

**Mesoporous CdO/Al<sub>2</sub>O<sub>3</sub> nanocomposite with enhanced optoelectronic properties for visible-light photocatalysis and bactericidal applications**

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## **Abstract**

Pristine  $\text{Al}_2\text{O}_3$  and CdO are known to possess poor photocatalytic activity individually. The formation of CdO/ $\text{Al}_2\text{O}_3$  heterojunction was investigated for the enhancement of photocatalytic performance. High resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) has been used to determine the crystalline feature and elemental composition of the NCs respectively. Peaks ascribed to Cd-O and O-Al-O was noted in fourier-transform infrared spectroscopy (FTIR) analysis. The NCs exhibits a high surface area ( $27.23 \text{ m}^2/\text{g}$ ) to their contributing particles which was analysed using BET analyser. The band gap energy of CdO/ $\text{Al}_2\text{O}_3$ NCs was observed to be 2.95 eV which shows a considerable energy shift from its individual particles, CdO (2.73 eV) and  $\text{Al}_2\text{O}_3$  (3.94 eV). The results displayed that the degradation efficiency of the CdO- $\text{Al}_2\text{O}_3$  NCs was enhanced 14 times than pristine  $\text{Al}_2\text{O}_3$  and 3.5 times than pristine CdO. The MB dye has showed the half life period of 80 min. TOC analysis of degraded product supported high mineralization of the pollutants. The dye degradation was driven by  $\text{OH}^\cdot$  radicals and the CdO- $\text{Al}_2\text{O}_3$  nanocomposite possessed high reusability which was confirmed by six cycle test. Growth inhibition of *E. coli*, *P. aeruginosa* and *B. subtilis* was attained by exposure to CdO/ $\text{Al}_2\text{O}_3$  NCs. The CdO- $\text{Al}_2\text{O}_3$  NCs can be a viable solution for degradation of organic contaminants effectively under natural sun light as well as an efficient antibacterial agent.

**Key words:** Photocatalysis; CdO- $\text{Al}_2\text{O}_3$ ; Nanocomposites; Antibacterial activity.

## 1. Introduction

The growing industrialization and urbanization led to a disposal of diverse range of toxic pollutants to the environment [1]. One among of them is the complex dyestuffs, which are difficult to degrade due to their high chemical stability [2]. The urge for an innovation or an efficient modification has become vital one to sort out this environmental threat. Although the current wastewater treatment is applicable, the recently emerged advanced oxidation process (AOP) is far better as it is cost efficient [3, 4, 5]. The production of hydroxyl radicals upon exposure to the light source is the basic mechanism behind this light driven catalytic process. The fabrication of photocatalyst with the metal oxide semiconductors is quite appreciable as it enhances the oxidation effectively.

$\text{Al}_2\text{O}_3$  is an insulator oxide with a wide bandgap range reported in literatures over 3.4 - 9 eV [6-9]. It has taken a lot of attention as it has a high surface area with an orderly arrangement of the nanopore structures and a non-toxic cost effective compound with high thermal stability [10]. This orderly arrangement of nanopores makes it an excellent photocatalyst and its appreciable usage in the drug delivery, biosensors and electronic devices [11]. It has been explored that nanostructure has appreciable optical properties and finds its usage in the optoelectronic devices [12]. The method by which they are synthesized also has an effect over the photocatalytic activity. These nanostructures can be synthesized through sol-gel, thermal treatment and anodization. Among them, the anodization is the refined one to fabricate with reliability [13].

As a n-type semiconductor, CdO has a bandgap of 2.2 – 2.9 eV [14]. It is a cost effective semiconductor with high electrical conductivity as it has shallow donors [15]. These shallow

donors are offered by the oxygen vacancies and the cadmium atoms. It has been widely used in the photocatalytic applications and other electrochemical devices such as the supercapacitors. Though CdO is cheapest with high surface-volume ratio yet it is less preferred due to toxicity. The size and structure of the semiconductors has direct effect over the catalytic efficiency. They can be synthesized through chemical co-precipitation method as it is a reliable cost effective one which brings forth excellent homogeneity [16]. In the present study, CdO-Al<sub>2</sub>O<sub>3</sub> photocatalytic activity compared with pristine CdO and Al<sub>2</sub>O<sub>3</sub>. *B. Subtilis*, *P. aeruginosa*, *E. coli* and *S. aureus* has been used to evaluate the antibacterial activity of NCs.

