograph of post microwave treatment has revealed the effective incorporation of SnO₂ nanoparticles into the CNT. Thus, under microwave irradiation, the molecular vibrations and interfacial polarization have lead to the effective incorporation of guest into host and generation of more defect sites and heterojunctions in SnO₂-CNT nanocomposite.

Characterization of the synthesized SnO₂-CNT nanocomposites. The morphology of the as synthesized CNTs and SnO₂-CNT nanocomposites were examined using transmission electron microscopy. The TEM micrographs (Fig. 2(a,b)) revealed quasi-aligned clean uniform >10 µm long hollow nanotubes formed due to CVD treatment of sunflower oil. These CNTs have an empty and uniform central core and open at one end. The nanotubes have long-range uniformity in the diameter with outer and inner diameters of ~35.2 nm and ~19.6 nm respectively. The HRTEM (Fig. 2(c)) suggested the as-grown nanotubes to be consisting of concentrically nested ~25 graphene sheets. The lattice fringes between two adjacent planes are 0.332 nm apart, which resembles the interlayer distance of (002) plane of the graphitic carbon. The SAED (Fig. 2(d)) revealed concentric rings that are characteristic of graphitic carbon (ICPDS 23-0064). Undesirable structures like amorphous carbon are negligible albeit with some structural defects. In SnO₂-CNT, the tin oxide nanoparticles of nearly spherical shape are evenly distributed over the surface of CNTs (Fig. 2(e,f)). The SnO₂ nanoparticles are of uniform size with average particle size of 2.25 ± 0.3 nm (Fig. S4(a)). The lattice fringes showed a separation of 0.176 nm (Fig. 2(g)) which may be indexed to (211) plane of tetragonal rutile tin oxide (ICPDS 21-1250). The high crystallinity of SnO₂-CNT nanocomposite was revealed by the SAED pattern (Fig. 2(h)) and the various lattice planes were identified and found to be in consistence with the XRD pattern (Fig. 3(a)). The energy dispersive X-ray analysis (Fig. S4(b)) confirmed
the composition of SnO₂-CNT nanohybrid. The weight ratio of Sn and C was approximately 0.76 which indicated some loss of carbon may be due to heat treatment. Also the atomic ratio of O to Sn was found to be 1.26 indicating a high number of oxygen vacancies in the synthesized sample⁴³. A comparative study of the morphologies of the
SnO₂-CNT nanohybrids with recent reports has been summarized in Table S1 (ESI). It was evident that low cost, biogenic, additive free fabrication of SnO₂-CNT resulted better control over hybridization and growth of SnO₂ nanoparticles, keeping the morphological characteristics of the CNT unscathed.

The X-ray diffraction pattern of the synthesized CNT and SnO₂-CNT nanohybrid is shown in Fig. 3(a). Pristine CNT showed Bragg's diffractions at 20 values 26.52°, 44.61°, 54.67° and 59.7° corresponding to the (002), (101), (102) and (103) crystallographic planes of hexagonal graphitic carbon (JCPDS Card No 23-0064). The dominant diffraction planes of SnO₂-CNT were indexed to be (110), (101), (200), (211), (220), (002), (310) and (301) of rutile tetragonal tin oxide (JCPDS Card No. 21-1250) possessing space group P4₃/mmm (136), lattice parameters a = 4.738 Å and c = 3.188 Å. Comparing with the XRD pattern of pristine CNT, the distinct reflection peak of (002) facet of hexagonal graphitized carbon seemed to be overlapping with (110) facet of SnO₂. The decrease in FWHM values of the diffraction peaks after carbonization indicated the increase in crystallinity of the sample. The average crystallite size is calculated by using the Debye-Scherrer’s equation, $D = \frac{k \lambda}{\beta \cos(\theta)}$, where $D$ is the crystallite size in nanometers, $k$ is the shape factor (0.89), $\lambda$ is the wavelength of CuKα radiation ($\lambda = 1.54056$ Å), $\beta$ is full width at half maximum (FWHM) of the particular peak and $\theta$ is the Bragg’s angle and was found to be 3.28 nm.

The FT-IR spectra of the as prepared compounds are shown in Fig. 3(b). The pristine CNT showed strong vibrations at 3443 cm⁻¹, 1620–1695 cm⁻¹ and 1050 cm⁻¹ which may be attributed to the O-H, C=O-C and C-O stretching vibrations respectively. This signifies that the CNT surface may contain some surface functional groups like -OH, -COOH, -CHO etc. Low intensity peaks at 2846 cm⁻¹ and 2914 cm⁻¹ may correspond to the -CH and =CH vibrations and moderate intensity bands at 1358–1460 cm⁻¹ are characteristics of CH₂/CH₃ banding vibrations. Pristine SnO₂ showed a strong band at 588 cm⁻¹ which is characteristic of Sn-O-Sn/Sn-OH stretching vibrations. Strong hydroxyl stretching (3443 cm⁻¹) and bending (1626 cm⁻¹) have appeared due to the physically absorbed H₂O on SnO₂ surface. The appearance of the C-O band (1050 cm⁻¹) retaining the characteristic Sn-O band (588 cm⁻¹) in SnO₂-CNT confirmed the composite formation.

Raman Spectroscopy is a sensitive and informative technique to investigate the interaction between carbon based materials with other components. The Raman spectra (Fig. 3(c)) of the pristine CNT and SnO₂-CNT exhibited characteristic first order D- and G-bands at ~1333.39 cm⁻¹ and ~1596.37 cm⁻¹ respectively, indicating the carbon backbone. The G band corresponds to the tangential stretching (E₂g) mode of the highly oriented pyrolytic graphite. The D-peak assigned to A₁g mode originates from the disorder in the sp²-hybridized carbon and indicated a lattice distortion in the graphitic carbon. Therefore, the intensity ratios ($I_D/I_G$) are a measure of the extent of modification and the associated defects on the CNT. Notably, The $I_D/I_G$ ratio for pristine CNT and SnO₂-CNT were found to be 0.85 and 0.92 respectively. The little increase in $I_D/I_G$ ratio implies a decrease of the average size of sp³ domains and increase in the atomic ordering of crystallinity of the CNT surface after being covered with SnO₂. Meanwhile, a slight up-shift of the G-band (From 1589–1603 cm⁻¹) was also observed with SnO₂ deposition which indicated efficient charge transfer between CNTs and SnO₂.

