Optimization Electrophotocatalytic Removal of Sulfanilamide From Aqueous Water by Taguchi Model

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Abstract: Sulfanilamide was a sulfonamideantibacterial. It was a molecule consisting of the sulfonamide functional group attached to aniline. Sulfanilamide resulted in irritation skin, allergic respiratory, and mutagenic effects. The goal of this applied-analytical research was to investigate of sulfonamide removal from 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. Various operating variables were tested; these included current density, initial concentration of sulfonamide, lamp intensity, layering of ZnO nanoparticles, pH, and radiation time.To prepare the ZnO films on the Zn electrode, dry methods were used. The sample was prepared by adding 100-300 milligrams of sulfonamide per ml of deionized water. The studied variables werepH(3-11), the sulfonamide concentration (100-300 mg/L), the lamp intensity (360-600 mW/cm^2), radiation time (0-45 min), layering of zinc oxide nanoparticles (1-3), and current density (6-12.5 mA/cm^2). The sulfonamide concentration was measured by a high-performance liquid chromatography / mass spectrometry. The optimal removal(0) was obtained at pH 3, radiation time of 15 minutes, 2- layer of ZnO nanoparticles, lamp density 600 mw/cm^2, and current density of 9 mA/cm^2. The sulfonamide decay followed a first order reaction. The results of sulfonamide removal efficiency by Taguchi model indicated that the reaction time was the most important variable. The electrochemical(E) process was the least efficiency. The rate of decay decreased at higher concentrations. Thus, batch experiments showed that the EPC reactor could be considered as a promising technology for treating sulfonamide-polluted water.

Keywords: Aqueous water, Electrophotocatalytic, Sulfonamide, Taguchi model, Zinc oxide

1. Introduction

Sulfanilamide, a prototype of carbonic anhydrase inhibitor, was a sulphonamide antibacterial [1]. Connections of heterocyclic groups such as aniline resulted in increasing antibacterial action [2]. Also, derivatives of azetidinone, thiazolidinone, and oxazoles were reported with antibacterial action [3-4]. As a sulfonamide antibiotic, it functioned by competitively inhibiting enzymatic reactions involving para-aminobenzoic acid (PABA) [5]. PABA was needed in enzymatic reactions that produce folic acid which acted as a coenzyme in the synthesis of purine, pyrimidine and other amino acids. Sulfanilamide resulted in irritation skin, allergic respiratory, and mutagenic effects. Groundwater withdrawals provided approximately more than 52% of public water supplies in Iran country. The antibiotics were in ten entries of recommended drugs in Iran country. Therefore pharmaceutical compounds could be presented in wells of

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groundwater use for public drinking-water supply in Iran country. The increase in sulfanilamide levels in groundwater had been mainly attributed to disposal of domestic and hospital wastes, profligate utilization of animal manure, and runoff and infiltration from cattle farms [6]. Sulfanilamide was not readily biodegradable. Processes such as chemical oxidation methods were effective for transforming sulfanilamide and sulfonamide derivatives from water. However, creating disinfection byproducts (DBP$_S$) during using free chlorine, relatively low rate of reaction, and forming carcinogenic bromate ion during using ozone were some of the disadvantages of the above processes [7-8].Electrophotocatalytic (EPC) method had been considered as a promising and innovative method for water treatment [9]. This process was a combination of external electric filed and the heterogeneous photocatalytic, so as to avoid of recombination hole / electron [10]. This process was an advanced oxidation processes (AOPs) in water treatment [11]. The advantages of thin layer electrophotocatalyst stabilized on metal surface were: not requiring stir for homogeneous mixing, and more homogeneous radiation of UV to catalyst [12]. Effective factors on the optimal performance of thin layer electrophotocatalyst stabilized on metal surface were: catalyst characteristics such as gap bond, improvement of photocatalytic efficiency, layer thickness, light source, light intensity, and water quality such as the presence of particle associated microorganisms [13].Recent research had shown that EPC technologies proposed a good opportunity to remove microbial and chemical pollutants. The application photoelectrolytic fuel cell (PECFC) technology by using tungsten trioxide /visible light for the treatment of organic pollutants (pentachlorophenol (PCP), dichlorophenol (DCP)), and pathogenic strains of *Esherichia coli* were reported [14]. Different studies had shown degradation effects for photocatalytic method using boron-doped diamond (BDD) anode and UVA light against pollutants (complete degradation of *Legionnelapneumophila* after 20 hour) [15]. Degradation of pharmaceutical effluents on carbon based electrodes was reported [16]. 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 degradation of sulfanilamide. The aim of this study was the degradation sulfanilamide, a pollutant which was considered a pollutant tolerant to chemical agents, from drinking water using a thin layer of photocatalyticZnO nanoparticles stabilized on Zn. The studied variables were the current density, the lamp intensity, the layering of zinc oxide nanoparticles, the pH, the radiation time, and the sulfanilamide concentration. This pollutant was studied as the model pollutant in this study.

