

Visible Light Activated Photocatalytic Degradation of 2,4-Dichlorophenol using Silver Halide Photocatalysts

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In this study, highly efficient silver halide (Ag/AgX where X= Cl, Br, I), photocatalysts were successfully synthesized through hydrothermal method. The prepared samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and Brunauer-Emmett-Teller (BET). All three compounds were confirmed to be pure with the associated planes being identified. The photocatalytic activity of these photocatalysts were evaluated through the degradation of 2,4-dichlorophenol (2,4-Di-2,4-DCP) under UV and visible light irradiation. Variant photocatalytic efficiency was exhibited dependent on the material used. The Ag/AgBr photocatalysts exhibited the best efficiency among all three catalysts, resulting in an 83.37 % and 89.39 % photodegradation under UV and visible light after 5 h, respectively, at a catalyst loading of 0.5 g/L.

1. Introduction

Water contamination with chlorinated organic compounds such as chlorophenol (CPs) and chlorophenoxy herbicide are reported as major environmental threats. Chlorinated organic compounds are generally utilized in the production of biocides, pesticides as well as wood preservatives (Liu et al., 2019). 2,4-Dichlorophenol (2,4-DCP) is a photodegradation product of triclosan, a common antimicrobial agent and 2,4-dichlorophenoxyacetic acid herbicide (Melián et al., 2013). 2,4-Dichlorophenol has been listed as a priority pollutant by the United States Environmental Protection Agency (USEPA (Melián et al., 2013)), as it creates serious threats to both aquatic and human health due to its high toxicity, recalcitrant, mutagenic, and carcinogenic properties (Liu et al., 2019). Furthermore, the World Health Organization (WHO) has established a limit to the concentration of CPs in drinking water to less than 1.0 mg/L (Organization, 2003). In order to reduce the risk of 2,4-dichlorophenol in the environment, remediation through the development of suitable removal methods is thus essential. Several methods have been investigated for the removal of 2,4-DCP in aqueous solutions, namely adsorption (Melián et al., 2013), ozonation (Aziz et al., 2018) and electrochemical (Liu et al., 2019) treatment. Most of these methods have disadvantages such as high operational cost, low efficiency, and the production of excessive by-products. As such, the development of effective methods for the degradation of 2,4-DCP is imperative. Recently, photocatalysis has been identified as an economically efficient and environmentally friendly advanced oxidation process (AOP), that is capable of mineralizing a wide range of organic compounds including recalcitrant phenolics (Adenuga et al., 2019). The most widely investigated photocatalysts are the TiO₂-based nanoparticles (NPs) as they are inexpensive, non-toxic and structurally stable (An et al., 2016). However, the large band gap of TiO₂ (3.2 eV (Cui et al., 2015)), has limited its application. TiO₂ can be directly excited by ultraviolet (UV) irradiation, which accounts for only 4% of the solar spectrum. Consequently, efforts have been made to develop photocatalysts that can absorb visible light which accounts for approximately 43% of the solar spectrum (Ma et al., 2012), thus, providing green energy source, economical and an eco-friendly strategy of environmental remediation. Thus, it is imperative to develop visible light responsive photocatalytic materials. Plasmonic photocatalysts made of noble metals nanoparticles (Au, Ag, Pt, Cu), indicate high adsorption coefficients in a broad UV-Visible-near infrared spectral range, due to their strong surface plasmon (Cui et al., 2015). Silver nanoparticles exhibit efficient plasmon resonance in the visible region. Silver halides are highly photosensitive and can be utilised as metallic silver precursor. AgX photocatalysis on organic degradation process, is similar to, general

photocatalysis mechanism, whereby, AgX can absorb photons and excite electrons from its VB to CB leaving holes in VB. When photons are absorbed, AgX (X=Cl, Br, I) produces an electron and a hole causing an electron transfer and subsequently, Ag⁺ reduced to surface plasmon effect (Fan et al., 2018). The localized surface plasmon effect of metallic Ag⁰ activate the self-generated electrons and holes engaging in the photocatalytic degradation. Herein, Ag/AgX (X =Cl, Br, I) photocatalysts were synthesized by simple hydrothermal method and characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and Brunauer-Emmett-Teller (BET). The obtained particles photocatalytic activities were evaluated through the degradation of 2,4-dichlorophenol under UV and visible light irradiation.