The surface area and pore structures of the synthesized SnO₂-CNT nanohybrids were investigated using BET surface area analysis (Fig. 3(d)). The materials showed typical type IV isotherms with H₂ hysteresis loops which are characteristics of mesoporous materials having narrow mouths or channel-like pores structures. The porosification process i.e., the blocking of narrow mouth pores due to condensation of adsorbate at the neck resulted in the steepness of the desorption branches of H₂ hysteresis loops. The BET surface area of pure SnO₂-CNT was found to be $9.76 \times 10^3$ cm²/g. Also, SnO₂-CNT exhibited high BJH pore diameter and mesopore volume of 3.7 nm and 0.136 cm³/g respectively. The high surface area and superior mesoporous nature are likely to benefit the adsorption behavior and catalytic performance of the SnO₂-CNT nanocomposite.

**Oxidative adsorption of As (III) on SnO₂-CNT nanocomposite.** The arsenic adsorption properties were investigated both at high arsenite concentrations as well as at low concentration ranges. Figure 4(a) demonstrated the decrease in arsenite concentration with time at two different initial concentrations. The As (III) removal efficiency was increased with increase in SnO₂-CNT dosage and an optimal dose of 0.1 g/L could reduce the As (III) concentration from 100 μg/L to below WHO drinking water permissible limit within 120 min of treatment time. The SnO₂-CNT adsorbent showed a good adsorption performance at high concentration range as well. A dose of 1.0 g/L could eliminate ~93% of the initial 1.0 mg/L As (III) concentration with in 120 min.

The pseudo first order and pseudo second order model were employed to study the adsorption kinetics of arsenite from the experimental data. The linear equations of the models are represented in Eq. (1) and Eq. (2) respectively.

$$\log(q_t - q_e) = \log q_e - \left(\frac{k_1}{2.303}\right) t$$  \hspace{1cm} (1)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \frac{t}{q_e}$$  \hspace{1cm} (2)

where $q_t$ and $q_e$ are the amounts of arsenic adsorbed per unit weight of adsorbent in equilibrium and at time $t$ respectively. $k_1$ and $k_2$ are the rate constants of pseudo first order and pseudo second order kinetic model respectively.

The kinetic parameters obtained from the fitting of the experimental data are summarized in Table 1. From the correlation coefficients ($R^2$) it was found that the pseudo second order model (Fig. 4(b)) fitted better than the pseudo first order model (Fig. S5(a,b)). Further, pseudo second order model showed a close agreement of the theoretical and the experimental values $q_t$ for both the concentration ranges. The best fitting of the pseudo second
order model suggested that the As (III) adsorption rate is dependent on both the concentrations of As species and the adsorption sites\(^4\). Moreover, chemisorption i.e., interaction through valency forces involving sharing or exchange of electrons between As (III) and SnO\(_2\)-CNT may be responsible for the adsorption process\(^5\).

The adsorption capacities of the SnO\(_2\)-CNT adsorbent in different concentrations of As (III) were evaluated using equilibrium adsorption isotherms. The adsorption data were fitted with the Langmuir and Freundlich isotherm models given by the Eqs (3) and (4) respectively.

\[
\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (3)
\]

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)
\]

where \(C_e\) is the equilibrium concentration of As (III) in water sample and \(q_e\) is the equilibrium amount adsorbed. \(K_L\) and \(q_m\) are the Langmuir adsorption constant and maximum monolayer adsorption capacity respectively. \(K_F\) and \(n\) are Freundlich adsorption capacity and adsorption intensity respectively.

**Table 1.** Pseudo first order and pseudo second order kinetic model fitting parameters for As (III) adsorption.

| Kinetic models       | Kinetic parameters | Values for As(III) adsorption \((C_0= 100 \text{ppb})\) | Values for As(III) adsorption \((C_0= 1 \text{ppm})\) |
|----------------------|--------------------|----------------------------------------------------------|----------------------------------------------------------|
| Pseudo-first order   | \(q_e\) experimental | 19600 \(\mu g/g\) | 25.20 mg/g |
|                      | \(q_e\) calculated  | 8511.38 \(\mu g/g\) | 22.38 mg/g |
|                      | \(K_1\)             | \(9.21 \times 10^{-3} \text{min}^{-1}\) | \(2.17 \times 10^{-2} \text{min}^{-1}\) |
|                      | \(R^2\)             | 0.795 | 0.980 |
| Pseudo-second order  | \(q_e\) calculated  | 20283 \(\mu g/g\) | 24.45 mg/g |
|                      | \(K_2\)             | \(2.5 \times 10^{-4} \text{g} \mu g^{-1} \text{min}^{-1}\) | \(5.1 \times 10^{-4} \text{g} \text{mg}^{-1} \text{min}^{-1}\) |
|                      | \(R^2\)             | 0.998 | 0.993 |

**Figure 4.** (a) Adsorption kinetics of arsenite on SnO\(_2\)-CNT nanocomposite with different dosage and initial concentrations (b) The pseudo second order kinetic model fitting at \(C_0= 100 \mu g/L\) and \(C_0= 1 \text{mg/L}\) (c,d) Langmuir and Freundlich adsorption isotherms for \(C_0= 1 \text{mg/L}\) (e,f) Freundlich and Langmuir adsorption isotherms for \(C_0= 100 \mu g/L\) respectively.
The experimental data were fitted with both Langmuir and Freundlich models and the parameters were presented in Table 2. It is evident from the $R^2$ values that at the higher concentration range the adsorption data were fitted well with both Langmuir and Freundlich models (Fig. 4(c,d)). However, at low concentration range, Freundlich model (Fig. 4(e)) can describe the adsorption behavior effectively. The maximum adsorption capacity ($q_m$) from the best fitted Langmuir model is found to be 106.95 mg/g. The separation factor ($R_L$), given by, $R_L = 1/(1 + K_L \times C_0)$ was found to be 0.87 ($<1$) implying favorability of the Langmuir adsorption process at higher concentration range. Also, $1/n$ is found to be 0.404 ($<0.5$) suggesting favorable Freundlich adsorption at low concentration range51. Thus among the various As (III) nanoadsorbents, SnO$_2$-CNT demonstrated superior arsenite adsorption behavior both at low and high arsenic concentrations (Table S2 ESI).

