

Ternary Ag/AgCl/BiOCl Synthesis and the Effects of its Constituents on Phenol Degradation

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Mineralisation of organic constituents in wastewaters emanating from petrochemical processing plants, coal powered energy generation, nuclear power and processing of algal infested waters could render the waste streams reusable for the purpose of reduction of water consumption and protection of the environment from harmful pollutants. Semiconductor photocatalysis, a particle physics based class of advanced oxidation processes (AOPs) has been tried as greener technology for removal of organic pollutants in gaseous phases (e.g. air and steam) and in aquatic phases. Pioneering investigators utilised titanium as a photocatalyst using UV light as the energy source resulting in an electron band-gap of 3.2 eV. The UV lamps consumed a lot of electricity which makes the technology operationally non-feasible. This study focussed on the synthesis and evaluation of an alternative photocatalyst comprised of Ag/AgCl/BiOCl with the potential of achieving photocatalysis of organic compounds under solar irradiation. All degradation tests were carried out on synthetic phenol wastewater. The effect of the components that make up the composite was also investigated. The catalysts were characterised using X-ray diffraction (XRD) and Fourier-transform infrared (FTIR). The degradation efficiency of Ag/AgCl/BiOCl, AgCl/BiOCl and BiOCl under UV light were 60 %, 56 % and 55 %. The visible light irradiation achieved degradation of 52 %, 51 % and 15 % for the same catalysts after 4.5 h of irradiation. These results suggest a more practical and realistic application of photocatalysis in the industry through the development of a visible-light responsive catalysts.

1. Introduction

Petrochemical pollutants such as phenol, chlorophenols, polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs), if discharged to the environment can cause lasting damage to natural ecosystems (Singh et al., 2018). These compounds are most known for their persistence and recalcitrance in the environment. The non-derivatised phenol was chosen in this study as a simplified model to demonstrate the degradation pathway under photocatalytic conditions. Photocatalysis makes use of a semiconductor catalyst suspended in aqueous medium which when illuminated with UV or visible light produces photogenerated electrons and holes on the surface of the catalyst. These photogenerated sites then act as sites for the oxidation of organic pollutants through the production of free radicals. Titanium dioxide is the most widely researched photocatalyst due to its high chemical stability and low cost. However, its commercial use has been limited by the need for UV light activation due to the wide band-gap of 3.20 eV (Magalhaes et al., 2017). This has led to concerted efforts in the development of photocatalysts with bandgap energies compatible with the energy of photons of visible light emitted by the sun (Ganeshraja et al., 2018). Two strategies have been used in this regard, sensitisation of TiO₂ through the introduction of doping agents or the synthesis of new catalysts and catalyst combinations. The current study builds on previous work from our research group where a composite photocatalyst comprising of Ag/AgCl/BiOCl was synthesised and tested for its efficiency under UV and visible light irradiation (Adenuga et al., 2019).

Bismuth-based oxides with 3D hierarchical structures such as Bi₂O₃, Bi₂WO₆, Bi₂MoO₆, BiPO₄ and BiOX (X=Cl, Br and I) have received considerable attention as semi-conductor catalysts due to the nature of their valence bands which are hybridised by O 2p and Bi 6s and therefore reduce the potential for electron-hole recombination (Lin et al., 2016). Bismuth oxychloride (BiOCl) is a p-type semiconductor that is characterised by an internal structure of [Bi₂O₂]²⁺ layers which are interleaved by double slabs of Cl⁻ (Gao et al., 2015).

