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Tetracycline removal from aqueous solution through photo-anodic oxidation process using rotating graphite cylinder anode

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Abstract

In the present work, tetracycline (TC) was removed from a simulated wastewater through a new photo-anodic oxidation process with a rotating graphite cylinder anode. The effects of current density, pH, rotation speed, and NaCl addition were evaluated. The results confirmed that increasing the current density results in improving the removal of TC. However, increasing the current density beyond 5 mA/cm^2 had little effect on TC removal. Results revealed that TC removal using photoanodic oxidation can be achieved at high performance with an initial pH of 5. Increasing or decreasing pH beyond this value has a negative effect on TC removal. Increasing rotation speed gave better performance for TC removal due to the increase in mass transfer. The addition of NaCl improved the removal efficiency of TC due to the participation of indirect anodic oxidation within the oxidation process. The best conditions were: current density of 5mA/cm^2, pH=5, 250 rpm, and the addition of 1 g/L NaCl, in which TC removal of 84% was achieved that claims (103 kWh/m^3) as a total electrical energy consumption. In comparison with the anodic oxidation process alone, photo-anodic improved TC removal by an increment of (13.73%), confirming the photo-anodic process can be adopted successfully for treating wastewaters.

Keywords: Tetracycline; anodic oxidation; photo-oxidation; rotating anode; graphite; wastewaters.

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1- Introduction

Antibiotics were used widely in medicine infectious diseases in both human and animal residents. Tetracycline (TC) is one of the most typical broad-spectrum antibiotics used in the world [1]. However, the overuse of TC results in entrance and accumulate TC within the environment, causing a significant threat to human health [2]. Therefore, searching for an effective method to degrade TC from wastewater would be a challenge. Different approaches have been used to remove TC from wastewater, including biological treatment [3], physical treatment such as adsorption [4] or membrane technology [5], and recently advanced oxidation processes (AOPs) [6]. The removal of TC by biological methods is limited due to the bio-resistance and chemical stability characteristics of TC [7]. Furthermore, biological methods claim a long processing time combined with complexion in isolation of bacterial strains, in addition to generating a large quantity of sludge [7]. Physical treatment can separate but not degrade TC from wastewaters which could be made a risk of generating secondary contaminations by used adsorbent which needs further processing [8]. In contrast, AOPs proved to be effective processes with high decomposition or degradation capacity for TC due to the powerful oxidation potential of the generated reactive oxygen species, which have the ability to attack organic pollutants in a non-selective manner [9]. Furthermore, AOPs have become the focus of many researchers as techniques with environmental friendliness, no secondary generations of contaminants, and cost effectiveness [10]. Different types of AOPs were used to remove TC, including ozone oxidation [11], Fenton/photo-Fenton [12], Heterogeneous photocatalytic [13-16], persulphate,peroxymono/disulphate [17-18] and electrochemical oxidation [19-22].

Electrochemical oxidation, in some time known as anodic oxidation (AO), is a well-known promising method in AOPs which had been used efficiently to treat refractory organic pollutants due to its environmental compatibility, simple operation, small footprint, low cost, and high oxidation capacity [21]. The degradation of organic pollutants by anodic oxidation can be happened either by direct transfer of electrons from organic molecules on the surface of the anode (direct oxidation) or by heterogeneous reactive oxygen species generated indirectly as a results of water oxidation or existing ions in the bulk, such as chloride ions [23]. In this framework, anodes in which radicals are strongly adsorbed (chemisorbed) on its surface would have a lower overpotential for oxygen generation and called active

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anodes since liberation of O_2 is easy. Consequently, a selective oxidation would be happened toward the pollutants. On the other hand, anodes in which radicals weakly adsorbed (physiosorbed) on its surface would have higher over potential for oxygen generation and called non active anodes. Consequently $^{\bullet}$OH formation is preferred [24]. The efficiency of direct oxidation depends on the catalytic property of anodic materials, while indirect oxidation is governed by the diffusion rate, pH, and temperature [25].

