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Optimization Electrophotocatalytic Removal of *Streptococcus faecalis* from Water by Taguchi Model

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Application of electrophotocatalytic (EPC) methods for drinking water disinfection was broadly used in the recent years. These methods led to producing of strong oxidant agents such as hydroxyl (OH^-) radical. The goal of this applied-analytical research was to investigate of *Streptococcus faecalis* (*S. faecalis*), as a microbial indicator, removal from urban drinking water by batch EPC reactor with using zinc oxide (ZnO) nanoparticles immobilized on zinc (Zn) sheet-copper electrode, and lamp emitting dynode (LED) ultraviolet-A (UV-A) lamp. The contaminated water sample was prepared by adding 5×10^1-5×10^2 cells of *S. faecalis* bacteria per ml of drinking water. The studied variables were pH (6-8), the number of bacteria (5×10^1-5×10^2 cells / ml), the lamp intensity (120-360 mW cm^{-2}), radiation time (5-30 min), the distance between lamp and electrode (1.5 cm), layering of zinc oxide nanoparticles (1-3), and current density (3-9 mW cm^{-2}). The results showed the correlation between removal of cells and UV-A lamp intensity, current density, and radiation time. Optimal removal (0) was obtained at pH 8, radiation time: 5 minutes, 2- layer of ZnO nanoparticles, and current density of 3 mW cm^{-2}. The findings indicated that removal efficiency was increased with increasing current density, radiation time, and lamp intensity.

Key words: Bacterium; Lamp emitting dynode; Electrophotocatalytic; *Streptococcus faecalis*; Urban drinking water.

The drinking water quality obeyed the strict regulations about microbial and chemical pollutants (Belhacova•*et al*, 1999). *Fecal streptococci* (*FS*) were Gram-positive, catalase-negative, non-spore forming coccid that grew at 35°C in a medium containing bile salts and sodium azide (João, 2010). The ratio of *fecal coliforms* to *FS* had been considerate as a tool for characterizing pollution origin of surface water resources. *FS* were resister than *fecal coliforms* (*FC*). *FS* was a bacterial group that had been applied as an index of fecal pollution in recreational water. *FS* might be more resistance to chlorination process than *FC* and survive longer in water resources, but usually died off quickly outside the host. If found it would indicated recent pollution (Bitton, 2005). *FS* or enterococci were considered as *Streptococcus spp.* effect on host physiology and nutrition, and they possibility acted as direct and indirect agent of illness in human (Riaz, 2005). Occasional opportunistic infections were associated with other genera of streptococci such as *Peptostreptococcus* (p. 340) and *Abiotrophia* ('nutritionally variant streptococci'). The genus *Streptococcus* included important pathogens and commensals of mucosal membranes of the upper respiratory tract and, for some species, the intestines. Chlorination was the most economical process of drinking water chemical disinfection in Iran country. This process produced several varieties of disinfection byproducts such as trihalomethanes (THMs) which were known

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carcinogen for bladder, rectal, and colon cancer (Mishra *et al*, 2014). The alternative methods had been applied for elimination of microbial pollutants, including; ozone, and ultraviolet (UV). The expensive equipment, maintenance and operational costs, and requiring to be supplemented with free chlorine were attributed to these methods (Khaleghi *et al*, 2012). There was need of applying more effective-cost technologies for water disinfection (Lazar *et al*, 2012). Electrophotocatalytic (EPC) water disinfection method had been considered as an eco-friendly and novel technology for all aspects of water treatment such as disinfection. The presence of a catalyst in the electrical field or combined and direct photoelectrochemical application increased the treatment efficiency with lower energy consumption (Ratiu *et al*, 2010). This process was a coupling of electrochemistry with the heterogeneous photocatalytic, so as to avoid of recombination photohole / photoelectron (Sirés, Brillas, 2012). This process was an advanced oxidation processes (AOPs) in water treatment (Comninellis *et al*, 2008). The advantages of thin layer electrophotocatalyst stabilized on metal surface were: not requiring stir for homogeneous mixing, more homogeneous radiation of UV to catalyst, and avoiding of filtration (Georgieva *et al*, 2012). Effective factors on the optimal performance of thin layer electrophotocatalyst stabilized on metal surface were: electrode material, catalyst characteristics such as gap bond, layer thickness, light intensity, oxygen, and water quality such as the presence of particle associated microorganisms (Guy, Yaron, 2011). Recent research had shown that EPC technologies could proposed a good opportunity to remove microbial and chemical pollutants. The application EPC technology by using zinc oxide (ZnO) nanoparticles immobilized on zinc (Zn) sheet-copper electrode, and lamp emitting dynode (LED) ultraviolet-A (UV-A) lamp for the treatment of pathogenic strains of *Pseudomonas aeruginosa* were reported (Kashi, 2015). Different studies had shown bactericidal effects for PEC method using titanium/titanium dioxide-argent (Ti/TiO_2-Ag) photoanode against *Mycobacterium kansasii* and *Mycobacterium avium* (with rate constant of 6.2×10^{-3} and 4.2×10^{-3} min^{-1}, respectively, after 240 mi) (Brugnera *et al*, 2013). In this study the coupling of light emitted dynode (LED) UV-A lamp and immobilized zinc oxide (ZnO) semiconductor on zinc (Zn) electrode had introduced a new method to meeting a more efficient kill of *SF* cells. The aim of this study was the removal *SF*, a Gram-positive bacterium which was considered water borne bacterial pathogen tolerant to antibacterial agents, from drinking water using a thin layer of photocatalytic ZnO nanoparticles stabilized on Zn. The studied variables were pH, the number of bacteria, the lamp intensity, the radiation time, layering of zinc oxide nanoparticles, and current density. As safe drinking water should not contained *FS*, this organism was studied as the model organism and an indicator in this study.

