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Effect of Electric Voltage on Simultaneous Electrocoagulation-Photocatalysis Process in Removal of Ciprofloxacin-Methylene Blue Mixture and Hydrogen Recovery

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In recent years, the number of health problems and hospital activities have increased with the amount of liquid waste produced. Therefore, this study aims to observe the effectiveness of wastewater treatment of antibiotics ciprofloxacin and methylene blue mixture using electrocoagulation and photocatalysis processes simultaneously. The observation focuses on the effect of the electric voltage used in electrocoagulation, considering the process is simultaneously conducted with photocatalysis. The smaller electrical voltage (20 V) increases the effectiveness of removing ciprofloxacin and methylene blue by 92.5% and 98.5%, respectively. Furthermore, hydrogen yields reached 2.07 mmol/g photocatalyst at 50 V voltage, while 0.98 mmol/g hydrogen gas photocatalyst was obtained when 20 V voltage was used in the process. A simultaneous process was developed by increasing the performance of the photocatalyst in terms of its ability to produce hydrogen. Similarly, the electrocoagulation voltage is sufficiently to maintain the effectiveness of removing dissolved pollutants.

Keywords: Electrocoagulation, Photocatalysis, Voltage, Hydrogen.

INTRODUCTION

The generation of liquid wastes from hospitals increases linearly with the growth of the world population. One type of waste generated quite a lot and its impact has not been completely overcome is liquid waste, which contains the antibiotics ciprofloxacin and methylene blue. According to several statistical reports, the antibiotic content reaches 65%, with ciprofloxacin as the most frequently detected component [1-4]. Various wastewater treatment technologies have been applied to diminish environmental pollution. One of these methods is electrocoagulation technology, which is efficient as well as easy to use [5,6]. However, the technology that produces this coagulant only adsorbs dissolved pollutants since they are easily removed. This situation has consequences that still need to be monitored since the pollutants emitted do not harm the environment.

Organic and inorganic wastes can be degraded through oxidation-reduction reactions on the surface of photocatalyst. The efficiency of the process in photocatalysis technology is determined by its ability to capture the energy of the released photon and to control the recombination rate of electrons and holes in a way that the oxidation-reduction reaction can proceed optimally [7-9].

The combination of two processes of electrocoagulation and photocatalysis is intended to increase the ability to remove pollutants dissolved in wastewater. A study has been conducted to combine the electrocoagulation and photocatalysis processes in sequence [10]. Ates *et al*. [11] also combined two techniques sequentially and compared the final results obtained when the process sequence was reversed. Both results concluded that the combination of the two processes can increase the ability to remove pollutants [11,12]. However, electrocoagulation has a better removal ability for effluents with high pollutant concentrations while photocatalysis can degrade pollutants with a concentrations of up to 800 mg/L [13].

A study development which concerns about the combined process system and the photocatalyst used. Photocatalyst modification is conducted to increase its ability to degrade dissolved pollutants. Slamet & Kurniawan [14] carried out both processes simultaneously in one reactor vessel. Furthermore, photocatalyst titania nanotube arrays (TNTAs) were used to improve the performance of the process. Observations were made to analyze the ability of this simultaneous process to remove tartrazine dye waste [14] and the photocatalyst capacity of TNTA is expanded by adding Cu dopants [15].

The magnitude of the electric voltage, which is one of the variables determining the performance of electrocoagulation was observed when the combined-photocatalysis system was applied. Meanwhile, the existence of two processes in one system is expected to affect the reaction mechanism. Previous studies have provided a direct correlation between the ability of electrocoagulation to remove dissolved pollutants and the amount of electric voltage used, when the process is not conducted simultaneously with photocatalysis [14,15]. The ability of TiO_2 photocatalyst was improved by modification with Fe as dopants. It lowers the energy level of the conduction band and narrows the bandgap of TiO_2 energy [16]. Additionally, it increases the ability of photocatalysts to capture photon energy from visible light to increase the performance of photocatalysts in degrading antibiotic waste.

