Enhanced photocatalytic degradation of lindane using metal–semiconductor Zn@ZnO and ZnO/Ag nanostructures

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ABSTRACT

To achieve enhanced photocatalytic activity for the degradation of lindane, we prepared metal–semiconductor composite nanoparticles (NPs), Zn@ZnO core–shell (CS) nanocomposites, calcined ZnO, and Ag-doped ZnO (ZnO/Ag) nanostructures were prepared using pulsed laser ablation in liquid, calcination, and photodeposition methods, respectively, without using surfactants or catalysts. The as-prepared catalysts were characterized by using X-ray diffraction (XRD), field-emission scanning electron microscopy, high-resolution transmission electron microscopy, ultraviolet-visible (UV–vis) spectroscopy, and photoluminescence spectroscopy. In addition, elemental analysis was performed by energy dispersive X-ray spectroscopy. The obtained XRD and morphology results indicated good dispersion of Zn and Ag NPs on the surface of the ZnO nanostructures. Investigation of the photocatalytic degradation of lindane under UV–vis irradiation showed that Zn@ZnO CS nanocomposites exhibit higher photocatalytic activity than the other prepared samples. The maximum degradation rate of lindane was 99.5% in 40 min using Zn@ZnO CS nanocomposites. The radical trapping experiments verified that the hydroxyl radical (·OH) was the main reactive species for the degradation of lindane.

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Introduction

The development of exhaustive agricultural production has improved intensely from the last few years to safeguard the food quantity based on the substantial growth of population. Significantly enriched production has achieved by intensifying the usage of pesticides and fertilizers, as an essential part of modern agriculture (Morillo and Villaverde, 2017). However, as pesticides are frequently used nowadays to control pests, they are causing contamination of the environment, water, and soil. Owing to their potential for environmental harm, the removal of pesticides has become a major and serious problem (Adeleye et al., 2016; Reddy and Kim, 2015). Environmental deterioration can be caused by the generation of abundant pollutants, which can directly affect human health. Thus, reasonable and sustainable technologies must be established and employed for environmental protection.

Lindane, the gamma-isomer of hexachlorocyclohexane (γ-HCH), is one of the most persistent organic pollutants (POPs), and it has been widely used against soil-dwelling and

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plant-eating insects (Shoiful et al., 2016). Lindane has low solubility, high stability, high persistence, and is resistant to degradation in the environment (Antonaraki et al., 2010). Typically, it has been observed in groundwater and in aquatic environments (Antonaraki et al., 2010). Although it is a prohibited material because of its high toxicity, it is still used in some emerging countries (Hiskia et al., 1997). Therefore, purification of water and degradation of lindane has become an essential problem. In order to address this problem, novel techniques, commonly described as advanced oxidation processes (AOPs), have emerged to replace conventional degradation methods (Gong et al., 2018). However, AOPs and biological approaches are costly, not effective at low concentrations, and require long reaction times (Aba-Guevara et al., 2017). Alternatively, metal–semiconductor composite nanomaterials, alone or in combination with other metal oxides, can decompose POPs efficiently (Rani et al., 2017).

Recently, photocatalytic degradation using metal nanoparticles (NPs) has been established as a promising process. Furthermore, this technique produces water and carbon dioxide as the final products. Therefore, this technology is a fascinating way to degrade toxic organic pollutants (Salam and Das, 2015). In particular, zinc oxide (ZnO) nanostructures, which possess a direct bandgap of 3.37 eV and a high exciton binding energy of 60 meV, are one of the most promising materials for photocatalytic reactions in the ultraviolet-visible (UV–vis) region (Khayatian et al., 2017; Ong et al., 2018). Moreover, ZnO NPs are economical, non-toxic, and biocompatible and, thus, have been widely used as drug carriers and cosmetics (Bhuyan et al., 2018). Compared with other semiconductors, ZnO shows high electron mobility and an extended photo-excited lifetime, which are favorable for photocatalytic degradation of organic pollutants (Margan and Haghighi, 2018). Many techniques have been reported for the production of ZnO nanostructures, including electrodeposition, hydrothermal methods, sol–vapor thermal methods, and atomic layer deposition (Ma et al., 2017; Nan et al., 2017; Rokade et al., 2017; Sagadevan et al., 2017). However, most of these techniques are expensive and complicated. A simpler and more environmentally friendly method, pulsed laser ablation in liquid (PLAL), has been established recently for the fabrication of nanomaterials (Navas et al., 2017; Zhang et al., 2017a).