## **2. Materials and methods**

### **2.1. Materials**

*Staphylococcus aureus* (MTCC 3160), *E. coli* (ATCC 14948), *Pseudomonas aeruginosa* (MTCC 1688), *Bacillus subtilis* (ATCC 11774) were procured from MTCC and ATCC. Methylene blue dye (Purity – 99%), Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, CdSO<sub>4</sub> and CdSO<sub>4</sub> are marketed from Merck (Germany).

### **2.2. Synthesis of CdO nanoparticles**

Chemical co-precipitation was exploited for synthesis of CdO with 0.1 M CdSO<sub>4</sub> as the precursor. The precursor was dissolved in an aqueous solution and was homogenized under heat for a period of 30 min. Then 25 mL of alkaline NH<sub>4</sub>OH was added up in a drop wise manner. Then the solution was vigorously heat stirred for 30 min. The obtained precipitate has been centrifuged for 10 min at 10000 rpm. The pellets obtained after centrifugation were dried under hot air oven at 90 °C for 2 h. The obtained CdO nanoparticle was calcinated at 500 °C for 1 h.

### **2.3. Synthesis of CdO/Al<sub>2</sub>O<sub>3</sub>NCs**

The synthesis of CdO/Al<sub>2</sub>O<sub>3</sub> nanocomposite involves sonication and thermal treatment. The calcinated CdO (0.1 M) was dispersed in H<sub>2</sub>O under sonication followed by addition of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (0.05M) to the suspension. The mixture was then sonicated for 30 min. The obtained solution was heat stirred for 30 min and 25 ml of NH<sub>4</sub>OH was added to the solution alongside. The precipitate collected was centrifuged at 10000 rpm for 10 min which was followed by water and ethanol wash. The collected NCs were calcinated for 1 h at 500 °C. Al<sub>2</sub>O<sub>3</sub> was prepared in a similar procedure as that of CdO/Al<sub>2</sub>O<sub>3</sub> without CdO, followed by thermal treatment for 1 h.

#### **2.4. Characterization of nanoparticles**

The elaborated details of instrumentations are provided in the supplementary material text S1.

#### **2.5. Photocatalysis experimental arrangement**

Photocatalytic efficiency of the NCs has been estimated based on the degradation of MB under visible light irradiation. The synthesized nanocomposite (10 mg) was dispersed in 20 mL of the methylene blue dye (25 mg/L). The obtained solution was placed in dark to attain adsorption/desorption equilibrium. The setup was then shifted under 800 W halogen lamp until the absorbance decrease ceases. The degradation kinetics of the sample was studied for every 20 min. UV-spectrophotometer was used for the determination of MB degradation at 550-750 nm.

The formulae given below was used for the calculation of percentage of degradation,

$$Degradation(\%) = \frac{A_0 - A_t}{A_0} \times 100 \quad (1)$$

A<sub>0</sub> – absorbance at initial time (t=0).

A<sub>t</sub> – absorbance at time t.

#### **2.6. Reusability and scavenging**

The scavengers chosen for carrying out the experiment includes 1 mM silver nitrate for oxidizing the electron radicals ( $e^-$ ), benzoquinone for superoxide anion oxidation ( $O_2^-$ ), isopropyl alcohol for the hydroxyl radical oxidation ( $OH\cdot$ ) and EDTA for hydrogen radical oxidation ( $h^+$ ). The same protocol was followed to study photocatalytic effect of NCs under the presence of 1 mL of each scavenger separately. The leftover dye in the sample was quantified by recording the absorbance at 665 nm. The scavenging efficiency was indicated based on the degradation percentage.

The reusability of the particles was checked to determine its efficient stability and practical use aside to the exhibited activity. The activity of NCs was tested in six successive photocatalytic cycles by MB dye degradation. During each cycle, the particles were collected, washed and employed for next set of runs by injecting fresh MB dye solution.

## **2.7. Antimicrobial activity**

The bacterial species listed below were used to evaluate the antimicrobial activity of the NCs: *P. aeruginosa*, *S. aureus*, *B. subtilis* and *E. coli*. The species were cultured in LB broth for duration of 12-16 h, after which the bacterial cells were obtained upon centrifugation. Different concentrations of CdO/Al<sub>2</sub>O<sub>3</sub> (0.1, 1, 10 and 100 mg/L) were used for evaluation of antibacterial activity. Plate count method and dilution method were exploited to determine the viable cells count after 4 h of bacterial-NCs interaction.