A previous study showed that the electrocoagulation and photocatalysis processes produce hydrogen gas [17,18]. The magnitude of the electric voltage used in the electrocoagulation process has a linear correlation with the amount of hydrogen gas produced [5,19]. Similarly, the modified TiO_2 photocatalyst using Fe-dopant will have a bandgap energy easily activated by visible light to increase hydrogen production [20]. Analysis of combined effects of the system on the amount of hydrogen produced was also observed since the presence of two reaction mechanisms may affect the ability to produce hydrogen.

EXPERIMENTAL

The ingredients used were ciprofloxacin manufactured by PT Bernofarm, while methylene blue, TiO_2 Evonik P25, NH_4OH (25%), $Fe(NO_3)_3{\cdot}9H_2O$, HNO_3 (65%) and methanol (99.9%) were procured from Merck, India. Furthermore, a vessel made of acrylic was used as a photocatalytic reactor as well as electrocoagulation and the process was conducted simultaneously using the power supply as a voltage source. The vessel is equipped with a quartz and pyrex tube in the photocatalyst and electrocoagulation section. Two 250 watt Philips lamps (17.25% UV and 82.75% Vis Light) were used as photon sources.

General procedure: The synthesis of nanocomposites using the sonophotodeposition method begins with dissolving $Fe(NO_3)_3{\cdot}9H_2O$ at a particular concentration in 100 mL distilled water. Meanwhile, 1.5% Fe content was used, which gave the optimal performance of Fe-TiO_2 nanocomposites in the photocatalysis process. Then TiO_2 nanoparticles were added with distilled water and HNO_3 dispersed in a solution of iron(III) nitrate ultrasonically for 90 min and exposed to light from a 24 watt UV-A lamp. Furthermore, Fe-TiO_2 nanocomposites were obtained by a deposition process followed by centrifugation to optimize the separation. The residue was washed with distilled water, and after drying, it was calcined at 300 ºC for 1 h.

Detection method: The characterization of the resulting nanocomposite was carried out using XRD to identify the crystals formed, while the SEM-EDX was used to analyze the presence of Fe in the crystals of titania.

The degradation of ciprofloxacin and methylene blue as pollutants were conducted during the simultaneous electrocoagulation-photocatalysis process. Fig. 1 showed samples of liquid waste containing ciprofloxacin and methylene blue with a concentration of 10 ppm and pH 10 introduced into the reactor. The reactor was equipped with 1 g of Fe-TiO_2 nanocomposite particles/L solution, an aluminum plate as cathode and a stainless steel plate as anode. The two plates were connected to a power supply, which conducts direct current at a voltage of 20 V. The homogeneity of solution was maintained by using a magnetic stirrer at the bottom of the reactor. The light source in the form of two Phillips lamps 250 W was placed parallel to the reactor and on two sides opposite each other. The process was conducted for 4 h and after every hour, a sample solution and gas were used to analyze the content of pollutants and hydrogen.

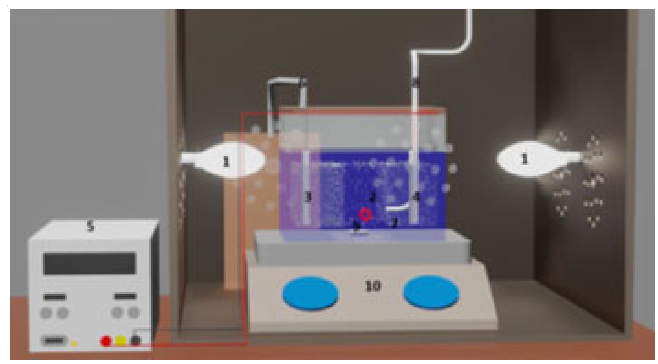

Fig. 1. A series of apparatus for the simultaneous electrocoagulation-photocatalysis process (1. Light source, 2. Waste sample solution, 3. Aluminium cathode, 4. Stainless steel anode, 5. Power supply, 6. Hydrogen output line, 7. TiO_2-Fe nanoparticle, 8. Inert gas inpt line, 9. Magnetic stirrer, 10. Hot plate)

