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Visible-solar-light-driven photo-reduction and removal of cadmium ion with Eosin Y-sensitized TiO_2 in aqueous solution of triethanolamine

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ABSTRACT

Cadmium is toxic to humans, animals, and plants, and show persistence because of its non-degradability. Photo-reduction of cadmium ion (Cd (II)) was studied with Eosin Y-sensitized TiO_2 photocatalyst for the reduction/removal of Cd (II) in an aqueous medium under visible-solar light. Triethanolamine (TEOA) was used as a sacrificial electron donor. The band-gap of Eosin Y-sensitized TiO_2 photocatalyst was reduced by ~1 eV, and visible light activity was observed for Cd (II) photo-reduction. Parametric studies were performed for visible-solar light intensity, solution pH, and initial concentrations of metal ion, dye, photocatalyst, and an electron donor. Complete photo-reduction of Cd (II) was achieved in 3 h at a pH of 7.0 and a light intensity of 100 $mW\,cm^{-2}$. The photo-reduction rate of Cd (II) in TEOA solution followed Langmuir-Hinshelwood rate equation. The highest apparent quantum yield (~0.3%) for Cd (II) photo-reduction was observed at the lower visible light intensity with illuminated Eosin Y-sensitized TiO_2.

1. Introduction

Heavy metals are toxic to living organisms and are difficult to eliminate from the aquatic ecosystem due to their non-biodegradability and bio-accumulation in living tissues. For that reason, heavy metals are considered as priority pollutants according to the US EPA. Numerous past tragedies from heavy metal contamination are reported all over the world. In Japan, a notable incident was the 'Itai-Itai' disease outbreak due to cadmium contamination in the aquatic stream, which occurred post World War II. According to WHO and the US EPA, the maximum contaminant levels of cadmium are 0.003, and 0.005 $mg\,L^{-1}$, respectively [1]. The toxicity of cadmium compounds significantly depends on their solubility in aqueous medium. Cadmium in its free ionic form (Cd (II)) is readily absorbed and accumulated in an aquatic organism, and eventually endures toxic reactions. Cadmium in metallic form (Cd (0)) is not soluble in aqueous medium and thus poses a lesser threat to aquatic life [2,3].

Cadmium could be introduced into the aquatic system via agricultural practices and chemical industries, including electroplating industries, metallurgical alloying, metal-finishing industries, ceramics, photography, cadmium-containing pigments, textile printing, plastic production, polymerization processes, cadmium-containing phosphate fertilizers, refined petroleum products, and detergents [4,5]. Conventional treatment methods for heavy metal contaminated water include different techniques such as precipitation, ion-exchange, reverse osmosis, adsorption, and biological processes [4]. However, such technologies have an inadequate affinity and selectivity to reduce residual cadmium concentration to a level imposed by environmental and health regulatory bodies [6]. In addition, heavy metals such as Cd (II) is only captured and transformed from one phase to another and still exist in its toxic form [7]. Therefore, it is important to develop a method where Cd (II) can be reduced to Cd (0), which is non-toxic.

The photocatalytic process is considered to be a promising technology in addressing the above requirements. Photocatalysis has received considerable attention in last few decades as a suitable alternative for the treatment of wastewater containing organic compounds and some heavy metals [1,8–13]. Heavy metal removal mainly involves reduction reaction producing metal ion at a lower oxidation state. Only arsenic exists in anionic form and requires oxidation reaction to convert it to non-toxic higher oxidation state. Unlike other advanced oxidation processes (AOPs), heterogeneous photocatalysis has the capability to undertake both oxidation and reduction reactions [1]. It is a renowned method where light energy is employed to excite the semiconductor material

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Nomenclature

C	Cd (II) concentration, ppm	h^+_{VB}	valence band hole
C_0	initial concentration of Cd (II), ppm	h	Plank's constant
I_{Vis}	visible-solar light intensity, mW cm^{-2}	ν	frequency of light, Hz
K_A	adsorption rate constant, ppm^{-1}	ϕ	quantum yield, %
k_{app}	apparent kinetic constant, min^{-1}	$\phi_{Cd\ (II)}$	apparent quantum yield, %
r	reaction rate, ppm min^{-1}	α	light adsorption coefficient of the photocatalyst
t	time, min	β	constant
e^-_{CB}	conduction band electron	λ	wavelength of light, nm

producing electron-hole pairs. The photo-generated electrons in the conduction band are used by the metal ions and get reduced to the non-toxic form. Photo-reduction has been extensively studied for a number of heavy metals, including chromium, nickel, platinum, zinc, cadmium and mercury [1].