Senthilnathan and Philip (2010) synthesized nitrogen-doped titanium oxide (N-doped TiO₂) photocatalysts with various nitrogen-containing compounds using a sol–gel technique and found that triethylamine-doped TiO₂ exhibited moderate photocatalytic activity for the degradation of lindane under visible light for 120 min. Jamil et al. (2016) synthesized bismuth oxybromide (BiOBr), bismuth oxyiodide (BiOI), and a heterojunction (BiOI0.5Br0.5) via co-precipitation, a low-temperature solution route, and chemical etching, respectively. All these bismuth oxyhalide catalysts exhibited significant photocatalytic activities for lindane degradation under visible light irradiation. During the photocatalytic process, hydroxyl radicals (·OH) and holes (h⁺) played a key role in the photodegradation of lindane. Singh et al. (2011) fabricated zero-valent iron NPs (nZVI) using an ultrasonication method, and they determined a reaction rate constant (k) for the degradation of lindane on the order of 0.012 min⁻¹. Based on this k value, they predicted that nZVI was efficient for enhancing the degradation of lindane.

In this study, we initially fabricated Zn@ZnO core–shell (CS) nanocomposites using a PLAL technique. Subsequently, two different types of photocatalysts ZnO and Ag-doped ZnO (ZnO/Ag) nanostructures were prepared by calcination and photodeposition methods, respectively, from the Zn@ZnO CS nanocomposites obtained by PLAL. The prepared photocatalysts were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), high-resolution transmission electron microscopy (HRTEM), UV–vis spectroscopy, and photoluminescence (PL). The enhanced photocatalytic performance of the Zn@ZnO CS nanocomposites and ZnO/Ag nanostructures was evaluated for the photodegradation of lindane.

1. Materials and methods

1.1. Materials

The zinc plate (99.99%), lindane (97%) and benzoquinone (BQ, ≥ 98%) were obtained from Sigma Aldrich Co., Ltd., Korea. The silver nitrate powder, and isopropyl alcohol (IPA, > 99.5%) were purchased from Daejung Co., Ltd., Korea. All chemicals were used directly without further purification.

1.2. Synthesis of Zn@ZnO CS nanocomposites

The typical experimental setup has been described elsewhere (Jung and Choi, 2014). Briefly, a Q-switched Nd:YAG laser (1064 nm, 10 Hz, 7 nsec) was focused onto a solid Zn plate immersed in deionized (DI) water. The Zn plate was placed at the center of a 20 mL Pyrex vial filled with 12 mL of DI water and vigorously stirred. A focusing lens with a focal length of 25 mm was used to focus the laser beam on a ~1 mm spot on the surface of the Zn metal plate. Laser ablation was carried out for 30 min at a laser energy of 90 mJ/pulse. Subsequently, the ablating colloidal solution was centrifuged at 13,000 r/min for 3 min several times.

1.3. Synthesis of calcined ZnO NPs

After PLAL, the Zn@ZnO CS nanocomposites were calcined for 60 min in a furnace at temperatures from 100 to 700°C at intervals of 100°C.

1.4. Synthesis of ZnO/Ag nanostructures

ZnO/Ag nanostructures were prepared by a photodeposition method. Briefly, 0.005 g ZnO (calcined at 500°C) was suspended in 9 mL of ethanol and then 1 mL of 0.1 mmol/L AgNO₃ in ethanol was added. The suspension was then exposed to UV irradiation produced by a xenon lamp (400 W) for 2 hr. Subsequently, the ZnO/Ag sample was centrifuged at 13,000 r/min for 10 min, washed with ethanol and DI water, and dried in an oven at 50°C.

1.5. Photocatalytic degradation of lindane

The photocatalytic degradation of lindane was investigated under UV–vis light using a 200 W xenon lamp. The prepared
sample (0.005 g) was mixed with 10 mL of lindane solution (5.0 × 10⁻⁵ mol/L) under magnetic stirring for 20 min in the dark to achieve adsorption equilibrium between lindane and the photocatalysts. Afterwards, the mixture was exposed to UV–vis light at room temperature.

