Surface modification of Ag–CdO with polyaniline for the treatment of 3',3''',5',5'''-tetrabromophenolsulfonphthalein (BPB) under UV-visible light irradiation

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ABSTRACT

The quality of natural waters could be deteriorated by organic pollutants which can impose a risk to the ecosystem as well as human health. These organic contaminants are often needed to be removed with adequate techniques. In this study, the photocatalysts of CdO nanoparticles (NPs), Ag–CdO nanocomposites (NCs), and Ag–CdO/polyaniline (PANI) NCs were successfully synthesized in order to investigate their degradation performance against 3',3''',5',5'''-tetrabromophenolsulfonphthalein (bromophenol blue, BPB) dye. The crystal structure, functional groups, morphological change, and degradation efficiency of as-synthesized photocatalysts were characterized using XRD, FTIR, SEM and UV-Visible spectroscopic techniques respectively. The SEM result showed that the surface morphology of the nanomaterials seems the agglomerated micron-scaled grains as compared to CdO NPs and Ag–CdO NCs. The FT-IR spectrum demonstrated the absorption peaks which strongly confirmed that Ag–CdO NCs surface was successfully modified with PANI. The highly sharp and intensive XRD patterns attributed to the cubic structure for CdO NPs and Ag–CdO NCs structures with decreasing crystalline size from 40.58 nm to 36.43 nm and 10.29 nm upon CdO NPs photocatalyst surface treatment with Ag metal and PANI. The decreased particle size brought about to narrow the bandgap from 2.76 eV to 1.61 eV and 1.58 eV respectively. Among the synthesized photocatalysts, Ag–CdO/PANI NCs exhibited the best degradation efficiency of 97.30 % at pH 6, 10 ppm concentration of dye, 0.140 g of catalyst load, and 210 min irradiation time. Moreover, the kinetics of
1. Introduction

Water is one of the most important natural resources for human beings and other biological organisms. However, as a result of various human activities such as industrialization and urbanization the water quality of aquatic ecosystem is deteriorating all over the world, which further influences human health as well as other living organisms including aquatic life. Aquatic ecosystems receive multiple types of organic and inorganic contaminants due to the aforementioned human activities. Organic dyes are among the common water pollutants which could be discharged from the textile, leather, paper, cosmetics, and printing industries [1, 2]. Some of these contaminants are pharmaceuticals, personal care products, pesticides, disinfection by-products, and synthetic chemicals such as dyes [3]. The list is ever-expanding due to the advanced instruments to detect contaminants in water bodies and by-product formed during wastewater treatment processes [4] in the concentrations range of $\mu$g/L to ng/L [5]. Organic dyes are non-biodegradable, highly toxic to aquatic organism, and carcinogenic to humans. Textile industry uses colored dyes such as acid red 14, methylene blue, reactive blue 19, remazol red RR and methyl orange [6]. Nowadays, $\text{ZnO}$, $\text{Fe}_2\text{O}_3$, $\text{CdO}$, $\text{CdS}$, $\text{ZnS}$, and $\text{NiO}$ are the most promising catalysts as they incorporate CdO NPs under light irradiations for the degradation on crystal violet (CV). The study indicated that, an addition of ceramic and oxidative polymerization for the photodegradation against MB and $\text{CdO}$ NPs and similar oxides suffer from decreasing recombination times between the electron-hole pairs [2]. Such challenges could be avoided through a combination of various nanostructured semiconductors in order to produce a nanocomposite so that the mutual transfer of electrons-holes pairs from one to other semiconductor [2].

Wang et al. [18] synthesized a series of TiO$_2$ doped with ceramics by sol-gel method and applied them for the degradation of rhodium B (RhB) under UV light irradiation. The result showed that the modification of TiO$_2$ by ceramic not only prevents phase transfer, but also provides facile recovery of the catalyst after use. Suarez-Parra et al [19] described that the combination of TiO$_2$ nanoporous with CdO nanostructures has improved the photocatalytic degradation of blue azo-dye under light irradiation. The photocatalytic activity of CdO–NiO nanocomposite has also investigated. According to the study, CdO having a small bandgap was mixed with a wide bandgap NiO semiconductor and results in new bandgap formation due to the interaction of their conduction or valence bands. In the combination of CdO with NiO, an electric field can be created at the interface that enhanced the migration of photoinduced charge carriers and photoinduced electron-hole pairs are efficiently separated to slowdown the recombination phenomena [2].