The effect of change in pH and the presence of competing ions on the arsenite removal efficiency have also been scrutinized. Fig. S6(a) (ESI) showed the decrease in arsenic removal efficiency with increase in pH from 2 to 10. High adsorption capacity at low pH is because of the favorable protonation of the adsorbent surface, thereby, increasing the electrostatic attraction between the sorbate and sorbent49. However, the decrease in adsorption efficiency at high pH may be due to the competing OH$^-$ ions and hence high pH conditions are beneficial for desorption studies. Figure S6(b) (ESI) demonstrated the effect of co-existing anions on arsenic removal efficiency of the adsorbent. The concentrations of different interfering anions like Cl$^-$, NO$_3^-$, SO$_4^{2-}$ and PO$_4^{3-}$ have been adjusted from 0.05 M to 0.2 M while the initial arsenite concentration (1.0 mg/L), adsorbent dose (1.0 g/L) and pH (7) were kept constant. Phosphate showed the maximum interference because of the chemical similarity with arsenite. However, the arsenic removal efficiency of the SnO$_2$-CNT was found to be ~70% even in presence of 200 times higher PO$_4^{3-}$ concentration than that of As (III).

The regeneration and reusability of the adsorbent even after several adsorption-desorption cycles is an important criterion for practical applications. The regeneration was conducted using 0.1 M NaOH solution as eluent and even after five successive cycles, adsorption percentage was found to be almost constant (~86%) (Fig. S6(c) (ESI)). These results demonstrated the good regeneration potential of the adsorbent. Thus, SnO$_2$-CNT possesses great adsorption efficiency even at very low concentration, good selectivity, easy regeneration and better reusability which render it as a superior adsorbent towards treating arsenic contaminated water in future.

| Isotherm models | parameters | Values for As(III) adsorption (Low concentration range) | Values for As(III) adsorption (High concentration range) |
|-----------------|------------|------------------------------------------------------|------------------------------------------------------|
| Langmuir model  | $q_m$ (mg/g) | 22.22 | 106.95 |
|                 | $K_L$       | 358.6 | 0.148 |
|                 | $R_L$       | 0.025 | 0.87 |
|                 | $R^2$       | 0.913 | 0.999 |
| Freundlich model| $K_F$ (mg/g) | 123.59 | 16.82 |
|                 | $1/n$       | 0.404 | 1.024 |
|                 | $R^2$       | 0.986 | 0.992 |

Table 2. Langmuir and Freundlich parameters for As(III) adsorption over SnO$_2$-CNT nanocomposite.

The nonionic nature of the As (III) species renders inefficiency towards adsorption technologies. Oxidative adsorption includes oxidation of As (III) to more favored As (V) species followed by simultaneous adsorption. The role of SnO$_2$ in the photocatalytic adsorbent SnO$_2$-CNT is to absorb sufficiently energetic light to produce photogenerated electron-hole pairs. The electron accepting capability of CNTs and the potential barrier across SnO$_2$-CNT heterojunction further stabilizes the excitons. In aerated solutions, O$_2$ serves as the primary electron acceptor to generate superoxide anion radicals (O$_2^-$) which can actively take part in the oxidation process as shown below52.

$$\text{SnO}_2 + \text{h}_\nu \rightarrow \text{SnO}_2(e^-_{CB} + h^+_{VB})$$

$$\text{SnO}_2(e^-) + \text{CNT} \rightarrow \text{SnO}_2 + \text{CNT}(e^-_e)$$

$$\text{CNT}(e^-_e) + \text{O}_2 \rightarrow \text{CNT} + \text{O}_2^-$$

$$\text{O}_2^- + \text{H}_2\text{O} \rightarrow \text{HO}^- + \text{HO}_2^-$$

$$2\text{HO}_2^- \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$$

$$\text{H}_2\text{O}_2 \rightarrow \text{2HO}^-$$

$$\text{H}_4\text{AsO}_3 + \text{O}_2^- + 2\text{H}^+ \rightarrow \text{H}_4\text{AsO}_3^+ + \text{H}_2\text{O}_2$$

Plausible mechanism of oxidative adsorption. The nonionic nature of the As (III) species renders inefficiency towards adsorption technologies. Oxidative adsorption includes oxidation of As (III) to more favored As (V) species followed by simultaneous adsorption. The role of SnO$_2$ in the photocatalytic adsorbent SnO$_2$-CNT is to absorb sufficiently energetic light to produce photogenerated electron-hole pairs. The electron accepting capability of CNTs and the potential barrier across SnO$_2$-CNT heterojunction further stabilizes the excitons. In aerated solutions, O$_2$ serves as the primary electron acceptor to generate superoxide anion radicals (O$_2^-$) which can actively take part in the oxidation process as shown below52.
The identification of photo induced reactive species can be done from the ESR measurement using N-tert-butyl-α-phenylnitrone (PBN) as spin trapping agent. Figure 5(a) showed typical six peak ESR signal confirming the generation of superoxide anion radicals (O$_2^-$) in the process. Further, X-ray photoelectron spectroscopy was utilized before and after the adsorption process to elucidate the adsorption mechanism. The binding energies of Sn 3d and As 3d were centered at ~484.2 eV and ~410.6 eV respectively which were assigned to Sn 3d5/2 and As 3d3/2. The binding energies of the C 1s before and after the adsorption were 284.5 and 283.9 eV respectively which were assigned to C–O and C–C bonds.

The reaction mechanisms are as follows:

$$\text{H}_3\text{AsO}_3 + \text{HO} + \text{H}^+ \rightarrow \text{H}_2\text{AsO}_3^+ + \text{H}_2\text{O}$$

$$\text{H}_2\text{AsO}_3 + \text{SnO}_2(h_{VB}) \rightarrow \text{H}_2\text{AsO}_3^+$$

$$\text{H}_2\text{AsO}_3^+ + \text{HO} \rightarrow \text{H}_2\text{AsOO}^- + 2\text{H}^+$$

$$\text{H}_3\text{AsO}_3^+ + \text{HO} \rightarrow \text{H}_2\text{AsO}_4^- + 2\text{H}^+$$