RESULTS AND DISCUSSION

XRD studies: The XRD results in Fig. 2 showed the anatase phase in the form of a tetragonal structure. It has a characteristic peak when 2θ = 25.3º, 37.7º, 48º, 54º, 55º, 68.8º, 70.6º and 75º corresponds to the diffraction peak at (101), (103), 004, (211) and (220) planes following the Joint Committee on Powder Diffraction Standards (JCPDS No. 21-1272). The rutile phase was also observed at position 2θ = 27.3º, 36º, 41.2º, 56.8º, and 62.7º in correspondence with the diffraction peaks in the (110), (101), (111), (220), and (002) planes (JCPDS

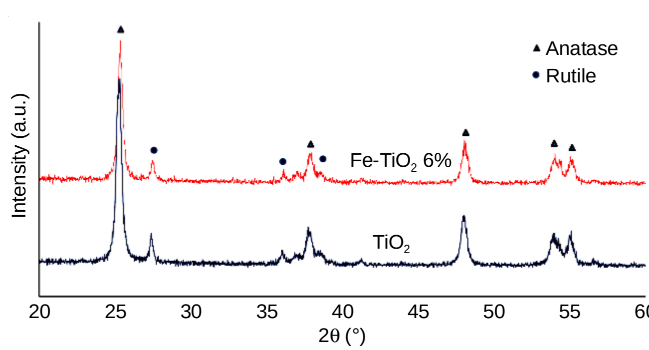

Fig. 2. XRD spectra of TiO_2 and Fe-TiO_2 nanocomposite

No. 21-1272). The characterization result did not find the presence of Fe dopant in the form of an iron oxide structure. The new diffraction peak at 6% Fe-TiO_2 showed that the characterization technique used is not sensitive enough to measure the presence of Fe^{3+}. This can also be attributed to the Fe^{3+} ion successfully substituting Ti^{4+} in the TiO_2 lattice structure.

Table-1 showed that the analysis of crystal size of TiO_2 photocatalyst with Fe dopant has a larger crystal size. Furthermore, the existence of a sintering effect as a result of heat treatment obtained at the nanocomposite annealing stage was also proven.

TABLE-1
CRYSTALLINE SIZE (nm)

Samples	Anatase	Rutile
Bare TiO_2	20	23
6% Fe-TiO_2	23	25

FESEM studies: The presence of Fe on the surface of TiO_2 was proven by FESEM results as shown in Fig. 3. The characterization showed that Fe is relatively distributed on the surface of TiO_2 with concentrations ranging from 0.25 to 0.33% by weight. There is a considerable difference in the amount of Fe used in the synthesis process, 1.5%. Therefore, the synthesis process carried out is not very successful in embedding Fe on the TiO_2 surface. The EDS results also showed the derivation of N and C elements from precursor materials in the nanocomposite synthesis process.

Effect of voltage: Previous studies showed that the electrocoagulation process requires higher applied voltage to produce more coagulant and increase the ability to remove pollutants as well as the amount of hydrogen gas recovered [21-23]. As shown in eqn. 1, the magnitude of the electric current (I) which is correlated with the voltage causes an oxidation-reduction reaction. It is represented by the weight of the resulting oxide (ω) while the reactions of oxidation and reduction at the anode and cathode are described in eqns. 1 and 2, respectively.

$$\omega = \frac{I.t.M_w}{n.F} \quad (1)$$

$$Al(s) \longrightarrow Al^{3+}(aq) + 3e^- \quad (2)$$

$$2H_2O_{(aq)} + 2e^- \longrightarrow 2OH^-_{(aq)} + H_{2\,(g)} \quad (3)$$

$$Al(OH)_{3(s)} + Pollutant \longrightarrow Pollutant\text{-}Al(OH)_{3\,(s)} \quad (4)$$

In this study, electrocoagulation and photocatalysis processes were carried out simultaneously to impact the competitive effect of the reaction on the results obtained. Furthermore, the theory regarding the voltage impact used in the electrocoagulation process was investigated and compared with the previous studies.

