접착 및 계면 제19권 제3호, 2018년
〈연구논문(Original Article)〉

Journal of Adhesion and Interface Vol.19, No.3, 2018
http://dx.doi.org/10.17702/jai.2018.19.3.101

전기화학 계면반응에 기초한 DSA 전극을 사용한 고성능 폐수처리 시스템

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(2018년 05월 26일 접수, 2018년 07월 10일 수정, 2018년 08월 27일 채택)

The wastewater treatment system with high performance based on electrochemical interface reaction using dimensionally stable anode with simple manufacturing

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(Received May 26, 2018; Revised July 10, 2018; Accepted August 27, 2018)

요 약: 도시의 산업화와 인구의 빠른 증가로 인해, 지구상에서 여전히 7억 8천만명이 물자원 사용에 어려움을 격고 있으며, 이에 따라 깨끗하고 저렴한 물자원 확보 방안에 대한 관심이 집중되고 있다. 그러나, 현존하는 폐수처리 시스템은 낮은 공정효율, 높은 운영비용, 그리고 넓은 부지 요구 등의 다양한 이슈에 직면하여 있는 실정이다. 따라서, 저렴하고 효율적인 폐수 처리 시스템의 개발이 시급히 요구된다. 이러한 노력의 일환으로 rutile type RuO_2를 기반으로 한 DSA전극을 이용한 전기 화학적 방법에 기초한 폐수 처리 시스템을 제안하였고, 이를 성공적으로 시연하였다. 우리의 폐수 처리 시스템은 생활폐수의 경우, 생화학적 산소 요구량 (BOD), 화학적 산소 요구량 (COD) 및 총 유기탄소 (TOC) 제거 효율이 52.0 %, 77.8 % 및 65.6 % 로 우수한 특성을 보였다. 또한 축산 폐수의 경우, BOD, COD, 총 질소 (TN), 총 인 (TP)의 제거 효율이 각각 92.9 %, 75.6 %, 35.1 %, 100 %로 획기적인 감축 효과를 거두었습니다. 이 장치의 탁월한 제거 효율과 작은 크기를 고려할 때, rutile RuO_2로 코팅된 DSA를 사용한 전기화학적 폐수 처리는 생활 및 축산 폐수의 처리를 위한 유망한 방안이 될 수 있음을 제안하고자 합니다.

Abstract: With the rapidly growing of the population and industrization of cities, the clean and affordable water resources have gained immense interest because of remaining about 780 million people still lack access to it. However, present wastewater treatment systems have been faced with various issues, such as low processing efficiency, high operational costs and the requirement of a large area for manufacturing. It is therefore urgently required to develop an inexpensive and efficient wastewater treatment system. As the one of these efforts, we suggested and successfully demonstrated the wastewater treatment system using and electrochemical method via a dimensionally stable anode (DSA) based on rutile type RuO_2. Our system achieved biochemical oxygen demand (BOD), chemical oxygen demand (COD), and total organic carbon (TOC) removal efficiently at the respective rates of 52.0%, 77.8%, and 65.6% from household wastewater. In addition, we were able to remove BOD, COD, total nitrogen (TN), and total phosphorus (TP) from animal husbandry wastewater at rates of 92.9%, 75.6%, 35.1%, and 100%, respectively, thereby achieving dramatic reductions. Considering the excellent removal efficiency and the small size of this device, electrochemical wastewater treatment using a DSA coated in rutile RuO_2 presents a promising option for the treatment of both household and animal husbandry wastewater.

Keywords: *Wastewater treatment system, Dimensionally stable anode, Rutile type RuO_2, Household and animalhusbandry wastewater, Electrochemical method.*

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1. Introduction

Clean and affordable water is the most important reso urce for the global human population. Unfortunately, access to it has remained a huge challenge throughout the 21st century. Presently, approximately 780 million people do not have access to clean and affordable drinking water resources (WHO, 2012). Furthermore, it is urgent to supply inexpensive wastewater treatment system not only in developing countries where it was not existed, but also industrialized countries where it was successfully existed. Because scarcity of the clean water resources is exacerbated by human being related issues, like a rapidly growing population, the improvement of living standard continuously drives up the demand and the global climate changes[1-2]. Therefore, lots of researchers have studied to solve these issues via various wastewater treatment systems including nanotechnology, photocatalytic oxidation, adsorption/separation processes, and bioremedia tion[3-7]. However, these efforts have been faced with many problems such as low processing efficiency, high operatio nal costs, and the requirement for large manufacturing areas. In an effort to solve the aforementioned issues, electroche mical water treatment has gained interest amongst researchers. An issue that needs to be overcome with this system is that of electrode corrosion.