BiOCl has a bandgap in the 3.2 - 3.4 eV range but electron flow is better due to its metal doped components (Sánchez-Rodríguez et al., 2018). BiOCl is an ideal photocatalyst due to its high photo activity, chemical stability and its distinctive electrical, optical and magnetic properties. However, like TiO₂, its wide bandgap permits activation mainly within the UV range (Cai, 2015). It has therefore been hypothesised that coupling the BiOCl with photoactive AgX (X = Cl, Br, I) may improve the response of the catalyst to visible light at various bandgaps (Ao et al., 2014). Previous work has illustrated the potential of the Ag/AgCl/BiOCl composite catalyst in the degradation of dyes such as methyl orange, rhodamine B and tetracycline (Zhao et al., 2018). Our recent work also highlighted the effectiveness of the composite catalyst in the degradation of phenol under both UV and visible light irradiation (Adenuga et al., 2019). Whilst the effectiveness of the ternary composite catalyst has been illustrated, the contribution of the individual compounds that make up the composite have not been reported. The current study investigates the influence of BiOCl and AgCl/BiOCl towards the photocatalytic degradation of phenol under UV and visible light irradiation and compares the results to the ternary composite. Based on the results obtained, a photocatalytic reaction mechanism is proposed highlighting the interaction of the constituent compounds.

2. Experimental

2.1 Synthesis

BiOCl was synthesised using a simple hydrolysis method at room temperature. The synthesis materials consisted of hexadecyltrimethylammonium chloride (CTAC) dissolved in water and bismuth (III) nitrate pentahydrate (Bi(NO₃)₃·5H₂O) dissolved in a mixture of ultrapure water and glacial acetic acid. AgCl/BiOCl was synthesised by adding AgNO₃ to the prepared BiOCl solution and stirring in the dark. For the Ag/AgCl/BiOCl synthesis step, the AgCl/BiOCl solution was irradiated under visible light for 1 h. All particles were collected, centrifuged and washed with ethanol, followed by water then dried at 80 °C for 8 h. The synthesis method is depicted in Figure 1.

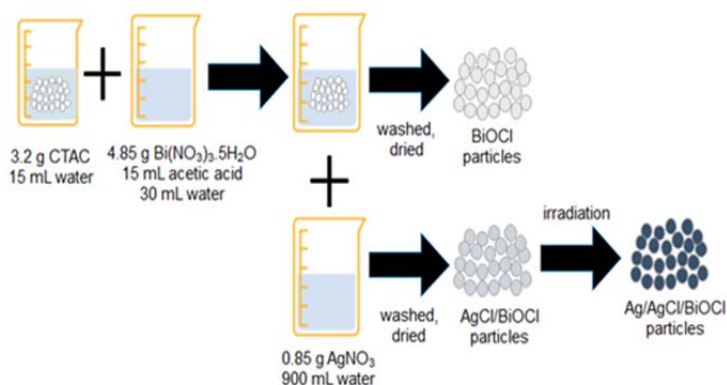


Figure 1: BiOCl, AgCl/BiOCl and Ag/AgCl/BiOCl synthesis

2.2 Characterisation

The sample was analysed using a PANalytical X'Pert Pro powder diffractometer in θ - θ configuration with an X'Celerator detector and variable divergence and fixed receiving slits with Fe filtered Co-K α radiation ($\lambda = 1.789 \text{ \AA}$). The phase identification was determined by selecting the best-fitting pattern from the ICSD database to the measured diffraction pattern, using X'Pert Highscore plus software.

Infrared spectra (FTIR) were recorded using a Perkin Elmer Spectrometer with a MIRacle ATR with Zn/Se. The spectra were obtained in the wavenumber range of 4,000 cm⁻¹ to 550 cm⁻¹ with a resolution of 2 cm⁻¹.

2.3 Photocatalytic activity

The photocatalytic activities of BiOCl, AgCl/BiOCl and Ag/AgCl/BiOCl composite were evaluated by monitoring the degradation of phenol under UV and visible light irradiation. The experimental setup involved the use of a 36 W lamp for UV irradiation and six 36 W OSRAM Fluora lamps for visible light irradiation. For each test, 0.83 g/L concentration of catalyst power was added to a 10 mg/L phenol solution. The solution was stirred for 30 min in the dark to reach absorption-desorption equilibrium prior to irradiation. During the irradiation experiment, 2 mL samples were collected and centrifuged at 9,000 rpm for 10 min. The collected solution was further filtered, and the resultant solution was then analysed using a Waters High-Performance Liquid

Chromatography (HPLC) with Empower software. The mobile phase was a combination of 1 % acetic acid in water and 1 % acetic acid in acetonitrile. The efficiency of degradation was calculated by Eq(1):

$$\% \text{ Degradation} = (C_0 - C) / C_0 \times 100 \quad (1)$$

where C_0 is the initial concentration of phenol and C is the concentration of phenol at any given time, t .