MATERIALS AND METHODS

Materials

The ZnO nanoparticles with special area 50 $m^2 g^{-1}$ and particle size 20 nm were supplied from Amohr Co. (Germany). Azide dextrose broth, PSE agar, brain heart infusion (BHI), nutrient agar, sodium chloride, sodium hydroxide, and nitric acid were purchased from Merck Co. (Germany). Nitric acid and sodium hydroxide (1 N) were applied for pH adjustment.

Preparation of ZnO nanoparticles

5 grams of ZnO nanoparticles were placed into 100 ml of distilled water. The suspension was mixed with a magnetic stirrer for 30 min and then sonicated in an ultrasonic bath (MATR. N.B., Italy) at a frequency 50 kHz for 22 min improved the dispersion of ZnO in distilled water. The weight of zinc electrode was measured after hydroxylation, and washing with distilled water.

Preparation of electrodes

The Zn electrode was used as the substrate for the immobilization of ZnO nanoparticles. The Zinc electrode was pre-treated by detergent and sodium hydroxide solution at 0.01 N to increase the number of OH groups.

Immobilization of ZnO nanoparticles

To prepare the ZnO films, dry methods were used (Malato *et al*, 2013: Zuolian *et al*, 2010). In this study a Zn plate was used for immobilization. After the pre-treatment, the Zn electrode was weighted, immersed in the colloidal solution, and dried in an oven at 35°C for 30 min. The coated particles were then calcined in a muffle furnace at

105 and 320°C for 60 min. The thermal treatment of immobilized ZnO films led to developing good mechanical stability of the films. For 2- and 3-layer coatings, the process were repeated twice and three times. They were washed with distilled water to remove any free ZnO nanoparticles.

Batch EPC reactor

The experimental setup was shown in Fig. 1. The batch reactor was a 360-ml glass vessel (10×6×6 cm). The characteristics of electrodes were as follows: two electrodes of thin layer ZnO nanoparticles immobilized on Zn (anode), and copper electrode (cathode). The area of each electrode was 36 cm^2 (9×4×0.1 cm). The distance between the bottom of the reactor and the electrodes was 1 cm, and the distance between the LED UV-A lamp and the Zn/ZnO electrode was adjusted 1.5 cm. The alternative current (AC) electrical source had an electrical energy production equal to 1-5 A, and a maximum electrical power of 60 W. The LED UV-A lamp had an electrical power of 1 W, radiation intensity of 120 mW cm^{-2}, a wavelength of 395 nm, and a voltage of 3.4 V. To evaluate the effect of the current densities, catalyst, and UV light on the disinfection process, samples underwent LED UV-A lamp treatments (at 360, 480, and 600 mW cm^{-2}), with an electrode of thin layer ZnO nanoparticles immobilized on Zn (at 5%, 10%, and 15%), different current densities (at 3, 6, and 9 mW cm^{-2}), different pHs (at 6, 7, and 8), and different radiation times (at 7.5, 15, and 30 min). A magnetic stirrer was used for homogeneous mixing of the contaminated water samples. The Log bacterial reduction was calculated using the equation below and was converted to percentage cell killed (K. Mwabi *et al*, 2012):

$$\text{Log reduction} = (\text{Log}_{10} \text{ bacterial count}_{\text{before treatment}} - \text{Log}_{10} \text{ bacterial count}_{\text{after treatment}}) \quad ...(1)$$

$$\text{The kill \%} = 100 - \frac{\text{Survivor count}}{\text{Initial count}} \times 100 \quad ...(2)$$