Ag metal is used as a dopant and is preferred for its easily oxidizable nature and brings CdO nanoparticles to considerable bandgap [20]. The preparation of doped CdO nanomaterials is possible and common via successive ion exchange, chemical reaction, hydrothermal methods, and sonochemical and sol-gel techniques. Mohanraj, K. et al [21] found that the synthesized particles were cubic in structure and decreased in particle size with the increase concentrations of dopant. Recently, the conjugated polymers (CPs) become the most important class of semiconductor materials with conceivable applications in photocatalytic degradation under UV-Vis light [22]. Furthermore, CPs are applicable in solar cells, fuel cells and rechargeable lithium batteries [23, 24]. The wide range of CPs’ application is due to their unique behavior such as low-cost, facile synthesis, excellent electrical and electrochemical activity, high carrier mobility and mechanical properties [25]. The hybrid nanomaterials based on CPs such as polyaniline (PANI), polypyrrole, polystyrene, poly (3-hexylthiophene) and other semiconductors can be used for the degradation of water pollutants [26]. PANI is one of the most commonly used polymers as a result of its decent stability, low synthesis cost, non-toxicity, good optical and electrical properties. The PANI hybrid nanocomposites are photocatalytically active under UV-Vis because of HOMO-LUMO excitation and increased electron-hole pairs separation [22]. The incorporation of such CPs into NPs is in order to stabilize or cap the surface of catalyst. Gulce et al [27] developed PANI/CdO NCs and evaluates the catalytic activity of PANI incorporated CdO NPs under light irradiations for the degradation on methylene blue (MB) and malachite green (MG) dyes. The report indicated that the apparent rate constant ($k_{app}$) values of the NGS are higher than the bare PANI.

TiO$_2$ nanoparticle has been modified by ceramic and polymer (n-TiO$_2$/C/PANI) using sol-gel method accompanied by in-situ chemical oxidative polymerization for the photodegradation against MB and crystal violet (CV). The study indicated that, an addition of ceramic and polymer to TiO$_2$ enhances its photocatalytic efficiency under visible light illumination. The degradation efficiency could be associated with high conductivity of the polymer, decreasing in the degree of agglomeration and the smallness of the particles size [28].

Bu and Chen [29] investigated PANI/Ag/Ag$_2$PO$_4$ heterostructure formed through in-situ deposition of Ag$_2$PO$_4$ nanoparticles on PANI chains and concluded that the nanocomposite had superior photocatalytic ability and stability because of an improved interfacial
electric field resulting in profound electron-hole separation and migration efficiency. The Authors found the formation Ag⁺ on the PANI surface because of PANI-assisted reduction of Ag⁺ to Ag₀, which played an important role in the separation of photogenerated electron and holes. Similarly, PANI/TiO₂ nanocomposites was successfully synthesized via a hydrothermal method and followed by a low-temperature calcination treatment process. Consequently, this nanocomposite exhibited the higher photocatalytic activity and stability than bare TiO₂ and TiO₂-Nₐ toward the liquid-phase degradation of methylene orange (MO) under UV and visible light irradiation. In general, the photocatalysis process involves three major steps: light absorption by photocatalyst, separation of photogenerated electron, and the interfacial catalytic redox reactions [30]. When UV/Visible light irradiates CP such as PANI, the charge-transfer excitation from the HOMO to LUMO can lead to the excited photogenerated electrons transfer to the conduction band of semiconductor oxide and it accepts the holes from the valence band of photocatalyst. The lifetime of charge carrier over the photocatalyst is prolonged, which is comfortable with the formation of a large number of radical species with strong oxidation capability, such as OH⁻ and O₂ species which further react with pollutant and degrade to the environmentally friendly compound such as H₂O and CO₂ [31].

This study is limited to the synthesis of CdO NPs, Ag–CdO NPs and Ag–CdO/PANI NCs using sol-gel method, characterization of the as synthesized nanomaterials with the help of FT-IR, XRD, SEM and UV-VIS spectroscopic techniques, investigating the effect of irradiation time, pH, initial concentration of dye and catalyst load on photocatalytic degradation of BPB dyes with its degradation mechanisms. It is anticipated that, this research work could provide valuable information about the optimum working conditions through preparing the cost effective and adequate alternative photocatalysts for industrial wastewater treatment.

2. Methodology

2.1. Experimental site

The synthesis of CdO NPs, Ag–CdO NCs, and Ag–CdO/PANI NCs using UV-Vis spectrophotometer were conducted in Chemistry Research Laboratory of Ambo University, Ethiopia. To verify the molecular and crystalline structure of the as-synthesized photocatalysts, ATR-FTIR and XRD measurements were conducted at the National Taiwan University of Science and Technology, Advanced Electrochemical Laboratory, Taiwan. The morphology of photocatalysts were measured using SEM at Addis Ababa Science and Technology University, Materials Science and Engineering Laboratory, Ethiopia.