$$\text{H}_3\text{AsO}_3^+ + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{AsO}_4^- + \text{O}_2^- + 3\text{H}^+$$
Sn (IV) in SnO₂ (Fig. 5(b)). After adsorption, a slight decrease in the intensities of the Sn 3d spin–orbit doublet was observed along with a slight tilt towards high binding energy. This indicated the existence of strong chemical interaction between SnO₂ and As species. The high resolution As 3d spectrum of the aqueous solution before and after the adsorption process was represented in Fig. 5(c,d) respectively. The signal can be deconvoluted into two individual component peaks centered at ~42.49 eV and ~46.48 eV assigned to As (III) and As (V) respectively. A momentous decrease in the intensity of the As (III) peak centered at ~42.96 eV after the adsorption was observed. Comparing the area under the curve before and after adsorption (Table S3 ESI), it was evident that peak area of As (III) has been decreased from 40.27% to 12.15%, thereby, indicating oxidation of As (III) to As (V) during oxidative adsorption process. Further, The C 1s spectrum before adsorption (Fig. 5(e)) can be deconvoluted into three peaks at ~283.7, ~284.6 and ~287.8 eV corresponding to three functional groups C–C, C–O and C=O respectively. The curve fitting parameters of C 1s before and after adsorption (Table S3 ESI) demonstrated that C–O content decreases from 10.97% to 5.72% while C–O increases from 29.20% to 45.81% with arsenic adsorption, thereby, indicating chemical interaction during adsorption process. Thus, photocatalytic oxidation of As (III) over SnO₂-CNT surface has been established and was found to be the driving force of the adsorption process. The neutral As (III) species (H₃AsO₃) has lesser affinity towards the adsorbent surface but the oxidation of As (III) to As (V) on SnO₂-CNT surface generated anionic H₂AsO₄⁻ species. The hydroxyl groups present on adsorbent surface (as evident from FTIR spectra) may undergo ligand exchange with anionic H₂AsO₄⁻ thereby, facilitating enhanced adsorption behavior.

Catalytic reduction of 4-nitrophenol. A popular line of investigation of catalytic performance of nanomaterials is catalytic reduction of nitroarenes. The reduction of 4-nitrophenol to 4-aminophenol by NaBH₄ in presence of SnO₂-CNT nanocatalyst have been monitored using UV-Vis spectroscopy. Aqueous solution of yellow colored 4-nitrophenol showed strong absorption at ~317 nm. In presence of NaBH₄ a red-shift was observed at ~400 nm due to the formation of nitrophenolate anion (Fig. S7(a))24. In absence of catalyst, the reduction did not occur as the peak at 400 nm remained the same even after 2 days (Fig. S7(b)). However, in presence of catalyst, the peak at 400 nm diminished gradually with time along with the concomitant rise of characteristic peak of 4-aminophenol at ~300 nm. Hence, the changes in the absorbance at 400 nm have been screened to track the progress of the reduction reaction.

The time-dependent reduction kinetics was studied with varied amounts of catalyst doses (Fig. 6(a–d)). The reaction conditions were optimized by varying concentrations of NaBH₄ and 4-nitrophenol. The excess NaBH₄ concentration (~100 times higher than that of 4-nitrophenol) induced the reaction to comply with pseudo-first order kinetics26. Since the ratio of concentration of 4-nitrophenol at time t (C) to that at time t = 0 (C₀) is directly proportional to the corresponding absorbance ratio (A/A₀), therefore, the pseudo first order kinetics can be estimated as follows

\[
\ln\left(\frac{C}{C_0}\right) = \ln\left(\frac{A}{A_0}\right) = -kt
\]

where k is the pseudo first order rate constant and t is the reaction time in minutes. A₀ is the initial absorbance of the nitrophenolate anion and A is that during the progress of reduction reaction. The nature of the ln (A/A₀) vs. time was a straight line with negative slope (Fig. 6(e)) the rate constants at different catalyst dose (m) were calculated using Eq. (5). Moreover, the catalytic activity parameters \((k_s)\), the ratio of rate constants to catalyst doses \(k/m\), have been calculated for different catalyst doses and represented in Table 3. It has been found that the reduction rate became faster with an increase in catalyst amount, however, with a trivial decrease in catalytic activity. A comparative study of pseudo first order rate constants and activity parameter of the SnO₂-CNT nanocatalyst with other reported catalysts has been summarized in Table S4 ESI. It is evident that the SnO₂-CNT nanocatalyst showed better activity than most of the reported catalysts.

The reusability of the catalyst was tested by regenerating the catalyst after three successive rounds of catalytic reduction. Common regeneration method involving sonication, centrifugation, vacuum drying etc were employed and the regenerated catalyst showed good catalytic activity with some loss at successive runs. The slight decrease in catalytic conversion after each run may be due to detachment of SnO₂ nanoparticles from the CNT surface (Table S5 ESI). However, after three cycles of regeneration and reuse, appreciable catalytic activity was found which supports the potential practical applicability of the catalyst.

Plausible mechanism of catalytic reduction. Previous reports explain the mechanism of the reduction on catalyst surface by Langmuir Hinshelwood model15. The substrates first get adsorbed over the catalyst surface, where the hydride transfer occurs followed by desorption of the product. In this respect, SnO₂-CNT provided low crystallite size (3.28 nm), large surface area (9.76 × 10⁶ cm²/g) and surface functional groups which in turn directly affected the active site of the catalysis in reaction medium and hence increased the catalytic activity. Moreover, the reduced feasibility of the reduction process in absence of catalyst is due to the large potential barrier between the donor and the acceptor molecules. The heterojunction structure of the SnO₂-CNT plays a crucial role for electronic interaction between the NaBH₄ and 4-nitrophenol. The SnO₂ can absorb electrons from BH₄⁻ anions which may be transferred through CNT to the nitro groups of adsorbed 4-nitrophenol, thereby increasing the reduction rate. Hence, the small particle size, morphology, high surface area and the heterojunction structure of the SnO₂-CNT are the factors responsible for the greater efficiency of the catalyst towards catalytic reduction of 4-nitrophenol.
Photocatalytic degradation of Alizarin red S dye and Metronidazole. The applicability of the synthesized SnO$_2$-CNT nanoheterojunctions to waste water treatment has also been explored by their degradation performance towards model water pollutants like Alizarin red S dye and metronidazole. The adsorption
performance under dark condition for Alizarin red S and metronidazole were found to be only 16.5% and 11.8% respectively (60 min duration) and hence neglected in further studies. The photocatalytic performance was investigated under UV irradiation with initial contaminant concentrations in the range 10 mg/L to 80 mg/L and the catalyst dose in the range 0.1 g/L to 1.5 g/L. The progress of the degradation process was monitored by tracking the absorbance intensity at \( \lambda_{\text{max}} = 260 \text{ nm} \) for Alizarin Red S and \( \lambda_{\text{max}} = 322 \text{ nm} \) for metronidazole.\(^{27,28}\) The degradation efficiency has been determined using the following equation:

\[
\text{Degradation efficiency (\%) } = \left( \frac{A_0 - A}{A_0} \right) \times 100
\]

where \( A_0 \) is the initial absorbance and \( A \) is absorbance at different interval of time.