The percentage cell reduction was calculated according to the following equation:

$$R(\%) = (1 - B_t / B_{t0}) \times 100 \quad ...(3)$$

Where R was the percentage of cell kill, B_{t0} and B_t were the average of initial and survival count of live cells per milliliter.

The operational cost required to *FS* removal was calculated to the following Eqn (4):

$$\text{Operational cost} = C_{energyt} + C_{electrod} + C_{UVlamp} \quad ...(4)$$

Where the operational cost ($C_{operational}$, Rial kWh per kg of *FS* removed), the consumed electrical energy cost (C_{energy}, kWh kg^{-1}), consumed electrode cost ($C_{electrode}$, Rial per kg of *FS* removed), and the consumed LED UV-A lamp cost ($C_{UV\text{-}A}$, kWh kg^{-1}) expressed.

The electrical energy required to *FS* removal was calculated to the following Eqn (5):

$$EE\left(\frac{kWh}{kg} FS\ removed\%\right) = \left(\frac{VIt \times 1000_t}{60 \times (C_{to} - C_t)}\right) \quad ...(5)$$

Where the consumed electrical energy cost (EE, kWh per kg *FS* removed), the electrical voltage (V, volt), the electrical current (I, A), and the electrochemical time (t, min) expressed.

Kinetics reaction models were calculated according to the following Equations (6) and (7):

$$\ln Bt = \ln Bt0 - K1t \quad ...(6)$$

$$1/Bt = K2t + 1/Bt0 \quad ...(7)$$

Where K_1 and K_2 were the first, and second order reaction constants, respectively. Values of K_1 and K_2 could be calculated from the slope of the plots ln B_t versus t, and $1/B_t$ versus t, respectively (Ifelebuegu *et al.*, 2013).

Preparation of FS

Suspension of *FS* (ATCC 29212) in water was obtained following the technique proposed by other researchers (Gholami *et al*, 2014). *FS* was reactivated from frozen stock (15% glycerinated azide dextrose broth) in a 100-ml Erlenmeyer flask containing 50 ml of azide dextrose broth (Merck). The sample was incubated at 37°C for 18-24 h. The bacterial cell was isolated at 5000 rpm for 15 min after inoculating strain in azide dextrose broth at 37°C. Strain was stored on trypticase soy agar at 4°C. The strain was grown on BHI agar at 35°C for 24-48 hrs. The optical density (OD) of the cell suspension was measured with a spectrophotometer at 650 nm. The described procedure resulted in suspensions with a cell concentration of 5×10^1 and 5×10^2 CFU/ml. The *FS* was measured by standard method 9230 B (APHA-AWWA-WEF, 2012). In this method, the bacteria could be confirmed by production of brownish-black colonies with brown halos. This method reported the number of microorganisms as most probable number (MPN). After each round of the study, reactor water was picked and cultured on zide dextrose broth tubes, and PSE agar to evaluate the efficiency of the removal process. After incubation at 35°C for 48h, the number of cells was

counted, and the results were expressed as MPN. EPC reactor without microbe, and electrophoto was used as the test control. EPC experiments were at least duplicated and all samples are analyzed in triplicate.

RESULTS AND DISCUSSION

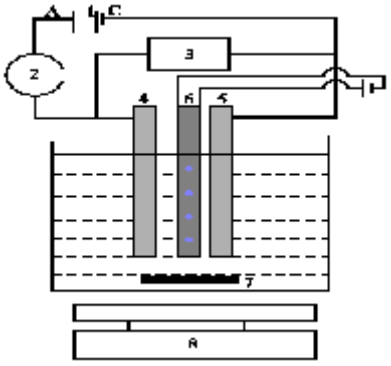

Fig. 1. The batch EPC reactor of thin layer ZnO nanoparticles immobilized on Zn (1. Power supply; 2. Current volume; 3. Voltage volume; 4. Copper electrode; 5. Zinc/Zinc oxide electrode; 6. Light emitted dynode ultraviolet-A lamp; 7. Magnetic stirrer bar; 8. Magnetic stirrer)