## **3. Results and discussion**

### **3.1. Characterization**

#### **3.1.1 EDAX, SAED and HRTEM**

The structure and morphology of Al<sub>2</sub>O<sub>3</sub> loaded CdO was represented in TEM photograph (Fig. 1a). The image depicts partially rough crystal structure. Fig. 1b represents HRTEM image of Al<sub>2</sub>O<sub>3</sub> and CdO with lattice fringes. The lattice fringe with d-spacing of 0.19 nm and 0.23 nm can be seen corresponding Al<sub>2</sub>O<sub>3</sub> and CdO. SAED analysis was done to determine the crystalline nature of NCs. The result indicated the polycrystalline nature of the NCs as shown in Fig. 1a. Supplementary material fig. S1a represents the SEM image of CdO/Al<sub>2</sub>O<sub>3</sub> NCs. The SEM images of CdO and Al<sub>2</sub>O<sub>3</sub> was represented in supplementary material fig. S1b and c that represents the uneven morphology of prepared NPs. The EDAX showed three peaks corresponding to cadmium, aluminium and oxygen.

### 3.1.2 XRD

XRD was used to clarify the crystal phase of CdO/Al<sub>2</sub>O<sub>3</sub> and the XRD patterns of pristine Al<sub>2</sub>O<sub>3</sub>, CdO and the NCs CdO-Al<sub>2</sub>O<sub>3</sub> was represented in Fig. 1d. The XRD pattern of CdO could be well indexed to a cubic CdO with peaks at 2 $\theta$  value of 29.4, 35.1, 48.9, 52.0, 56.0, 64.4, 67.0, and 74.3°. The presence of Al<sub>2</sub>O<sub>3</sub> was inferred from the peaks spotted at the 2 $\theta$ value of 22.6, 25.2, 28.8, 37.4, 38.6, 45.9, 52.3, 54.4, 57.9 and 67.4 [19, 20]. On the surface of CdO, the loading of Al<sub>2</sub>O<sub>3</sub> NPs in NCs was supported by peaks corresponding to both CdO and Al<sub>2</sub>O<sub>3</sub>.

### 3.1.3 FTIR

The various bonds present in the NCs were determined by FTIR analysis based on the vibrational transition of bonds (Fig. 2a). In CdO/Al<sub>2</sub>O<sub>3</sub>, the peak denoting M-O for Al-O and Cd-O are noted at 421 cm<sup>-1</sup> [21]. The peak obtained at 1067 cm<sup>-1</sup> and 1406 cm<sup>-1</sup> denotes the non bridging M-O terminal group and O-H bending respectively [22]. In CdO, peak at 1405 cm<sup>-1</sup> has indicated O-H bond [22]. Peaks at low wavenumbers were due to M-O bond [21]. Wide peak observed at 3276 cm<sup>-1</sup> was ascribed to stretching of OH [23]. In Al<sub>2</sub>O<sub>3</sub>, Al-O-Al bond was

denoted by the bands near 650 and 967  $\text{cm}^{-1}$  and the peak obtained at 500 and 1068  $\text{cm}^{-1}$  were resulted from non-bridging Al-O terminal group [21, 22].

### 3.1.4 UV-visible-DRS

The optical bandgap of the NCs was determined by DRS analysis and Kubelka-Munk method by the below equation [24]:

$$F(R)hv^2 = A(hv - E_g) \quad (2)$$

where planck's constant, bandgap, Kubelka-Munk function and the light frequency were denoted as  $h$ ,  $E_g$ ,  $F(R)$  and  $v$  respectively. From Kubelka-Munk plot, the calculated  $E_g$  values of pure CdO,  $\text{Al}_2\text{O}_3$  NPs and CdO/ $\text{Al}_2\text{O}_3$  NCs were 2.73, 3.94 and 2.95 eV (Fig. 2b). The synergistic effect facilitates visible-light sensitization compared to pure  $\text{Al}_2\text{O}_3$ . Hence, more amount of energy from natural sunlight will be utilized by the fabricated nanohybrid.