1.6. Radical trapping experiments

It is well-known that the hydroxyl radical (·OH) and superoxide radical (·O₂⁻) anions are the main reactive species involved in the photocatalytic degradation processes. In order to determine the active radical species involved in the photodegradation of lindane, trapping experiments were conducted by introducing various scavengers including IPA (1.0 × 10⁻³ mol/L) and BQ (1.0 × 10⁻³ mol/L) for ·OH and ·O₂⁻ radicals, respectively. The experimental procedure was similar to the process of the photocatalytic degradation of lindane (Section 1.5).

1.7. Characterization

The as-prepared samples were examined by XRD (D8 Discover with GADDS, Bruker, Germany) with Cu Kα radiation (wavelength (λ) = 0.15418 nm), FE-SEM (XL30S FEG, Philips, Netherlands), HRTEM (TF30ST, Fei-Tecnai, USA), energy dispersive X-ray spectroscopy (EDS, INCA system, Oxford, UK) with Mn Kα radiation (λ = 138 eV), PL (F-7000, Hitachi, Japan), and UV–vis spectroscopy (UV-3600, Shimadzu, Japan).

2. Results and discussion

2.1. Structural analysis of photocatalysts

Fig. 1 shows the XRD patterns of the Zn@ZnO CS nanocomposites, calcined ZnO, and ZnO/Ag nanostructures, respectively. The XRD pattern of the Zn@ZnO CS nanocomposites (Fig. 1a) displays two sets of diffraction peaks. The strong diffraction peaks (black) resemble the wurtzite hexagonal phase of ZnO (JCPDS#01-089-0510), whereas the weak peaks (red) resemble the hexagonal phase of Zn (JCPDS#00-004-0831) (Gritsenko et al., 2017; Jeen Maria et al., 2016). The peaks at 31.75, 34.40, 36.29, 47.54, and 56.59° can be assigned to the reflections of the (100), (002), (101), (102), and (110) planes of ZnO, respectively. The peaks at 39.01, 43.19, and 55.20° can be indexed to the (100), (101), and (110) facets of hexagonal Zn, respectively. Thus, the formation of Zn@ZnO CS nanocomposites via PLAL is confirmed.

Fig. 1b shows the XRD pattern of ZnO calcined at 500°C. For reference, the XRD patterns of ZnO calcined at different temperatures from 100 to 700°C are shown in Appendix A Fig. S1. The XRD peaks sharpened above 500°C owing to the enhanced crystallinity of the samples at high calcination temperatures (Parra and Haque, 2014). It is clear from the XRD spectra (Appendix A Fig. S1) that the average grain size of the ZnO NPs increases as the calcination temperature increases, and the Zn@ZnO phase is transformed into ZnO at around 500°C, indicating that Zn has been completely oxidized to ZnO (Zhang et al., 2014, 2012; Zhao et al., 2015).

The average grain size, d, of the ZnO NPs produced by calcination of the Zn@ZnO CS nanocomposites was obtained using Scherrer’s formula (Rauwel et al., 2017). The mean grain sizes corresponding to the (100), (002), and (101) planes were calculated at calcination temperatures of 500, 600, and 700°C (Table 1). The size of the ZnO NPs was observed to gradually increase as the calcination temperature increased, which is due to particle aggregation (Kayani et al., 2015).

Fig. 1c shows the XRD pattern of the ZnO/Ag nanostructures produced using a photodeposition method. Representative Ag peaks at 2θ of 38.15 and 44.34° correspond to the (111) and (200) facets, respectively, of the face-centered cubic structure (fcc) (JCPDS#01-089-3722) (Mehta et al., 2017). Furthermore, no other peaks were detected in the XRD pattern, which indicates the purity of the ZnO phase.

2.2. Electron microscopy studies

Fig. 2a shows the FE-SEM and HRTEM images of the Zn@ZnO CS nanocomposites. From the FE-SEM image (inset a-iv), it is observed that the particles are spherical in shape. The HRTEM image (inset a-i) shows the presence of Zn@ZnO with a CS structure consisting of a Zn core and a ZnO shell. Thus, it is evident that the Zn NPs are coated with a ZnO surface. Appendix A Fig. S2 shows a size distribution histogram for the Zn@ZnO CS nanocomposites, which indicates that the mean size of the NPs obtained by PLAL is 11.74 ± 0.27 nm. Furthermore, the high-resolution images (insets a-ii and a-iii) reveal lattice fringes with spacing’s of 0.209 and 0.247 nm.