2.2. Apparatus and instruments

The crystal structures of CdO NPs before and after surface modification with Ag and PANI were examined by in-house X-ray diffractometer (XRD, D2 phaser, Bruker). The determination of functional groups of as-synthesized photocatalysts was studied with help of Fourier-transform infrared spectroscopy (FTIR, JASCO FT/IR-6700) in the wave number from 400-4000 cm⁻¹. The absorbance of the samples was determined using a UV-Visible spectrophotometer (Sunny Uv-vis spectrophotometer, UV-7804 Cprint). The morphology of the photocatalysts was examined using scanning electron microscope (SEM) (JCM-6000PLUS Bench Top SEM, JEOL, Japan). Muffle furnace (PYRO THERM FURNACES), centrifuge (Centri. model 800, China), round bottom flask, volumetric flask, conical flask, beaker, magnetic stirrer, aluminum foil, measuring cylinder, desiccators, refrigerator (MRF-451), drying oven (DHG-9070A), funnel, filter paper, electronic balance, burette, pipette, the crucible, iron stand, glove, spatula, pestle and mortar and pH meter (CPI-501) were apparatus used for this studies.

2.3. Chemicals and reagents

All the chemicals and reagents are analytical grade reagents which are used without further purification. Briefly, cadmium acetate dihydrate (Cd(CH₃COO)₂.2H₂O, oxalic acid dihydrate (COOH)₂.2H₂O, Ethanol (CH₃CH₂OH) (99.8%, FDR-626031), 2% (w/w) AgNO₃ (99.9%, Alpha Chemical, India), aniline (C₆H₅NH₂) (99%, Nice Chemical, China), sulfuric acid (H₂SO₄), hydrochloric acid (HCl), distilled water (DI), ammonium per sulfate (APS) (98%, Sisco Research Lab, India) were chemicals used to prepare NPs and NCs. 3,3',5,5'-tetrabromophenol sulfonphthalein (BPB) (Scheme 2.1) is used as the model organic dye intended for investigating photocatalytic activities of CdO NPs, Ag–CdO NCs, and Ag–CdO/PANI NCs.

2.4. Preparation of CdO NPs

CdO NPs was prepared by sol-gel method via dissolving 13.32 g of Cd(CH₃COO)₂.2H₂O in 100 mL ethanol (Solution A) under continuous stirring for 30 min. Another solution was prepared in a separate beaker by dissolving 2.51 g of (COOH)₂.2H₂O in 40 mL of ethanol (Solution B). Then after, Solution A has slowly added to Solution B through continuous stirring for 3 h to get a new solution (Solution C). The resulting white solid has settled down for 24 h, filtered by Whatman 540 filter paper, and washed by DI water and ethanol. Then, the formed precipitate has dried at 80 °C for the period of 12 h followed by calcination at 500 °C for 3 h in a muffle furnace. After calcination, the samples are grinded using mortar and pestle which then keep in desiccators for further characterization and degradation [2].

2.5. Synthesis of Ag–CdO NCs

Once solution C was prepared, it was stirred continuously for 2 h which then form the white sol. To this sol, 2% (w/w) AgNO₃ was added and stirred for additional 3 h. The obtained sol-has dried at 80 °C till the xerogel is formed. The xerogel then calcinated at the temperature of 500 °C in muffle furnace at 5 °C/min heating rate for 2 h. Then, the samples are ground and kept in desiccators for further characterization and degradation of dye [21].

2.6. Synthesis of PANI

PANI has synthesized through the in-situ polymerization method via dissolving 0.1 mL of the monomer (aniline) in 90 mL of 1 M HCl solution. The oxidant solution has prepared via dissolving 0.25 g of APS in 1M HCl which the polymerization reaction takes place at 0 °C for 24 h. The molar ratio of monomer to APS was 1:1. The precipitated samples are centrifuged and washed successively three times with water and ethanol followed by drying at 70 °C for 24 h [27]. The polymerization mechanism of

Scheme 2.1. Molecular structure of 3,3',5,5'-tetrabromophenolsulfonphthalein (BPB) dye.
PANI (conductivity \( \approx 30-200 \text{ S\,cm}^{-1} \) and bandgap \( \approx 2.8 \text{ eV} \)) has indicated in Scheme 2.2 [32].