### 3.1.5 Photoluminescence

The electron-hole pair migration in semiconductor nanohybrids was determined by photoluminescence. The CdO/ $\text{Al}_2\text{O}_3$  NCs PL spectrum was measured at excitation wavelength of 400 nm in room temperature. The result implied the decrease in PL intensity of NCs than that of their individual precursors ( $\text{Al}_2\text{O}_3$  and CdO) due to quenching mechanism. The  $e^-/h^+$  pair recombination of CdO/ $\text{Al}_2\text{O}_3$  NCs was prevented by interface formation indicating the presence of defects. Here the better photocatalytic efficiency corresponds to the enhanced lifetime of charge carriers.

### 3.1.6 $\text{N}_2$ adsorption/desorption studies

The photocatalytic performance of CdO/ $\text{Al}_2\text{O}_3$  was critically influenced by the surface area and porosity. The CdO- $\text{Al}_2\text{O}_3$ , CdO and  $\text{Al}_2\text{O}_3$  NPs possess the surface area of 27.23, 19.11 and 21.42  $\text{m}^2/\text{g}$  respectively. The high surface area of NCs provides more active sites. The mean pore

volume and mean pore size of CdO/Al<sub>2</sub>O<sub>3</sub> were 0.151 cm<sup>3</sup>/g and 3.2 nm respectively. The pore volume and size of CdO was 0.123 cm<sup>3</sup>/g and 2.4 nm and for Al<sub>2</sub>O<sub>3</sub> were 0.134 cm<sup>3</sup>/g and 2.7 nm respectively.

### **3.1.7 X-ray photoelectron spectroscopy**

Chemical states in NCs were determined using XPS analysis (Fig. 3). The major components of CdO/Al<sub>2</sub>O<sub>3</sub> NCs were observed as Al, O and Cd with no unwanted elements and contaminants. A peak at 530.2 eV was observed in O1s core level scan. A peak at 66.8 eV was noted in Al2p core level scan ascribed to Al<sub>2</sub>O<sub>3</sub> presence [27]. The core level scan of Cd3d spectrum showed two components at 403.8 eV (Cd3d<sub>5/2</sub>) and 410.6 eV (Cd3d<sub>3/2</sub>) [28].

### **3.1.8 EIS analysis**

The charge transfer in NCs was examined by EIS analysis (Supplementary material Fig. S2). The small arc radius in NCs indicates the better migration of charges than CdO and Al<sub>2</sub>O<sub>3</sub>. The results suggest us that the NCs have effective e<sup>-</sup>/h<sup>+</sup> migrations.

## **3.2. Photocatalytic activity**

### **3.2.1 Dye degradation**

During photocatalysis, the MB dye degradation in presence of CdO-Al<sub>2</sub>O<sub>3</sub> under visible light irradiation was recorded for 120 min. Fig. 4a depicts the MB spectra that possess the absorption maximum at 665 nm [29, 30, 31]. The chromogenic group in MB dye resulted in the absorption at 665nm in the visible light spectrum. The reducing absorbance value of  $\lambda_{\max}$  directly corresponds to the decolourization of cationic MB dye indicating the degradation of MB chromophore.

### **3.2.2 Half-life calculation**

The intersection of graph plotted between the time and  $C_t/C_0$  and  $1-C_t/C_0$  was used to evaluate the half life of MB dye and it is represented in Fig. 4b. The  $t_{1/2}$  of MB was found to be 80 min in the presence of NCs.

### 3.2.3 Synergetic effect

The degradation efficiency of CdO/Al<sub>2</sub>O<sub>3</sub> was compared with pristine CdO and Al<sub>2</sub>O<sub>3</sub> to ensure the enhanced synergetic effect of fabricated CdO/Al<sub>2</sub>O<sub>3</sub>. In fig. 5a, the combined effect of NCs as CdO-Al<sub>2</sub>O<sub>3</sub> was observed; this indicated the better efficiency of NCs than individual CdO and Al<sub>2</sub>O<sub>3</sub> in dye degradation. The kinetic rate constant of CdO/Al<sub>2</sub>O<sub>3</sub> was observed to be  $14 \times 10^{-3}$  which was 3.5 times higher than CdO ( $4 \times 10^{-3}$ ) and 14 times higher than the pristine Al<sub>2</sub>O<sub>3</sub> ( $1 \times 10^{-3}$ ) (Fig 5b). The degradation percentage of CdO-Al<sub>2</sub>O<sub>3</sub>, CdO and Al<sub>2</sub>O<sub>3</sub> are represented in Fig. 5c, obtained after 220 min of visible light irradiation. The degradation percentage of CdO-Al<sub>2</sub>O<sub>3</sub> was 97.3%, and it was higher compared to CdO (64%) and Al<sub>2</sub>O<sub>3</sub> (27%) which might be the result of increased photocatalytic activity of NCs by enhanced light absorption. The heterojunction formation results in reduced recombination of photogenerated e<sup>-</sup>/h<sup>+</sup> pair [33]. Further, total organic carbon (TOC) analyzer was used to measure TOC of the treated solution to provide some mineralization results as indicated in following equation:

$$TOC \text{ removal (\%)} = 100 \times \left( 1 - \frac{[TOC]_t}{[TOC]_0} \right)$$

where  $[TOC]_0$  and  $[TOC]_t$  are the TOC values of the solution in mg L<sup>-1</sup> at time 0 and time  $t$ , respectively. Similar to decolourization (97.3%) in 160 min, high TOC removal (87%) was attained for CdO/ZnFe<sub>2</sub>O<sub>4</sub> NCs. MB molecules come in contact with ·OH and oxidize incompletely that may lead to the production of several intermediates. The high TOC removal indicates the high level of mineralization of MB under visible light irradiation.

### 3.2.4 Influence of NCs dosage

The effect of NCs in dye degradation was evaluated by using varying amount of photocatalyst from 5 to 20 mg. It has been observed that the increase in NCs amount enhanced the degradation efficiency which is represented in the supplementary material in fig.S3a. The increasing concentrations of the NCs quantity correspond to the better degradation of the MB dye. The active sites in the NCs played a vital role in degradation of MB dye. More active sites were observed when the concentration of MB (25 mg/L) was kept constant with an increasing NCs quantity. Here, the path length remained constant whereas the number of photons reaching to the NCs surface increased as the colour intensity of the MB is same. This paved the way for more generation of free radicals.

### 3.2.5 Kinetics study

Several degradation processes are understood based on the degradation kinetics using Langmuir and Freundlich isotherm. Langmuir isotherm is the best method to understand active sites with same energy whereas the available sites with unequal energies and heterogeneity are indicated by Freundlich isotherm [34]. At weak absorbance and lower concentration of MB, Langmuir Hinshelwood equation (L-H) is exploited for evaluating the reaction kinetic [35]. The simplified L-H given as follows:

$$R = \frac{dC}{dt} = -kC \quad (3)$$

The above equation is integrated to:

$$\ln(C) = -kt + \ln(C_0) \quad (4)$$

where  $k$  and  $C_0$  denotes the first order kinetics reaction constant and the initial concentration of MB respectively. The graph plotted between  $\ln C_t/C_0$  and time (0 to 220 min) was used to evaluate first order kinetics constant for varied NCs quantity [36]. As per the literatures,

experimental data with high regression coefficients ( $R^2 = 0.923$  to  $0.962$ ) for varied NCs concentration best suits for Langmuir isotherm model [37, 38]. MB molecules have an equal affinity on the active sites of NCs, hence at the time of absorption, MB could provide a monolayer coverage on surface of NCs. The  $k$  value was found to be  $18 \times 10^{-3}$ ,  $17 \times 10^{-3}$ ,  $14 \times 10^{-3}$  and  $9 \times 10^{-3}$  for varying quantity of NCs as 20, 15, 10 and 5 mg respectively (Supplementary material Fig. S3b). The rate constant of MB in the absence of CdO/Al<sub>2</sub>O<sub>3</sub> has been obtained as  $0.9 \times 10^{-3}$  under irradiation of visible light, which proves that the dye degradation was carried by the action of NCs indeed.

### **3.2.6 Stability and reusability**

In dye degradation, the particle stability is a critical factor as the photocatalytic activity. The similar protocol is followed on subsequent repeated cycles for degradation. The degradation percentage of MB was calculated on each cycle (fig 6a). The degradation percentage of MB for the 1<sup>st</sup> run was observed to be 97.3%, which was sustained with a negligible difference even after the 6<sup>th</sup> run (96.6%), indicating the high stability and reusing capacity of CdO-Al<sub>2</sub>O<sub>3</sub>. In addition, the structural stability of the photocatalyst was monitored by performing XRD, TEM and XPS analysis of recovered NCs. The XPS showed negligible change in the pattern and intensity that ensured that the particles were free from photo-corrosion. Stability was further confirmed by XRD analysis of the recycled NCs irradiated under light after photocatalysis. The negligible changes in peak indicate the photostability and non-corrosive nature of particles (Supplementary figure S4a). Further the TEM analysis (Supplementary figure S4b) verified that there was no change in morphology of NCs.