The performance of the electrocoagulation process for two voltage values (20 V and 50 V) was observed and used to treat waste samples consisting of a mixture of ciprofloxacin and methylene blue solution of 10 ppm. Fig. 4 showed that there is a better ability to remove dissolved pollutants at 50 V, and according to Faraday's law, the amount of electric current directly proportional to the voltage affects the intensity of the oxidation-reduction reaction on the surface of the electrode.

The oxidation reaction of aluminium plate takes place at the anode according to eqn. 2, which forms Al^{3+} ions, then binds dissolved hydroxyl ions to form $Al(OH)_3$ coagulant (eqn. 4). The greater the voltage, the more coagulant is formed to increase the processability of removing dissolved pollutants. However, in experiments using a combination system of electrocoagulation and photocatalysis as shown in Fig. 5, the opposite results were obtained. The ability of the combined process to remove a mixture of ciprofloxacin and methylene blue as pollutants occurs better under a lower voltage (20 V). Based on the observations, the use of a larger electric voltage produces more coagulant to increase the cloudiness of solution due to the presence of coagulant. It disrupts the photocatalytic process, where the turbidity makes it difficult for the light exposure to be received by the photocatalyst. Therefore, the performance of the process

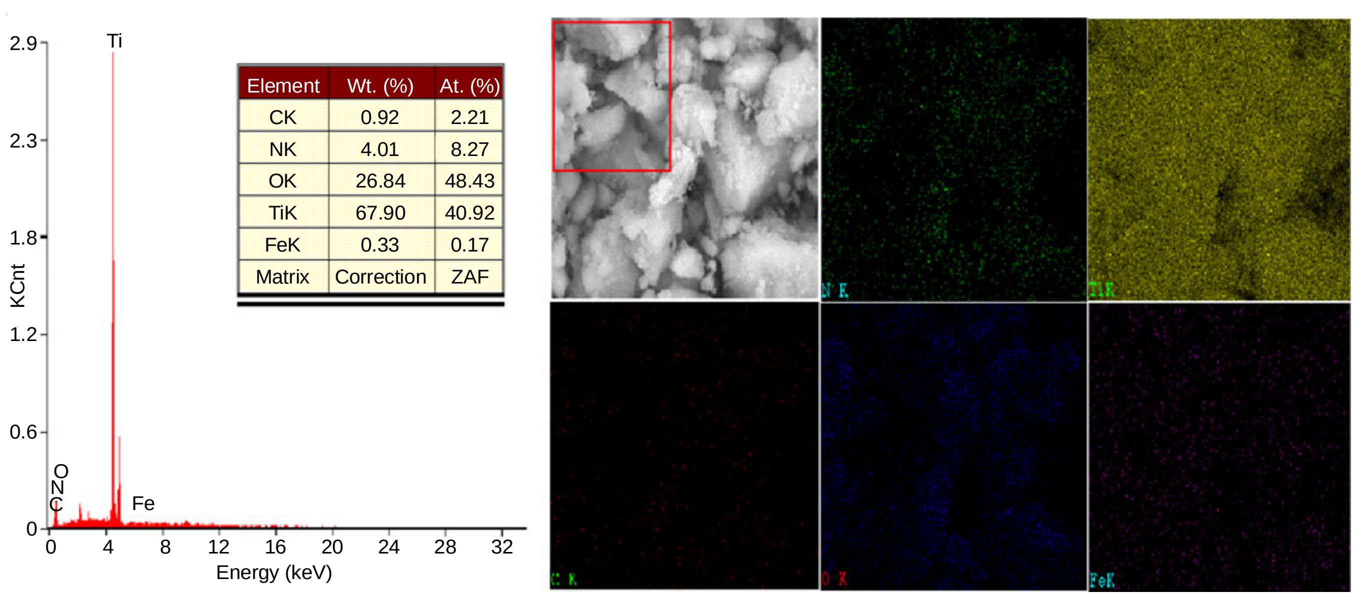

Fig. 3. SEM images, element distribution, and EDX spectra of Fe-TiO_2 nanocomposite