TC has been removed successfully using different anodic materials, including Pt [26], boron-doped diamond (BDD) [27-30], and dimensionally stable anode (Ti-based anode) [31-34] SnO_2 [35-37] and PbO_2 [38-39]. BDD is the best anodic material, but its cost is relatively high that restricts its industrial application [40]. Pt and DSA anodes have the ability to degrade TC, but they can't remove the chemical oxygen demand (COD) and total organic carbon (TOC) completely [28]. SnO_2- or PbO_2- based anodes have good activity and are economic, but their short life time and the risk of possibility releasing toxic metals (Pb) from their surface limit their industrial applications [41]. Graphite is another anodic material that has been used extensively in wastewater treatment. It has many benefits, like low cost and high hydrogen peroxide formation over-potential. However it suffer from its inability in removal of organic compounds completely at low current density while using high current density results in corrosion issues [42]. Hence combining AO using graphite anode with other advanced process may be resulted in making the treatment process more efficient, economic, and easy to scale-up [43]. Direct photolysis, although not characterized as an AOP, has been used in TC degradation [44-47]. In this process, the interaction between organic pollutants with UV can lead to the occurrence of photochemical reactions via the transfer of electrons from the excited-state molecule to ground-state oxygen, in which degradation can be processed directly or by hemolysis [48].

The aim of the present work is to remove TC from a simulated wastewater using AO with a rotating cylinder anode in combination with photolysis, as a new system not studied before. Adopting a rotating cylinder anode would enable the use of high current densities, hence improving the application of graphite anode for the oxidation process as a cost-effective anode. Furthermore, previous studies confirmed the successful application of rotating cylinder electrode (RCE) in wastewater treatment as a result of its high mass transfer, uniform potential and current distributions on its surface, and easy to scale-up [49]. Accordingly, it would be expected to improve the TC removal via photo-anodic process with a rotating electrode as a result of increasing the mass transfer during the oxidation process. The effect of current density, pH, rotation speed, and the addition of NaCl on the removal efficiency of TC was investigated thoroughly.

2- Experimental work

2.1. Materials and chemicals

Tetracycline was purchased from Sigma-Aldrich (Singapore). NaCl was purchased from Fisher Chemicals. pH adjustment was performed using 1M HCl or 1M NaOH. All chemical reagents used in this work were of analytical grade; hence, no further purification was performed.

2.2. The photo-anodic oxidation system

The photo-anodic oxidation system is shown in Fig. 1. It was composed of a photoelectrochemical cell, an overhead electric motor (PHOEN RSO 20D), a magnetic hot-plate (ISO LAP), an air compressor (HAILEA(aco-280)) with an air flow meter at a range of 0.5-5 L/min, a DC power supply (UNI-T(UTP-3315TFL) provided with an ammeter (UNI-UT90A).

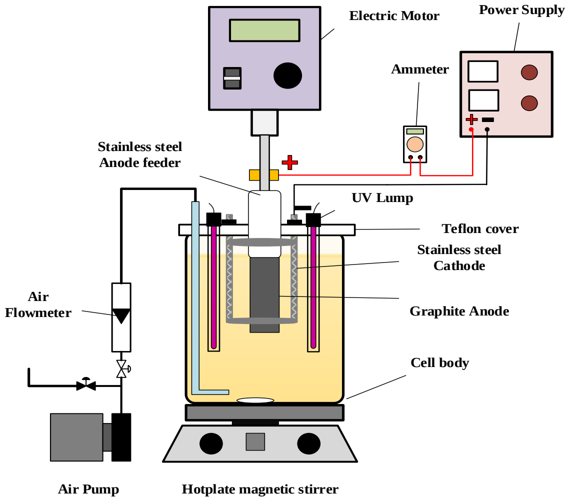

Fig. 1. Photo-anodic oxidation system

The photo-electrochemical cell is a Perspex cylindrical reactor having dimensions (inside diameter of 10 cm with length of 19.5 cm). The photo-reactor was provided with a cover made of the same material and having an outside diameter of 12 cm and a thickness of 1 cm. Three holes were drilled in this cover; the first was at the centre with a diameter of 2.5 cm, while the others were located along the bisector line at equal distance (2.5 cm) from the center, and each one has a diameter of 2 cm and used for fixing the houses of two UVC lamps. Each lamp has a power of 10W and λ of 253.7 nm. It was type (Sterilight R-CAN, Texas, USA). The choice of UVC in the present work is based on the work of López-Peñalver et al.[47]. They found that the best photodegradation of TC occurred when using UV with λ = 254 nm.

