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An ecological new approach for treating Cr(VI)-containing industrial wastewater: Photochemical reduction

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ABSTRACT

An ecological new approach for photochemical reduction of Cr(VI) in aqueous solution by adding into water-soluble copolymer, polyethylene glycol (PEG), was investigated. Various influences including light intensity, initial solution pH value, PEG molecular weight and initial concentration ratio of PEG to Cr(VI) on photochemical reduction of Cr(VI) were discussed, and a possible reaction mechanism was proposed. Experimental results revealed that Cr(VI) could be reduced to Cr(III) by PEG under sunlight irradiation. The photo-reduction rate of Cr(VI) increased with the decrease of solution pH and PEG molecular weight, but increased with the light intensity. The reduction percentage of Cr(VI) increased with the initial concentration ratio of PEG to Cr(VI). When the initial solution pH value was below 3.0, almost all of Cr(VI) was completely reduced to Cr(III) within 20 min of 50×10^3 lux solar irradiation in the presence of PEG. After photo-reduction, PEG and Cr(III) in aqueous solutions could be recovered by adding into a high-concentrated Na_2SO_4 aqueous solution to induce the formation of a stable PEG-based aqueous biphasic system. By doing so, Na_2SO_4 in aqueous solution could also be removed. The present work highlights a promising new route for treating the industrial wastewater containing toxic Cr(VI) ions by adding into environmental-friendly PEG for photo-reduction of Cr(VI) to Cr(III), and then salting-out recovery of PEG and removal of Cr(III) in wastewater by adding into another high-salt wastewater, so that the high-salt wastewater could also be treated.

1. Introduction

Chromium is widely applied in various fields such as chrome plating, steel fabrication, metal processing, canning, leather tanning, pigment synthesis, wood preservation, etc (Malaviya and Singh, 2011). Extensive application of chromium in industries result in an increased flux of chromium into the environment (Gode and Pehlivan, 2007). Though the oxidation states of chromium range from −2 to +6 (Greenwood and Earnshaw, 1997; Cotton et al., 1999; Schlautman and Han, 2001), only the hexavalent chromium [Cr(VI)] and trivalent chromium [Cr(III)] are environmentally stable (Losi et al., 1994; Xie et al., 2011b). Cr(VI) is notoriously known as a human carcinogen and genotoxic agent and is responsible for various chronic health disorders including organ damage, dermatitis and respiratory impairment. Cr(VI) can move throughout aquifers to contaminate groundwater and other sources of drinking water as well as adversely affect the growth of plants, livestock and wildlife (Mohapatra et al., 2005). Therefore, Cr(VI) is considered as a priority pollutant and the discharge of Cr(VI) into surface water is strictly regulated (Park et al., 2007). In comparison with Cr(VI), Cr(III) is 500–1000 times less toxic (Max, 2003) and less mobile. Cr(III) can be readily precipitated in the form of $Cr(OH)_3$ from neutral or alkaline solution (Loyaux-Lawniczak et al., 2001). Therefore, various technologies including bioremediation, photocatalytic reduction and chemical treatment have been explored for conversion of Cr(VI) to Cr(III) to decrease the toxicity and bioavailability of this metal.

Bioremediation of Cr(VI) can be conducted using strains of bacteria that are able to enzymatically reduce Cr(VI) to Cr(III) (Joutey et al., 2015; Pan et al., 2014a, b). Although these microbial systems function in the laboratory under defined culture conditions, the bioremediation method practically requires strict monitoring of process conditions and is likely to be spoiled by the

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toxicity of chromium. Photocatalytic reduction of Cr(VI) using semiconductor, metal oxide or sulfide nanoparticles (Kush et al., 2015; Pandikumar and Ramaraj, 2013), e.g. TiO_2, WO_3, CdS and ZnO, is a relatively new technique, but it was criticized as being uneconomical due to its inherently low efficiency and the limitations of immobilization, which may increase the overall costs. Among those reported methods, chemical reduction was considered more effective and gains popularity over others. For chemical reduction of Cr(VI) to Cr(III), strong reducing agents (e.g. SO_2, H_2S, H_2O_2) (Kim et al., 2001; Pettine et al., 2002) and other metals or metal salts (e.g. metallic iron, $FeSO_4$) (Pan et al., 2014a, b) were usually used. However, these inorganic reductants exhibit toxicity themselves or introduce additional environmental problems (Xu et al., 2004). Recently, chemicals such as citrate, tartrate and oxalate (Kantar and Keskin, 2015), ascorbic acid (Xu et al., 2004) and C_1–C_4 aliphatic alcohols (Mytych et al., 2003), were employed as the reducing agents for Cr(VI) treatment. It was demonstrated that Cr(VI) reduction was possible by using those organic compounds with low molecular mass under solar irradiation. However, secondary pollution with the addition of those chemicals into water was still unavoidable.