2. Material and methods

2.1 Chemicals and Materials

Sodium chloride (NaCl), sodium bromide (NaBr), potassium iodide (KI), silver nitrate (AgNO₃) and glacial acetic acid (CH₃COOH) were obtained from Glassworld (Johannesburg, South Africa). 2,4-Dichlorophenol and HPLC grade acetonitrile were purchased from Sigma-Aldrich (St Louis, MO, USA) and Merck (South Africa), respectively. All reagents were utilized without further purification. Deionized water was used throughout this study.

2.2 Synthesis of Ag/AgX (X=Cl, Br & I)

The Ag/AgCl catalyst was produced using a hydrothermal method adapted and modified from (Kuai et al., 2010). The preparation of AgCl followed a typical procedure of dissolving 105 mg of AgNO₃ in 30 mL of deionized water, thereafter, 0.0016 mol of NaCl was added to the above solution. After 10 min of vigorous stirring, the mixture was transferred into an autoclave and kept for 2 hours at 120 °C. After cooling to room temperature, the product was collected and washed several times with deionized water and ethanol. Ag/AgCl was obtained through the dispersion of the obtained products in 10 mL of deionized water and irradiating under visible light for 3 hours to convert some Ag⁺ ions on the surface region of AgX (X = Cl, Br & I) to Ag⁰ species. Thereafter, the product was collected and dried at 60 °C for 12 hours. The preparation of Ag/AgBr and Ag/AgI followed the above procedure using NaBr and KI reagents, respectively.

2.3 Characterization

X-ray diffraction (XRD) spectra of the prepared samples were analysed using a PANalytical X \square Pert Pro powder diffractometer in θ - θ configuration with an X \square Celerator detector and variable divergence and fixed receiving slits with Fe filtered Co-K α radiation (λ =1.789 Å). The particle morphology was detected using a Zeiss 540 Ultra FEGSEM scanning electron microscope. The specific surface areas of the catalysts were characterized by a nitrogen adsorption-desorption and BET method by a surface area analyser (Micrometrics Tristar II 3020). All samples were degassed overnight at 150 °C under pure nitrogen atmosphere prior to analysis for the removal of all adsorbed species from the catalysts.

2.4 Photocatalytic activity

The photocatalytic activities of the as-prepared Ag/AgX were evaluated by 2,4-dichlorophenol (2,4-DCP), using a photochemical reactor with visible light and UV light irradiation. A 72 W LED lamp with a wavelength from 380-800 nm was used as the visible light source and the UV light source was the 36 W LED (PHILIPS TUV 36 W/C36 T8) lamp. Before irradiation, 125 mg of photocatalyst was added into 250 mL of the 2,4-DCP (10 ppm) and kept stirred in the dark for 1 hour to reach the adsorption-desorption equilibrium. During photodegradation, 2 mL of aliquots were sampled at certain time interval and collected for subsequent analysis after centrifugation and filtration for the removal of photocatalysts.

2.5 Analytical procedure

The concentration of 2,4-DCP was determined using HPLC (Water 2695 separation module with a 2489 UV/Visible detector). The HPLC was equipped with a Water PAH C18 (250 x 4.6 mm) and worked at 25 °C with the detector performing at 280 nm. The mobile phase was 60:40 (v/v) acetonitrile and deionized water and the flow rate at 1 mLmin⁻¹. The mobile phase solvents consisted of 0.1 % of acetic acid in both the acetonitrile and water. 2,4-DCP was identified through the comparison of the retention times with standard samples, thereafter, quantified with the calibration curve method. 2,4-DCP was identified at a retention time of 4.40 minutes. Empower software was used to collect data.