## **3.3 Possible mechanism**

### **3.3.1 Scavengers study**

The reaction mechanism of the dye degradation was evaluated by scrutinizing the role of each reactive species. The available free electrons were quenched by the scavengers and thus declining the photocatalytic activity. Higher reduction in the degradation activity corresponded to the vital role of a particular radical. In this report, EDTA, AgNO<sub>3</sub>, isopropyl alcohol, and p-benzoquinone were exploited to quench the h<sup>+</sup>, e<sup>-</sup>, OH<sup>-</sup> and O<sub>2</sub><sup>-</sup> respectively. In fig. 6b reduction in degradation has been observed in the order of isopropyl alcohol > EDTA > AgNO<sub>3</sub> > p-benzoquinone. It indicates the ·OH as a major contributor followed by h<sup>+</sup> and e<sup>-</sup>.

### 3.3.2 CdO catalyst performance

Due to the narrow bandgap of CdO (2.73 eV), it is active in visible region (Fig. 7 Scheme 1) [39]. The photoinduced e<sup>-</sup> excited from the Valence band (VB) of CdO to the conduction band (CB) under visible light irradiation. Nevertheless, as a single system photocatalyst, the photoinduced e<sup>-</sup>/h<sup>+</sup> pair recombines faster. This results in decreased lifetime of charge carriers. This makes fewer e<sup>-</sup>/h<sup>+</sup> pairs available for the photo-degradation of dye. The h<sup>+</sup> react with water to generate free radical (OH<sup>·</sup>). The MB dye is attacked and oxidized by generated radicals with the release of H<sub>2</sub>O and CO<sub>2</sub>.

### 3.3.3 Al<sub>2</sub>O<sub>3</sub> catalyst performance

Al<sub>2</sub>O<sub>3</sub> possess relatively large bandgap (3.94 eV) that makes it active in UV region [40]. The Under visible-light irradiation, there is no photo-excitation of e<sup>-</sup> in Al<sub>2</sub>O<sub>3</sub>. It resulted in reduced photocatalytic performance compared to CdO under visible light (Fig. 7 Scheme 2).

### 3.3.4 Photocatalytic activity of CdO/Al<sub>2</sub>O<sub>3</sub> NCs

The schematic representation was photocatalysis mechanism is represented in (Fig. 7 Scheme 3). The bandgap of 2.95 eV facilitates visible light photocatalysis with enhanced utilization of energy [41]. The e<sup>-</sup> jumps from (VB) valance band to the (CB) conduction band of CdO under

visible light irradiation, which leaves behind an  $h^+$  in VB of CdO. Although  $Al_2O_3$  CB potential is higher, the photo-excited  $e^-$  from CdO tends to migrate to low lying  $Al_2O_3$  defect levels. Owing to its amorphous nature, the  $Al_2O_3$  act as electron sink as it contains more number of defect sites [42]. This aids  $e^-/h^+$  pair separation [8]. The role of  $Al_2O_3$  is to provide support and not used to facilitate activity in visible region. The position of CB in  $Al_2O_3$  does not be able to participate in charge transfer. Therefore,  $Al_2O_3$  alone does not give any activity. On contrary, CdO with a small bandgap is sensitive in the visible region.  $Al_2O_3$  was selected as support due to its low cost, non-toxic and stable nature [43]. Further, electric field induced between n-type CdO and p-type  $Al_2O_3$  heterojunction, the photo-generated  $e^-/h^+$  separations are made quite comfortable. This interfacial charge transfer increases the life time of  $e^-/h^+$ . Hence, photocatalytic activity is enhanced for NCs. The enriched  $h^+$  accumulation on VB of CdO reacts with available water to form radicals. The formed  $OH\cdot$  radicals subsequently degrade the dye molecules by releasing  $CO_2$  and  $H_2O$  [44].