The aim of the present work is to demonstrate the feasibility of using polyethylene glycol (PEG), a commercial available nonionic copolymer, to perform an effective photochemical reduction of Cr(VI) under solar irradiation. Compared with those reducing agents previously reported, PEG has environmental benign characteristics (Chen et al., 2005; Luo et al., 2005; Su et al., 2009). PEG is on the FDA's GRAS list (compounds Generally Recognized as Safe) and has been approved by the FDA for internal consumption. PEG is highly water-soluble, nonvolatile, nonflammable, and biodegradable and has been found to be stable to acid, base as well as high temperature. Hence, one main advantage of photochemical reduction of Cr(VI) by PEG is to avoid the use of toxic chemical reducing agents, and thus provides a green approach for removal of Cr(VI). Other advantages include better control of the reduction process under solar irradiation without the need of high temperatures. In addition, the use of natural sunlight in the photochemical process will reduce energy costs since solar energy is an enormous and clear energy source. To our knowledge, employing water-soluble polymer such as PEG for photochemical reduction of Cr(VI) in industrial wastewater has hitherto not been reported. The possible mechanisms for photochemical reduction of Cr(VI) by PEG remain not clear.

Another aim of the present work is to explore whether or not it is possible to recover PEG and Cr after photochemical reduction process. Here, we suggest to add a high-concentrated salt aqueous solution into the Cr-containing aqueous solution after photochemical reduction. Our experiments revealed that addition of a high-salt aqueous solution would result in an effective recovery of PEG due to formation of a stable PEG-based aqueous two-phase systems, in which the up-phase was enriched with PEG, and Cr was also enriched into the up-phase, while the bottom-phase was mainly salt-rich aqueous solution. During the process of two-phase separation, salt could also be removed from the high-salt aqueous solution and enriched into the PEG-rich phase under some special conditions after phase separation. Such a kind of PEG-rich phase could be further treated for recycling PEG and reusing. Therefore, it is feasible for future application to treat those typical high-salt wastewater, which is commonly derived from dyeing industrials and pesticide production, by mixing with the Cr-containing industrial wastewater after photochemical reduction. Not only the high-salt wastewater can be consumed, but the Cr-containing wastewater can also be disposed, and Cr in wastewater can be removed. The present work highlights an ecological new approach by using one kind of wastewater to treat another wastewater, which completely accords with the sustainable requirements for environmental protection.

2. Experimental

2.1. Chemicals

PEGs, $[HO-(CH_2CH_2O)_n-H]$, with different average molecular weights from 400 (denoted as PEG 400) to 10,000 (denoted as PEG 10000), were purchased from Sino-pharm Chemical Reagent Co., Ltd. Stock solutions of 50% (w/v) PEGs were prepared by dissolving the PEGs (with different molecular weights) in deionized water, respectively. Stock solution (5 g L^{-1}) of Cr(VI) was prepared by dissolving analytical grade potassium dichromate ($K_2Cr_2O_7$) into deionized water. Working solutions of Cr(VI) with different initial concentrations were prepared by diluting the stock solution of Cr(VI) with deionized water. Na_2SO_4 and other reagents used in experiments were of analytical grade.

2.2. Procedure for photo-reduction and recovery

2.2.1. Photochemical reduction

Required volume of PEG stock solution was added into a transparent borosilicate glass beaker to mix sufficiently with a certain volume of Cr(VI) working solution at room temperature (25 °C). The glass beaker has a total volume of 25 mL and an internal diameter of 32 mm. The above Cr(VI)-containing mixed solutions were diluted with deionized water to the volume of 20 mL, and then determined the initial Cr(VI) concentrations. The initial pH values of the Cr(VI)-containing mixed solutions were adjusted to the pre-seted values with 1 mol L^{-1} H_2SO_4 or 1.5 mol L^{-1} NaOH aqueous solutions. And then the Cr(VI)-containing mixed solutions were stored in the darkroom or exposed to a steady state solar simulator as a light source for a required time. The light intensity was adjusted by placing pieces of glass with different light transmittance in front of the solution. Samples were withdrawn at proper time intervals and the concentration of Cr(VI) was determined.

2.2.2. Recovery of PEG and recycling

A certain amount of solid Na_2SO_4 were dissolved into water to prepare Na_2SO_4 aqueous stock solution with appropriate concentrations. Then, required volumes of Na_2SO_4 aqueous stock solution were added into above-mentioned Cr-containing aqueous solution after photochemical reduction. After stirring and mixing for 10 min, the mixtures were let stand at room temperature for enough time so that to obtain a stable two-phase system. The up and bottom two phases of the two-phase system were separated between each other by a separating funnel. The volumes of up and bottom phases were determined respectively. If the initial concentration of Na_2SO_4 aqueous solution before mixing with Cr-containing solution is higher than 0.7 mol/L, the obtained up-phase, enriched with most of PEG, could be reused and added into another Cr(VI)-containing aqueous solution to perform photochemical reduction as mentioned above. The bottom-phase, enriched with Na_2SO_4, was returned for reusing. If the initial concentration of Na_2SO_4 aqueous solution before mixing with Cr-containing solution is higher than 0.3 mol/L but less than 0.7 mol/L, the obtained up-phase, enriched with PEG and salt, could be mixed with the bottom-phase previously mentioned for treating the Cr-containing solution by adding Na_2SO_4 aqueous solution with concentration of higher than 0.7 mol/L. By doing so, PEG could be recovered further after two-phase separation. The samples were withdrawn from the salting-out bottom phases in PEG-based aqueous biphasic system for determination of the concentrations of total Cr, Cr(VI) and Cr(III), respectively.