3. Results and discussion

3.1 Characterisation

Figure 2 shows the XRD patterns of BiOCl, AgCl/BiOCl and Ag/AgCl/BiOCl photocatalysts. The peaks are indexed from the ICSD database. The sharp peaks showed that the materials are of high purity and crystallinity with no impurities being detected. AgCl/BiOCl and Ag/AgCl/BiOCl had similar XRD patterns. This indicates that no Ag was detected. This is likely due to the low composition of Ag. This observation is consistent with work from Zhao et al. (2018). The weak peaks at 32.2° , 57.5° observed coincide with AgCl patterns.

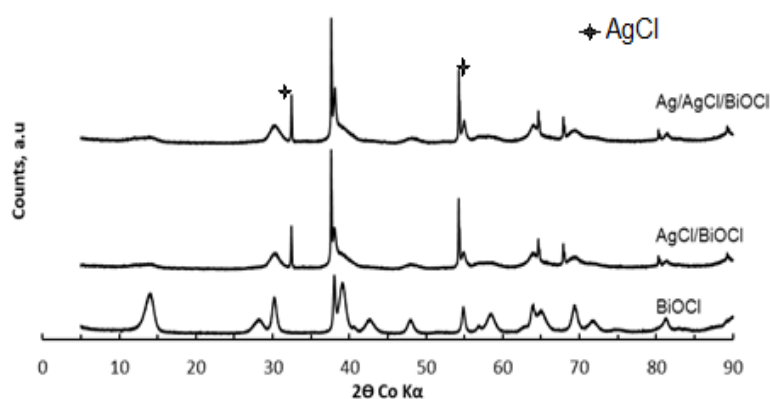


Figure 2: XRD analysis for BiOCl and AgCl/BiOCl

Figure 3 shows the FTIR analysis that was carried out in order to understand the functional groups present on the catalyst surface. A broad band noticed at the $3,400 - 3,500 \text{ cm}^{-1}$ range could be as a result of interactions with water by hydrogen bonds (O – H) (Sánchez-Rodríguez et al., 2018). The bands at $2,923$, $1,600$ and $1,357 \text{ cm}^{-1}$ correspond to carboxyl and alkanes groups which are as a result of remnants from the synthesis process such as CTAC and acetic acid and could also be as a result of adsorbed CO_2 (Singh et al., 2018). The band at 550 cm^{-1} for BiOCl is attributed to the Bi – O bond which is an important characteristic for this compound.