To overcome the issue of electrode corrosion, a dimensionally stable anode (DSA) can be used in the chlor-alkali production process. Beer, who demonstrated mixed metal oxide electrode based on ruthenium chloride and titanium chloride on titanium substrate via pyrolysis method[8]. Other studies have reported based on iridium dioxide (IrO_2), ruthenium dioxide (RuO_2), titanium dioxide (TiO_2),zirconium dioxide (ZrO_2)[9-14].

Ruthenium (RuO_2) is a famous element that can easily change oxidation states from −II to +VIII. For this reason, it is able to combine many elements resulting in compounds with interesting and unique properties[15-16]. Ruthenium is included as a chemical catalyst in various organic reactions[17-18]. Promoted metallic ruthenium is a good hydrogenat ion catalyst for converting nitrogen to ammonia, making it the most active catalyst in ammonia synthesis[19-20].

Furthermore, ruthenium is an excellent oxidation catalyst in heterogeneous catalysis and electro-catalysis[21-22].

Unfortunately, it is a relatively rare metal with limited commercial uses. The market price of ruthenium is high due to limited production, which is estimated to be between 20 and 25 ton/year[23]. Even if the price of ruthenium is about 10 times lower than that of platinum. In 2010 about 3 or 4 ton/year of ruthenium was used into the fabrication of dimension nally stable anodes (DSAs) for chlor-alkali electrolysis, while most of the ruthenium is deployed as buffer layers and thin film resistors in the electronic industry (about 20 t in 2010). [24]

In this study, we successfully demonstrated the wastewater treatment system based on various wastewaters, such as wastewater of household and of animal husbandry, by electrochemical method with DSA based in rutile type RuO_2. Remarkably, the BOD, COD, and TOC removal efficiencies of the wastewater of the household were 52.0%, 77.8%, and 65.6%, respectively. In addition, we achieved good BOD, COD, TN, and TP removal rates from animal husbandry wastewater. These were 92.9%, 75.6%, 35.1%, and 100%, respectively. These results show a dramatic reduction in BOD, COD, TN, and TP values. Considering the excellent removal efficiency relative to the small size of this device, the wastewater treatment system using an electrochemical method employing DSA coated with rutile RuO_2 is a promi sing example for wastewater treatment method for both household and animal husbandry wastewaters.

2. Materials and Methods

A ruthenium (RuO_2) ink solution used to coat the DSA. This was prepared by mixing the ruthenium chloride hydrate ($RuCl_3$-xH_2O, Sigma-Aldrich, 6.5wt%) and isopropyl alcohol ($(CH_3)_2CHOH$, Sigma-Aldrich, 93.4wt%) in a solvent withhydrochloric acid (HCl, Sigma-Aldrich, 0.1wt%) as catalyst for 24 h. We used titanium plates (10×10×1 mm, 99.9%) as the substrates for the DSA coated with rutile RuO_2. To increase their surface area, the titanium plates were sanded using sandpaper. The plates were then etched by 3wt% hydrofluoric acid for 3 mins and 10wt% oxalic acid (Sigma-Aldrich) for 1 h. To plate the DSA with rutile RuO_2, we dipped the grinded and etched titanium plates into the RuO_2 ink solution 10 times using a semi-automatic dip-coating machine. Thereafter, the plates were fired at 450°C in a programmable furnace. Fig 1. shows a schematic illustration of the DSA plating with rutile RuO_2 using dip-coating and firing method.

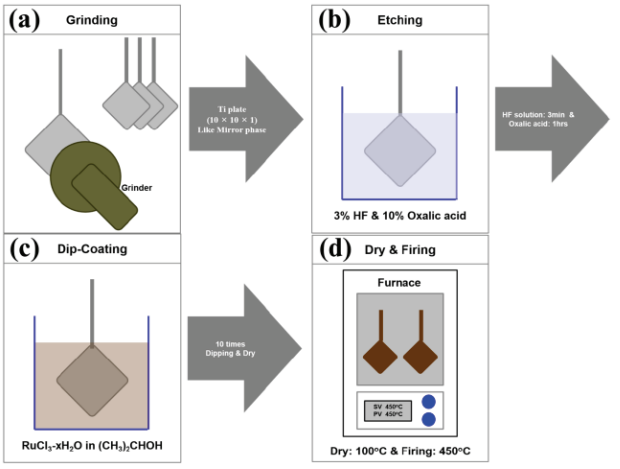

Figure 1. Schematic illustration of the manufacturing routes for dimensionally stable anode with RuO_2 by using dip-coating & firing method.

