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Solar photocatalytic degradation of Zn^{2+} using graphene based TiO_2

Gloria Kumordzi [a], Ghodsieh Malekshoar [a], Ernest K. Yanful [b], Ajay K. Ray [a,*]

[a] Department of Chemical and Biochemical Engineering, University of Western Ontario, London, Ontario N6A 5B9, Canada
[b] Department of Civil and Environmental Engineering, University of Western Ontario, London, Ontario N6A 5B9, Canada

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ABSTRACT

The improvement of photocatalytic efficiency under an abundant natural resource, sun light, presents the next step in the large-scale application of photocatalysis for the treatment of dissolved organic and inorganic pollutants in wastewater. In this study, a composite catalyst of TiO_2 and Graphene synthesised by a hydrothermal treatment method is used to photo-reduce Zn^{2+}, the most abundant heavy metal found in combined sewer overflows (CSOs). The performance of this composite photo-catalyst was assessed under various process conditions such as pH, light intensity, catalyst loading and light source. The TiO_2-Graphene composite photo-catalyst showed a 20.3 ± 0.04% increase in the photo-reduction of Zn^{2+} under solar light compared to un-doped TiO_2 when reaction rate constants are compared. This enhancement is a result of the availability of more sorption sites, decrease in band-gap of the TiO_2, and effectiveness of the charge separation in the TiO_2-G composite catalyst.

1. Introduction

The application of heterogeneous photocatalytic technology for degradation of various dissolved organic and inorganic pollutants has been widely studied in recent years because of its potential in environmental remediation [7,8,17,21,24,37,41,43,54,57,68]. One such application, for which solar photocatalytic treatment can be extended to, is the removal of dissolved components in Combined Sewer Overflows (CSOs) in wastewater treatment plants. CSOs comprising industrial, domestic wastewater and surface run-offs commonly occur during wet weather events in most urban areas using aged combined sewer systems. Although storm water run-off pollutant concentration is greatly influenced by the land use in a particular area, CSOs may generally contain significant levels of suspended solids, heavy metals, nutrients, oxygen demanding organic material, pathogens, suspended solids, oil and grease [16,26].

At present, CSOs discharge requirement are not stringent. For example, in Ontario Canada, the minimum level of treatment is primary treatment or equivalent corresponding to 30% $CBOD_5$ and 50% TSS removal [73]. For these reasons there is increased concern over their occurrence because overflows are detrimental to the overall receiving surface water quality [48,64] and this becomes even more critical when the same water body is the source of drinking water [12]. To this effect, the need to develop high-rate treatment technologies with the ability to also treat the dissolved components in anticipation of future requirements is laudable.

Heavy metals as a major constituent of overflows find their way into wastewater streams by a number of means such as domestic activities, industrial wastewater, storm water runoff etc. [22]. Focusing on dissolved metal ion pollutants, some studies conducted on CSOs found aluminium (Al), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn) and zinc (Zn) concentrations exceeded that for tertiary treated wastewater. In addition, surface run-off contributes high concentrations of Cu and Zn to the wastewater while Fe and Al are also present in significant quantities [58]. These metal ions are non-biodegradable and they accumulate in concentration over time, which pose a long term effect [47]. However, for the purposes of this study, Zn^{2+} (−0.76 V) being the most abundant metal ion in most surface run-offs was used as the model compound. More so, studies showing severe environmentally unfriendly conditions arise when other heavy metals such as cadmium are present in significant quantities due to synergistic effects [60].

Photocatalytic reactions occur when electron-hole pairs are generated as a result of the irradiation of a photocatalyst with light, providing energy equal to or greater than the band-gap. These photo-generated electrons may react with electron acceptors such as oxygen and/or metal cations (photo-reduction), while the photo-generated holes may react with electron donors such as organic materials (photo-oxidation) [9]. In recent times, the goal

* Corresponding author.
E-mail address: aray@eng.uwo.ca (A.K. Ray).

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Nomenclature

C	concentration (ppm)
I	light intensity (mW/cm^2)
K_{ads}	adsorption equilibrium constant (ppm^{-1})
k_1	pseudo-first-order rate constant (min^{-1})
k_2	pseudo-second-order rate constant (g/mg min)
r	reaction rate (mg/L min)
q	adsorption capacity (mg/g)
NHE	normal hydrogen electrode
SHE	standard hydrogen electrode
T	temperature (K)
t	time (min)
V	volume (L)
λ	wavelength

Subscript/superscript

0	initial
app	apparent
cat	catalyst
m	maximum

of photocatalysis is to utilize direct sunlight, an enormous renewable energy source, for the photo-degradation process due to its potential of becoming cost effective and reliable in augmenting currently expensive and complicated conventional treatment methods [7]. However, Titanium Dioxide (TiO_2) as the most widely used semiconductor material, which has proven to be biologically and chemically stable, nontoxic, insoluble under most conditions and inexpensive, has a major drawback with respect of its wide band-gap (3.2 eV) [8,42]. This limits the light energy sufficient for the activation and continuity of reaction to the ultraviolet (280–390 nm) range of the solar spectrum. The sum of ultraviolet (UV) wavelengths makes up only approximately 4% of the entire solar energy spectrum [1] while the visible light reaching the surface of the earth represents about 43–46% of the solar radiation. This translates to reduced efficiency and the need to concentrate the energy in this small window and hence, the broad study of photo-reduction of metal ions using this UV range [11,29,62].

