Contents lists available at ScienceDirect

Process Safety and Environmental Protection

journal homepage: www.elsevier.com/locate/psep

Simultaneous photocatalytic treatment of Cr(VI), Ni(II) and SDBS in aqueous solutions: Evaluation of removal efficiency and energy consumption

*Javad Saien**, *Amir Azizi*

Department of Applied Chemistry, Bu-Ali Sina University, Hamedan 65174, Iran

ARTICLE INFO

Article history:
Received 17 July 2014
Received in revised form
12 January 2015
Accepted 28 February 2015
Available online 6 March 2015

Keywords:
Photocatalytic process
Hexavalent chromium
Divalent nickel
SDBS
Energy consumption
Titania

ABSTRACT

Simultaneous photocatalytic reduction of poisonous Cr(VI) and Ni(II) ions, coupled with photocatalytic oxidation of sodium dodecyl benzene sulfonate (SDBS) were studied with a trace amount of commercial titania nanoparticles and by means of a direct-photo-irradiation reactor. The co-presence of metal ions and SDBS causes metal ions reduction as well as SDBS oxidation to enhance and energy efficiency to improve. XRD, XPS and FTIR analysis were used to characterize TiO_2 particles before and after usage with the aim of evaluating the mechanism of reactions. The effect of major operating parameters, pH and temperature, was investigated. Under conditions of $[Cr(VI)]_0 = [Ni(II)]_0 = 5$ mg/L, $[SDBS]_0 = 10$ mg/L, $[TiO_2] = 40$ mg/L, pH 6 and $T = 35\,^{\circ}C$; the removal efficiencies of 55.4%, 71.2% and 57.2% were obtained, respectively, for Cr(VI) and Ni(II) reduction, as well as for SDBS oxidation, after 110 min operation. The relevant kinetic model jointed with the Arrhenius equation was introduced. Pseudo-first-order reactions are relevant. Energy consumption (electrical and thermal) evaluations revealed that operations at higher temperatures provide significant cost reduction. Meantime, a criterion was proposed for a consistent assessment of this kind of processes.

1. Introduction

Heavy metals in aquatic systems pose a potential danger to the ecosystem at various scales. They have infinite lifetime and can accumulate in places to a toxic level (Samarghandi et al., 2011). Metal ions such as Cr(VI) and Ni(II) are commonly occurring as toxic metals in natural ecosystems, originated from the effluent of refineries, electroplating, casting industries, storage batteries and particularly nickel–chromium plating plants (Doan et al., 2008; Donmez and Aksu, 2002; Kabra et al., 2008a). In aquatic environments, nickel and chromium usually appear as Ni(II), Ni^0, Cr(VI), and Cr(III) species (Chen and Ray, 2001). Though the high toxicity has been reported for Cr(VI) and Ni(II), only slight toxicity has been reported for Cr(III) and Ni^0 (Shirzad-Siboni et al., 2012). So, converting to less harmful species would be of beneficial use. On the other hand, wastewaters from electroplating units, for instance, contain some organic materials in addition to metal ions, which are used in different stages of the manufacturing process, as lubricant, surfactant, polisher and so on (Doan and Saidi, 2008). Salts of linear alkyl benzene sulfonates (LABS), such as sodium dodecyl benzene sulfonates (SDBS), are widely used in industries as detergents or surfactants (Doan and Saidi, 2008) despite their strong resistance nature in biodegradation treatment (Hidaka et al., 1986).

As documented in the literature, photocatalytic process is a promising method for treatment of different pollutants. The main step in the photocatalytic reduction process is the formation of electron–hole pairs ($e^-_{CB} - h^+_{VB}$) on the catalyst surface upon irradiation with the proper photon energy to overcome

* *Corresponding author*. Tel.: +98 81 38257407; fax: +98 81 38257407.
E-mail address: saien@basu.ac.ir (J. Saien).
http://dx.doi.org/10.1016/j.psep.2015.02.020

the band gaps. The electron–hole pairs are then separated between the valance and conduction bands and the adsorbed species on the sites of catalyst undergo photo induced redox reactions. Titanium dioxide has been mostly used as very efficient photocatalyst (Prairie et al., 1993; Bhatkhande et al., 2001), since the band gap of TiO_2 is around 3.2 eV with energy of conduction band −0.3 eV and valence band +2.9 eV at pH 5.6 (Blake et al., 1991; Vaez et al., 2012). Thus, any metal ions with a reduction potential of less negative than −0.3 eV are potentially reduced by photo-generated electrons of TiO_2. Also photo-generated holes, directly and indirectly, help in producing high reactive intermediates, mainly hydroxyl radicals.

In recent years, one new approach was the photocatalytic reduction of metal ions with simultaneous photocatalytic oxidation of organic pollutants (Doan and Saidi, 2008; Prairie et al., 1993). Photocatalytic reduction of individual Cr(VI) and Ni(II) has been investigated in the presence of organics such as low molecular weight compounds and different dyes, all with very high level of nano TiO_2 concentration, within 250–2000 mg/L (Kabra et al., 2008a; Shirzad-Siboni et al., 2012; Dozzi et al., 2012; Schrank et al., 2002; Testa et al., 2004). In a relevant work by Aman et al. (2011), simultaneous photo-reductive removal of Cu(II) and Se(IV) in the presence of formic acid and ethylene diamine tetra acetic acid (EDTA) has been examined. Initially, formic acid found to be slightly better for both copper and selenium reduction in comparison with EDTA. For this aim, SDBS surfactant can be one suitable organic substance that conventionally exists in relevant wastewaters. To the best of our knowledge, no work has been carried out on the simultaneous treatment of practically encountered, heavy metals and SDBS pollutants with photochemical process.

