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Uncovering results in electro-scrubbing process toward green methodology during environmental air pollutants removal

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ABSTRACT

Present findings uncovered the electro-scrubbing process as a green methodology. This green methodology was assessed by an analysis of electrode dissolution into an electrolyte and acid fumes emission to the atmosphere. As an initial experiment oxidation effect of Co(II) by PbO_2 electrode revealed an enhanced oxidation efficiency of ~20% compared to a Pt-coated Ti electrode. The mist concentration from the first scrubber test was approximately 30 times lower than that of the indoor air particles. In addition, molar mass of Co(II) and SEM analyses revealed no Co(II) or PbO_2 from the first scrubber. An analysis of the second scrubber showed no Co(II), PbO_2 or pH changes during a 24 h study confirming that no sulphuric acid escaped from the first scrubber or mediator containing electrolyte solution. This electro-scrubbing process was applied to the air pollutants removal process, in which a definite ratio between Co(III) and odor gases at given concentrations were identified. These results show that this electro-scrubber can maintain its initial concentration of Co(II) and H_2SO_4 by just adding water, and is become a highly sustainable and green methodology system without a loss of H_2SO_4 and Co catalysts to the environment.

Keywords: Sustainability; Green methodology; Mist particles; Mediated electrochemical oxidation; Electro-scrubbing; Air-Pollutants

1. Introduction

In recent past, combination of electrochemical generation of active mediators and wet scrubbing process, in the name of electro-scrubbing process, becomes emerge because of 'electrons' involved as reactants. Using this approach, along with development of effective conditions for active mediators, variety of air pollutant has been degraded using electro-scrubbing process (Muthuraman and Moon, 2013; Muthuraman et al., 2013). The sustainable generation of active mediators has been controlled by many ways like minimization of electrode fouling, membrane stability and these are the main issues among all, which were investigated thoroughly and still under up gradation (Martínez-Huitle and Ferro, 2006; Farmer et al., 1992). In this regard, we have engineered a special mode of operation and controlled time on/off, for sustainable generation of Ag(II) in nitric acid medium (Muthuraman et al., 2012a). One thing here to be pointed out is the solubility and generation of active metal ions, such as Ag(II), Co(III) and Ce(IV), were restricted to acid media due to only solubility of their activated state. This acidic medium gives positive hope in one way like acid alone as the acid wet scrubber in industries where acid wet scrubbers, particularly H_2SO_4, play important roles in various air pollutant removal process by absorption (Hasanoglu et al., 2010) or simple oxidation methods (Zhang et al., 2000). On the other way, use of acid in electro-scrubbing process is restricted to be considered it as a green methodology because acid aerosols and sulfates cause an increased prevalence of pulmonary diseases and acid rains.

Strong inorganic acid mists containing sulfuric acid (H_2SO_4) have been implicated as causes of lung and laryngeal cancers in humans (Bratveit et al., 2004; Shangina et al., 2006; Hsu et al., 2007). The specific chemical characteristics of sulfuric acid, such as low volatility, high reactivity, high acidity,

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high corrosivity, and high affinity for water (Hsu et al., 2007; CAS, 2001) have forced its continuing use in many applications. According to USEPA, packed bed wet scrubbers or packed towers can be referred to as acid gas scrubbers when used to control inorganic gases (ACGIH, 2010; Jiuan, 2005), but it is not considered for the removal of sulfuric acid. This both positive and negative synergetic effect of acid causes it to deviate from green chemical process considering humans and the environment. Certainly, electro-scrubbing processes have also been considered as non-green methodologies in environmental air pollutants removal processes. The aim of this study is to uncover some additional points to support the electro-scrubbing process also as one of the green methodologies. Here again, as a first preventive measure mentioned above, the sustainability of the electro-scrubbing process was assessed because the electro-generated homogeneous mediator in the electro-scrubbing process might migrate through the proton exchange membrane to the cathodic compartment and be reduced to the inactive metal or metal ions, which can be prevented by simply modifying the current supply mode (Muthuraman et al., 2012a). Another possible measure for the sustainable operation of the electro-scrubbing process is to prevent mediator ions and electrolytes from escaping from the electro-scrubbing process. Following our experience in the electro-scrubbing process, the aim of this study was to determine if the electro-chemical process can be used as a green methodology by examining the electrolyte and catalyst change and its loss.