2.7. Synthesis of Ag-CdO/PANI NCs

The Ag-CdO/PANI nanocomposite was prepared by in-situ polymerization of the monomer with Ag-CdO NCs in the APS solution. First, 1 g of Ag-CdO NCs is added to 100 mL H\(_2\text{SO}_4\). Then, a 1 mL of monomer has added to the first solution dropwise through continuous stirring for 30 min till the silvery-white color (second solution) is formed. Further, 2 g of APS oxidant in 100 mL H\(_2\text{SO}_4\) solution has added to the second solution dropwise under stirring for 30 min. Then, the dark green color solution is observed which confirms the formation of Ag-CdO/PANI NCs and the formed NCs was kept at room temperature for 24 h. The solution was filtered on the next day and washed with DI water till the filtrate converted to colorless. The precipitate has filtered and dried at 80°C for 6 h. The NCs product was collected in a sample holder and was kept in desiccators for further activities [21] as indicated in Scheme 2.3.

2.8. Characterization of photo-catalysts

The crystalline structural measurements for photocatalysts have performed using XRD. Their crystallite sizes are calculated using Debye-Scherer’s Eq. (2.1):

\[
D = \frac{0.9\lambda}{\beta \cos \theta}
\]

where \( \lambda \) - wavelength of radiation used in Cu K\(_\alpha\) (0.15406 nm), \( \beta \) - full width at half-maximum of the peak, and \( \theta \) - angle at the position of the maximum peak (in rad) [6]. The surface morphology of each sample has observed using an SEM.

The FT-IR spectrum CdO-based photocatalysts are recorded with ATR-FTIR in 400–4000 cm\(^{-1}\) wavenumber. The UV-Vis absorption and band gap (calculated using equation 2.2) of the synthesized photocatalyst were determined using a UV-Vis spectrophotometer equipped with a quartz tube scanning over 200–800 nm wavelength.

\[
E_g = \frac{hc}{\lambda}
\]

where \( h \) - Plank’s constant (6.62 \( \times \) \( 10^{-34} \text{ J\,s} \)), \( c \) - speed of light (3.0 \( \times \) \( 10^8 \text{ m\,s}^{-1} \)) and \( \lambda \) is irradiation light wavelength in nm.

2.9. Degradation of BPB

For the photocatalytic degradation study of the model dye (BPB) samples (Scheme 2.1) was used; the photocatalysts are CdO NPs, Ag-CdO NCs, and Ag-CdO/PANI NCs and evaluated under UV-Visible irradiation. Different amount of photocatalysts (0.10, 0.12, 0.14 and 0.16 g) are added to 250 mL BPB solution of 10, 15, 20 and 25 ppm initial
concentration. The suspension is constantly stirred for 30 min in a dark place to allow the formation of adsorption-desorption equilibrium condition. During light irradiation process, the photoreactor was maintained under magnetic stirring for achieving a homogeneous suspension to promote the adsorption of dye on the surface of photocatalysts. A light-emitting diode (LED) lamp that predominantly emits with the definite power of 30 W and 220 V was employed as the source of visible radiation and placed parallel to the photo-reactor. The λ_{\text{max}} of BPB in aqueous solution was analyzed by UV–Vis instrument with full scan mode and the optimum absorbance (λ_{\text{max}}) was observed at 592 nm which is comparable with the reported values [33]. Further, the signals were collected at every 30 min in order to determine the degradation efficiency of BPB using the following equation [34]:

\[
\% \text{ of degradation} = \frac{A_0 - A_t}{A_0} \times 100
\]

where \(A_0\) and \(A_t\) - the absorbance of BPB at initial stage and at the reaction time \(t\).

2.10. Degradation kinetic

The BPB degradation kinetic was studied by using the initial concentrations of 10, 15, 20, and 25 ppm. The catalytic activity of as-synthesized photocatalysts under UV-Vis light can be evaluated by comparing the apparent rate constants [35]. The degradation kinetics is also described using pseudo-first order (eq. 2.4) and pseudo-second order kinetics (eq. 2.5):

\[
\ln \left( \frac{A_t}{A_0} \right) = K_{\text{app1}} \cdot t
\]

(2.4)

\[
\frac{1}{A_t} = \frac{1}{A_0} + K_{\text{app2}} \cdot t
\]

(2.5)

where \(A_0\) and \(A_t\) - the absorbance of BPB at initial and time \(t\), \(K_{\text{app1}}\) and \(K_{\text{app2}}\) are apparent rate constants for pseudo-first and second-order reactions respectively [36].

