



Short Communication

Recovery of potassium from landfill leachate concentrates using a combination of cation-exchange membrane electrolysis and magnesium potassium phosphate crystallization



Xinyang Li ^{a,b}, Wei Zhu ^b, Yue Wu ^b, Chengwen Wang ^{b,*}, Jianzhong Zheng ^a, Kangning Xu ^c, Jiyun Li ^b

^a College of Resources and Environment, University of Chinese Academy of Sciences, Beijing 100049, China

^b School of Environment, Tsinghua University, Beijing 100084, China

^c College of Environmental Science and Engineering, Beijing Forestry University, Beijing 100083, China

ARTICLE INFO

Article history:

Received 22 September 2014

Received in revised form 5 January 2015

Accepted 7 January 2015

Available online 4 February 2015

Keywords:

Electrochemical oxidation

Nanofiltration

Cation-exchange membrane electrolysis

Gaseous chlorine

Potassium recovery

ABSTRACT

Simultaneous removal of high levels of organic pollutants and recovery of nutrients from concentrates generated from the nanofiltration (NF) or reverse osmosis membrane separation process is a significant environmental challenge. In this study, a combined cation-exchange membrane electrolysis (CEME)/magnesium potassium phosphate crystallization process for the recycling of NF concentrates generated from treating landfill leachate was developed. These NF concentrates contained high levels of organics, ammoniacal-nitrogen, chloride as well as valuable potassium ions. The removal of these pollutants and feasibility of potassium recovery were evaluated. This study demonstrated that the proposed combined process can effectively remove 82%, 99%, 34%, 99% of organic matter, ammoniacal-nitrogen, total nitrogen, and chloride ions, respectively, while simultaneously allowing recovery of chloride and potassium ions from NF concentrates as beneficial products (gaseous chlorine and valuable magnesium potassium phosphate precipitates, a buffered fertilizer, respectively) and collection of a further electrolysis by-product (hydrogen). The recovered gaseous chlorine was reused on site as a decolorizing agent for synthetic dye containing wastewater and complete decolorization was achieved. The results indicate that recycling of NF concentrate via the CEME electrolysis/magnesium potassium phosphate crystallization process is feasible.

© 2015 Published by Elsevier B.V.

1. Introduction

Recently, membrane separation processes such as nanofiltration (NF) and reverse osmosis (RO) have been used increasingly in wastewater treatment and water reclamation facilities. Nevertheless, the concentrates generated from membrane separation processes, especially when treating industrial wastewater (i.e., textile wastewater [1], landfill leachate [2], and pesticide wastewater

[3]), always contain high levels of refractory or toxic organic pollutants and inorganic salts [1–5], which must be properly treated before they can be safely discharged into the environment. Thus, proper disposal of concentrates is critically important.

Recently, regarding organic pollutants, advanced oxidation processes (AOPs) (i.e., electrochemical oxidation [6], electro-Fenton [2], electro-peroxone [7], and ozone/peroxide (O₃/H₂O₂) [3] processes) have found wide use in hazard-free treatment of NF or RO concentrates owing to their effectiveness in the degradation of refractory organic compounds. When conducting these AOPs, hydroxyl radicals ($\cdot\text{OH}$) are largely produced, which aid in mineralization of refractory organic compounds. It is important to note that the primary aim of using these processes is to effect the near-complete removal of organic compounds or to increase their biodegradability, and thus reduce the environmental hazards. However, such concentrates also contain various valuable and scarce inorganic species such as potassium ions (2059 mg potassium(1)/L of livestock wastewater [8] and 2200 mg potassium(1)/L of

Abbreviations: NF, Nanofiltration; RO, reverse osmosis; AOPs, advanced oxidation processes; CEME, Cation-exchange membrane electrolysis; RhB, Rhodamine B; CEM, cation-exchange membrane; COD, chemical oxygen demand; BOD₅, biochemical oxygen demand; TN, Total nitrogen; BMED, bipolar membrane electro-dialysis; ICP–AES, inductively coupled plasma–atomic emission spectroscopy.

* Corresponding author. Tel.: +86 10 62771551; fax: +86 10 62788148.

E-mail addresses: lixinyang@ucas.ac.cn (X. Li), zhuw11@mails.tsinghua.edu.cn (W. Zhu), yueyi918@126.com (Y. Wu), wangcw@tsinghua.edu.cn (C. Wang), jzzheng@ucas.ac.cn (J. Zheng), xukangning@bjfu.edu.cn (K. Xu), lijiyun2000@sina.com (J. Li).

landfill leachate [2,7]), a source of urgently needed fertilizer chemical, especially in China where imports are heavily relied upon due to lack of potassium resources. Unfortunately, beneficial recovery of potassium ions from concentrates has rarely been reported [9]. In addition, other valuable inorganic species (i.e., chloride ions) are also abundant in these concentrates [4,10,11] and should be effectively recovered. These ions are often oxidized to by-products such as gaseous chlorine or hypochlorite depending on pH, in the above AOPs [2,6,7,12], which can cause uncontrolled discharge of toxic gases into the environment, leading to potential human health hazards. Finally, hydrogen, a clean energy fuel, is another valuable compound that is electro-generated at the cathode, when electrochemical oxidation processes are used to treat concentrates [13]. Therefore, the current study aims to explore innovative and environmentally sustainable treatment processes for NF concentrate, which include (a) contaminant removal: organic pollutant and ammoniacal-nitrogen removal; (b) recycling and onsite reuse of chloride ions in the form of gaseous chlorine; (c) separation and beneficial recovery of potassium from NF concentrates.