The cathode was fixed on the cover from the bottom via two holes with a diameter of 5 mm. It was a hollow stainless steel cylinder having an outside diameter of 3.8 cm and a thickness of 0.1 cm. It was perforated laterally with holes of 5mm distributed equally along its surface. The anode was composed of two parts; the first is a current feeder, while the second is a solid graphite cylinder with dimensions (outside diameter of 2 cm, with length of 5 cm). The graphite cylinder was drilled from the top with a hole of 5 mm for fixing it on the current feeder. The current feeder was composed of two sections; an upper section is a stainless steel rod with dimensions (outside diameter of 0.7 cm and length of 8 cm) while the bottom is a stainless-steel rod with dimensions (outside diameter of 1 cm and length of 9 cm) covered with a Teflon cylinder (outside diameter of 1.8 cm and length of 9 cm) for preventing current feeder from attack with solution. The electrical connection of the anode feeder with the positive pole of the power supply was performed by a copper ring positioned around the anode feeder.

The photo-anodic oxidation was conducted at room temperature under galvanostatic operation for 240 min. Firstly, 1 L of a simulated wastewater was prepared by dissolving 0.5 g of TC to make a concentration of 50 ppm, then transferred to the photo electrochemical cell. The air pump was then switched for a period of 15 min for saturating of oxygen followed by switching the UV lamps and power supply to start the oxidation process. During the oxidation, 1 ml of the solution was taken every 30 min, then diluted 10 times. The concentration of TC was measured by detecting the absorbance of the sample at a wavelength of 357nm using a UV-spectrophotometer type (Shimadzu/Japan UV-Vis spectrophotometer). Then, the concentration of TC was found from a calibration curve presented in Fig. 2. All experiments were performed twice in this study, and the average values were considered.

TC removal efficiency at any time was evaluated using Eq. 1 [50]:

$$\mathrm{RE\%} = \frac{C_o - C_t}{C_o} \times 100 \qquad (1)$$

Where C_o represents the initial TC concentration (50 mg/L) while C_t represents the concentration of TC in mg/L at any time within the experiment.

According to the proposal of the Photochemistry Commission of the International Union of Pure and Applied Chemistry (IUPAC), the photo-electrical energy (PE) that is consumed during operation in kWh/m^3 can be calculated as follows [51]:

$$\mathrm{PE} = \frac{P \times t \times 1000}{V \log\left(\frac{C_o}{C_f}\right)} \qquad (2)$$

Where P represents UV lamp power (kW), V symbolizes the wastewater volume (L), and (t) denotes the operating time (h). C_f represents the final concentration of TC in mg/L.

The electrical energy (EE) that is consumed during the AO process in kWh/m^3 can be calculated as follows [50]:

$$\mathrm{EE} = \frac{E \times I \times t}{V} \qquad (3)$$

Where I denotes the current in amperes and E represents the voltage of the cell (Volt). Hence, for the photo-anodic process, the total electrical energy consumption in the process is the sum of PE and EE.