The effect of catalyst amounts on the degradation efficiencies of Alizarin red S and metronidazole was evaluated by varying the catalyst concentration and keeping other parameters constant. Figure 7(a) showed steep increase in the percentage degradation for both Alizarin red S and metronidazole with increase in the amount of SnO\(_2\)-CNT. A maximum degradation of \(~97\%\) for Alizarin red S and \(~82\%\) for metronidazole was achieved with catalyst amount 0.6 g/L and 0.8 g/L respectively. Whilst in the blank run, degradation efficiencies were found to be in the range 13–17% even after 60 min of illumination, suggesting the efficiency of the catalyst. The nearly stagnant degradation efficiencies beyond the optimized catalyst doses can be ascribed to the decreasing penetration power of the light with the increasing turbidity of the solution.

The effect of variation of initial contaminant concentrations on degradation efficiencies was studied by taking different concentrations of Alizarin red S and metronidazole in the range 10 mg/L to 80 mg/L with optimized catalyst doses (Fig. 7(b)). Maximum degradation efficiencies were recorded at initial concentration 50 mg/L for both the contaminants. The degradation performances were found to decrease with increase in initial contaminant concentrations. The reason being the increased number of adsorbed contaminants/degradation by-products on the surface of catalyst might have hindered the direct contact of reactive radicals (\( \text{O}_2^/-\text{OH} \)) with the contaminant molecules, thereby, retarding the degradation\(^{44}\).

The effect of initial pH on photodegradation of contaminants have also been investigated by varying the pH from 2–10. The pH of the solution was adjusted by appropriate amounts of 0.1 M HCl/NaOH solutions. Figure 7(c) demonstrated a slight increase in degradation efficiency for Alizarin red S while remained steady for Metronidazole up to pH 6. However, with further increase in pH, the degradation efficiencies were found to decrease steadily for both Alizarin red S and Metronidazole. The decrease in catalytic performance under high pH conditions may be attributed to the accumulation of negatively charged \( \text{OH}^- \) ions over the catalyst surface thereby repelling the electron rich contaminant molecules. Hence the optimization experiments result the best suited photodegradation conditions as, pH 6, 50 mg/L initial concentration and 0.6/0.8 g/L catalyst doses for Alizarin red S/Metronidazole respectively.

The absorbance intensities of Alizarin red S and Metronidazole as a function of time under optimized degradation conditions have been represented in Fig. 7(d,e). A gradual decrease of absorbance with increase in irradiation time can be noticed which is attributed to the decrease in concentration of the contaminants. The percentage degradation efficiencies calculated using Eq. (6) was found to be \(~97.2\%\) and \(~82\%\) for Alizarin red S and Metronidazole in time 50 min and 45 min respectively. No new absorbance peaks have emerged during the degradation process, which indicated the mineralization of the degraded products. The extents of mineralization of both contaminants were examined by TOC analyzer during degradation process. A maximum TOC removal of 82.4% and 69.7% were found for Alizarin red S and Metronidazole respectively (Table S6 ESI).

The kinetics of the photodegradation process catalyzed by SnO\(_2\)-CNT has been investigated and a comparative plot of \( \ln (A/A_0) \) vs. time for Alizarin red S dye and Metronidazole has been shown in Fig. 7(f). The pseudo first order rate constants for Alizarin red S and Metronidazole were calculated using Eq. (5) and found to be 0.048 min\(^{-1}\) and 0.024 min\(^{-1}\) respectively. The photocatalytic activity parameters were also calculated using the equation \( k = k/C_{\text{catalyst}} \) and were found to be 0.08 L min\(^{-1}\) g\(^{-1}\) and 0.03 L min\(^{-1}\) g\(^{-1}\) for Alizarin red S and Metronidazole respectively.

It can be noted from Fig. S8 ESI, under UV irradiation conditions, the SnO\(_2\)-CNT nanocomposite showed excellent degradation efficiencies for both Alizarin red S (\(~97.2\%)\) and Metronidazole (\(~82\%)\) while the pure SnO\(_2\) and CNT displayed poor performances even under prolonged UV irradiation (duration: 90 min). Moreover, the SnO\(_2\)-CNT photocatalyst catalyst showed a decrease in degradation efficiencies (\(~78\%\) and 63%) under direct solar irradiation condition (duration: 120 min). The catalyst showed good stability and maintained high activity over three consecutive cycles of regeneration and reuse. The degradation performance, however, decreased a bit with each run, which may be due to the dislodgement of the heterojunction.

To investigate the simultaneous multifunctional capability, the removal efficiencies of SnO\(_2\)-CNT nanohybrids towards a mixture of contaminants like As (III), alizarin red S and Metronidazole have been examined. To a 50 mL solution of As (III) (1 mg/L), Alizarin Red S (50 mg/L) and Metronidazole (50 mg/L), approximately 1 g/L nanocomposite was added and maintaining the similar conditions as earlier, the removal efficiencies have been measured (Fig. S9 ESI). Due to competitive adsorption and substrate selectivity, a varying degree of removal efficiencies have been observed\(^{55}\). A sharp decrease in As (III) removal efficiency was evident due to competitive adsorption of organic contaminant molecules on the surface of the nanocomposite. This preferential adsorption may be attributed to the superior concentration and various polar functional groups of the organic molecules. Since the concentration of As (III) is very low as compared to the concentrations of Alizarin red S and metronidazole, their removal efficiencies were negligibly affected by the presence of As (III). Further, substrate selective activity was observed with SnO\(_2\)-CNT nanocomposite, where removal of Alizarin red S being favored more over Metronidazole. The simultaneous removal efficiencies of As (III), Alizarin red S and Metronidazole were found...
to be ~62%, ~89% and 68%, respectively which are slightly lower than their individual counterparts (~93%, 97% and 82% respectively).