3. Results and discussions

3.1. Analysis of surface morphology

Figure 1 (a - d) represents the SEM images of CdO NPs, Ag–CdO NCs, PANI, and Ag–CdO/PANI NCs. The morphology of as-synthesized photocatalysts is vital to determine whether the CdO is successfully modified with organic and inorganic additives. The image in Figure 1 (a) signifies that CdO NPs appeared a small and agglomerated particles with regular surface of spherical shapes which agree with the prior report [37]. Figure 1 (b) showed the nanoparticle formed was also small in size and similar shapes with more interconnected particles as compared to CdO NPs. Figure 1 (c) exhibited that pure PANI possesses much agglomerated grainy structure. Each particle is well intersected indicating that there is sufficient binding energy among neighboring molecules. The surface of the nanocomposite (Figure 1 (d)) seems to be composed of agglomerated nano-scaled grains which recognized the successful surface modification of Ag–CdO NCs with PANI.

3.2. Analysis of functional group

Figure 2 represents ATR-FTIR spectra of CdO NPs, Ag–CdO NCs, PANI, and Ag–CdO/PANI NCs between 400–4000 cm\(^{-1}\) vibration numbers. The spectrum corresponding the PANI (black line) exhibits the broadband at 3387–3240 cm\(^{-1}\) which represents N–H vibrations of polymer and the bending of N–H at 1607 cm\(^{-1}\) [38]. Absorption peaks observed at 1503 cm\(^{-1}\) corresponds to the bending mode of C=O in aromatic ring structures while the peak at 813 cm\(^{-1}\) is ascribed to the C–H out-of-plane bending in aromatic ring. The peak at 1314 cm\(^{-1}\) is assigned to C–N stretching of the secondary amine unit of PANI. The peak
corresponding to the wagging vibration of pure CdO NPs (red line) is detected at 1363 cm\(^{-1}\). The formation of the absorption band at 530 cm\(^{-1}\) represents Cd–O stretching vibrations while absorption bands around 1222 and 1736 cm\(^{-1}\) are the distinctive bands of CdO NPs which agree with the spectra investigated by [2]. The ATR-FTIR spectra of Ag–CdO NCs (blue line) showed the weak band near 530 cm\(^{-1}\) is attributed to stretching vibrations of Cd–O bond while the new absorption peak at 857 cm\(^{-1}\) represents the formation of Ag–O bond and confirms the proper doping of Ag in CdO nanoparticles [21].

The weak band observed between 1227 and 1400 cm\(^{-1}\) corresponds to O–H functional group. The slightly increased absorption peaks around 1743 cm\(^{-1}\) signify the absorption band of CdO NPs after Ag doping [2]. The spectrum for Ag–CdO/PANI NCs (green line) at 558 and 857 cm\(^{-1}\) shows the absorption peak corresponds to CdO and the formation of Ag–O bond in Ag-doped CdO [39]. The absorption band at 1023 and 1211 cm\(^{-1}\) corresponds to in-plane deformation of C–N and in-plane vibration of C–H in PANI structure. The peaks that appeared at 1314, 1363, 1607, and 3421–3222 cm\(^{-1}\) correspond to C–N stretching of secondary amine, wagging vibration of pure CdO NPs, bending vibrations of N–H, and stretching vibration of N–H in PANI respectively [38]. Thus, from the ATR-FTIR spectrum, its strongly confirms that the nanoparticles are highly incorporated to PANI molecular chain and in-situ polymerization was successful during surface modification of Ag-doped CdO NPs with PANI.

### 3.3. Analysis of crystalline structure

Figure 3 depicts the XRD spectrum of CdO NPs, Ag–CdO NCs and Ag–CdO/PANI NCs. These patterns delivered highly sharp and intensive diffraction peaks of CdO NPs and Ag–CdO NCs. From the XRD results, the crystalline phase of pure and Ag doped CdO NPs were determined that all peaks are clearly matched to the cubic phase. The XRD pattern for CdO NPs (red line) demonstrated the intense diffraction peak at \(2\theta = 32.64^\circ, 38.12^\circ, 55.04^\circ, 65.77^\circ\), and 69.13\(^\circ\) corresponding to the plans (111), (200), (220), (311) and (222) respectively which exactly agree with the result of [2, 21]. Thus, the sharp peaks signify that the synthesized CdO NPs and Ag–CdO NCs possess a good crystalline structure [27]. Upon Ag doping, the XRD pattern of CdO NPs exhibits the slight shift in diffraction peaks at \(2\theta = 33.02^\circ, 38.37^\circ, 55.35^\circ, 65.93^\circ\), and 69.30\(^\circ\) corresponding to the plans (111), (200), (220), (311), and (222) respectively with the additional pattern observed at 44.23\(^\circ\) and 77.36\(^\circ\) signify that the metal oxide was successfully doped with Ag metal.