### 3.4 Anti-bacterial activity

In Fig. 8a, the role of NCs against *S. aureus*, *B. subtilis*, *P. aeruginosa* and *E. coli* as an antibacterial agent has been shown. Varying NPs concentration (0.1 to 100 mg/L) has been studied for toxicity. It has been observed that the toxicity increased in accordance with the NPs concentration. As compared to *S. aureus*, *P. aeruginosa* and *B. subtilis*, the *E. coli* has been observed to be more sensitive. After NCs interaction, *P. aeruginosa*, *S. aureus*, *B. subtilis* and *E. coli* growth was inhibited to 71, 55, 46 and 87% for 10 mg/L and all species showed 100% growth inhibition for 100 mg/L NCs concentration. The toxicity of individual particle (CdO and  $Al_2O_3$ ) exhibited the same tendency but with lower toxicity in comparison with NCs. (Fig 8b and c) This in turn indicated the higher ROS generation in NCs. When subjected to 100 mg/L of

nanoparticle, CdO toxicity upon *P. aeruginosa*, *S. aureus*, *B. subtilis* and *E. coli* were observed as 73, 46, 35 and 84% respectively and for Al<sub>2</sub>O<sub>3</sub> it was 49, 28, 23 and 67% respectively. As gram negative bacteria with a thin peptidoglycan wall, *E. coli* showed enhanced penetration of NCs leading to its increased toxicity [46]. The nano-sized particles led to generation of more amounts of ROS species. ROS interaction leads to damage in cellular proteins that induce apoptosis. When NPs incorporate cytoplasm, they can induce plasma membrane damage alters cell permeability. Further the NPs penetrate inside the nucleus which may lead to DNA damages via point mutations. This results in arrested cell division. Therefore the growth is inhibited. Also, positive ions release from NPs, if any will interact with the negatively charged bacterial cell membrane. This action prohibits the permeability of the proteins by entering into the cell membrane ultimately lead to bacterial death [47].

#### **4. Conclusion**

The photocatalytic activity of CdO NCs was enhanced after fabrication of Al<sub>2</sub>O<sub>3</sub>. The NCs was prepared by chemical co-precipitation method. XRD, TEM, FTIR, XPS and BET analysis were used for the characterization of NCs. The kinetic rate constant was  $14 \times 10^{-3}$  for NCs which was 14 times higher than Al<sub>2</sub>O<sub>3</sub> ( $1 \times 10^{-3}$ ) and 3.5 times higher than CdO ( $4 \times 10^{-3}$ ), respectively. The NCs also exhibited excellent antimicrobial activity against all the mentioned bacteria. The degradation exhibited first order kinetic trend. The hydroxyl radical served a vital role in the mechanism of dye degradation. Even after six cycles, the NC expressed good stability and reusability.

#### **Acknowledgement**

Authors sincerely thank the management of Bannari Amman Institute of Technology, Tamil Nadu for providing the necessary facilities for carrying out this work.

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### Figure captions

**Figure 1.** Characterization of CdO/Al<sub>2</sub>O<sub>3</sub> NCs: (a) TEM (inset – SAED), (b) HRTEM, (c) EDAX and (d) XRD pattern of CdO/Al<sub>2</sub>O<sub>3</sub>.

**Figure 2.** (a) FT-IR spectrum, (b) Kubelka Munk function vs energy plot and (c) CdO/Al<sub>2</sub>O<sub>3</sub> photoluminescence emission

**Figure 3.** Full-scan XPS spectrum and corresponding deconvoluted peaks in the high resolution for O1s, Al2p and Cd3d elements of NCs.

**Figure 4.** (a) UV-vis spectral change of MB dye after addition of CdO/Al<sub>2</sub>O<sub>3</sub>. (b) The plot of C/C<sub>0</sub> and 1-(C/C<sub>0</sub>) versus time.

**Figure 5.** (a) The plot of C/C<sub>0</sub> versus time, (b) the plot of lnC<sub>0</sub>/C versus time and (c) degradation (%) for CdO/Al<sub>2</sub>O<sub>3</sub>, CdO and Al<sub>2</sub>O<sub>3</sub>.

**Figure 6.** (a) Photocatalytic performance of CdO/Al<sub>2</sub>O<sub>3</sub> during six successive cycles and (b) Effect of different scavengers on photocatalytic performance.

**Figure 7.** Schematic representation of photocatalytic mechanism of CdO/Al<sub>2</sub>O<sub>3</sub>, CdO and Al<sub>2</sub>O<sub>3</sub>.

**Figure 8.** The antimicrobial influence of (a) CdO/Al<sub>2</sub>O<sub>3</sub>, (b) CdO and Al<sub>2</sub>O<sub>3</sub> on *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *Escherichia coli* and *Bacillus subtilis*