| Table 1 – Average grain size (d) of ZnO nanoparticles at different calcination temperatures. |
|---------------------------------|-----------------|-----------------|-----------------|
| Diffraction plane              | d value (nm) at various calcination temperatures (°C) |
| (100)                          | 20.75           | 22.14           | 24.23           |
| (002)                          | 19.39           | 21.08           | 22.37           |
| (101)                          | 19.73           | 21.55           | 22.36           |
Fig. 2 – High-resolution transmission electron microscope images of (a) Zn@ZnO CS nanocomposites, (b) calcined ZnO and (c) ZnO/Ag nanostructures. The insets are the lattice fringes (a-i, a-ii, a-iii, b-i, b-ii, c-i, c-ii) and field-emission scanning electron microscope images (a-iv, b-iii, c-iii) of the corresponding samples.
corresponding to the (101) plane of Zn and the (101) plane of the wurtzite hexagonal phase of ZnO, respectively (Trejo et al., 2009). Fig. 3a shows the corresponding selected area electron diffraction (SAED) pattern, which further confirms the formation of Zn@ZnO CS nanocomposites. The EDS spectrum (inset a-iv) reveals the elemental composition of the prepared sample, indicating the presence of Zn and O. Chemical mapping of Zn and O atoms (inset a-i, a-ii, and a-iii) is represented by red and green, respectively.

Fig. 2b shows the FE-SEM and HRTEM images of ZnO calcined at 500°C. The FE-SEM image (inset b-iii) reveals that the calcined ZnO nanostructures are larger than the Zn@ZnO CS nanocomposites and ZnO/Ag nanostructures (Appendix A Fig. S3). The HRTEM image in Fig. 2b shows that the calcined ZnO nanostructures have mixed hexagonal (marked by blue hexagonal structures) and spherical shapes with non-uniform grain sizes (Koupaei et al., 2016). The lattice fringe patterns (insets b-i and b-ii) with spacings of 0.260 and 0.281 nm confirm the presences of the (002) and (100) planes of ZnO, respectively (Liu et al., 2012).

Fig. 2c shows the FE-SEM and HRTEM images of the ZnO/Ag nanostructures. The ZnO/Ag nanostructures (inset c-iii) are spherical and exhibit slight agglomeration. The HRTEM image in Fig. 2c reveals a small distribution of Ag NPs (marked by yellow circles) on the ZnO surface. The lattice fringes (insets c-i and c-ii) with spacings of 0.204 and 0.247 nm correspond to the (200) plane of Ag and the (101) plane of ZnO, respectively (Agnihotri et al., 2014). The TEM images of samples before and after photo-irradiation are shown in Appendix A Fig. S4. After photo-irradiation, the Ag NPs were more aggregated on the surface of ZnO than those before photo-irradiation. Hence, we think that the ZnO/Ag nanostructures have low photocatalytic nature than the Zn@ZnO CS nanocomposites. Fig. 3b shows the SAED pattern, which confirms the formation of ZnO nanostructures and Ag NPs. EDS analysis and chemical mapping of the ZnO/Ag nanostructures are shown in Fig. 3b.

Fig. 3 – Selected area electron diffraction patterns (a and b) and energy dispersive X-ray spectroscopy (insets a-i, a-ii, a-iii, a-iv, b-i, b-ii, b-iii, b-iv) analysis of (a) Zn@ZnO CS nanocomposites and (b) ZnO/Ag nanostructures.
The EDS spectrum (inset b-iv) reveals the presence of Zn, O, and Ag in the prepared sample. The chemical mapping of Zn, O, and Ag atoms (insets b-i, b-ii, and b-iii) is represented by blue, green, and yellow, respectively. No other peaks related to any impurity were detected, which confirms that the prepared samples have the desired composition.

2.3. UV–vis and PL spectroscopic studies

Fig. 4a shows the UV–vis absorption spectra of Zn@ZnO CS nanocomposites, calcined ZnO, and ZnO/Ag nanostructures. The absorption bands observed at 352, 367, and 369 nm for Zn@ZnO CS nanocomposites, calcined ZnO and ZnO/Ag nanostructures, respectively, are attributed to ZnO (Kahouli et al., 2015). In addition, the absorption band observed at around 455 nm for the ZnO/Ag nanostructures is due to the surface plasmon resonance (SPR) of Ag NPs (Zhang et al., 2017b).