The maximum diffraction peak for PANI was observed around \(2\theta = 25.10^\circ\) which is ascribed to parallel and perpendicular polymeric chains structure [27]. The XRD pattern of nanocomposite was observed at \(2\theta = 25.10^\circ, 27.07^\circ, 28.00^\circ, 35.1^\circ,\) and 37.5\(^\circ\) describing that the pattern represents the cubic structures of CdO NPs, Ag–CdO NCs, and PANI homopolymer. As observed from the patterns, it is also indicated that the diffraction peaks of CdO is slightly shifted to higher \(2\theta\) and hence decreased crystalline size with the addition of Ag which agree with the previous studies [2, 21]. The crystalline size of CdO NPs, Ag–CdO NCs, and Ag–CdO/PANI NCs were calculated using Eq. (2.1). Hence, the calculated crystallite size (D) for each photocatalysts using the most intense peaks at \(32.64^\circ, 38.12^\circ,\) and \(55.04^\circ\) for CdO NPs; 33.02\(^\circ, 38.37^\circ,\) and 55.35\(^\circ\) for Ag–CdO NPs and 25.10\(^\circ, 27.07^\circ\) and 28.00\(^\circ\) for Ag–CdO/PANI NCs are found to be 40.58, 36.43 and 10.29 nm respectively.

### 3.4. Study of degradation properties

#### 3.4.1. Effect of photocatalysts

Figure 4 showed the photocatalytic degradation performances of CdO NPs, Ag–CdO NCs, and Ag–CdO/PANI NCs. It was evaluated using an initial concentration of dye (10 ppm), catalyst load (0.140 g), and pH (6) under UV-Vis light irradiation. The maximum absorption peak was found at 592 nm and the degradation tendency was increased with the irradiation time and become constant after 210 min indicating that it is the maximum degradation time of BPB dye. The photocatalytic degradation performances of each photocatalyst were calculated using Eq. (2.3) and summarized in Table 1. The percentage degradations of BPB dye at CdO
Table 1. Photocatalytic degradation of BPB dye using 10 ppm dye concentration, 0.140 g catalyst load, and pH 6 at room temperature under UV-visible light radiation.

| Photocatalyst | Degradation efficiency (%) at different irradiation times (min) |
|---------------|-------------------------------------------------------------|
|               | 0 | 30 | 60 | 90 | 120 | 150 | 180 | 210 |
| CdO           | 0 | 40.24 | 44.87 | 58.53 | 63.17 | 63.65 | 64.63 | 64.87 |
| Ag–CdO        | 0 | 50.48 | 55.60 | 59.75 | 68.29 | 75.36 | 87.80 | 88.29 |
| Ag–CdO-PANI   | 0 | 78.29 | 81.21 | 83.90 | 89.02 | 93.17 | 97.07 | 97.30 |

Figure 5. (a) Degradation of BPB dye using a different initial concentration with 0.14 g Ag–CdO/PANI load, (b) at different Ag–CdO/PANI catalyst load under fixed dye concentration to 10 ppm, pH of 6 and 25 °C.

Figure 6. (a) Degradation of BPB dye at different pH values, (b) Pseudo-first order kinetics, (c) Pseudo-second order kinetics of Ag–CdO/PANI nanocomposite.
NPs, Ag–CdO NCs, and Ag–CdO-PANI NCs catalysts surface after the optimum time were found to be 64.87, 88.29, and 97.30 % respectively. The best photodegradation efficiency was recorded by Ag–CdO/PANI NCs and considerably the promising result which is more efficient as compared to the previous results. For instance, the best photodegradation efficiency of MO dye was achieved only 60% at the optimum degradation condition using 0.12 wt% of CdO photocatalyst [6]. However, the photocatalytic activity of Co catalyst against ARS showed 98% degradation efficiency at 105 min while the Ni catalyst assisted photodegradation of ARS showed 78% at the same UV irradiation time. As stipulated in the report, the degradation efficiency of Co nanocatalyst is pronounced as a result of its lower crystalline size (31.43 nm) when compared to Ni nanocatalyst (33.24 nm) [30].