**Plausible mechanism of photodegradation.** In order to evaluate the mechanistic aspect of photodegradation process, the photo induced reactive species was identified using Electron Spin Resonance (ESR) spectroscopy. The active species formed during photodegradation process was trapped using N-tert-butyl-α-phenylnitrone (PBN) and ESR measurements were carried out to detect the generation of reactive radicals under UV irradiation (Fig. 8(a)). When a sample during an intermediate stage of degradation was exposed to UV irradiation, six typical ESR signals were detected indicating the generation of superoxide anion radical (O$_2^-$). Further, PL quenching effect was utilized to investigate the effect of heterojunction structure on recombination rate of photogenerated electron-hole pairs. Commonly, high PL emission intensity refers to superior recombination of electron-hole pairs and hence lower photocatalytic performance. Figure 8(b) displayed the PL quenching effect.
spectra of Pristine SnO$_2$ NPs, and SnO$_2$-CNT nanohybrids at an excitation wavelength of 272 nm. It was evident that both the samples exhibited similar shape of emission peaks at ~350 nm which corresponds to the band-gap recombination of electron-hole pairs in SnO$_2$ generated under UV irradiation. The decrease in PL emission intensity indicated that the recombination rate of photogenerated excitons was much lower in SnO$_2$-CNT than that in pristine SnO$_2$. The decreased rate of recombination in SnO$_2$-CNT would contribute to the enhancement of photocatalytic performance.

Based on the above discussion, the mechanism of photodegradation can be explicated by the electron transfer model in SnO$_2$-CNT nanoheterojunctions under UV irradiation. The SnO$_2$ nanoparticles can interact with the suitable frequency of the incident irradiation to undergo photoexcitation. Electrons from valence band (VB) of SnO$_2$ may get transferred to the conduction band (CB), thereby, generating electron-hole pairs. However, the rapid recombination of the excitons, thus formed, lowers the activity of pristine SnO$_2$. The electron accepting capacity and the charge mobility of the CNT makes the SnO$_2$-CNT heterojunction crucial for superior synergistic performance. The relative positions of conduction band edge of SnO$_2$ (−4.2 eV vs. vacuum) and the work function of CNT (5.6 eV) supports electron transfer from SnO$_2$ (CB) to CNT$^{57}$. The relocation of electrons from CB to the conjugated $\pi$-system of the CNT inhibits the charge recombination due to the potential barrier at the interface. The prolonged existence of the excitons, because of the electronic structure of the SnO$_2$-CNT heterojunction, is responsible for greater photocatalytic performance. The electrons in the conduction band (e$_{CB}^-$) may reduce the surface oxygen (O$_2$) to generate superoxide anion radicals (O$_2$$^-$) and the holes in the valence band (h$_{VB}^+$) may oxidize the water molecules (H$_2$O) to generate OH$^-$ radicals. These highly active radicals can degrade the organic contaminants more effectively and in a very short time span. A schematic representation of the degradation process is represented as follows$^{54}$.

\[
\text{SnO}_2 + h\nu \rightarrow \text{SnO}_2(e_{CB}^- + h_{VB}^+) \\
\text{SnO}_2(e_{CB}^-) + \text{CNT} \rightarrow \text{SnO}_2 + \text{CNT}(e^-) \\
\text{CNT}/\text{SnO}_2(e^-) + O_2 \rightarrow \text{CNT}/\text{SnO}_2 + O_2^- \\
2O_2^- + 4\text{H}_2\text{O} \rightarrow 2\text{H}_2\text{O}_2 + 2\text{O}_2 \\
\text{H}_2\text{O}_2 \rightarrow 2\text{HO} \\
\text{SnO}_2(h_{VB}^+) + \text{H}_2\text{O} \rightarrow \text{HO}^- + \text{SnO}_2 \\
X + \text{HO} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \\
X + e_{CB}^- \rightarrow \text{Reduced product} \\
X + h_{VB}^+ \rightarrow \text{Oxidised product; } X = \text{contaminants}
\]

**Identification of intermediate products of photodegradation.** To identify the intermediates generated during photodegradation process, samples of both Alizarin red S and Metronidazole were collected after
25 min and 20 min of illumination respectively. The samples were analyzed using LC-MS technique and the chromatograms were furnished in Fig. S10 (ESI). The mass spectra of Alizarin red S taken at 11.1 min and 16.8 min of retention time have revealed major peaks at m/z–148.13, 104.08, 77.14 and m/z–122.08, 105.07, 94.06 and 78.02 corresponding to compound A3 and A4 respectively (Fig. S11(a,b)). From the mass spectral data, a plausible degradation pathway of Alizarin red S is represented in Fig. 9(a). The attack of photogenerated OH˙ radicals on the dye molecule have resulted the cleavage of C-C bond near C=O of Alizarin red S thereby forming phthalic acid (A1) and hydroxylated intermediate (A2)\(^58\). The polyhydroxylated intermediate (A2) being very unstable, immediately undergo cleavage to mineralization. The relatively stable phthalic acid undergo several steps of radical attack and elimination to form radical-ions of phthalic anhydride (A3), benzoic acid (A4), phenol (A5) and finally smaller carboxyls and mineralized products\(^59\).

The mass spectra of Metronidazole recorded at 4.2 min and 5.9 min of retention time revealed major peaks corresponding to compounds M1 (m/z 128.04) and M2 (m/z 98.03) (Fig. S11(c,d)). The LCMS analysis, the probable fragmentation pathway of Metronidazole is represented in Fig. 9(b). The attack of hydroxyl radical on the parent molecule (M) have resulted the elimination of lateral N-ethanol group thereby forming 2-methyl-5-nitro-1H-imidazole (M1)\(^60\). Subsequent hydroxylation and denitration yielded 2-methyl-1H-imidazole-5-ol (M2). Further degradation and ring opening of the imidazole moiety resulted in the formation of low molecular mass carboxylic acids which on decomposition gives mineralized products\(^61\).

The m/z values of all the proposed intermediates correlates well with the observed LC-MS data and hence it is evidenced that the photodegradation products of both Alizarin red S and Metronidazole are low molar mass aliphatic carboxyls, carboxylic acids, amides etc. or mineralized products.

**Antimicrobial activity of SnO\(_2\)-CNT Nanohybrids.** In this study, SnO\(_2\)-CNT nanohybrids exhibited synergistic activity against five bacterial and two fungal strains. The effect of antimicrobial susceptibility test was evaluated against standard antibiotics and summarized in Fig. S12(a,b).