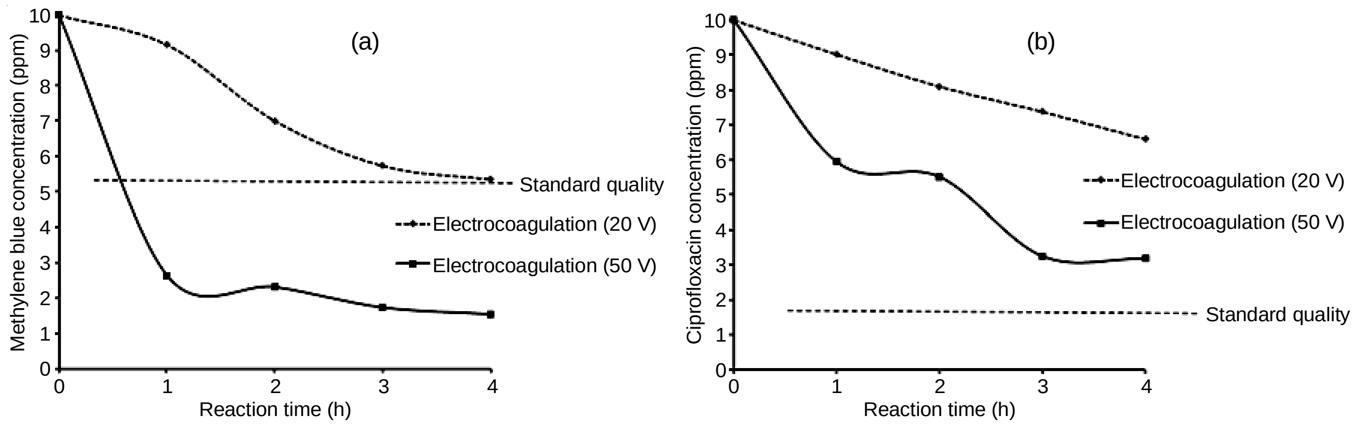

Fig. 4. Effect of electric voltage on the performance of the electrocoagulation process when run individually in its ability to remove (a) MB and (b) CIP pollutants in mixed liquid waste

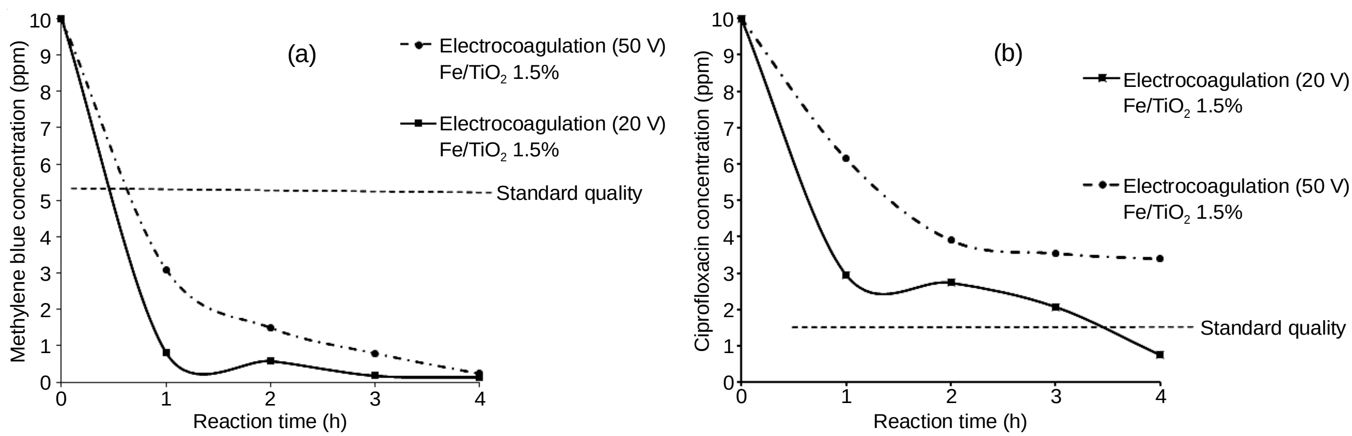

Fig. 5. Performance of combination process (electrocoagulation-photocatalysis) to eliminate (a) methylene blue and (b) ciprofloxacin at a various electric voltage