Cadmium photo-reduction has been attempted by several researchers with few semiconductor photocatalysts under UV light [4,14–16]. However, the thermodynamic driving force is low in case of Cd (II) photo-reduction, and thus require a hole scavenger to initiate the photo-reduction process [4]. Formic acid and methanol are two such hole scavengers that have been widely used for the photo-reduction of different metal ions including Cd (II) [4,17–19]. Hole scavengers mainly suppress the charge carrier recombination to accomplish the photo-reduction. They also produce secondary reducing radicals such as $CO_2^{-\cdot}$ (from $HCOO^-$) and $^{\cdot}CH_2OH$ (from CH_3OH) which also contribute to the photo-reduction process [4]. Till date, most of the Cd (II) photo-reduction studies have been performed with UV light which is a minor fraction (4%) of the solar spectrum. Visible light, on the other hand, comprises of 46% of the solar spectrum [20]. Moreover, UV light is not readily available and is expensive; in the future, we expect the use of solar light for large-scale applications of photocatalysis [21]. Visible and solar light assisted photocatalytic reduction studies have been reported for a few heavy metals with different photocatalysts [9,22–25]. However, so far no study has been performed for Cd (II) photoreduction under visible light. Therefore, enabling the reduction of Cd (II) using visible-solar light illuminated photocatalyst would be a breakthrough in the field of heavy metal removal via photocatalysis [26].

Dye-sensitization process is a well-known technique to expand the active spectral range of photocatalyst. It has been applied for degradation of carbon tetrachloride, trichloroethylene, hydrazine, pesticides, phenol, chlorophenols, and benzyl alcohol. In dye-sensitization process, sensitization of a larger band gap semiconductor to the visible region is achieved with a dye at the molecular level [27]. Among these dyes, transition metal-based dyes are the best but are very expensive and not environment-friendly. On the contrary, organic dyes are less toxic, less expensive and can be used for dye sensitization processes. Several organic dyes such as Eosin Y, Rose Bengal, Merocyanine, Cresyl Violet, and Riboflavin have been utilized for spectral sensitization of semiconductors [21,28]. Visible-light-driven photocatalytic reduction of heavy metals with dye-sensitized photocatalyst is rarely documented in the literature. Only Cr (VI) photo-reduction with Alizarin Red S dye-sensitized ZnO was reported recently under visible light irradiation [29]. To the best of our knowledge, no single study has been reported on Cd (II) photo-reduction with dye-sensitized photocatalyst under visible-solar light. The present study aims for the photo-reduction of Cd (II) from aqueous solution into its non-toxic form (Cd (0)), utilizing a dye-sensitized TiO_2 photocatalyst. Eosin-Y dye was used for the dye-sensitization of TiO_2. We have chosen Triethanolamine (TEOA) as a sacrificial agent which is proven to be an effective electron donor used in several studies of dye-sensitized photocatalysis [20,21]. The originality of the present study is the exploration of Eosin-Y dye-sensitized TiO_2 for the photo-reduction of toxic Cd (II) under visible-solar light.

2. Experimental

2.1. Chemicals

All reagents were of analytical grade and were used without further treatment. Aeroxide TiO_2 P25 (80% anatase, and 20% rutile) from Evonik Degussa Corporation was used as the photocatalyst. Eosin Y dye (99%, Sigma-Aldrich Canada Ltd.) was used as the sensitizer for TiO_2; TEOA (98%), and Formic acid (95%) were also purchased from Sigma-Aldrich Canada Ltd. Ultrapure water (18 MΩ) was prepared from an in-house EASY Pure RODI system (Thermo Scientific, Ontario, Canada). Cadmium nitrate tetrahydrate ($Cd(NO_3)_2 \cdot 4H_2O$), (98% purity) was purchased from Sigma-Aldrich Canada Ltd. and used to make standards and aqueous solutions for the photocatalytic reactions.

2.2. Light source

Simulated air mass (AM) 1.5 solar light was generated using a solar simulator (model SS1KW, Sciencetech, Ontario, Canada, with a 1000-W Xe arc lamp and an AM 1.5 G filter). AM is a ratio of the direct beam solar irradiance path length through the atmosphere at a certain solar zenith angle to the path length when the sun is in a vertical position (i.e. a zenith angles of 0°). An air mass of 1.5 corresponds to a solar zenith angle of 48.19° [20]. The light source was also equipped with a 420 nm cut-off filter (Omega optical, USA) to remove all the UV light. The solar simulator produced identical simulated 1-Sun irradiance of 100 mW cm^{-2} at full power that matched the global solar spectrum at sea level. Spectral analysis of their radiation from the solar simulator with a StellarNet EPP2000C-25LT16 spectrometer for UV–vis-NIR spectroscopy showed 6.5% UV, 64.5% visible light, and the remaining was NIR light [20].

2.3. Photocatalyst characterization

Phase composition and the degree of crystallinity in the photocatalysts were determined by X-ray diffraction (XRD). The XRD data were obtained using a Rigaku–MiniFlex II, powder diffractometer (Japan), using CuKα (λ for $K\alpha = 1.54059$ Å) over the desired 2θ range with a step width of 0.05°. DRS (diffuse reflectance spectra) were recorded on a Shimadzu UV–vis-NIR spectrophotometer (UV-3600) equipped with an integrating sphere using $BaSO_4$ as a reference. The Specific surface areas of photocatalysts were measured using a Micrometritics Chemisorption Controller ASAP 2010.