The biosynthesized SnO\(_2\)-CNT nanocomposites exhibited a broad-spectrum activity with consistent microcidal efficiency against all the seven microbes, represented in Fig. S13(a,b) where 100% of the microbes
were susceptible to the sample. Among them, the sample showed highest activity against *E. coli* with ZOI 32.23 ± 0.62 mm at 0.04 M (Fig. 10). The bacterial strains were susceptible for *S. pneumoniae* at 0.01, 0.02 and 0.04 M concentrations with ZOI, 9.33 ± 0.88, 13.73 ± 0.93 and 17.47 ± 1.79 mm respectively. However, at 0.02 M lowest activities showed against *B. subtilis* with ZOI 10.17 ± 0.44 mm. In Fig. S13(b), antifungal activity of *C. albicans* displayed ZOI; 0, 13.40 ± 1.25, and 31.03 ± 0.78 mm at 0.01, 0.02 and 0.04 M respectively whereas the lab isolated fungus *A. niger* exhibited 0, 11.07 ± 1.35 and 31.03 ± 0.78 mm respectively. The results unveiled the potential activity of bio-fabricated SnO2-CNT nanohybrids towards clinically isolated pathogenic microorganisms. The plausible mechanism of microcidal activity might be the capturing of the microbial cells by quasi-aligned uniform >10 μm long nanotubes and disrupting the cell wall by SnO2 nanoparticles. Approximately 10 numbers of *E. coli* cells (each having diameter ≤1 μm) can be captured and wrapped tightly by a single CNT strand, thereby, inactivating the microorganism by rupturing the cell membranes3. The presence of SnO2 nanoparticles over the CNT surface may enhance the microcidal action by diffusing into the cell membrane and altering the cell functioning62. Moreover, the heterojunction structure may lead to the generation of reactive oxygen species, which may interact with the cell wall, thereby resulting in lethal activity towards microbes63.

**Conclusion**

In conclusion, we have synthesized SnO2-CNT nanoheterojunction using a biogenic, economically viable, environmentally sustainable strategy. Sunflower oil, a commonly available bio-precursor was utilized for the preparation of MWCNTs and were decorated with SnO2 nanoparticles using *Coccinia grandis* extracts. The various phytochemicals present in the plant extract played the role of complexing agents and no surfactants, capping agents, templates, solvents etc. were required to control growth of SnO2 nanoparticles over CNT surfaces.

The efficiency of bio-fabricated SnO2-CNT nanocomposites towards adsorption, catalysis and disinfection was exploited to provide one stop solution for the abatement water contaminants. The SnO2-CNT showed excellent efficiency of towards As (III) and a maximum Langmuir adsorption capacity of 106.95 mg/g was observed at high arsenite concentration (C0 = 1 mg/L). The nanoabsorbent was also found to be equally efficient in low arsenite concentration ranges (C0 = 100 μg/L) as it could bring down the arsenic concentration below maximum permissible limit within 120 minutes of operation time. It was found that the redox environment on SnO2-CNT surface is the active site for oxidation of As (III) to As (V) and the surface -OH groups of CNTs facilitated the adsorption process by anion exchange. One of the biggest challenges of application of CNTs in water treatment processes was their recollection after treatment. Hybridisation of CNTs with SnO2 nanoparticles has rendered the recovery of the adsorbent by gravitational sedimentation, coagulation and filtration after use. The SnO2-CNT nanoabsorbent showed effective removal in presence of interfering ions, good regeneration with NaOH and maintained a constant removal efficiency of ~86% after five consecutive adsorption-desorption cycles.

Moreover, the SnO2-CNT nano-heterojunctions have revealed their catalytic efficacy towards pollutants utilizing reduction of 4-nitrophenol as a model reaction. The manifestation of surface chemical properties of the heterojunction structure, and their ability to coerce the adsorbed nitrophenolates for a facile reaction has suggested the potential catalytic efficiency towards emerging organic water pollutants. Also, the catalyst showed...
great effectiveness towards photocatalytic degradation of model water contaminants like Alizarin red S dye and Metronidazole. Under UV irradiation, impressive degradation efficiencies of 97% and 82% were achieved for Alizarin red S and Metronidazole within 50 min of exposure. The catalyst retained good efficiency after three consecutive rounds of application, thereby, signifying potential applicability to treat waste water. Moreover, the degradation intermediates were identified using LC-MS technique and mechanism of degradation has been explained using ESR and PL studies.

Additionally, the nanocomposite displayed comparative antimicrobial action against both bacterial strains (Bacillus subtilis, Escherichia coli, Streptococcus pneumoniae etc.), and fungal strains (Candida albicans and Aspergillus niger). These multifunctional performances of SnO2-CNT nanohybrids suggest the promising applicability of hierarchical nano-heterojunctions to combat against natural, biological and man-made water contaminants.