In recent research works, scientists are purposely modifying the catalyst surface with PANI owing to its versatile importance. For example, Kumar et al. [40] studied the photocatalytic removal of a mixture of PPCPs by PEDOT alone under UV light. The authors found that an excellent photocatalytic ability of PEDOT with removal efficiency of >99% of the PPCPs in the mixture which further have been applied to the real wastewater matrix and demonstrated the effective removal efficiency. Mahanta et al. [41] utilized a layer-by-layer (LbL) approach to fabricate thin layers of TiO2 nanoparticles and polyaniline-grafted chitosan (CPANI) with poly (styrene sulfonate) as a bridging layer between the two. CPANI containing films showed a better photocatalytic ability for both cationic and anionic dye because of doped and undoped regions in CPANI chains, which were responsible for adsorption of anionic and cationic dyes, respectively which ascribed to the increased porosity of thin-film and adsorption sites [40]. Moreover, the visible-light driven Bi2MoO6/CdO NCs. The electron accepted part would then react with an oxygen molecule to form O2− radicals, whereas holes react with H2O to form •OH [45, 46]. Deng et al. [47] and Zhu et al. [48] indicated that holes and superoxide both played an important role in visible light photocatalysis by PANI/TiO2 and PPy@Ag/C3N4, respectively. However, a recent study by Ghosh et al. [49] disclosed that holes, hydroxyl radicals, and superoxide radicals are the main reactive species in the photocatalytic activity of a PEDOT hybrid structure. This principle works for the PANI modified Ag doped CdO NPs in the way that the photosensitized polymer performs the electrons excitation from HOMO to LUMO which further jumped to the CB of Ag–CdO NCs. The electron accepted part would then react with an adsorbed O2 to form O2− radicals, whereas holes react with H2O to form •OH. Consequently, the activated superoxide and hydroxide free radicals effectively split the pollutant (BPB dye) in to environmentally friendly compounds such as H2O and CO2. The degradation mechanism using nanocomposites is shown in Scheme 2.4.

3.4.2. The effect of initial concentration of dye

The effect of the dye initial concentration on photocatalytic degradation efficiency was studied using 10, 15, 20, and 25 ppm dye concentrations. The other parameters such as the amount of catalyst load and pH were kept at 0.14 g and 6 respectively. The highest degradation efficiency was obtained at 10 ppm as indicated in Figure 5 (a). The result signify that the degradation rate of BPB dye was decreased with increased BPB concentration which attributed to the adsorption of dye molecules at the catalyst surface so that the significant amount of UV-light could be absorbed and the OH* formation become decreases since the active sites of Ag–CdO/PANI NCs is occupied with dye molecules [43].

3.4.3. The effect of catalyst load

The effect of catalyst dose is studied through varying the amount of Ag–CdO/PANI NCs The 0.10 g, 0.12 g, 0.14 g, and 0.160 g doses were investigated while the pH of the solution, dye concentration, and temperature was kept at 6, 10 ppm, and 25 °C (Figure 5 (b)). The degradation efficiency of dye is increased up to 0.140 g which then decreased to 0.160 g. These results indicated that as active sites of catalyst surface are occupied by the molecules of dye, the reaction becomes controlled. Furthermore, it has been reported that as the particles’ concentration become excessive, the turbidity of the solution become significant. Consequently, the penetration of UV-Vis light get decreasing on account of light scattering effect is pronounced, and subsequently the photocatalytic degradation becomes ineffective [44].

3.4.4. The effect of pH

Figure 6 (a) illustrates the effect of pH on degradation of BPB dye keeping its initial concentration to 10 ppm, and catalyst load to 0.140 g under 25 °C. Thus, the degradation results of BPB dye were 58.54 %, 77.56 %, 97.30 % and 83.41 % at pH of 2, 4, 6 and 8 respectively. The results showed that the pH of the solution had a direct influence on the heterogeneous photocatalytic process. The percent degradation rate of dye at the Ag–CdO/PANI surface was found to increase with increasing pH until it reach 6 and then started to decrease beyond this optimum value. It can also be observed from the result that as the pH of solution becomes higher, the degradation performances of the catalyst has a tendency to decline owing to the generation of a negative charge at the catalyst surface, which encourages repulsion on the negatively charged dye molecules [38]. In this study, it is concluded that the optimum degradation efficiency (97.30 %) was found at pH of 6.