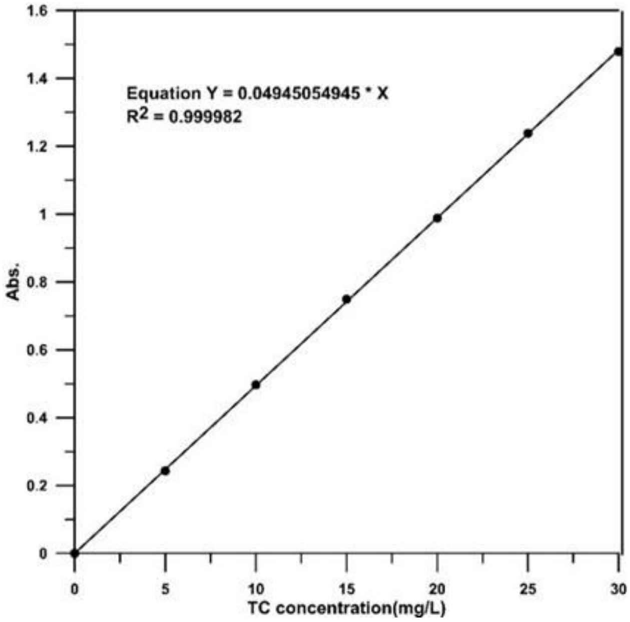

Fig. 2. Calibration curve for TC

3- Results and discussion

3.1. Effect of current density

Fig. 3 shows the effect of current density on the degradation of TC at a pH of 5 and rotation speed of 250 rpm. It can be seen that increasing the current density results in increasing RE%. However a little increase in RE% is occurred at a current density of 8 mA/cm^2 with a significant increase in the energy consumption from ($130.86 kWh/m^3$) to be ($181.65 kWh/m^3$). So it is recommended to use a current density of 5 mA/cm^2. The increase in RE% with increasing current density can be attributed to the increasing of active radicals as the current density increases [20]. However, a little improve at RE% was observed as the current density became higher than 5mA/cm^2. This is possibly attributed to the limited mass transfer rate of organic compounds toward the anode at a higher current density [52]. Similar observations were noted by previous works using anodic oxidation alone[20, 24, 28, 32, 34, 35-37, 42-53]. Shi et al. [31]found a similar behavior as the voltage across the electrode increases. Wang et al. [33] found that no significant effect of current density beyond 15 mA/ cm^2 in the treatment of TC using Ti/Ti_4O_7 anode, suggesting that higher current densities could not further accelerate the electrochemical oxidation.

3.2. Effect of pH

The pH of the solution can affect the rate of generating the active radicals with the AO process as well as the photolysis process. Besides it has an effect on the forms of organic molecules existing in the polluted water [54]. Fig. 4 shows the effect of pH on the degradation of TC at a constant current density of 5 mA/cm^2 and rotation speed of 250 rpm. It seems that increasing or degreasing pH beyond 5 results in a decrease in RE%. The reason can be attributed to the structure of TC at different pH. Previous studies confirmed that TC has three p*K*a values: p*K*a1 =9.7: p*K*a2 =7.7, and p*K*a3 =3.3, resulting in existing TC as an anion, neutral/amphiprotic ion, and cation forms, respectively [55-56]. In other words, at low pH<3, more TC molecules would have positive charges causing few TC molecules near the anode hence decreasing RE% [57]. While higher pH >7 leads to increasing oxygen evolution rather than radical formation [58]. Similar observations were noted by previous works using anodic oxidation alone [32, 35, 52]. Shi et al. [31]found that pH has no significant effect in the range 4-11 when using NiO@Co_3O_4/Ti anode. While Köktaş et al. [42] found that acid solution is preferred in comparison with alkaline solution for treating TC using graphite anode because oxygen precipitation was inhibited under acidic conditions. Similarly, Santos et al. [24] preferred acidic solution in the removal of TC using the DSA anode. Additionally, Liang et al. [34]removed TC using a Magnéli phase Ti_4O_7 porous anode at pH=6.

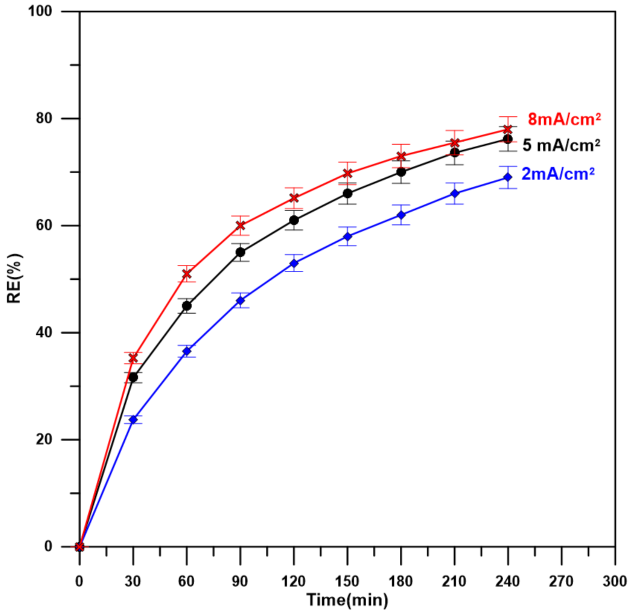

Fig. 3. Impact of current density on RE%. TC concentration =50 mg/L, pH=5, 250 rpm