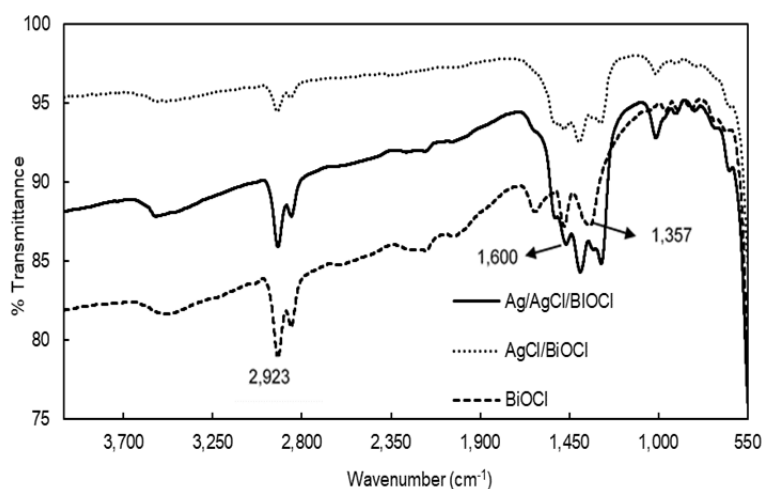


Figure 3: FTIR spectrum for BiOCl, AgCl/BiOCl and Ag/AgCl/BiOCl

3.2 Photocatalytic activity

The photocatalytic potential of the prepared photocatalyst composite was investigated based on its ability for the degradation of phenol. Figure 4 shows the photocatalytic activity of BiOCl, AgCl/BiOCl and Ag/AgCl/BiOCl under UV irradiation. The results show that an average of 15 % phenol was adsorbed on the surface of the catalysts in the first 30 min of the experiment. After 4 h of UV irradiation, a total photocatalytic degradation efficiency of 55 %, 56 % and 60 % was attained by BiOCl, AgCl/BiOCl and Ag/AgCl/BiOCl. This shows that all three catalysts can be activated by UV light.

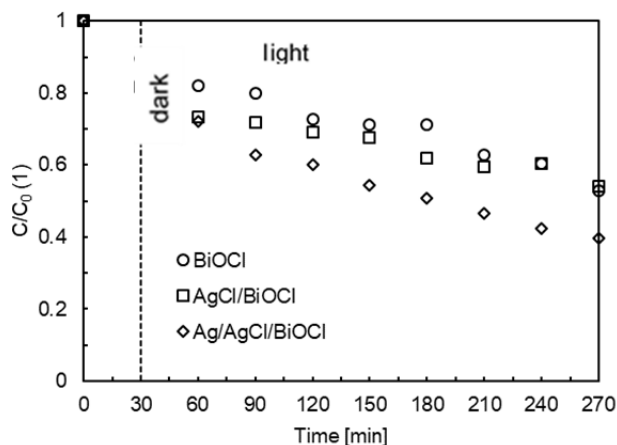


Figure 4: BiOCl, AgCl/BiOCl and Ag/AgCl/BiOCl degradation of phenol under UV irradiation

Figure 5 shows that phenol degradation efficiency of the catalysts under visible light irradiation was 15 %, 50.6 % and 52 % at 4 h for the different experiments with BiOCl, AgCl/BiOCl and Ag/AgCl/BiOCl. These results correlate with the work done by Wang et al. (2014) where the degradation efficiency of 4-nitrophenol using BiOCl was tested under both UV and visible light irradiation. They found that while 47.61 % degradation was obtained in UV light, only 5 % degradation was observed under visible light after 120 min. Figure 5 shows that BiOCl adsorbed 20 % of the phenol after contacting the catalyst with the simulated wastewater for 30 min in the dark. A slight change in concentration was noted after visible light irradiation, this suggests that the bandgap of the catalyst is too wide for it to be activated by visible light. Zhang et al. (2008) synthesised BiOX (X= Cl, Br, I) powders and investigated their activity in the degradation of methyl orange (MO). They found the degradation of MO under UV-visible light using BiOCl to be 17 % and its degradation in 3 h under visible light to be 15 %.

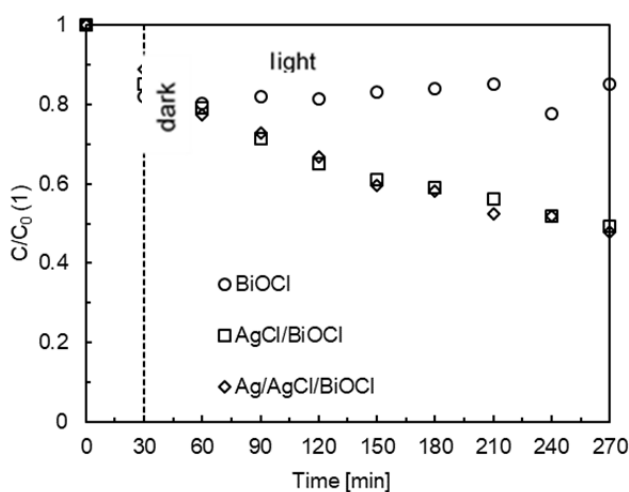


Figure 5: BiOCl, AgCl/BiOCl and Ag/AgCl/BiOCl degradation of phenol under visible light