3. Results and discussion

3.1 Characterization

XRD analysis was conducted to investigate the crystal structure of the of the as-prepared Ag/AgX (X=Cl, Br, I) photocatalysts. The typical XRD spectra of the prepared photocatalysts are presented in Figure 1. The XRD pattern of Ag/AgCl shows the cubic phase of AgCl (Cui et al., 2015), with distinct diffraction peaks at a 2θ of 33° , 54° and 66° which can be assigned to (200), (311) and (400) planes, respectively. The peaks centred at 38° and 64° can be attributed to the cubic phase of Ag (Wang et al., 2011). The XRD pattern of the Ag/AgBr catalyst shows the coexistence of cubic phase Ag and cubic phase AgBr (Wang et al., 2011). Ag phase can be characterized by the distinct peaks at a 2θ of 38.5° and 78.5° which are assigned to (111) and (311) planes, respectively. AgBr peaks are located at a 2θ of 32.5° , 52.5° and 65.5° correlating to (200), (311) and (400) plane, respectively. XRD patterns of Ag/AgI photocatalyst match the reported data by An et al. (2014) of hexagonal phase β -AgI and cubic phase γ -AgI. The presented diffraction peaks are sharp and intense, indicating the high degree of crystallinity of the Ag/AgX species.

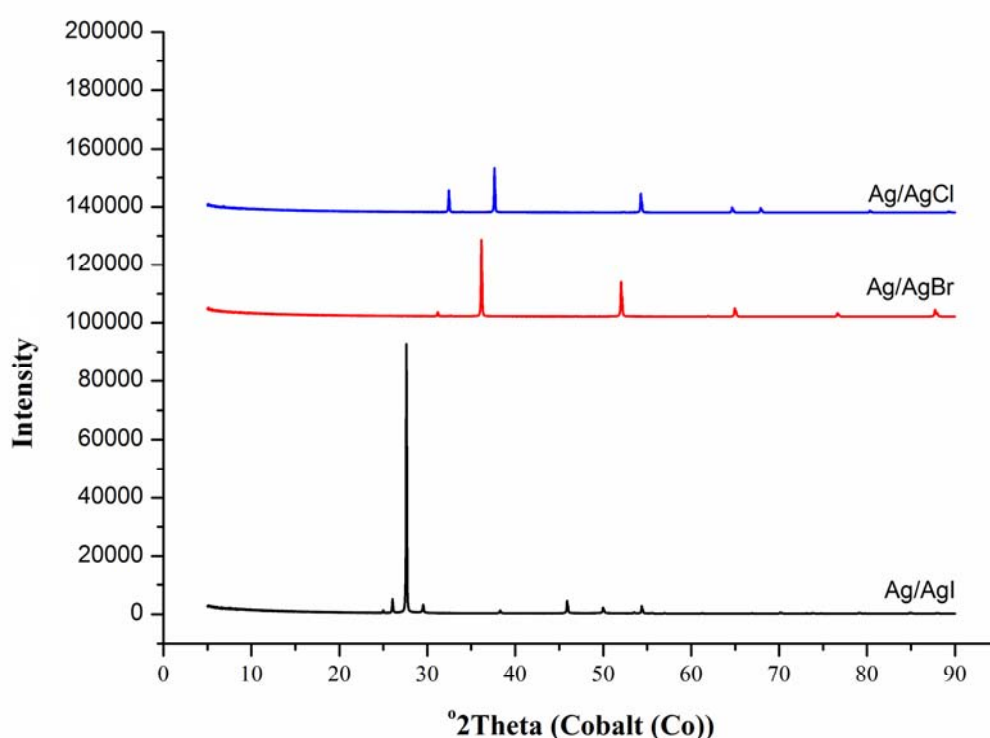


Figure 1: XRD spectra of the as-prepared Ag/AgX (X=Cl, Br, I) photocatalysts

The morphology of the Ag/AgX particles have an effect on the their photocatalytic properties, as different morphologies lead to different surface area, which directly determine the photocatalytic performance (Cui et al., 2015). The surface morphologies of the as-synthesized Ag/AgX were characterized by SEM and are presented in in Figure 2(a-d). As shown in Figure 2(a), the as-synthesized Ag/AgCl exhibits irregular and near-spherical morphology. Ag/AgBr exhibits irregular spherical-like shape presented in figure 2(b). Figure 2(c-d) show the polygonal plates of the as-synthesized Ag/AgI. Most of the as prepared catalysts are agglomerated with a non-uniform distribution of particles, which is a characteristic of surfactant-free precipitation reactions in aqueous media (Reddy et al., 2015).

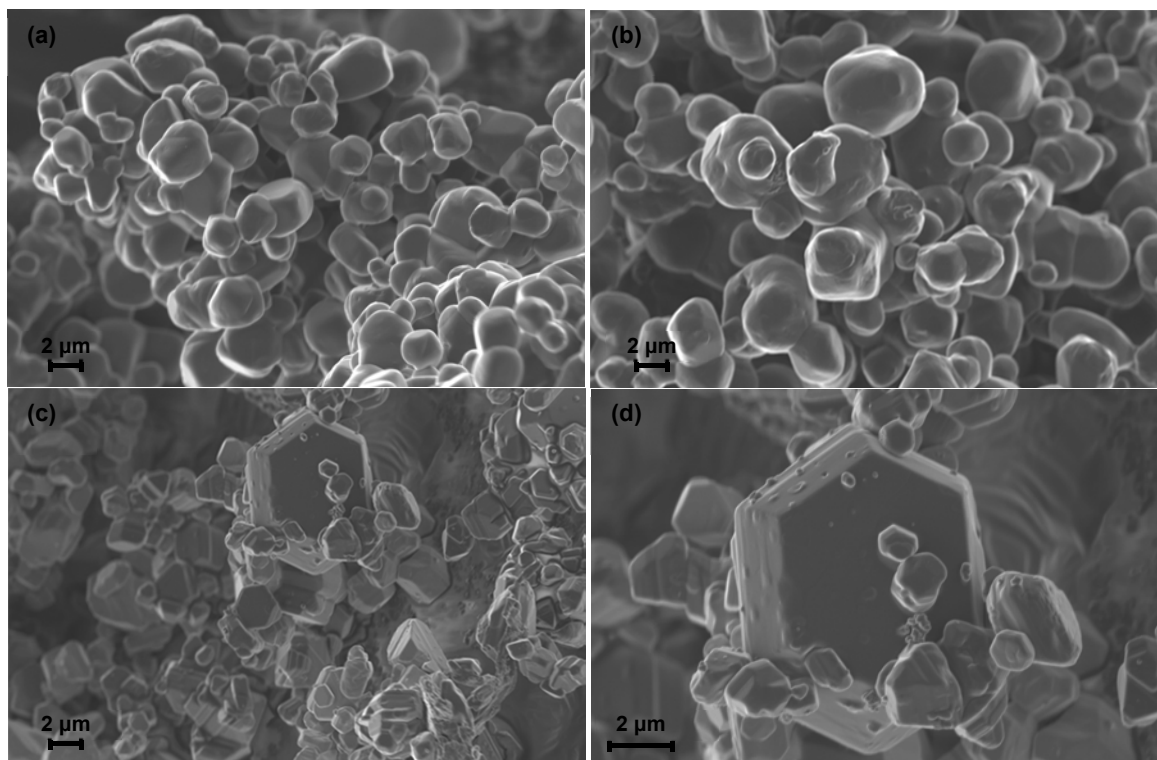


Figure 2: SEM images of the as-prepared catalysts (a) Ag/AgCl, (b) Ag/AgBr, (c) Ag/AgI and (d) high magnification of Ag/AgI