An additional consideration was the ability of the PbO_2 electrode to generate active reactants. To increase the number of active mediators, several electrode materials, such as Pt, Ti/Ir, and PbO_2, were assessed (Leffrang et al., 1995; Matheswaran et al., 2007; Chen et al., 2012). Among the many electrodes, the BDD (boron doped diamond) electrode showed a high current efficiency, but its cost expensive nature is restricted to use in large industrial scale applications. A Pt-coated titanium electrode is significantly less expensive than BDD with moderate timing applications (Muthuraman et al., 2012b). PbO_2 showed similar water splitting potential to BDD (Panizza and Cerisola, 2009) with high current efficiency. The PbO_2 electrode is used in the direct oxidation of water pollutants (Panizza and Cerisola, 2004). Recently, the use of PbO_2/Sn_2O_3–SnO_2/Ti anode for the oxidation of Ce(III) and its uses in acetaminophen oxidation were reported (Chen et al., 2012). A previous study showed that the oxidation of Ce(III) was totally contradictory to Co(II), particularly the temperature effect (Matheswaran et al., 2008; Comninellis et al., 1979). In particular, the rate of Co(II) oxidation was inversely proportional to temperature but there are no reports on the oxidation of Co(II) by PbO_2.

Exploring the green methodology of the electro-scrubbing process, PbO_2 was used as an anode in this investigation to increase the oxidation efficiency of Co(II) and compared with the conventional Pt-coated Ti electrode. The emission of the scrubbing liquid (4 M H_2SO_4 + Co(III)) was examined by a range of analyses, such as mass balance of Co(II), solid particle capture by a filter, mist number concentrations at the outlet of the scrubber, and pH changes in spraying water at the second scrubber downstream of the first scrubber. Finally, the electro-scrubbing system was tested to remove a mixture of odor gases.

2. Experimental

2.1. Materials

Cobalt sulfate ($Co(SO_4)_2{\cdot}7H_2O$, 99.9%) from TERIO Corporation, China, sulfuric acid (H_2SO_4, 60%) from Sam Chun Chemicals, Korea, and ferrous sulfate ($FeSO_4{\cdot}7H_2O$) from Junsei Chemical Co., Ltd, Japan were used as received. A Nafion® 324 membrane was purchased from DuPont, USA, and the mesh-type Pt-coated-Ti and Ti plate electrodes were obtained from Wesco, Korea. All the solutions were prepared using water purified by reverse osmosis (Human Power III plus, Korea). The air pollutants in cylinder H_2S (2% H_2S in N_2), NH_3 (10%), $(CH_3)_3NH$, CH_3CHO were supplied by P.S. Chem. Co., Ltd., Korea.

2.2. Methods

The experimental scheme used for the sustainability and green methodology of the electro-scrubbing process consisted of two main units: an electrochemical cell and a wet scrubber reactor column, as described elsewhere (Muthuraman et al., 2012b). The electrochemical cell used for Co(III) generation included a plate-and-frame type narrow gap divided flow cell configuration with a mesh type Pt-coated-Ti and PbO_2 anode and Ti cathode separated by a Nafion 324 membrane. The inter-electrode gap was maintained at 5 mm with the help of two Viton rubber gaskets (thickness = 2 mm). The electrochemical cell set-up was fastened tightly to the stainless steel end plates using a screw bolt. Provisions were made with separate channel paths, through which the anolyte and catholyte solutions could flow to their respective electrodes. A 0.7 L solution of cobalt (II) sulfate (0.1 and 0.75 M) in 4 M sulfuric acid (sufficient protection was taken during preparation) and 0.5 L of 4 M sulfuric acid, which were taken into separate anolyte and catholyte glass tanks, respectively, were circulated continuously through the anode and cathode compartments of the electrochemical cell, at a range of constant flow rates ($L\,min^{-1}$), via a magnetic pump (Pan World Co., Ltd., Taiwan). Electrolysis for the generation of an active Co(III) mediator was conducted galvanostatically by applying a constant current of 2.5 A or 3.5 A via a current source from Korea Switching Instruments. The effective surface area of each electrode exposed to the solution was 35 cm^2.

To examine the emission of the mists, two wet scrubbers were used, as shown in Fig. 1. The first scrubber contained an electrolytic liquid of 4 M H_2SO_4 and 0.75 M Co(II) and second was an additional scrubber to remove the acid components assumed to have arrived from the first scrubber. Two scrubbers were made from Pyrex glass and had an inner diameter of 50 mm and height of 100 cm. They were filled with rasching ring packing with a diameter of 10 mm and height of 10 mm. The total height of the packing was approximately 80 cm. Clean compressed air (oil free air compressor was supplied by Kyungwon Co., Korea) with a controlled flow rate of 30 $L\,min^{-1}$ using a mass flow controller (MFC) model (1179A13CS1BK-S, MKS Co. Ltd., USA) and electrolyte liquid with a liquid flow rate of 4 $L\,min^{-1}$ were introduced via a counter-current flow pattern to the first scrubber until the volume of the electrolyte liquid was reduced to approximately 3/4 of its initial volume. Similarly, the desired concentration and flow rate of the air pollutants were introduced to the first scrubber for their removal. The size distribution of the mist particles generated