3.3. Effect of anodic rotation speed

Fig. 5 shows the effect of rotation speed on the degradation of TC at a constant current density of 5 mA/cm^2 and pH of 5. It can be seen that increasing rotation gives better performance in removal of TC due to the increase in mass transfer towards the anode as a results of reducing the boundary layer thickness around the anode [59] . However, a slightly increase was observed at a rotation speed greater than 250 rpm. Similar observations were reported by previous works [59, 60-64].

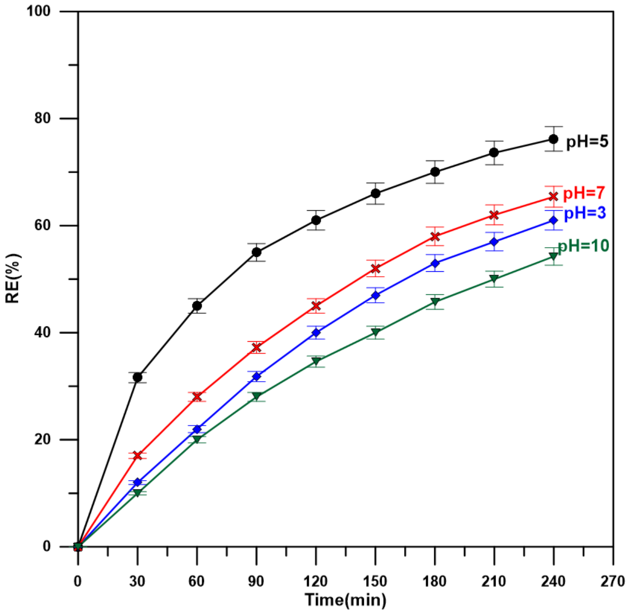

Fig. 4. Impact of pH on RE%.TC concentration =50 mg/L, 250 rpm, current density =5 mA/cm^2

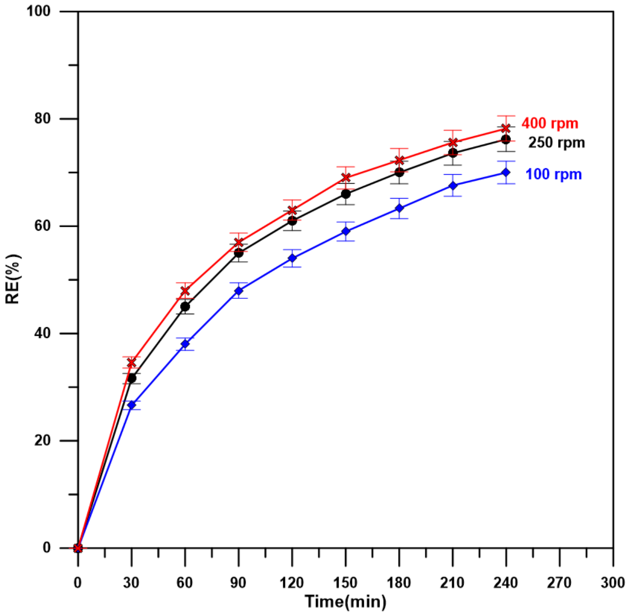

Fig. 5. Impact of rotation speed on RE% TC concentration =50 mg/L, current density =5 mA/cm^2, pH=5

3.4. Effect of the addition of NaCl with comparison against anodic oxidation

Fig. 6 shows that adding NaCl results in improving the TC removal where RE% increased from (76.2%) to (84%) with adding Cl^- at a concentration of 1 g/L in addition to reducing the total energy consumption from 130.86 to 103 kWh/m^3. This can be interpreted as chloride ions are oxidized at the anodes to give reactive chlorine species such as Cl_2 (aq) (E^O=1.36V/SHE), HClO (E^O=1.49V/SHE), ClO^- (E^O=0.89V/SHE) as shown in Eqs. 4-6 which can attack TC hence lowering its concentration [65].