In this work, the simultaneous photocatalytic reduction of chromium and nickel ions, coupled with oxidation of SDBS, is investigated using only 40 mg/L of titania nanoparticles. Low dosage catalyst is practically interested due to difficulties in separation and regeneration. The effects of important operating parameters, pH, temperature and mutual interactions of substrates are investigated. The kinetic of reactions in the mixed solution, within the conventional temperature range, is also investigated. Another important parameter is the energy consumption. In this regard, the process cost-effectiveness is estimated with respect to energy consumption. The results are then compared with other similar processes.

2. Experimental

2.1. Chemicals

All the chemicals used in this work were of analytical grade and were used as received. Potassium dichromate as the source of chromium ion (>99.9%); nickel nitrate hexa-aqua as the source of nickel ion (>99.0%) as well as 1,5-diphenylcarbohydrazide (DPC) and 1-(2-pyridylazo)-2-naphthol (PAN) (both of them with high purity, for metal indication); acetone (>99.5%); ethanol (>99.9%) and Triton X-100 (gas chromatography grade) were all Merck products. Sulfuric acid (>99.9%) and sodium hydroxide (>97%) were used for pH adjustment; methylene blue (>99.5%) and chloroform (>99.5%) were also purchased from Merck. SDBS with purity of 80% (mixture of homologous LABS) was purchased from Fluka. Titanium dioxide nanoparticles (P-25, purity more than 99.5%) were supplied by Plasma Chem with BET surface area of 50 m^2/g and the average particle diameter of 21 nm. All aqueous solutions were prepared using deionized water with conductivity less than 0.08 μS/cm.

2.2. Photo-reactor and experimental procedure

A 1.25 L cylindrical photo-sono reactor made of glossy stainless steel and dimensions of 90 mm diameter and 200 mm height was used (Saien et al., 2010). The light source was a 250 W mercury lamp (165 mm body length and 80 mm arc length) with wavelength range of 280–400 nm and the maximum emission of 365 nm. The lamp was located centrally and immersed directly in the aqueous solution. This configuration allows a homogeneous irradiation and perfect reflection for the beams contacting the reactor wall. To break any particle clusters and provide homogenous TiO_2 nanoparticle suspensions at the beginning of each experiment, an ultrasound source (28 kHz, 60 W) was used, located at the outside bottom of the reactor which propagates ultrasonic waves into the reaction media. The temperature during each experiment was maintained constant by means of a stainless steel water-flow jacket from a thermostat bath.

To run each experiment, a solution (1 L) containing the desired concentration of Cr(VI), Ni(II) and SDBS was prepared and was transferred into the reactor after pH adjustment (using either sulfuric acid or sodium hydroxide dilute solutions). Temperature was then set to desired value. The needed amount of the catalyst particles was added and prior to light irradiation, the suspension was sonicated for 5 min and then maintained mixing for 60 min in dark to ensure adsorption/desorption equilibria of the pollutants on TiO_2 particles surface. All the experiments were performed while the content was continuously mixing with a simple impeller. Initial total concentration of pollutants in mixed solution was maintained at 20 mg/L, including 5, 5 and 10 mg/L of Cr(VI), Ni(II) and SDBS, respectively. The selection of metals initial concentration was with respect to the feasible reduction by the end of treatment, to be close to the permissible limit for discharge into surface water as 0.1 and 2 mg/L for Cr(VI) and Ni(II) respectively (WHO, 2008). Accordingly, SDBS initial concentration was the amount that frequently found in the electroplating wastewaters (Doan and Saidi, 2008). It is noteworthy that during each experiment, the solution pH was almost constant.

To follow the reaction progress, 3 mL samples were withdrawn at different times and after vigorous centrifuging to separate nanoparticles, were divided into three 1 mL samples, each for analyzing either of Cr(VI), Ni(II) and SDBS.

2.3. Analytical method and photocatalyst characterization

The concentration of Cr(VI), Ni(II) and SDBS was determined from their absorption in the spectra obtained by a UV-vis spectrophotometer (Jasco, model 760). For Cr(VI) ions, colorimetry at λ_{max} = 542 nm, relevant to the complex formation with DPC in acidic solutions (pH 2.5) (Clesceri et al., 1998), was used. Similarly, the amount of Ni(II) ions was determined with colorimetry at λ_{max} = 568 nm using PAN as the color agent. Accordingly, the best complex formation for Ni(II) conditions was provided using 2.5 mL of 1.0% Triton X-100 in water solution, 2 mL of universal buffer solution (pH 8.5), 1.0 mL of 0.01% PAN solution in ethanol, together with 1 mL of collected sample, all added into a 10 mL standard flask and volume was made up to the marked level with deionized water (Clesceri