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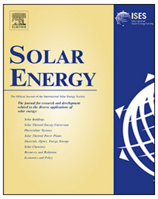

Sunlight mediated passive wastewater treatment technology using photochemical reduction of ferric iron for decontamination of various aqueous contaminants

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ABSTRACT

This paper demonstrates the feasibility of a very simple and novel, “passive” sunlight mediated photochemical process using ferric chloride for degradation of a wide range of organic contaminants. Batch experiments were conducted under natural sunlight to study the degradation of carbamazepine (CBZ), sulfolane and acid extractable organics of oil sands process water (OSPW) in the presence of 100 mg/L of ferric chloride at pH 2.7–3. The efficacy of the process was also evaluated by studying the degradation of the contaminants in actual wastewater and groundwater samples. All three contaminants were resistant to photodegradation under sunlight in the absence of ferric chloride. CBZ in wastewater and pure water was completely degraded in the presence of ferric species under sunlight within 2 h. Kinetics of degradation of CBZ was fastest in groundwater as more than 99.9% of CBZ was degraded within 30 min. Rate of reduction of Fe(III) to Fe(II) was proportional to kinetics of CBZ degradation in aqueous samples. Over an irradiation period of 7 h, more than 50% of TOC was removed by sunlight mediated iron reduction of CBZ in spiked water and secondary treated wastewater. In contrast to CBZ, sulfolane degraded faster in deionised water (4.5 h^{-1}) with more than 50% reduction in TOC. Unaltered rates of increase in Fe(II) concentration in groundwater spiked with sulfolane and CBZ signifies the presence of easily degradable organics in groundwater competing with sulfolane for the reactive species. GC–MS analysis showed more than 60% reduction in acid extractable organics present in OSPW 7 h of sunlight irradiation in the presence of ferric chloride. Overall, photochemical iron reduction shows great promise as highly sustainable treatment process for decontamination of variety of recalcitrant contaminants in their inherent aquatic environments with marginal effects imparted by other aquatic species.

1. Introduction

“Emerging Contaminants” (ECs) include multitudes of contaminants such as: pharmaceuticals, antibiotics, personal care products and detergents originating from domestic activities; pesticides and animal antibiotics from agricultural activities; novel process chemicals arising form industrial activities(Bell et al., 2011; Geissen et al., 2015; Hamza et al., 2016; Sui et al., 2015). Though these contaminants occur in very low concentrations, evidence has shown that many of these compounds have harmful effect on receiving aquatic waters and human health by chronic exposure (Jarvis et al., 2014; Quinn et al., 2008). Many ECs are recalcitrant to biological degradation due to which they may pass through conventional wastewater treatment plants(Chen et al., 2006; Clara et al., 2004; Fatta-Kassinos et al., 2011; Petrie et al., 2015). Advanced oxidative processes (AOPs) and membrane technologies have shown to effectively treat and remove ECs from domestic and industrial wastewaters(Bolong et al., 2009; Dolar et al., 2012; Mehrabani-Zeinabad et al., 2015; Snyder et al., 2007; Somathilake et al., 2017).

Abbreviations: CBZ, carbamazepine; AOPs, advanced oxidation processes; OSPW, oil sands process water; TOC, total organic carbon; ECs, emerging contaminants; UV, ultraviolet radiation; UVC, ultraviolet C (λ = 254 nm) radiation; UVA, ultraviolet C λ = 365 nm) radiation; NA, naphthenic acid; HPLC, high performance liquid chromatography; DI, deionised water; GW, groundwater; WW, wastewater; SUL, sulfolane; AEO, acid extractable organics; PTFE, polytetrafluoroethylene; GC, gas chromatography; FID, Flame Ionization Detector; BSTFA, tert-butyldimethylsilyl trifluoroacetamide; OH, hydroxyl radicals

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However, application of these technologies to remove ECs are limited even in highly industrialised countries as they require installation of large infrastructure or changes to existing tertiary treatments based on the technology adopted. Moreover, these technologies are energy intensive and incur significant operational and maintenance costs. Use of energy and chemical intensive processes for removal of very low concentration of ECs is not sustainable(Shannon et al., 2008). The unique challenge of treating low concentration of ECs in large volumes of water underpins the necessity of effective unconventional wastewater treatment with low costs.

In the recent past, development of “passive” sunlight driven AOPs for treatment of ECs has been the focus of some research efforts(Alalm et al., 2015; Leshuk et al., 2016; Senthilnathan and Philip, 2012; Sivagami et al., 2014). AOPs generate highly reactive species such as $^{\cdot}OH$ which are nonspecific in their attack and have shown promise in degradation of numerous ECs. The idea of harnessing solar energy to produce highly reactive species without the need for infrastructure makes passive solar AOPs the most suitable technologies for treatment of ECs. Solar driven AOPs have been mainly centered on modifications of photo-Fenton (Alalm et al., 2015; Garcia-Segura et al., 2016; Rodríguez et al., 2005)and visible light active photocatalytic process (Brienza et al., 2016; Kaur et al., 2018, 2016; Leshuk et al., 2016; Magalhães and Lago, 2009). Though these processes have been successfully demonstrated to degrade wide variety of ECs in laboratory experiments, there is no evidence of the use of these technologies for commercial applications. Major setbacks such as the highly sensitive process control required for photo-Fenton and exorbitant processes involved in synthesis of visible light active photocatalysts and their stability are some of the reasons due to which these technologies have not been used for field applications.