$$2Cl^{-}_{aq.} \rightarrow Cl_2 + 2e^{-} \quad (4)$$

$$Cl_{2(aq)} + H_2O \rightarrow HClO + Cl^{-} + H^{+} \quad (5)$$

$$HClO = ClO^{-} + H^{+} \quad (6)$$

In the present work, NaCl was added at a concentration of 1g/L since most previous work confirmed that increasing NaCl concentration higher than 1 g/L has a little effect on TC removal [32]. Besides increasing NaCl concentration could results in an adverse effect due to the reaction of excess Cl^- with •OH leading to producing inactive chlorine species such as ClO_2^-, ClO_3^-, ClO_4^- [28, 31]. Other studies confirmed that high concentrations of Cl^- could result in the formation of organic chlorine compounds, which have an adverse effect on human health [42].

Fig. 6 shows that combining anodic with photolysis results in the enhancement of TC removal due to the synergistic effect of the two processes. Using direct photolysis alone for tetracycline solutions does not induce the generation of HO· radicals [47], but it can increase the concentration of reactive oxygen species in the solution [66].

Generally, using photolysis alone can remove TC, but at low percent. Frontistis and Meriç [66] found that using photolysis removed only 17% of TC. The use of light can increase the concentration of reactive oxygen species in the bulk of the solution, so it is expected that the rate of TC degradation by photolysis is low. However, it would be enhanced in combination with other AOPs. Therefore, combining photolytic with AO results in an enhancement of AO as shown in Fig. 6, where RE% is increased from (67%) to (76.2%) due to the photolysis effect. Also, it is appeared that in the absence of air, the RE% for the photoanodic process reduced to72% confirming the role of dissolved oxygen in the enhancement of the photolysis mechanism. Most previous works confirmed the role of oxygen in enhancement the UV activity by increasing the generation of reactive oxygen species [67].

Table 1 shows a comparison with similar works. It can be seen that BDD and DSA can remove TC completely within 240 min, but using higher current density and current concentration. While the present work used low current density and current concentration and system has the ability to degrade 84% of TC confirming the successful application of photolysis with rotation to degrade TC at lower current density and very low current concentration. Increasing the current concentration would be expected to remove TC totally at a lower operation time. However, the increase in current concentration in the present work is limited by the dimensions of UV lamps. In comparison with Ru/Graphite, which used 7.8 times the current concentration used in the present work, it would be expected that Ru/Graphite would require a time greater than 240 min to reach 84% removal of TC if using the same current concentration, which additionally confirms the effect of photolysis and rotation to enhance the anodic oxidation processes.

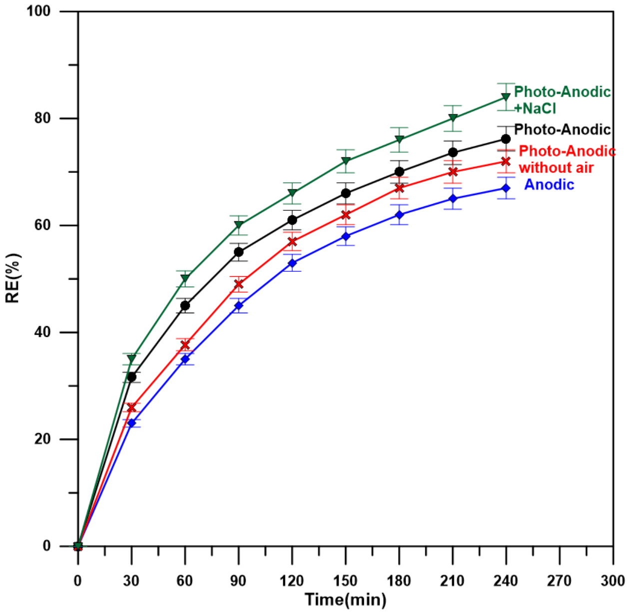

Fig. 6. Comparison between anodic and photo-anodic in the presence of NaCl. TC concentration =50 mg/L, pH=5, 250 rpm, current density =5 mA/cm^2

Table 1. Comparison with different works using different anodes for tetracycline removal