We examined the DSA with rutile RuO_2 plating using X-ray diffraction (XRD) and scanning electron microscopy (SE M). X-ray diffraction (XRD) patterns were collected (New D8-Advance/Bruker-AXS) at a scan rate of 1 s−1within the 5°−80° 2θ range using Cu Kα1 radiation (λ=0.154056 nm). We observed the morphology of the samples using a scaning electron microscope (JSM-5200, JEOL Co.).Water quality tests were used to determine the efficiency of the waste water treatment using the Rutile RuO_2 plated DSA. The water quality analyses methods (BOD, COD, and TOC) are described in supporting information.

3. Results and Discussion

The surface morphologies of the DSA coated with rutile structure RuO_2 are shown in Fig 2(a). In the SEM images of the electrodes, several cracks and lots of hollows with sub-micron sizes (the inset) can be observed, which could provide a high surface area for the large electrochemical reaction area of the DSA. Fig 2(b) exhibits the XRD patterns of the DSA with rutile structure RuO_2. The data contains rutile type RuO_2(space group: P42/mnm (136), JCPDS #43-1027), which are four main peaks centered at 2θ 28.0, 35.1, 40.0, 54.3 and 69.5corresponding to the (110), (101), (200), (211) and (301). We confirmed that the DSA with rutile type RuO_2 were successfully demonstrated via dip-coating and firing method using sol-gel RuO_2 ink solution.

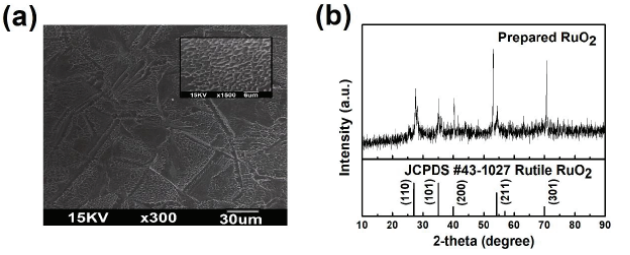

Figure 2. Materials analysis of dimensionally stable anode with RuO_2 (a) SEM image and (b) XRD patterns.

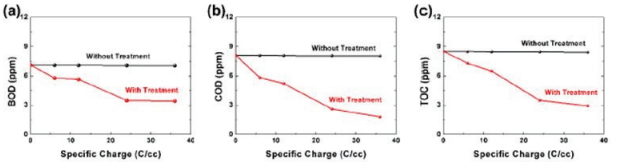

Figure 3. Water treatment effects of the wastewater of the household in Seoul, Korea via electrochemical treatment method using dimensionally stable anode with RuO_2 (a) BOD changes (b) COD changes and (c) TOC changes.

To confirm the wastewater treatment performances of prepared DSA based on rutile type RuO_2, we examined the water quality tests which are BOD, COD, TOC, TN, TP,and fluoride ions concentrationsusing test methods listed and described in the water quality conservation act, Ministry of Environmental of Korea (No.2004-188).

Fig 3. shows the results of the water quality tests (Fig 3(a) BOD, Fig 3(b) COD, and Fig 3(c) TOC) of the household wastewater in Seoul, Korea via electrochemical treatment method. The BOD, COD, and TOC contents of the household wastewater samples were 7.11 ppm, 8.10 ppm, and 8.49 ppm, respectively, before electrochemical treatment with the DSA. As increasing the specific charge (C/cc) of the anode, the BOD, COD, and TOC contents of wastewater samples dramatically decreased. Notable decreases were observed in BOD which decreased by 52% to 3.41 ppm, COD which decreased by 77.8% to 1.80 ppm, and TOC which decreased by 65.6% to 2.92 ppm; all at 36 C/cc (adding current 5A, sample volume 250cc, and treatment time 30 mins). The electrochemical treatment using a rutile RuO_2 plated DSA is therefore more efficient at removing COD than BOD or TOC.

In general, the treatment of the wastewater of household was more efficient than that of animal husbandry. Especially, TN and TP removal of the wastewater of animal husbandry is quite important.

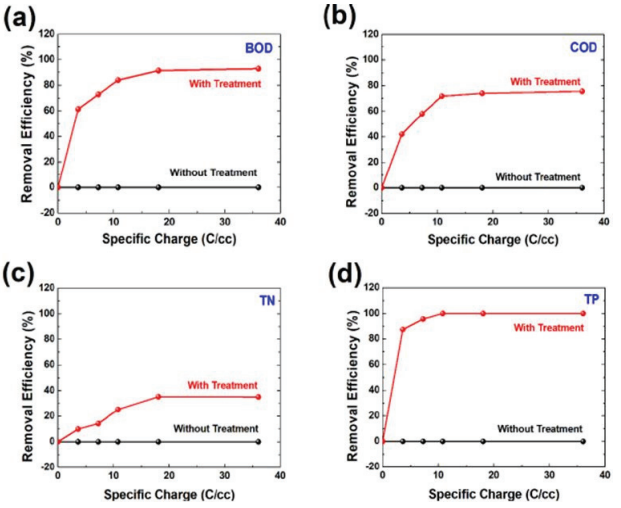

Figure 4. Removal efficiencies of the wastewater of the animal husbandary via electrochemical treatment method using dimens ionally stable anode with RuO_2 (a) BOD (initial concen tration : 61.6 ppm) (b) COD (initial concentration: 131.0 ppm) (c) TN (initial concentration: 53.0 ppm) and (d) TP (initial concentrate on: 2.4 ppm).