Fig. 4b shows the PL spectra of Zn@ZnO CS nanocomposites, calcined ZnO, and ZnO/Ag nanostructures at an excitation wavelength of 340 nm at room temperature. In PL spectra, the two major emission bands were observed for the Zn@ZnO CS nanocomposites: a near UV emission band around 378 nm consistent with near band edge (NBE) emission of ZnO originating from the recombination of excitons in ZnO and a broad yellow emission band about 482–649 nm attributed to emission from oxygen vacancies (Bekkari et al., 2017; Mannam et al., 2017; Xian et al., 2017). The strong UV emission peak indicates a high optical density of the prepared ZnO (Rehana et al., 2017). Calcined ZnO and ZnO/Ag nanostructures exhibit relatively strong bands around 384 nm, which correspond to the NBE emission of ZnO (Xu et al., 2017). It is clear that the Zn@ZnO CS nanocomposites showed less PL intensity compared to the calcined ZnO, and ZnO/Ag nanostructures, which is due to the high content of electron-trapping defects (broad yellow emission) (Flores et al., 2014). The weak PL intensity signifies the suppression of electron-hole recombination rate; thus, the Zn@ZnO CS nanocomposites exhibit an extended lifetime of the photogenerated carriers.

2.4. Photocatalytic degradation of lindane

Photocatalytic processes depend on the production of electron-hole pairs under bandgap radiation to form reactive radical species. In this study, we used lindane as an organic dye to explore the advantages of the as-prepared samples for photocatalytic degradation under UV–vis irradiation. In the dark and in the absence of photocatalysts, no photodegradation of lindane was observed. However, a significant enhancement in photodegradation efficiency was observed when the photocatalysts were added to the lindane solution. The results for photodegradation of lindane using a 320 nm light source and Zn@ZnO CS nanocomposites, calcined ZnO, and ZnO/Ag nanostructures as catalysts are shown in Fig. 5. The degradation performance can be expressed as \( C/C_0 \), where \( C_0 \) is the initial concentration of lindane and \( C \) is the concentration of lindane after the photocatalytic reaction.

As illustrated in Fig. 5, the Zn@ZnO CS nanocomposites degraded lindane faster than the other photocatalysts. After 40 min of photo-irradiation (indicated by a dashed vertical line), about 99.5% of lindane was decomposed. However, the photocatalytic activities of calcined ZnO and ZnO/Ag nanostructures were lower than that of the Zn@ZnO CS nanocomposites. The photocatalytic performance of the synthesized photocatalysts at 40 min decreased in the following order: Zn@ZnO CS nanocomposites (99.5%) > ZnO/Ag nanostructures (77.8%) > calcined ZnO (19.3%). The slightly lower photocatalytic performance of ZnO/Ag nanostructures may result from the low dispersion of Ag NPs on the ZnO surface (Kubo and Tatsuma, 2005). Nevertheless, both Zn@ZnO CS nanocomposites and ZnO/Ag nanostructures exhibited enhanced photocatalytic activity (~100%) after 94 min of photo-irradiation. Based on these results, the Zn@ZnO CS nanocomposites and ZnO/Ag nanostructures exhibit desirable photocatalytic activities for the degradation of lindane under UV–vis irradiation. However, in the case of calcined ZnO, the photocatalytic activity is considerably lower, which may be due to the decreased surface area after calcination (Jing et al., 2013). Furthermore, ZnO is a pure semiconductor photocatalyst, whereas the other two samples are metal–semiconductor photocatalysts.

To understand the reaction kinetics of lindane removal by the as-prepared samples, the photocatalytic reaction rate constants (k) were calculated using pseudo-first-order model, \( \ln(C/C_0) = kt \). The calculated values of k were 0.0625, 0.0069, and 0.0352 min\(^{-1}\) for the Zn@ZnO CS nanocomposites, calcined ZnO, and ZnO/Ag nanostructures, respectively (Naseri et al.,

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Fig. 4 – (a) Ultraviolet–visible (UV–vis) absorption and (b) photoluminescence spectra of Zn@ZnO CS nanocomposites, calcined ZnO and ZnO/Ag nanostructures.
These results suggest that the Zn@ZnO CS nanocomposites have the highest efficiency among the prepared samples for the degradation of lindane.