Effect of initial number of FS

The effect of the initial number of *FS* on the removal efficiency of the EPC process was shown in figure 2. The removal efficiency was decreased by an increase in the cell number from 5×10^1 to 5×10^2 CFU/ml. The EPC reactor showed the removal percentage for *FS* cells (5×10^1 in ml) increased from 90% to 100% as the pH increased from 6 to 8, with 7.5 min irradiation. The EPC reactor showed the removal percentage for *FS* cells (5×10^2 in ml) increased from 84% to 99% as the pH increased from 6 to 8, with 7.5 min irradiation. This effect was attributed to increasing the number of *FS* cells accordingly fixed the number of photocatalytic sites and UV-A light. This phenomenon was the same as *E. coli* bacterium. They were investigated the effect of photocatalytic disinfection on *E. coli*. These experiments were performed an initial cell concentration in the range of 10^2 to 10^3 cells in ml at pH 7, radiation time 5 minute, distance between the UV-A lamp and Zn/ZnO electrode 2 cm, voltage 10 V, ZnO nanoparticles 5% wt, and LED UV-A lamp power 240 mw cm^{-2}. At higher concentration, the efficiency started to lessen (Rezaee *et al*, 2011). The EPC reactor reached the highest efficiency (100%) at pH 8, radiation time 7.5 minute, and a cell concentration of 5×10^1 and 5×10^2 CFU/ml. Photocatalytic exposure time required for complete cell inactivation (5×10^1 and 5×10^2 in ml) were 7.5 min. At lower concentration, photocatalytic exposure time required for complete cell inactivation started to lessen. The influence of ultrasound (US) dose on *E. coli* inactivation was studied at two different sonolysis time (15 and 30 minutes). The results showed a synergistic effect of US on *E. coli* reduction at 15 minute (Naddeo V *et al*, 2009). Dehgani *et al*. found that the fun-gi population decreased with increasing sonication time (Dehghani *et al*, 2007).

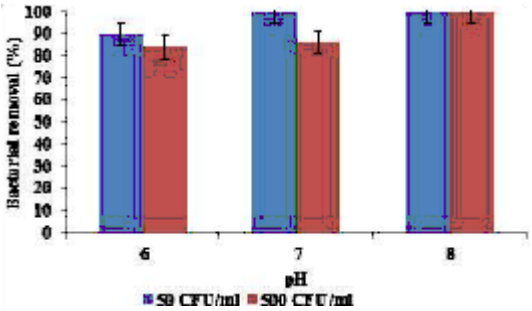

Fig. 2. Effect of the initial number of *FS* and pH on efficiency of bacterial removal (pH 6-8; Temperature 25°C; Radiation time 7.5 min; UV-A lamp intensity 480 mw cm^{-2}; Initial bacterial number 5×10^1-5×10^2; Current density 3 mA cm^{-2}; Zinc oxide concentration 10% wt)

Effect of pH

The pH was a significant operating variable affecting the performance of the EPC process. The bactericidal effect of this method was strongly dependent on pH, and was enhanced by an increase in pH. In the EPC process, different concentrations of OH^- radical from water were formed depending on the pH. These products played an important role in the removal of *FS* cells in the EPC process. This effect was attributed to an increase in the OH^- concentration at a higher pH. This observation was consistent with other previously studies (Mendez-Arriaga *et al*, 2008). Endocrine disrupting chemicals (EDC) bisphenol-A however get increasingly very significant at alkaline pH. The initial and final pH values were

measured in this study in order to investigate the effect of pH more effectively. The initial pH enhanced during EPC studies. The effect of the pH on the removal efficiency of the EPC process was shown in figure 2, and figure 3. The EPC reactor reaches the highed efficiency (100%) at pH 8, radiation time 15 minute, ZnO nanoparticles 10% wt, distance between the LED UV-A lamp and Zn/ZnO electrodes 1.5 cm, LED UV-A lamp intensity 480 mw cm^{-2}, current density 3 mA cm^{-2}, and a cell concentration of 5×10^1 and 5×10^2 CFU/ml. The pH 8 needed lower current density, compared with the two other current densities. It was concluded that optimum pH for reaching to microbial standard (MPN 0) was pH 8. It was expected that positive surface charge of *FS* logarithmic growth phase could affected the solution pH during photocatalytic oxidation. This observation was consistent with the significant of the pH effect for certain organics destruction in a basic pH as reported by Torres *et al*. (Torres *et al*, 2008).