The BET surface areas and, the pore size of the as-prepared catalysts are presented in Table 1. The BET surface area of Ag/AgI is $0.33 \text{ m}^2\text{g}^{-1}$, which is higher than Ag/AgBr ($0.14 \text{ m}^2\text{g}^{-1}$) and Ag/AgCl ($0.09 \text{ m}^2\text{g}^{-1}$). Furthermore, the obtained pore size of Ag/AgCl, Ag/AgBr and Ag/AgI are 130.30, 102.45 and 59.9Å, respectively, indicating that the reduction of pore size produce an increased surface area. Higher surface areas are beneficial in enhancing adsorption capability and transfer ability of organic pollutant onto the surface of photocatalysts to enhance photodegradation (Shi et al., 2013).

Table 1: BET surface area and pore volumes of the as-prepared samples

Samples	$S_{\text{BET}} (\text{m}^2\text{g}^{-1})$	Pore size (Å)
Ag/AgCl	0.09	130.3
Ag/AgBr	0.14	102.5
Ag/AgI	0.33	59.9

3.2 Photocatalytic activity

The photocatalytic performance of the as-prepared Ag/AgX photocatalyst were evaluated in the photodegradation of 2,4-DCP, under UV and visible-light irradiation. Control tests were conducted to investigate the effect of UV and visible-light irradiation as well as, adsorption of 2,4-DCP. Figure 3(a). present the degradation effect of UV and visible-light irradiation on 2,4-DCP in the absence of the catalysts over 5 hours. A photodegradation of approximately 36.37 % and 30.97 % was exhibited under UV and visible-light irradiation, respectively. Presented in Figure 3(b). is the catalysis performance of the as-prepare Ag/AgX. Ag/AgCl exhibited an adsorption of 63.36 % after 5, slightly higher than Ag/AgBr (53.36 %) and Ag/AgI (55.11%), this can be attributed to the polarity of the catalysts surface. The polarity of the catalysts surface played a critical role in adsorbing 2,4-DCP over the specific surface area (Sobiesiak, 2017).

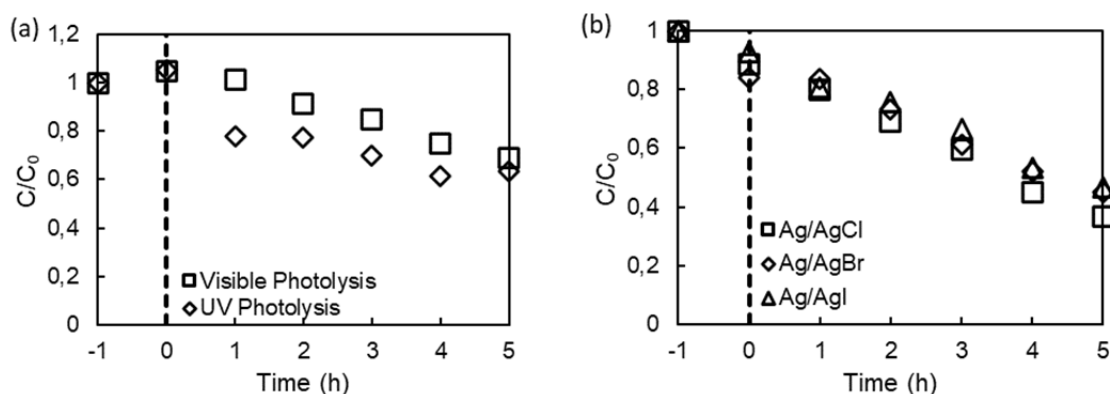


Figure 3:(a) Photolysis test (without catalysts) under UV and visible light irradiation and (b) adsorption test (in the dark) of the as-prepared samples of 2,4-dichlorophenol