The three factors that are crucial to the effectiveness of photo-reduction are; pollutant adsorption onto the catalyst surface, light absorption of semiconductor photocatalyst and the charge transportation and separation [70]. For these reasons, improving the ability of the semiconductor to absorb light in the visible light region while hindering photo-generated charge recombination has proved to directly translate into the improvement of overall quantum efficiency of the process and also reduce future cost for larger-scale implementation. Therefore, modification to TiO_2 is necessary. Semiconductor catalyst enhancement can be achieved either by augmenting the band-gap (band-gap engineering) or photo-sensitisation technique [3,18,19,52]. Even though transition metal particle doping and other material combination with TiO_2 has been studied widely as a form of increasing the catalyst activity in the solar spectrum [52], carbon based TiO_2 composite materials are becoming of great interest [65]. At the center of these carbon-based material, is the use of graphene [20,23,27,38,41,51,56] due to its unique characteristics such as chemical inertness, stability in both acidic and basic mediums, relatively large theoretical surface area (2630 m^2/g), its abundance, flexible structure, high transparency, and good electrical and thermal conductivity (2000–5000 W/m/K) [65]. It is made up of a single layer of graphite and is recognised as the thinnest and hardest material known currently (mechanical strength of 2.4 ± 0.4 TPa) [2,5,25,70]. Another interesting finding in recent studies indicates that graphene and its derived materials exhibit anti-microbial activity, which is essential for the disinfection of wastewater [34].

Graphene-semiconductor composites, synthesised by different methods have been used for the degradation of various dyes and other recalcitrant organic [45,55]. However, its application in photo-reduction reactions has not yet been systematically studied to the best of our knowledge. Liu et al. Liu et al. [39] reported the enhancement in photocatalytic activity of a ZnO-TiO_2-RGO (10 wt% graphene) composite for the reduction of Cr(VI) to Cr(III) as compared with pure ZnO-RGO. Zhang et al. Zhang et al. [71] reported that TiO_2-RGO (5 wt% graphene) composite enhance reduction of Cr(VI) under natural sunlight. The enhanced performance of TiO_2-RGO for the visible light removal of Cr(VI) to Cr(III) was discussed by Zhao et al. Zhao et al. [72] while Lee and Yang [32] investigated the adsorption capacity of TiO_2-G based on the hydrothermal treatment period of the composite semiconductor for the adsorption of Zn^{2+}, Cd^{2+} and Pb^{2+}.

Until date, there is extensive research on photocatalytic heavy metal ion reduction efficiencies and viabilities under various conditions. Metals such as Cr, Se, Ag, Pb and Cu that are more easily photo-reduced due to the position of their standard reduction potential, have been widely studied [13,14,30,31,33,35,53,63,66,72]. Ku and Jung [31] studied the kinetics of Cr(VI) photo-reduction, while Canterino et al. Canterino et al. [6] studied that of Cu(II). However, the application of photocatalytic treatment method for other metal ions such as Cd, Zn, Mn and Al, which are thermodynamically less favoured has been scarcely studied [10,44]. Therefore, further studies is required in this area due to the coexistence of metal ions in polluted wastewater streams such as CSOs [58].

So far, small concentrations of Zn^{2+} has been photo-reduced in the presence of TiO_2 under UV light irradiation [10] and also in the presence of natural sunlight (65–80 mW/cm^2) and hydrogen peroxide [28,61]. This study investigates and reports a systematic study of the effects of various process parameters such as pH, light intensity, light source and initial metal ion concentration on the photo-reduction of Zn^{2+} (the most abundant heavy metal ion found in CSOs) in suspended TiO_2 and TiO_2-G composite catalyst for the application in CSO treatment. It also reports the effect of the catalyst modification using graphene on the photo-reduction of the selected model compound Zn^{2+}.

2. Experimental section

2.1. Materials

Degussa P25 titanium dioxide (Evonic Degussa Corporation) was used. Zinc nitrate [$Zn(NO_3)_2{\cdot}6H_2O$ - 99%], trizma base, sodium hydroxide, hydrochloric acid, formic acid and ethanol (99.5%) were purchased from Sigma-Aldrich Canada Ltd. All chemicals were used without further purification.

2.2. Photocatalyst preparation and characterization

TiO_2-G composite was prepared using a hydrothermal process as reported by Malekshoar et al. [41]. X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS), UV spectra analysis, transmission electron microscope (TEM) and the scanning electron microscope (SEM) for structural and morphological analysis of the composite TiO_2-G 1% (mass ratio) were carried out and