is significantly reduced and ultimately contributes to reduced overall system performance.

Fig. 6 showed the performance of photocatalysis, electrocoagulation and the simultaneous combination of both. The electrocoagulation process carried out separately can remove ciprofloxacin and methylene blue as pollutants well. However, it cannot reduce the concentration of the two pollutants below the quality standard required by the Ministry of Environment even though it was conducted for 4 h. The ability to remove the dissolved pollutants was excellent by observing the photocatalyst process carried out separately. This is due to the modification of titania nanoparticle using Fe dopant, which results from the characterization that nanocomposite Fe-TiO_2 has a smaller energy bandgap. This condition resulted in a better performance of photocatalysts in degrading pollutants to obtain a good result in the simultaneous process. The operation for 4 h removed the ciprofloxacin and methylene blue to concentrations below the required quality standard. The combination process was conducted using a voltage of 20 V based on the best results of the previous experiment as shown in Fig. 5. The

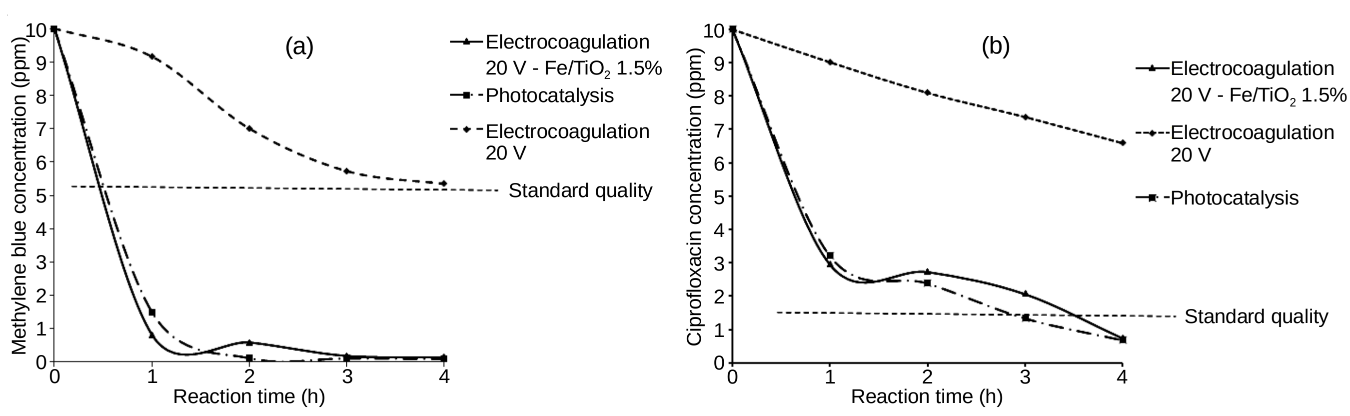

Fig. 6. Comparison of the ability of various processes (electrocoagulation, photocatalysis, and combination electrocoagulation-photocatalysis) to eliminate (a) methylene blue and (b) ciprofloxacin pollutants in mixed liquid wastewater