AgCl/BiOCl and Ag/AgCl/BiOCl had similar photodegradation activity under visible light. Jiao et al. (2019) explains that while Ag nanoparticles advance the visible light absorption and photodegradation activity, its presence in excess on the surface of a catalyst may block incident light and reduce photocatalytic activity. These results show that coupling Ag/AgCl with BiOCl significantly improves the photocatalytic activity of BiOCl under visible light. This is as a result of efficient separation of photo-generated electron-hole pairs due to the modification in the spherical structures of the as-synthesised photocatalysts composites and the presence of the metallic Ag (Liu et al., 2017). The surface plasmon resonance (SPR) and dipolar effect of Ag traps visible light and the absorbed photon is efficiently separated into an electron and a hole thereby decreasing recombination (Ye et al., 2012).

3.3 Proposed photocatalytic mechanism

Figure 6 shows a proposed mechanism for the photo-degradation of phenol in visible light based on the results obtained. During degradation of phenol in visible light, AgCl absorbs light and excites electron hole pairs by the photosensitive effect which are then transferred to the BiOCl (Zhao et al., 2019). The results show that BiOCl on its own is unable to absorb visible light but could absorb UV irradiation. The transferred electrons combine with O_2 which generates the $O_2^{\cdot-}$ radical. It should be noted that the photogenerated hole in AgCl could also oxidise organic pollutant molecule (Chen et al., 2016). Hydroxy radicals (HO^{\cdot}) are formed in the presence of dissolved O_2 which then reacts with phenol until mineralization is achieved (Chowdhury et al., 2017). Therefore, Cl^- , OH^- and $O_2^{\cdot-}$ are directly responsible for the oxidation of the organic pollutant. The use of AgCl and BiOCl as a composite material in photocatalysis ensures that the transportation of the photogenerated carriers is fast thereby reducing recombination (Zhao et al., 2019).

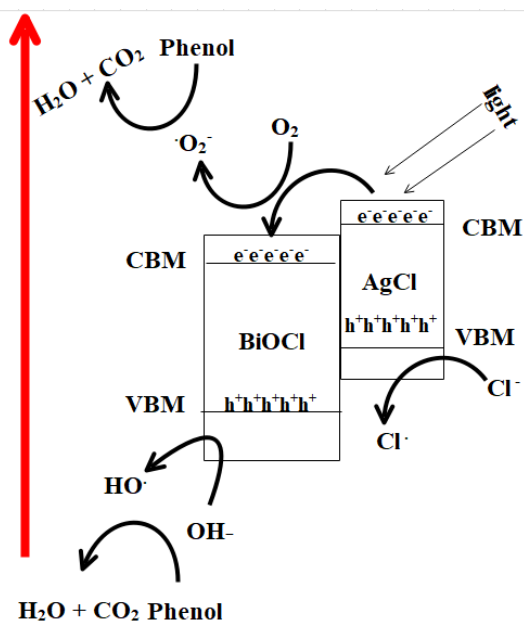


Figure 6: Proposed photocatalytic mechanism

4. Conclusions

BiOCl, AgCl/BiOCl and Ag/AgCl/BiOCl were successfully synthesised, and the main physical characteristics were determined using XRD and FTIR. All three catalysts showed significant photocatalytic activity under UV irradiation, with more than 50 % phenol being degraded by all the catalysts. The ternary and binary catalyst composites, Ag/AgCl/BiOCl and AgCl/BiOCl, exhibited substantial photocatalytic degradation efficiencies towards phenol under visible light. However, the BiOCl alone was unresponsive to visible light activation. This confirms that it is necessary to couple the BiOCl with AgCl in order to promote the synergistic interaction of the band gaps of the two materials for visible light activation. The positive results obtained under visible light irradiation indicate that natural sunlight can potentially be used to activate this composite catalyst, rendering the photocatalysis remediation process economically viable and sustainable.

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