Photochemical reduction of Fe(III) in natural waters under sunlight has been identified as one of the cause of natural attenuation of many ECs. Under irradiation of sunlight Fe(III) hydroxy complexes undergo photoinduced electron-transfer mechanism where ferric is reduced to ferrous and the ligand is oxidized (Balzani and Moggi, 1990). Due to the electron transfer between excited Fe(III) and a water molecule, extremely strong, non-reactive hydroxyl radicals are produced which can react with organic compounds in their vicinity (Weiss, 1969). This reaction is known to play a significant role in photodegradation of organic contaminants in sunlit surface waters. Indirect photodegradation of antibiotics (sulfadiazine and sulfathiazole) and artificial sweeteners (acesulfame, saccharin, cyclamic acid and sucralose) promoted by photochemical reduction of Fe(III) has been reported in the literature (Batista et al., 2014; Perkola et al., 2016). Photodegradation of estrogen estriol (E3) by photochemical Fe (III) redox reaction was enhanced by the presence of humic acids have acted as photosensitizer(Chen et al., 2013). Though the reaction mechanisms of photochemical reduction of Fe(III) have been very well understood, very few studies have demonstrated the use of simple ferric salts for the degradation of recalcitrant compounds using direct sunlight.

For the first time, this paper demonstrates the feasibility of using ferric chloride for degradation of recalcitrant aqueous contaminants using photochemical iron reduction mediated by natural sunlight. The process was tested on three dissimilar contaminants including carbamazepine (CBZ), sulfolane and a mixture of organics present in actual oil sands process water (OSPW). These compounds were selected based on their prevalence and resistance to natural attenuation and conventional treatment processes(Miao et al., 2005). CBZ is a pharmaceutical drug ubiquitously detected in wastewater effluent-impacted surface water and groundwater (Clara et al., 2004). On the other hand, sulfolane is an industrial chemical detected in aquifers surrounding natural gas processing plants. Sulfolane is a stable compound which has been known to degrade under active AOP conditions such as UV/H_2O_2, UV/TiO_2 and O_3. OSPW is a highly complex mixture of organic and inorganic compounds derived from oil sands operations (Yu et al., 2016). Organic contaminants of concern in OSPWs includes bitumen, naphthenic acids (NAs), asphaltenes, creosols, humic and fulvic acids, phenols, phthalates, polycyclic aromatic hydrocarbons (PAHs), benzene, toluene, ethylbenzene, and xylene (Allen, 2008). Large volumes of OSPW and the presence of numerous contaminants has left limited options for reclamation of water from OSPWs.

The objective of this paper is to investigate the feasibility of ferric ion assisted photooxidation under solar irradiation. To establish the applicability of the method a wide variety of recalcitrant contaminants were selected such as CBZ, sulfolane and naphthenic acids (NAs) which are used in dissimilar areas and found in various aqueous matrices. CBZ was blended with sulfolane and NAs to determine the effect of degradation and ferrous ion formation. The experiments were conducted in lab synthetic water and in real sulfolane contaminated groundwater, NAs contaminated Oil Sands Process Water (OSPW) and secondary treated municipal waste water.

2. Materials and methods

2.1. Chemicals

Analytical grade CBZ (99% purity), sulfolane (99% purity), $FeCl_3$ (97% purity), HCl (ACS reagent grade) and high-performance liquid chromatography (HPLC) grade methanol were purchased from Sigma-Aldrich Co. (Oakville, Ontario, Canada). HPLC grade DCM (dichloromethane) used for extraction of AEOs was purchased from VWR (Canada). tert-butyldimethylsilyl trifluoroacetamide (BSTFA) used as derivatizing agent was purchased from Sigma Aldrich, USA.

2.2. Solar experiments

Solar photochemical experiments detailed in this study were conducted on the campus of University of Calgary, Calgary, Canada located at coordinates of 51°4′47.8128″N and 114°7′31.9224″W at an elevation of 1111 m. All experiments in the study were conducted simultaneously at one location to avoid variation in solar irradiation applied to each experiment. The study was conducted on 30th May 2017 from morning to late afternoon spanning over a period of 7 h. The average solar irradiance for the experimented time period, as measured by University of Calgary Weather Research Station 51°4′445.687″N and 114°8′30.022″W; Elevation: 1114.2 m was 723 W/m^2.

Experiments were performed in batch mode using 250 mL cylindrical clear glass beakers with no markings. The effect of photochemical iron reduction to degrade contaminants was tested on CBZ, sulfolane and OSPW. The effects of various aquatic co-contaminants were also tested by studying the degradation of CBZ and sulfolane in spiked secondary treated effluent and sulfolane contaminated groundwater sample, respectively. The various experiments conducted in this study are described in Table 1. Experiments conducted without ferric chloride acted as controls to evaluate the degradation of contaminants by photolysis under direct sunlight. For experiments conducted in the presence of ferric chloride, 4 mL of 5 g/L $FeCl_3$ stock was spiked to maintain a dose of 100 mg/L. Treated effluent and groundwater were adjusted to pH 3 prior to the addition of $FeCl_3$. 5 N HCl was added dropwise to adjust the pH. Final pH of groundwater and treated effluent after spiking of $FeCl_3$ was 2.8 ± 0.1. Experiments conducted with CBZ were spiked with 10 mL of 100 mg/L of CBZ stock resulting in 5 mg/L of CBZ. Similarly, 10 mL sulfolane stock (1000 mg/L) was spiked to achieve 50 mg/L. In addition to sulfolane present in contaminated groundwater at a concentration 28 mg/L, a fresh sulfolane spike of 50 mg/L was made for experiments on sulfolane degradation in groundwater. 5 mL of sample was withdrawn from all batches at regular intervals and stored immediately at 4 °C in the dark. Analysis of CBZ and sulfolane were performed within 48 h of sample collection. Concentration of Fe(II) was determined immediately upon collection of samples to determine the level of reduction of Fe(III) to Fe(II).