Figure 4(a) and (b) illustrates the photocatalytic degradation efficiencies of 2,4-DCP for Ag/AgCl, Ag/AgBr and Ag/AgI under UV and visible-light irradiation. Ag/AgBr photocatalyst exhibited the highest photodegradation efficiency under both UV and visible-light irradiation for 2,4-DCP removal, presenting a degradation of 83.37 % and 89.39 % respectively. Ag/AgI had the lowest efficiency under both lights with approximately 72.71 % removal under UV irradiation and 38.16 % under visible light after 5 h of irradiation. Ag/AgCl presents an efficiency of 78.96% and 72.70 % under UV and visible light, respectively. Tian (2012) has reported on the visible light response of Ag/AgX illustrating that, for Ag/AgCl photocatalyst, the visible light photocatalytic activity is primarily relative to the plasmonic adsorption of Ag, whereas, in the case of Ag/AgBr and Ag/AgI, both Ag and AgX respond to the visible-light irradiation producing more electrons and holes. Thus, Ag/AgBr usually presents higher photocatalytic activity than Ag/AgCl. This correlate with the result of this study by which, Ag/AgBr photocatalyst exhibited the highest degradation under visible light irradiation.

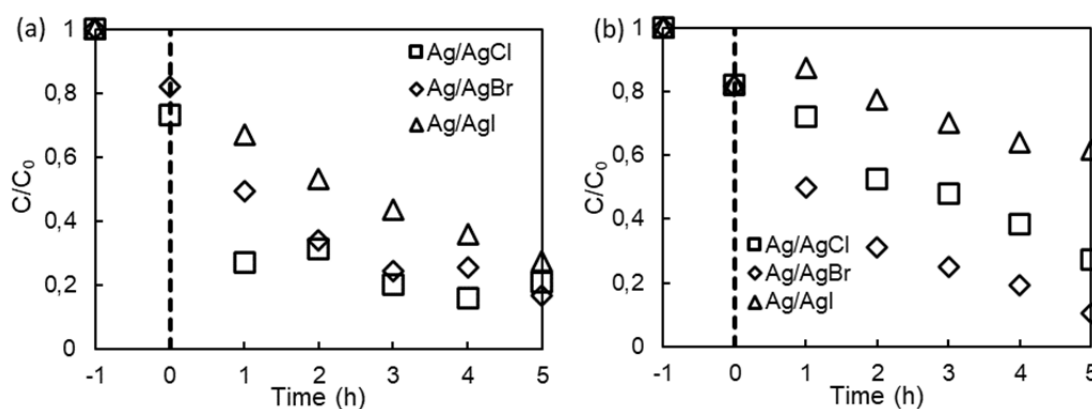


Figure 4: Photocatalytic activity of the as prepared samples under (a) UV light and (b) visible light irradiation

4. Conclusions

Ag/AgX (X=Cl, Br, I) photocatalysts were successfully synthesized through a hydrothermal method. The prepared photocatalysts crystallinity were confirmed through XRD characterization with SEM presenting near-spherical, spherical-like and polygonal plate morphologies in Ag/AgCl, Ag/AgBr and Ag/AgI catalysts, respectively. The photodegradation tests indicate the efficiency of the catalysts under both UV and visible light irradiation. Ag/AgBr exhibits the highest overall efficiency of approximately 89.39 % photodegradation of 2,4-dichlorophenol after 5 h. This study indicates the potential use of silver halides, specifically Ag/AgBr under visible light irradiation, for the remediation of 2,4-dichlorophenol in the environment.