Process	Anode	pH	TC conc. (mg/L)	Current density (mA/cm^2)	Solution volume (cm^3)	Applied current (mA)	Current conc. (A/L)	Time (min)	RE %	Ref.
AO	BDD	7	150	30	200	6000	30	240	100	[30],2012
AO	DSA(Ti/RuO_2 - IrO_2)	6	200	20	400	1000	2.5	240	100	[68],2012
AO	Pb/PbO_2	2	20	25	400	500	1.25	180	76	[39],2013
AO	Ru/Graphite	2	88.9	5.68	80	100	1.25	100	93.8	[42],2023
Photo-AO	Graphite	5	50	5	1000	160	0.16	240	84	This work

4- Conclusion

Removal of TC from a simulated wastewater was achieved successfully via photo-anodic oxidation using a rotating graphite cylinder anode. Increasing the current density gives better removal up to 5 mA/cm^2, with a slight improvement beyond this value. pH of 5 was found to be the best for degrading TC. More acidic or alkaline conditions result in decreasing TC removal. The rotation speed has a positive effect on degrading TC on the surface of the anode. Using air is essential for the photolysis process, and adding NaCl improved the removal of TC due to the effect of indirect oxidation that generates other oxidizing species rather than •OH. The preferred conditions for removing of TC were a current density of 5 mA/cm^2, a rotation of 250 rpm, a pH of 5, and adding 1g/L NaCl, where RE% of (84%) was achieved during 4h of oxidation that required a total electrical energy consumption of (103 kWh/m^3). Using graphite as anodic material with adopting a rotation design of the cell would make the process more economic and easy to scale up.

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إزالة التتراسيكلين من المحلول المائي من خلال عملية الأكسدة الضوئية باستخدام أنود أسطوانة الجرافيت الدوارة

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الخلاصة

في هذا العمل، تمت إزالة التتراسيكلين (TC) من مياه الصرف الصحي المحاكاة من خلال عملية أكسدة ضوئية أنودية جديدة باستخدام أنود أسطواني دوار من الجرافيت. تم تقييم آثار كثافة التيار والرقم الهيدروجيني وسرعة الدوران وإضافة كلوريد الصوديوم. أكدت النتائج أن زيادة كثافة التيار تؤدي إلى تحسين إزالة TC. ومع ذلك، فإن زيادة كثافة التيار إلى ما يزيد عن ٥ مللي أمبير / سم ٢ كان لها تأثير ضئيل على إزالة TC. كشفت النتائج أنه يمكن تحقيق إزالة TC باستخدام الأكسدة الضوئية الأنودية بأداء عالٍ بدرجة حموضة أولية تبلغ ٥. إن زيادة أو تقليل الرقم الهيدروجيني بما يتجاوز هذه القيمة له تأثير سلبي على إزالة TC. أعطت زيادة سرعة الدوران أداءً أفضل لإزالة TC بسبب زيادة نقل الكتلة. أدى إضافة كلوريد الصوديوم إلى تحسين كفاءة إزالة TC بسبب مشاركة الأكسدة الأنودية غير المباشرة في عملية الأكسدة. كانت أفضل الظروف: كثافة تيار ٥ مللي أمبير/سم^2، ودرجة حموضة = ٥، وسرعة دوران ٢٥٠ دورة/دقيقة، وإضافة ١ جم/لتر من كلوريد الصوديوم، حيث تم تحقيق إزالة كربونات الصوديوم بنسبة ٨٤٪، أي ما يعادل ١٠٣ كيلوواط/ساعة/م^3 كاستهلاك إجمالي للطاقة الكهربائية. وبالمقارنة مع عملية الأكسدة الأنودية وحدها، حسّنت عملية الأكسدة الأنودية الضوئية إزالة كربونات الصوديوم بنسبة ١٣,٧٣٪، مما يؤكد إمكانية اعتماد عملية الأكسدة الأنودية الضوئية بنجاح لمعالجة مياه الصرف الصحي.

الكلمات الدالة: التتراسيكلين، الأكسدة الأنودية، الأكسدة الضوئية، الأنود الدوار ، الجرافيت، مياه الصرف الصحي.