To confirm the treatment effects of the wastewater of animal husbandry, we performed the electrochemical treatments and examined the water quality tests at the same methods, which were exhibited the Fig 4. Before treatment, the initial values of the BOD, COD, TN, and TP were 61.6 ppm, 131.0 ppm, 73.0 ppm, and 2.4 ppm, respectively. After treatment for 30 mins under the same test conditions, BOD, COD, TN, and TP were reduced to 4.4 ppm, 32.0 ppm, 47.7 ppm, and 0.0 ppm, respectively, which were dramatically reduced by electrochemical treatment with DSA based on rutile type RuO_2. Remarkably, TP were perfectly removed during electrochemical treatment using DSA plated with rutile RuO_2. The removal efficiency for BOD, COD, TN and TP were 92.9%, 75.6%, 35.1%, and 100%, respectively. These results show that we confirmed and successfully demonstrated not only the treatment of the wastewater of the animal husbandry but also that of the household via the electrochemical method with DSA based on rutile type RuO_2.

Fluoride ions in water pose a number of health risks. These include induced cancer, reduced kidney function, microcephaly and congenital abnormalities, abnormal thyroid activity, atherosclerosis, and many allergic reactions. To reduce these risks, it is important that wastewater treatment processes are able to remove

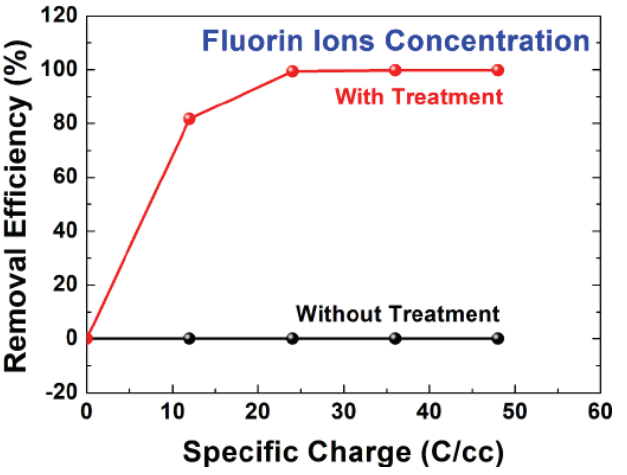

Figure 5. Removal efficiency for fluoride ions concentrations (initial concentration: 2,150 ppm) in the wastewater via electrochemical treatment using dimensionally stable anode with RuO_2.

fluoride form wastewater. To test the efficiency of wastewater treatment using a rutile RuO_2 plated DSA, we carried out water treatment under the same conditions as described above. Fig 5. exhibited the removal of fluoride ions in the wastewater by electrochemical treatment with a DSA plated with rutile RuO_2. The initial concentrationsof the fluoride ions was 2,150 ppm and it was dramatically reduced at about 5.2 ppm after electrochemical treatment at 36 C/cc, which was achieved at about 99.8 % removal efficiency. Considering the excellent removal efficiencies and small size of this device, our system should be a promising example for wastewater treatment applications of household and animal husbandry.

4. Conclusion

The electrochemical wastewater treatment system with DSA based on rutile type RuO_2 were investigated and demonstrated in use of wastewaters of household and animal husbandry. Furthermore, we could achieve the good removal efficiencies of BOD, COD, and TOC were 52.0%, 77.8%, and 65.6%, respectively in wastewater of household application. In additions, we also could get the best removal efficiencies of BOD, COD, TN, and TP were 92.9%, 75.6%, 35.1%, and 100%, respectively in wastewater of animal husbandry, which were dramatically reduced values.

Considering the excellent removal efficiencies and

small size of this device, our system should be a promising example for wastewater treatment applications of household and animal husbandry. Furthermore, in view of thehigh price and limitation of RuO_2, we will study on the wastewater treatment system with the various DSA based on metal oxides compounds, such as, iridium dioxide (IrO_2), titanium dioxide (TiO_2), and zirconium dioxide (ZrO_2).

Conflict of Interests

The author declares that there is no conflict of interestsregarding the publication of this paper.

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