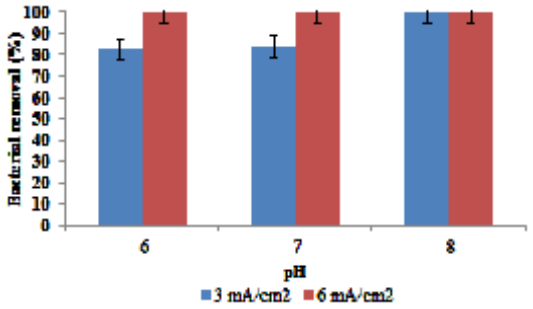

Fig. 3. Effect of the pH on efficiency of bacterial removal (pH 6-8; Temperature 25°C; Radiation time 7.5 min; UV-A lamp intensity 480 mw cm^{-2}; Initial bacterial number 5×10^2; Zinc oxide concentration 10% wt)

Effect of lamp intensity

The effect of the LED UV-A lamp intensity on the removal efficiency of the EPC process was shown in figure 4. The removal percentage for *FS* cells (5×10^2 in ml) increased from 97 % to 100% as the LED UV-A lamp intensity increased from 360 to 480 mw cm^{-2}, with 7.5 min of radiation, and pH 8. The removal efficiency of *FS* was proportional to the LED UV-A lamp intensity and enhanced by an increase in the LED UV-A lamp intensity. This observation was consistent with previously published data. When primary wastewater samples was exposed to UV irradiation, the number of *P. aeruginosa* (ATCC 15442) cells decreased progressively from 10^7 cells in ml to 10^4 as the UV-C lamp dose increased from 0 to 500 mW·s cm^{-2} (Mounaouer, Abdennaceur, 2012). It was also reported that the concentration of 2,4-dichlorophenoxyacetic acid (2,4-D) decreased from 45 to 20 mg L^{-1} as the UV-C lamp dose increased from 150 to 400 W (Kundua *et al*, 2007). At higher lamp intensity, the exposure time, and current density started to lessen. Optimum UV-A lamp intensity for reaching to microbial standard (MPN 0) was 480 mw cm^{-2}. The above increased optical activity was explained by higher formation of reactive oxygen species (ROS), such as electron donor OH^- radical from hydroxide anion of water, and superoxide radical anion ($O_2^{\cdot-}$). The linear increase trend of the degradation rate for *FS* at UV-A lamp intensity was explained by producing more electron / hole pairs due to being available more photons for excitation at the Zn/ZnO surface. This finding was consistent with photocatalytic experiments were performed using a ZnO nanoparticle (Kundua *et al*, 2007).

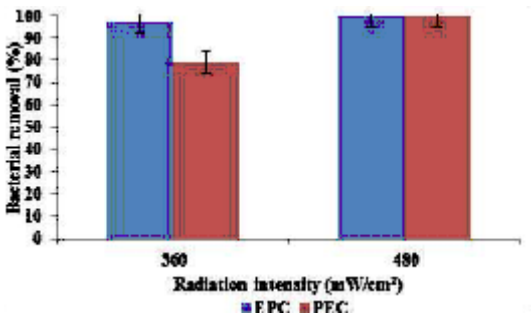

Fig. 4. Effect of the UV radiation and catalyst on efficiency of bacterial removal (pH 8; Temperature 25°C; Radiation time 7.5 min; UV-A lamp intensity 360-480 mw cm^{-2}; Initial bacterial number 5×10^2; current density 3 mA cm^{-2})

Effect of ZnO and LED UV-A lamp

The effect of the ZnO, and LED UV-A lamp intensity on the removal efficiency of the EPC process was shown in figure 5. The removal percentage for *FS* cells (5×10^1, and 5×10^2 in ml) dramatically increased in presence of ZnO photocatalyst nanoparticles and the LED UV-A lamp. At higher lamp intensity along with higher amount of ZnO catalyst up to solution 10% wt, the exposure time, and current density started to lessen. At fixed lamp intensity, it was that an

