Biological analogues in advanced water treatment with application in 3D printed graphene oxide and metal-halide BixOyClz/AgCl composite heterogeneous photocatalysis

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Abstract

Engineering can be made simple and more impactful by observing and understanding how organisms in nature solve eminent problems. For example, scientists around the world have observed green plants thriving without organic food inputs using the complex photosynthesis process to kick start a biochemical food chain. Observations have also been conducted on bacteria multiplying in diverse environments, some so unimaginable for life to exist. In several studies, complex biochemical pathways for detoxification and degradation of pollutants were emulated in AOPs and photocatalytic processes. This includes the development of heterogeneous nanoparticle materials for photocatalytic reactions and solar desalination for recovery of water mimicking the z-scheme photochemical process used by plants. How plants split water to H+ and O2 to produce the reducing equivalents (~e-) is still a subject of intensive research. If a material is found that is capable of releasing H2(g) from water, that will solve the world’s energy crisis for forthcoming generations. From the fundamental energy transduction processes in microorganism, the research group from the Water Utilisation Group at the University of Pretoria has studied and developed fundamental processes for degradation and remediation of unwanted compounds such as disinfection byproducts (DBPs), volatile organic compounds (VOCs) and pharmaceutical products from water. The research entailed the derivation, synthesis and characterisation of visible-light activated metal-halide heterogeneous photocatalysts for degradation of hard-to-degrade organic pollutants, intermediates and their congeners from wastewater and water from impaired sources. The processes of low energy photocatalysis and 3D printed graphene oxide solar desalination and degradation of compounds were evaluated as developments towards future applications.

**Keywords**: biological analogues, z-scheme, heterogenous photocatalysis, 3D printed graphene, organics degradation.

* 1. Introduction

While investigating the photoelectrolysis of water, the discovery by Fujishima and Honda in 1972 of the photocatalytic splitting of water on *n*-type rutile titanium dioxide (TiO2) electrodes opened the doors to numerous possibilities that the field of photocatalysis presents (Hashimoto *et al*., 2005). The limitation of TiO2 photocatalysis is due to its wide band-gap energy which is mostly activated using high-frequency UV light produced by high-pressure mercury lamps. Many studies have recently been undertaken to unravel the underlying principles of oxidative degradation of organic pollutants in aqueous phase (Mzimela et al., 2023), photodegradation pathways, as well as identification of intermediates produced during photocatalysis (Bamuza-Pemu and Chirwa, 2010).

Based on the predominant scientific understanding of the enzymatic redox processes in living cells, the redox processes in a photocatalytic semiconductor particle during the oxidation of water at the valance band (h+) and reduction of oxygen at the conduction band (e-) is presented as a set of equations, Eqs. (1-7):

|  |  |
| --- | --- |
| TiO2 + *hv* → TiO2 (e−CB + h+VB) | (1) |

|  |  |
| --- | --- |
| TiO2(h+VB) + H2Oad → TiO2 + •OHad + H+ | (2) |

|  |  |
| --- | --- |
| TiO2(h+VB) + OH− → TiO2 + •OHad | (3) |

|  |  |
| --- | --- |
| TiO2 (e−CB) + O2 → TiO2 + O2− | (4) |

|  |  |
| --- | --- |
| O2− + H+ → HO2• | (5) |

|  |  |
| --- | --- |
| TiO2(h+VB) + R-H → TiO2 + oxidized products | (6) |

|  |  |
| --- | --- |
| •OH + R-H → oxidized products | (7) |

The photogenerated electrons that are available to reduce oxygen to water are passed on through the Redox reactions, Eqs.(1-5). The photogenerated h+ oxidise organic pollutants, Eq.(6), and oxidation of organic compounds by •OH generated indirectly by photolytic reactions is illustrated by Eq.(7). The mineralization process is believed to involve the initial oxidation of surface hydroxyl groups (>TiIVOH) on the TiO2 to hydroxyl radicals (>TiIV OH•+), which oxidizes the pollutant and any intermediate(s).

Alternatively, visible-light activated metal-halide heterogeneous photocatalysts are suggested derived based on BiOCl stoichiometry. These studies have one theme in common, i.e., the catalysts activation following a model similar to the photoenergy transduction and electron generation using the z-scheme photosynthetic process in green plants. Surface interaction models followed standard Langmuir isotherms, however interactive conversion of species was highly non-linear with multi-species rate limiting levels following the simulation routine derived by Khuzwayo and Chirwa (2016). Complementary photocatalytic performance matrices were established to estimate parameters based on the Taguchi orthogonal arrays (Sendin et al., 2004).

The aim of this study was to develop efficient visible-light driven photocatalysts for degradation of toxic organics in water based on known processes from nature. Examples being the AgCl/BixOyClz (Adenuga et al., 2023) and porphyrin@Bi12O17Cl2 (Ogbeifun et al., 2023). Batch results for the above photocatalysts showed 80.3% and 83.4% degradation of phenol, respectively, after 6 hours exposure to visible-light.

* 1. Experimental Methods
     1. Synthesis of Heterogeneous Metal-Halide Photocatalysts

The synthesised Bi24O31Cl10 (0.2 g) was added into 50 mL of water with continuously stirring. A 10 mL solution containing 50 mg cetyltrimethyl ammonium chloride (CTAC) was added to the suspension and stirred for 1 h. AgNO3 (27 mg) dissolved in 10 mL water was slowly added into the Bi24O31Cl10/CTAC suspension and stirred continuously for 2 h. The collected precipitate was washed with ethanol and water before being dried at 60 oC for 8 h. This resulted in 10% AgCl on a mass basis being deposited on the BOC to form a composite photocatalyst. The process is illustrated in Figure 1.