References
1. Wang, Q. & Yang, Z. Industrial water pollution, water environment treatment, and health risks in China. Environmental Pollution 218, 358, https://doi.org/10.1016/j.envpol.2016.07.011 (2016).
2. Meinel, F. et al. The benefits of powdered activated carbon recirculation for micropollutant removal in advanced wastewater treatment. Water research 91, 97, https://doi.org/10.1016/j.watres.2016.01.009 (2016).
3. Wang, H. et al. Multifunctional and recyclable carbon nanotube ponytails for water purification. ACS applied materials & interfaces 6(12), 9426, https://doi.org/10.1021/am501811f (2014).
4. Vadahamambhi, S. et al. Arsenic removal from contaminated water using three-dimensional graphene-carbon nanotube-iron oxide nanostructures. Environmental science & technology 47(18), 10510, https://doi.org/10.1021/acs.est.3c00389 (2013).
5. Slivn, S. A. & Mitra, S. Adsorption of arsenic on multiwall carbon nanotubes. Zirconia nanohybrid for potential drinking water purification. Journal of colloid and interface science 375(1), 154, https://doi.org/10.1016/j.jcis.2012.01.063 (2012).
6. Tofighy, M. A. & Mohammadi, T. Adsorption of divalent heavy metal ions from water using carbon nanotube sheets. Journal of Hazardous Materials 185(1), 140, https://doi.org/10.1016/j.jhazmat.2010.09.008 (2011).
7. Sui, M., Xing, S., Sheng, L., Huang, S. & Guo, H. Heterogeneous catalytic ozonation of ciprofloxacin in water with carbon nanotube supported manganese oxides as catalyst. Journal of Hazardous materials 227, 227, https://doi.org/10.1016/j.jhazmat.2012.05.039 (2012).
8. Suriani, A. B. et al. Synthesis of vertically aligned carbon nanotubes using natural palm oil as carbon precursor. Materials Letters 63(30), 2704, https://doi.org/10.1016/j.matlet.2009.09.048 (2009).
9. Ghosh, P., Soga, T., Afre, R. A. & Jumbo, T. Simplified synthesis of single-walled carbon nanotubes from a botanical hydrocarbon: Turpentine oil. Journal of alloys and compounds 462(1), 289, https://doi.org/10.1016/j.jallcom.2007.08.027 (2008).
10. Nath, A., Purkayastha, D. D., Sharon, M. & Bhatchbarjee, C. R. Catalyst free low temperature synthesis and antioxidant activity of multiwalled carbon nanotubes accessed from ghee, clarified butter of cow’s milk. Materials Letters 152, 36, https://doi.org/10.1016/j.matlet.2015.03.070 (2015).
11. Suriani, A. B. et al. Vertically aligned carbon nanotubes synthesized from waste chicken fat. Materials Letters 101, 61, https://doi.org/10.1016/j.matlet.2013.03.075 (2013).
12. Duan, H., Wang, D. & Li, Y. Green chemistry for nanoparticle synthesis. Chemical Society Reviews 44(16), 5778, https://doi.org/10.1039/C4CS00363B (2015).
13. Mohanta, D. & Ahmaruzzaman, M. Tin oxide nonstructured materials: an overview of recent developments in synthesis, modifications and potential applications. RSC Advances 6(112), 11099, https://doi.org/10.1039/C6RA21444D (2016).
14. Gattu, K. P. et al. Bio-green synthesis of Ni-doped tin oxide nanoparticles and its influence on gas sensing properties. RSC Advances 5(89), 72849, https://doi.org/10.1039/C5RA13513C (2015).
15. Choudhury, R., Mahanta, C., Verma, S. & Mukherjee, A. Arsenic distribution along different hydrogeomorphic zones in parts of the Brahmaputra River Valley, Assam (India). Hydrogeology Journal 25(4), 1133, https://doi.org/10.1007/s10047-017-1584-2 (2017).
16. Sahu, T. K. et al. Efficient and rapid removal of environmental malignant Arsenic (III) and industrial dyes using re-usable, recoverable ternary Iron Oxide–ORMOSIL Graphene Oxide composite. ACS Sustainable Chemistry & Engineering 5, 5912, https://doi.org/10.1021/acssuschemeng.7b06632 (2017).
17. Zhang, G. et al. Synthesis of tin oxide nanospheres under ambient conditions and their strong adsorption of As (iii) from water. Dalton Transactions 44(41), 18207, https://doi.org/10.1039/C5DT03259H (2015).
18. Xu, T., Kamat, P. V. & O’Shea, K. E. Mechanistic evaluation of arsenite oxidation in TiO2 assisted photocatalysis. The Journal of Physical Chemistry A 109(40), 9070, https://doi.org/10.1021/jp054021x (2005).
19. Youn, S. H. & Lee, J. H. Oxidation mechanism of As (III) in the UV/TiO2 system: evidence for a direct hole oxidation mechanism. Environmental science & technology 39(24), 9695, https://doi.org/10.1021/et051148r (2005).
20. Forstier, A. H., Pereira, M. D. S. S., Rath, S. & Guimarães, J. R. Arsenic removal from water employing heterogeneous photocatalysis with TiO2 immobilized in PET bottles. Chemosphere 72(2), 319, https://doi.org/10.1016/j.chemosphere.2008.01.067 (2008).
21. Liu, H., Zhao, K. & Vecitis, C. D. Titanium dioxide–coated carbon nanotube network filter for rapid and effective arsenic sorption. Environmental science & technology 48(23), 13871, https://doi.org/10.1021/acs.est.1c03312 (2014).
22. Peng, X. et al. Ceria nanoparticles supported on carbon nanotubes for the removal of arsenate from water. Materials letters 59(4), 399, https://doi.org/10.1016/j.matlet.2004.05.090 (2005).
23. Chen, B. et al. One-pot, solid-phase synthesis of magnetic multiwalled carbon nanotube/iron oxide composites and their application in arsenic removal. Journal of colloid and interface science 434, 9, https://doi.org/10.1016/j.jcis.2014.07.046 (2014).
24. Sinha, T., Ahmaruzzaman, M., Adhikari, P. P. & Bora, R. Green and Environmentally Sustainable Fabrication of Ag-SnO2 Nanocomposite and Its Multifunctional Efficacy As Photocatalyst and Antibacterial and Antioxidant Agent. ACS Sustainable Chemistry & Engineering 5(6), 4645, https://doi.org/10.1021/acscemag.6b03117 (2017).
25. Sinha, A. K., Pradhan, M., Sarkar, S. & Pal, T. Large-scale solid-state synthesis of Sn–SnO2 nanoparticles from layered SnO by sunlight: a material for dye degradation in water by photocatalytic reaction. Environmental science & technology 47(5), 2339, https://doi.org/10.1021/acs.est.6b03413 (2015).
26. Aditya, T., Jana, J., Singh, N. K., Pal, A. & Pal, T. Remarkable Facet Selective Reduction of 4-Nitrophenol by Morphologically Tailored (111) Faceted Cu2O Nanocatalyst. ACS Omega 2(5), 1968, https://doi.org/10.1021/acsomega.6b00447 (2017).
27. Jabeen, U., Shah, S. M. & Khan, S. U. Photo catalytic degradation of Alizarin red S using ZnO and cadmium doped ZnS nanoparticles under unfilled sunlight. Surfaces and Interfaces 6, 40, https://doi.org/10.1016/j.surfint.2016.11.002 (2017).
28. Dong, S. et al. ZnSnO3, hollow nanospheres/reduced graphene oxide nanocomposites as high-performance photocatalysts for degradation of metronidazole. Applied Catalysis B: Environmental 144, 386, https://doi.org/10.1016/j.apcatb.2013.07.043 (2014).
29. Addae, E. et al. Investigation of antimicrobial activity of photothermal therapeutic gold/copper sulfide core/shell nanoparticles to bacterial spores and cells. Journal of biological engineering 8(1), 11, https://doi.org/10.1186/1754-1611-8-11 (2014).
30. Kang, S., Herzer, M., Rodrigues, D. F. & Elimelech, M. Antibacterial effects of carbon nanotubes: size does matter! Langmuir 24(13), 6409, https://doi.org/10.1021/la060531v (2008).
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Author Contributions
D.M. wrote the main manuscript text and figures. M.A. discussed results, commented, revised and corrected the whole manuscript. A.N. fabricated the samples, carried out the characterization, interpreted the data and managed figures.

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