optimum catalyst amount would present where the photocatalyst would form a maximum concentration of ROS which could take part in reaction at the outer film surface. The optimum amount of ZnO catalyst solution, and optimum intensity of the LED UV-A lamp for reaching to microbial standard (MPN 0) were 10% wt., and 480 mw cm^{-2}, respectively. While the removal efficiency decreased at the 1- and 3-layer Zno nanoparticle films, it reached the highest value (100%) at 2- layer Zno nanoparticle film. This finding was attributed to an increase the surface area for inactivation of *FS* cells (5×10^1, and 5×10^2 in ml). This finding was consistent with photocatalytic experiments were performed using ZnO. They concluded that the decay rate constant of Congo red (CR) was proportional to the ZnO concentration. The decay rate enhanced from 68.73 to 90.02% as ZnO concentration was increased from 0.25 to 0.5 g L^{-1}. However, increase in the ZnO concentration more than 0.5 g L^{-1} led to decreasing the decay rate of CR (Elaziouti *et al*, 2011). However, a limiting value was observed at thick films due to increase in opacity and light scattering leading to a decrease in the passage of irradiation through the film. At higher catalyst loadings (i.e. more than two layer), the removal efficiency of *FS* started to lessen. This phenomenon was attributed to a decrease in UV penetration to the outer layers of the film, and a decrease in protection effect of clusters blocking UV from reach catalyst surface. The presence of ZnO photocatalyst nanoparticles and UV-A was led to increasing the removal efficiency of *FS* due to the generation of OH^- radicals. This finding was consistent with photocatalytic experiments were carried out using

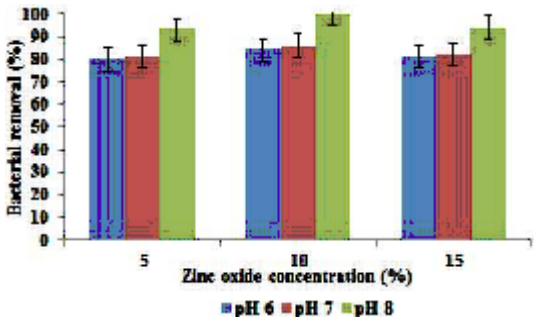

Fig. 5. Effect of the catalyst layer on efficiency of bacterial removal (pH 6-8; Temperature 25°C; Radiation time 7.5 min; UV-A lamp intensity 480 mw cm^{-2}; Initial bacterial number 5×10^2; current density 3 mA cm^{-2})

TiO_2 (Daghrir *et al*, 2012). OH^- radicals led to fat peroxidation of cellular membrane and degradation of the different compounds of the cell. $O_2^{\cdot-}$, hydro peroxyl radical and hydrogen peroxide, generated by the reduction of dissolved oxygen in anode, could also feed into the photocatalytic disinfection mechanism. These species were responsible for decaying the *FS*. The photoelectrocatalytic application by TiO_2 thin film photoanodes for disinfection process in water had been reported (Selcuk, 2010). UV dosage required for 99.9% destruction of *FS* was 8 mJ. cm^{-2}.

Effect of current density

A key variable parameter affecting the oxidation ability of EPC process was the applied current density since it regulated the amounts of generated OH^- radicals acting as oxidizing agents. The effect of the current density on the removal efficiency of the EPC process was shown in figure 6. At lower current density, and lower radiation time, the removal efficiency of *FS* started to lessen. On the other hand, at higher current density, the radiation time started to lessen. The optimum current density for reaching to microbial standard (MPN 0) was 3 mA cm^{-2}. At lower initial cell loadings, the photocatalytic treatment time required for complete cell inactivation started to lessen. The experimental results showed that the current density electrode enhanced the resulting gradient separated electron–hole, thereby diminishing its recombination rate, enhancing the photocurrent rate, and at length expediting the cell inactivation as shown in figure 3. Under higher applied current densities, the external electric field improved the direct and indirect electro-oxidation reactions at anode. The biocidal efficiency was proportional to the specific surface area of photocatalysts and the quantum yield of photocatalytic system because the number of OH^- was proportional to the specific surface area and inversely proportional to the electron-hole recombination rate. The photoelectrocatalytic accelerated the mass transfer by electro-migration of negatively charged bacterium cells towards the electrode. The selection of current densities was depended in the removal efficiency of bacterial, and the consumed electrical energy cost. This finding was the same as photocatalytic experiments were carried out using N-doped Ti/TiO_2 photoanode (Daghrir *et al*, 2012). The experimental results showed that the

more intensity the radiation penetrating the photocatalytic electrode was, the faster the cell inactivation progresses. As expected, for the current density and exposure time was enhanced, accordingly the removal efficiency of *FS* was enhanced as shown in Figure 3. This finding was the same as photocatalytic experiments were carried out using TiO_2 reactor (Mounaouer, Abdennaceur, 2012).