3.4.5. Photocatalytic degradation mechanism

In the case of CP-metal oxide hybrid, CP acts as a photosensitizer to absorb a wide range of visible light because of the lower bandgap compared to pure metal oxide. The excited electrons in the LUMO of CP chains are injected into the CB of transition metal oxide or hybrid materials, which reacts with an adsorbed water molecule to form O2− radicals, whereas holes may react with water to form *OH [45, 46]. Deng et al. [47] and Zhu et al. [48] indicated that holes and superoxide both played an important role in visible light photocatalysis by PANI/TiO2 and PPy@Ag/C3N4, respectively. However, a recent study by Ghosh et al. [49] disclosed that holes, hydroxyl radicals, and superoxide radicals are the main reactive species in the photocatalytic activity of a PEDOT hybrid structure. This principle works for the PANI modified Ag doped CdO NPs in the way that the photosensitized polymer performs the electrons excitation from HOMO to LUMO which further jumped to the CB of Ag–CdO NCs. The electron accepted part would then react with an adsorbed O2 to form O2− radicals, whereas holes react with H2O to form •OH. Consequently, the activated superoxide and hydroxide free radicals effectively split the pollutant (BPB dye) in to environmentally friendly compounds such as H2O and CO2. The degradation mechanism using nanocomposites is shown in Scheme 2.4.
3.5. The study of degradation kinetics

3.5.1. Pseudo-first order kinetics

Figure 6 (b) illustrates the relationship between time and degradation rate of BPB dye under UV-Vis light illumination. The study of degradation kinetic for BPB dye was determined using initial concentrations of BPB ranges from 10, 15, 20, and 25 mg/L. The photocatalytic activity of the as-synthesized nanocomposite under UV-Vis irradiation was evaluated by comparing the apparent rate constants (Eq. 2.4 and eq. 2.5). As identified from the result, the photocatalytic activity of Ag–CdO/PANI NCs was higher as compared to CdO NPs and Ag–CdO NCs. It was also supported by the regression coefficient ($R^2 = 0.9549$) for Ag–CdO/PANI NCs and $K_{app}$ value is $8.0 \times 10^{-3}$ min$^{-1}$.

3.5.2. Pseudo-second order kinetics

Figure 6 (c) represents the relationship between time and the concentration change of BPB dye. The regression coefficient ($R^2$) of Ag–CdO/PANI NCs and $K_{app}$ value are 0.999 and 8.56 $\times 10^{-2}$ M$^{-1}$ min$^{-1}$ respectively. Consequently, pseudo-second order is the appropriate kinetic model that provided the best fit to an experimental data. This kinetic model signify the BPB dye could be fully adsorbed to the Ag–CdO/PANI catalyst surface. The importance of PANI has been detected in the reduction of carrier recombination as a result of the existence of connecting doped CdO NPs and consecutive reduction of the surface resistivity of the entire photocatalysts to the photodegradation of BPB.

4. Conclusions

In the current report, CdO NPs, Ag–CdO NCs, and Ag–CdO/PANI NCs were successfully synthesized via sol-gel technique in order to evaluate their degradation efficiency against BPB dye in aqueous media. The surface properties of as-synthesized nanomaterials were characterized with the help of advance analytical tools such as ATR-FTIR, XRD, UV-Vis and SEM. The SEM images of photocatalysts showed that the nanoparticles appeared to be small and agglomerated, ranging from spherical shapes to amorphous ones. The ATR-FTIR spectrum revealed that Ag-doped CdO NCs was successfully modified with PANI as it confirmed from the broad vibration spectrum observed ~3250 cm$^{-1}$ ascribed to the presence of N-H bond of PANI. The XRD spectrum ascribed to the numerous sharp and highly intensive peaks confirmed the CdO NPs and Ag–CdO NCs structure is cubic with decreasing crystalline size while further decreasing after nanocomposite formation. The maximum photocatalytic degradation efficiency was achieved 97.30 % using Ag–CdO/PANI NCs against BPB dye at 10 ppm of initial dye concentration, pH 6, and 0.14 g catalyst dosage under UV-Vis light irradiation for 210 min. The photocatalysis kinetics of Ag–CdO/PANI was pseudo-second order reaction with a positive slope and $8.56 \times 10^{-2}$ M$^{-1}$ min$^{-1}$ rate constant.

The result of this research work showed that, Ag–CdO/PANI NCs is one of the promising photocatalytic nanocomposites which could be generally applicable to the treatment of wastewaters effluents containing acidic dye molecules.

Declarations

Author contribution statement

Tibebu Alemu: Conceived and designed the experiments; Wrote the paper.
Gutema Taye: Performed the experiments.
Girmaye Asefa: Analyzed and interpreted the data.
Lemessa B. Merga: Contributed reagents, materials, analysis tools or data.

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The authors declare no conflict of interest.

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No additional information is available for this paper.

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