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References

- Adenuga, D. O., Tichapondwa, S. M. & Chirwa, E. 2019. Synthesis and characterisation of potential visible-light photocatalyst and its photocatalytic activity in the decomposition of phenol.
- An, C., Wang, J., Liu, J., Wang, S. & Zhang, Q.-H. 2014. Plasmonic enhancement of photocatalysis over Ag incorporated AgI hollow nanostructures. *RSC advances*, 4, 2409-2413.
- An, C., Wang, S., Sun, Y., Zhang, Q., Zhang, J., Wang, C. & Fang, J. 2016. Plasmonic silver incorporated silver halides for efficient photocatalysis. *Journal of Materials Chemistry A*, 4, 4336-4352.
- Aziz, K. H. H., Miessner, H., Mueller, S., Mahyar, A., Kalass, D., Moeller, D., Khorshid, I. & Rashid, M. A. M. 2018. Comparative study on 2, 4-dichlorophenoxyacetic acid and 2, 4-dichlorophenol removal from aqueous solutions via ozonation, photocatalysis and non-thermal plasma using a planar falling film reactor. *Journal of hazardous materials*, 343, 107-115.
- Cui, L., Jiao, T., Zhang, Q., Zhou, J. & Peng, Q. 2015. Facile preparation of silver halide nanoparticles as visible light photocatalysts. *Nanomaterials and Nanotechnology*, 5, 20.
- Fan, Y., Han, D., Song, Z., Sun, Z., Dong, X. & Niu, L. 2018. Regulations of silver halide nanostructure and composites on photocatalysis. *Advanced Composites and Hybrid Materials*, 1, 269-299.
- Kuai, L., Geng, B., Chen, X., Zhao, Y. & Luo, J. 2010. Facile subsequently light-induced route to highly efficient and stable sunlight-driven Ag- AgBr plasmonic photocatalyst. *Langmuir*, 26, 18723-18727.
- Liu, Y., Yan, Z., Chen, R., Yu, Y., Chen, X., Zheng, X. & Huang, X. 2019. 2, 4-Dichlorophenol removal from water using an electrochemical method improved by a composite molecularly imprinted membrane/bipolar membrane. *Journal of hazardous materials*, 377, 259-266.
- Ma, X., Dai, Y., Guo, M. & Huang, B. 2012. The role of effective mass of carrier in the photocatalytic behavior of silver halide-based Ag@ AgX (X= Cl, Br, I): A theoretical study. *ChemPhysChem*, 13, 2304-2309.
- Melián, E. P., Díaz, O. G., Rodríguez, J. D., Araña, J. & Peña, J. P. 2013. Adsorption and photocatalytic degradation of 2, 4-dichlorophenol in TiO₂ suspensions. Effect of hydrogen peroxide, sodium peroxodisulphate and ozone. *Applied Catalysis A: General*, 455, 227-233.
- Organization, W. H. 2003. Atrazine in drinking-water: background document for development of WHO guidelines for drinking-water quality. World Health Organization.
- Reddy, D. A., Choi, J., Lee, S., Ma, R. & Kim, T. K. 2015. Green synthesis of AgI nanoparticle-functionalized reduced graphene oxide aerogels with enhanced catalytic performance and facile recycling. *RSC advances*, 5, 67394-67404.
- Shi, H., Chen, J., Li, G., Nie, X., Zhao, H., Wong, P.-K. & An, T. 2013. Synthesis and characterization of novel plasmonic Ag/AgX-CNTs (X= Cl, Br, I) nanocomposite photocatalysts and synergetic degradation of organic pollutant under visible light. *ACS applied materials & interfaces*, 5, 6959-6967.
- Sobiesiak, M. 2017. Chemical structure of phenols and its consequence for sorption processes. *Phenolic compounds-natural sources, importance and applications*. IntechOpen.
- Tian, B. & Zhang, J. 2012. Morphology-controlled synthesis and applications of silver halide photocatalytic materials. *Catalysis Surveys from Asia*, 16, 210-230.
- Wang, D., Duan, Y., Luo, Q., Li, X. & Bao, L. 2011. Visible light photocatalytic activities of plasmonic Ag/AgBr particles synthesized by a double jet method. *Desalination*, 270, 174-180.
- Yan, T., Zhang, H., Luo, Q., Ma, Y., Lin, H. & You, J. 2013. Controllable synthesis of plasmonic Ag/AgBr photocatalysts by a facile one-pot solvothermal route. *Chemical engineering journal*, 232, 564-572.