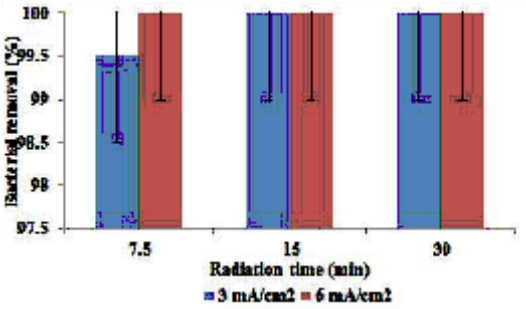

Fig. 6. Effect of the current density on efficiency of bacterial removal (pH 8; Temperature 25°C; Radiation time 7.5-30 min; UV-A lamp intensity 480 mw cm^{-2}; Initial bacterial number 5×10^2; current density 3-6 mA cm^{-2}; Zinc oxide concentration 10% wt)

Mechanism

EPC decay pattern for a Gram-positive bacterium *FS* was distinguished by complex structure of cell wall, peptidoglycan layers, and teichoic acids made of alcohol and phosphate groups. From the viewpoint of the cell wall structure, gram-positive streptococci's cell walls were notably thicker (200 Å) than gram-negative enterobacteria's. The negative charge of teichoic acids of the Gram-positive bacterium *FS* led to its absorption by the Zn/ZnO electrode and could be mineralized and disrupted by strong oxidants such as positive hole, and OH- radical or reduced by electron in the conduction band. The increase in current density, and exposure time led to faster generation of electrolysis products such as OH^- and Cl^- anions in cathode and anode electrodes, respectively. These products were responsible for *FS* inactivation. Increased current density led to an increased drift force on electrode surface, which was the main factor in electrochemical processes. Therefore, it was obvious that the generation adequate quantity of reactive oxygen species for *FS* oxidation needed optimum radiation time (7.5 min). This finding was the same as experiments were performed using N-doped TiO_2 photoanode (Daghrir *et al*, 2014). Clearly, the band gap of the ZnO semiconductor (Eg = 3.2 eV) was meagerly equal to that of UV-A radiation LED lamp (E_{UV-A} =3.4 eV). The photogenerated electron (e^-)-hole (h^+) pairs could be facilely isolated and transferred to the semiconductor/adsorbate interface efficiently, therefore enhancing the photocatalytic activity. This finding was the same as photocatalytic experiments were carried out using UV light (Tomasevic *et al*, 2009). The oxygen produced in anode electrode led to higher bactericidal effect against *FS*, because oxygen molecule played an important role in photocatalysis stage, and transformed to $O_2^{\bullet-}$ radical in capacity bond of ZnO photocatalyst nanoparticles. This finding was the same as photocatalytic experiments were performed using TiO_2 (Pelaez *et al*, 2012). The efficiency of *FS* absorption by Zn electrode layered by ZnO nanoparticles as positive pole (anode) was directly related to an increase in current density, and exposure time. This electrophotocatalytic mechanism was illustrated in the following equations:

$ZnO + h\square(\square = 390\ nm) \dashrightarrow ZnO\ (e^-_{(CB)} + h^+_{(VB)})$ …(4)

$O_2 + H_2O \dashrightarrow O_3 + 2H^+ + 2e^-$ …(5)

$e^-_{(CB)}\ (ZnO) + O_{2ads} \dashrightarrow O_{2ads}^{\bullet-} + ZnO$ …(6)

$O_{2ads}^{\bullet-} + H^+ \dashrightarrow HO_{2ads}^{\bullet-}$ …(7)

$HO_{2ads}^{\bullet-} \dashrightarrow O_2 + H_2O_2$ …(8)

$H_2O_2 + h\square \dashrightarrow 2\ OH^\bullet$ …(9)

$h^+_{(VB)} + OH^- \dashrightarrow OH^\bullet$ …(10)

$\bullet OH + FS \rightarrow$ degradation of the *FS* …(11)