Cation-exchange membrane electrolysis (CEME), the first stage of the combined process examined in this study, has been used to simultaneously remove organic pollutants from NF concentrates and recover chloride ions via electro-generated gaseous chlorine [14]. This process has often been used for chlorine and base production in chloralkali industries [15]. However, to the best of our knowledge, the application of CEME to organic pollutant removal and gaseous chlorine production from NF or RO concentrate waste-streams has not been investigated before. Notably, the gaseous chlorine produced does not need to be discharged, but can be reused onsite as a convenient agent to decolorize colored wastewater. The second stage in this study is the separation of potassium(I) from treated NF concentrates via electro-migration and subsequent potassium recovery using a magnesium potassium phosphate crystallization process, which has been used to recover potassium(I) from urine [16]. The magnesium potassium phosphate products are considered valuable and scarce slow-release fertilizers [16,17]; however, the application of magnesium potassium phosphate crystallization to recover potassium(I) from NF concentrates has never been reported before.

Therefore, the specific objectives of this study were: (1) achieving effective removal of organic pollutants and ammoniacal-nitrogen; (2) recycling Cl^- and producing gaseous chlorine for reuse as an agent for decolorizing synthetic dyeing wastewater (Rhodamine B (RhB) solution); (3) recovery of potassium ions (K^+) through magnesium potassium phosphate crystallization.

2. Materials and methods

2.1. Electrochemical oxidation of NF concentrates

The electrolysis was conducted three times in a divided electrolysis cell consisting of two cylindrical glass tubes (empty volume 220 mL), which acted as the anode and cathode chambers (Fig. 1(a)), respectively. These two chambers were separated by a cation-exchange membrane (CEM) (Grion7322-Q, Hangzhou Grion Environmental Technology Co., Ltd, China). A piece of $\text{Ti}/\text{RuO}_2\text{-IrO}_2\text{-TiO}_2\text{-SnO}_2$ electrode (Long Sheng Co., China) and a stainless steel plate were used as the anode and cathode, respectively. Both electrodes were rectangular (geometric area 25 cm^2) and positioned vertically and parallel to each other. The two electrodes were placed at an equal distance (5 cm) from the CEM membrane, with an inter-electrode gap of 10 cm.

The NF concentrates, clear dark brown liquids, were sampled from a municipal landfill site (Beijing, China), where raw landfill

leachates had been treated via a combined process of upflow anaerobic sludge blanket (UASB), anoxic-aerobic-oxic ($\text{A}_1\text{-A}_2\text{-O}$), and submerged membrane bioreactor treatment (MBR). The biologically treated leachates were then further treated with NF before it was discharged. The concentrates generated in the NF process were collected and stored in a refrigerator at $4\text{ }^\circ\text{C}$ before they were used in the electrolysis treatment tests. The composition of the concentrates were listed in Table 1. Before starting the experiment, a concentrate sample (200 mL) and 5% NaOH aq. (w/v) were added to the anode and cathode chambers, respectively. The electrolysis experiment was conducted under galvanostatic conditions (current density 40 mA cm^{-2}) for 8 h using a digital DC power supply (LeiCi Co., China). During electrolysis, gaseous chlorine and hydrogen gas were electro-generated in the anode and cathode chamber, respectively, while the volume of hydrogen was measured with water displacement method. The temperatures of the anodic and cathodic solutions were maintained at $20\text{ }^\circ\text{C}$ using cooling water.

After various reaction times, 3 mL of treated samples was collected and filtered through a $0.45\text{ }\mu\text{m}$ filter. The filtrate was analyzed for the characteristics described in Section 2.4.

2.2. Reuse of gaseous chlorine for decolorizing synthetic dyeing wastewater

During electrolysis, chloride ions from the NF concentrates were oxidized to gaseous chlorine in the anode chamber, which was continuously exhausted into a glass bottle containing 500 mL synthetic dyeing wastewater (RhB solution, 69.4 mg/L RhB, initially pH 3). The RhB concentrations were determined at various reaction times using ultraviolet-visible spectrophotometry.

2.3. Beneficial potassium recovery via magnesium potassium phosphate crystallization process

After 8 h electrolysis, the 200 mL electrolyte solution in the cathode chamber was collected and potassium (K) ions were recovered via magnesium potassium phosphate crystallization as follows: (1) the initial pH of the cathodic electrolyte was adjusted to 10 using $18.4\text{ M H}_2\text{SO}_4$; (2) sources of magnesium (MgSO_4) and phosphate ($\text{Na}_2\text{HPO}_4\cdot 12\text{H}_2\text{O}$) in solid phase (molar ratio of Mg:K:P is 3:1:3) were added into the cathodic electrolyte with stirring; (3) after 20 min of reaction and 20 min of sedimentation, the supernatant was collected for analysis.

2.4. Analytical methods

Solution pH was measured using a pH meter (H160NP, Hach Co., USA). COD was measured colorimetrically using a spectrophotometer (DR/2010, Hach Co., USA). Total nitrogen (TN) and ammoniacal-nitrogen ($\text{NH}_3\text{-N}$) were analyzed in accordance with standard methods [18]. The concentrations of potassium ions were measured using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (IRIS Intrepid II, Thermo Scientific Co., USA). Cl^- concentrations were determined with a chloride ion-selective electrode (7101, Luosu Co., China). Ultraviolet-visible absorption spectra of RhB solutions were recorded using a spectrophotometer (UV-2401PC, Shimadzu Co., Japan).

In addition, we measured the three-dimensional excitation-emission matrix (EEM) spectra [19] and quantitatively analyzed the fluorescence spectra according to the fluorescence regional integration (FRI) technique [20].

Download English Version:

<https://daneshyari.com/en/article/640740>

Download Persian Version:

<https://daneshyari.com/article/640740>

[Daneshyari.com](https://daneshyari.com)