*Figure 1. Schematic diagram illustrating the preparation process of Xwt%AgCl/BOC heterojunction photocatalyst.*

* + 1. Reactor Studies

All experiments were conducted in batch with different doses of the photocatalyst under visible-light with UV irradiation as a control. For systems with ultimate catalyst dose, the concentration of test compounds was varied to determine the effect of loading on reaction rates. Effective photocatalytic reaction was measured from the point when the light was turned on as time zero.

* + 1. Photocatalyst Characterization Studies

The crystal structure of the synthesized photocatalysis was determined using SEM. The composition of synthesized materials was verified by SEM-EDX, XRD, XPS and FTIR. Particle size distribution and surface area was determined by the Mastersizer 3000 — Particle Size Analyzer and BET analysis. XRD, SEM-EDX and XPS characterization results are shown in Figure 2 whereas particle size and surface area relationship data is discussed in Section 3.

* + 1. Parameter Analysis and Optimisation

The program Sugal 2.1 by Hunter (1995) was interfaced with the simulation program using Modified Sugal GA subroutine (Chirwa, 2001). The Genetic Algorithm uses the fitness function, , and an evolutionary search engine to find the best parameters for the system of equations (Eqs. 8-9):

|  |  |
| --- | --- |
|  | (8) |

|  |  |
| --- | --- |
|  | (9) |

where *RSS* = residual sum of squares, = fitness function, *n* = number of points to evaluate, *q* = number of parameters, ***y****i*pred = model prediction for a given set of parameters, and ***y****i*obs = a corresponding experimental value. The genetic algorithm was terminated with a coarse set of parameters within vicinity of the true optima. A faster converging gradient method, the Levenberg-Marguardt algorithm, was used to fine tune convergence to the global optimum.

(c)

(a)

|  |  |
| --- | --- |
|  |  |
| (d)  (b) |  |
|  |  |

*Figure 2. (a-b) Composition characterization using XRD and SEM for a BiOCl/AgCl system, and (c-d) XRD and SEM-EDS for the synthesized porphyrin@Bi12O17Cl2 photocatalyst.*

* 1. Results and Discussion
     1. Catalyst Performance Data - BiOCl/AgCl system

The compound *BiOCl/AgCl* was tested on phenol degradation under visible light irradiation and is reported in Figure 3a. Experiments were carried out under photolysis and adsorption conditions to investigate the individual effects of light and photocatalyst. The results show negligible degradation of phenol illustrating that light and photocatalysts are required for photocatalytic degradation to take place. The compound porphyrin@Bi12O17Cl2 achieved similar results as demonstrated by Figure 3b.

|  |  |
| --- | --- |
|  | (a)  (b) |

*Figure 3. (a) Degradation of phenol as a model compound using the BiOCl/AgCl system, and (b) degradation of RhB dye by the* *porphyrin@Bi12O17Cl2 photocatalyst.*

The results in Figure 3a show clearly that photocatalytic degradation of phenol in a complex matrix was highest under visible light using the *BiOCl/AgCl* heterogeneous photocatalyst. Notably, no degradation was observed in the absence of light even in the presence of the heterogeneous photocatalyst.

(a)

|  |  |
| --- | --- |
|  | (b) |

*Figure 4. (a) Correlation of date to the pseudo-first order rate kinetic which yielded the optimum operational condition for a z-scheme photocatalytic model using Rhodamine B (RhB) dye, and (b) light absorption conditions for different structural compositions.*

* + 1. Catalyst Performance Data - porphyrin@Bi12O17Cl2

Similar results were observed with the porphyrin@Bi12O17Cl2 photocatalyst (Figure 3b). In this version of photocatalyst, the best reaction was achieved with a 1% of porphyrin to the BiOCl composite. It was demonstrated here that there is still room of improvement in the development of metal-halide heterogeneous photocatalysts through inclusion of organic reactive compounds that were never studied before.

* + 1. Suggested Operational Model

The kinetics of RhB dye degradation were determined from the data obtained in the degradation study to be *pseudo-first order* kinetic equation. *First-order kinetic* –ln*C*/*Co* = *kt* where *C0* and *C* are the initial and final concentrations of RhB dye, *k*, the rate constant, and *t*, the time, was used to fit the experimental data. The *pseudo-first order* kinetic was confirmed from the linear curve in Figures 4 (a) and (b). The *R2* values for 0.02%Porph@BOC, 0.1%Porph@BOC, 0.4%Porph@BOC, 1%Porph-@BOC, 10%Porph@BOC and BOC were found to be 0.9566, 0.97107, 0.97808, 0.99063, 0.97548, 0.94701, 0.97018.

* 1. Conclusions

Semiconductor photocatalytic nano-particles prepared by facile combustion and hydrothermal methods produced stable AgCl/Bi24O31Cl10 and porphyrin@Bi12O17Cl2 photocatalysts capable of degrading phenolics and antibiotic pharmaceuticals under vis-light irradiation. The structural, optical, morphological, textural, and magnetic properties of the as-synthesised nanocomposites indicated degradation with 83.5% removal efficiency of phenol, 98% removal efficiency of RhB dye and 99.5% removal efficiency of tetracycline, with first-order degradation *k* = 0.020, 0.362, and 0.032 h-1, respectively. In this case, tetracycline and RhB were used as surrogate compounds for pollutants emanating from major industrial polluters around the world. The derived heterogeneous photocatalysts exhibited excellent chemical stability and recyclability after five runs without need for any significant alteration in its structural and morphological properties.

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