Kinetic studies

The results of *FS* removal efficiency by Taguchi model showed that concentration was the most important variable. This finding was not consistent with experiments were performed using iron electrodes (Chandra Srivastava1 *et al*, 2011). Figure 8 showed the plots of the kinetics first, and second order reaction models fitted with the *FS* removal experimental data in batch EPC reactor. The experimental data fitted better to the first order reaction. The regression coefficient for the fitted line was calculated to be $R^2 = 0.9882$ for *FS*. The apparent rate constant, K_1 and the half-life time, $t_{1/2}$ were calculated to be 0.028 min^{-1} and 0.7 min. This finding was consistent with electrocoagulation experiments were performed using Iron-Steel electrodes. They concluded that the degradation of the CR followed first-order kinetics

(Mohammadlou *et al*, 2014). Thereby, EPC reactor technology could be the basis of a point off use treatment system of water able to enhance water quality by producing high disinfection. According to optimum conditions (electrical current 0.03 A, electrical potential 30 V, reaction time 7.5 min, Zinc oxide concentration 10% wt, UV-A lamp intensity 480 mw cm^{-2}, and water need 40 L/day), it was calculated that the minimum operational cost of the EPC was initial bacterial number 5×10^{1} in mL with removal efficiency 100% (3860 = 370 (consumed electrode cost) + 2175 (consumed electrical energy cost) + 1315 (consumed LED UV-A lamp cost)) and the maximum operational cost of the EPC was initial bacterial number 5×10^{2} in mL with removal efficiency 99,5% (4538 = 1030 (consumed electrode cost) + 2186 (consumed electrical energy cost) + 1322 (consumed LED UV-A lamp cost)). Therefore, at higher efficiency, the operational cost started to lessen.

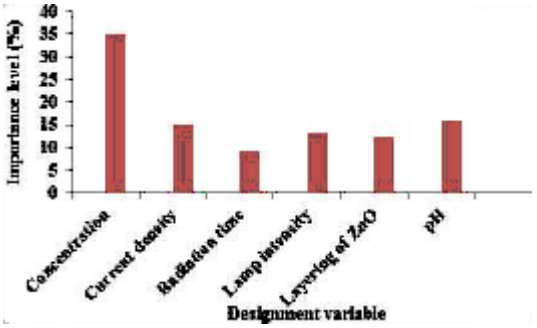

Fig. 7. The Taguchi model

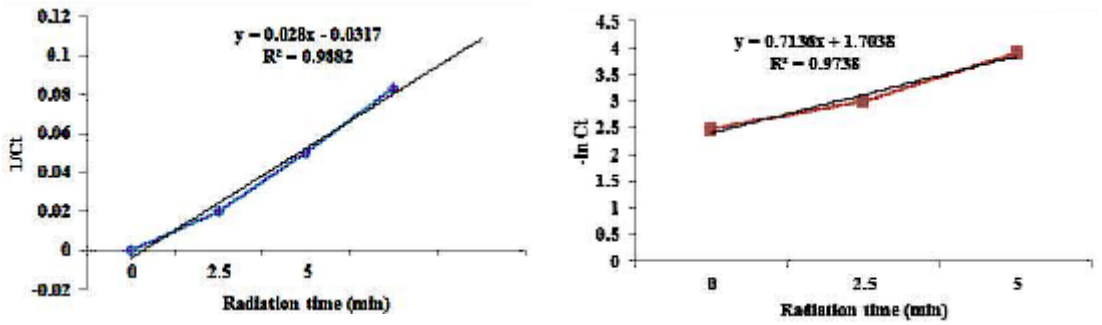

Fig. 8. The plots of first, and second order reaction models fitted with the *FS* removal experimental data in batch EPC reactor (experimental conditions: 25 ºC, pH: 7, reaction time: 0-5 min)

CONCLUSIONS

The experimental results suggested that ZnO thin layer nanoparticles immobilized on Zn photoanode in a batch EPC reactor was a promising method for the *FS* inactivation. The EPC was affected by pH, the number of bacteria, the lamp intensity, radiation time, the number of layers ZnO nanoparticles catalyst, and current density. The following conclusions were obtained from the experiments:

1. High removal efficiency of *FS* was obtained by the EPC reactor (97%) compared to the photoelrctrochemical (PEC) reactor (79%).
2. The EPC treatments were capable of *FS* removal at the pH value (8) investigated, with a radiation time less than 7.5 min.
3. Enhanced *FS* removal was obtained with an increase in the pH, the lamp intensity, radiation time, and current density.

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