2.4.1. Radical trapping experiments
To investigate the photocatalytic reaction mechanism, it is of vital importance to identify the primary active species. Thus, controlled experiments with different types of active scavengers are added in the catalyst system to understand the involvement of active radical species in the photocatalytic process. It is well known that the active intermediate species such as ·OH and ·O$_2^-$ radicals were the major reactive species in the photocatalytic dye degradation process. Thus, the radical trapping experiments have been conducted by using IPA and BQ which are known to trap ·OH and ·O$_2^-$ radicals, respectively, in the reaction mixture on the excitation of semiconducting material (Khan et al., 2018; Tanwar et al., 2017).

Fig. 6 shows the degradation ratio of lindane as a function of time in the absence and presence of the various scavengers containing Zn@ZnO CS nanocomposite photocatalysts under UV–vis irradiation. The photocatalytic degradation of lindane decreased remarkably after the addition of IPA as a ·OH scavenger. This behavior suggests that ·OH is the main active species in this system. However, upon addition of BQ as a ·O$_2^-$ scavenger, the degradation efficiency of lindane is also affected to some degree, but not as much as that of IPA. These results suggest that the degradation of lindane is mainly due to the ·OH radicals, and the ·O$_2^-$ radicals played a minor role under UV–vis irradiation.

2.4.2. Possible photocatalytic mechanism
Based on the above experimental results, a possible photocatalysis mechanism was proposed, as illustrated in Scheme 1. Irradiation of the Zn@ZnO CS nanocomposites using UV–vis light with an energy higher than the bandgap of 3.37 eV produces electrons (e$^-$) and holes (h$^+$) in the conduction band (CB) and valence band (VB) of ZnO, respectively. At the interface between Zn and ZnO, the electrons in the CB of ZnO moves to the Zn core resulting in the formation of a Schottky barrier, which could prevent the electron–hole recombination in the photocatalytic reaction (Babu et al., 2016; Chang et al., 2016). Subsequently, the photogenerated holes move to the surface and react with H$_2$O or OH$^-$ to produce hydroxyl radical species (·OH), whereas the electrons in Zn core react with oxygen molecules to form superoxide anion radicals (·O$_2^-$). The formed radicals are responsible for the degradation of lindane. Moreover, defects, such as oxygen vacancies, may act as electron donors to produce extra electrons which contribute to the photocatalytic degradation process.
acceptors that trap the photogenerated electrons and reduce the recombination of electrons and holes (Ma et al., 2013; Udayabhanu et al., 2016; Zeng et al., 2007).

3. Conclusions

In summary, enhancement of the photocatalytic degradation of the environmentally persistent chlorinated pesticide, lindane, was investigated. Zn@ZnO CS nanocomposites, calcined ZnO, and ZnO/Ag nanostructures were successfully prepared using PLAL, calcination, and photodeposition methods, respectively. Structural and morphology studies confirmed the purities of the prepared samples. The Zn@ZnO CS nanocomposites exhibited higher photocatalytic activity than the other prepared samples. The movement of electrons from the ZnO shell to the metallic Zn core was responsible for the enhanced photocatalytic activity. Furthermore, the mixed systems of metal (Zn and Ag) NPs and semiconductor ZnO reduce the recombinant of electron–hole pairs and improve the photodegradation of lindane. Additionally, the reactive species in the degradation of lindane were identified by adding a series of scavengers into the photocatalytic reaction and the ·OH radicals were determined to be the main reactive species in the photocatalytic process. Based on these results, the Zn@ZnO CS nanocomposites and ZnO/Ag nanostructures, which were prepared using facile methods, can be considered good candidates for enhancing the photodegradation efficiency of organic pollutants.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jes.2018.02.014.

REFERENCES


Agnihotri, S., Mukherji, S., Mukherji, S., 2014. Size-controlled silver nanoparticles synthesized over the range 5-100 nm using the same protocol and their antibacterial efficacy. RSC Adv. 4, 3974–3983.


Tanwar, R., Kaur, B., Kumar Mandal, U., 2017. Highly efficient and visible light driven NiO@ZnS@Fe3O4@PANI modified BiOCl heterocomposite catalyst for water remediation. Appl. Catal. B 211, 305–322.