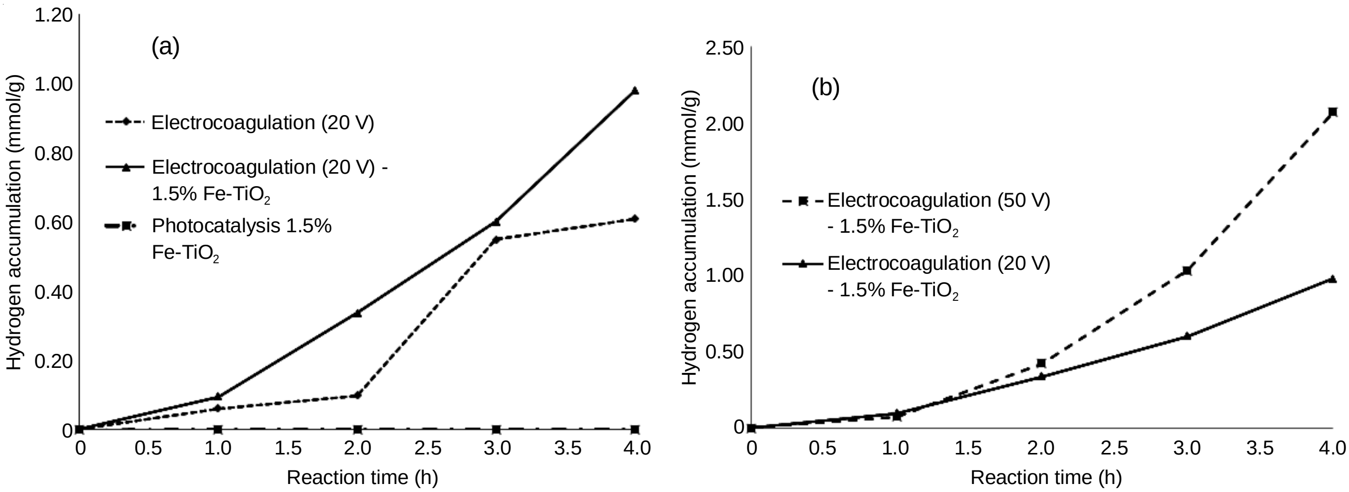

Fig. 7. (a) Hydrogen production from the various process, (b) Effect of voltage to the combination process performance on producing hydrogen

results are not better when the simultaneous process is compared with individual photocatalysts. This is because the turbidity of the solution affects the penetration of photons to the photocatalyst surface, thereby interfering with the process.

Generation of hydrogen gas: In the production of hydrogen gas from the simultaneous electrocoagulation-photocatalysis process, the amount increased compared to when the operation was conducted individually. This is because both processes produce hydrogen gas and the amount from the electrocoagulation is higher than that of photocatalysis (Fig. 7a). Further study is required to improve the performance of photocatalysis in producing hydrogen gas. This is because the ability to degrade waste is much better than electrocoagulation. The development can be conducted by modifying the photocatalyst to have better performance in converting liquid waste into hydrogen gas.

Fig. 7b showed the performance of the electrocoagulation-photocatalysis process in producing hydrogen when two different voltages were used. The voltage is directly proportional to the ability of hydrogen production because the greater the electric current supplied to the process, more electrons will be found on the cathode surface (eqn. 3). Furthermore, the use of 20 V produced 0.98 mmol of hydrogen gas, while at a voltage of 50 V the amount obtained reached 2.07 mmol. The $Fe-TiO_2$ photocatalyst is good in degrading ciprofloxacin and methylene blue as pollutants, and its ability to produce hydrogen is much smaller than the electrocoagulation or the simultaneous electrocoagulation-photocatalysis process.

Conclusion

The simultaneous electrocoagulation-photocatalysis process increases the ability to eliminate ciprofloxacin and methylene blue as toxic wastes. After a 4 h process, the conversion of ciprofloxacin and methylene blue removal was measured at 92.5% and 98.5%, respectively. Meanwhile, the Fe-doped titania nanoparticle photocatalyst can work well in the simultaneous process even though the synthesis has not produced the desired optimal concentration of Fe. The simultaneous process produced 0.98 mmol of hydrogen gas for each litre of the waste sample and it showed an increase of 60.88% compared to when the process was not conducted simultaneously. The production of hydrogen makes it necessary to conduct further study in improving the performance of photocatalysis.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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