2. Materials and Methods

Materials

The ZnO nanoparticles with special area 50 m^2/g and particle size 20 nm were supplied from Amohr Co. (Germany). Sulphuric acid, sulfanilamide, and sodium hydroxide were purchased from Merck Co. (Germany). Sulphuric 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 improve 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 [17-18]. 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 f0r 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 250-ml glass vessel (10×5×5 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 thedistance 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 degradation 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 6, 9, and 12.5 mA/cm^2), different pHs (at 3, 7, and 11), and different radiation times (at 15, 30, and 45 min). A magnetic stirrer was used for homogeneous mixing of the contaminated water samples.

Analytical Methods

All tests were performed in triplicate, and the mean data values were reported. The water samples were tested for sulfanilamide, oxidation reduction potential (ORP), pH, and temperature after EPC by using a high-performance liquid chromatography / mass spectrometry (HPLC / MS) (CECIL, America), ORP-meter (CG, Malesia), pH-meter (Hack, America), respectively. The percentage sulfanilamide removal was calculated according to the following equation [19]:

$$R~(\%) = (1 - C_t~/~C_{t0}) \times 100 \tag{1}$$

Where R was the percentage of sulfanilamide removal, C_{t0} and C_t were the average of sulfanilamide concentration milligrams per liter before and after treatment.

Kinetics reaction models were calculated according to the following Equations (2) and (3):

$$\ln Ct = \ln C0 - K1t \tag{2}$$

$$1/Ct = K2t + 1/C0 \tag{3}$$

Where C_0 and C_t were the concentration of sulfanilamide at the beginning and after time (t) of the reaction, respectively. 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 Ct versus t, and 1/Ct versus t, respectively.

Preparation of Water Sample

Sulfanilamide-contaminated water samples used for EPC experiments were obtained from urbane distribution system situated the site of a laboratory in Islamic Azad University Tehran Medical Sciences Branch in Tehran city. The samples were tested for the main physicochemical characteristics. The mean values of these water characteristics were presented in Table 1. The sulfanilamide was measured by HPLC / MS [20]. After each round of the study, reactor water

was picked and analyzed to evaluate the efficiency of the removal process. EPC reactor without sulfanilamide, and electrophoto was used as the test control. EPC experiments were at least duplicated and all samples were analyzed in triplicate.
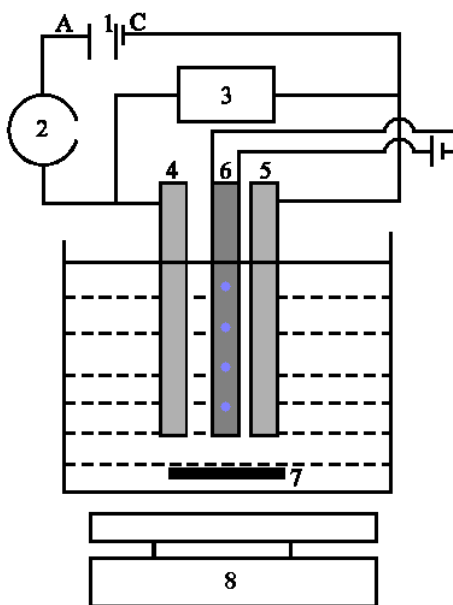
Fig. 1 The batch EPC reactor of thin layer ZnO nanoparticles immobilized on Zn (1.Power supply; 2.Current volume; 3.Voltage volume; 4.Copper electrode; 5. Zinc/Zinc oxide electrode; 6. Light emitted dynode ultraviolet-A lamp; 7. Magnetic stirrer bar; 8. Magnetic stirrer)

Table 1 The main physicochemical characteristics of sulfanilamide-contaminated urbane water

Parameter	Unit	Value
Calcium	mg/L as $CaCO_3$	162
Dissolved oxygen	mg/L	8.05
Nitrate	mg/L	9.5
ORP	mV	279
pH		7.19
Sulphate	mg/L	93.8
Temperature	°C	20
Total Alkalinity	mg/L as $CaCO_3$	122

3. Results and Discussion

The results obtained from this study were shown below. The effects of current density, the sulfanilamideconcentration, the lamp intensity, the layering of zinc oxide nanoparticles, the pH, and the different radiation times on the performance of EPC reactor in sulfanilamideremoval from sulfanilamide-contaminated urbane drinking water were investigated.

Effect of Initial Concentration of Sulfanilamide

The effect of the initial concentration sulfanilamideon the removal efficiency of theEPC process was shown in figure 2. The removal efficiency was decreased by an increase in the concentration from 100 to 300 mg/L. The EPC reactor showed the removal percentage forsulfanilamideconcentration (100 mg/L) decreasedfrom 100% to 80% as the pH increasesdfrom 3 to 11, with 30 min irradiation. The EPC reactor showed the removal percentage forsulfanilamide concentration (300 mg/L) decreasedfrom 80% to 60% as the pH increased from 3 to 11, with 30 min irradiation. This effect was attributed to a decrease in the path length of the photons entering in the EPC reactor and the concentration at a higher sulfanilamideconcentration. Therefore fewer photons reached to catalyst surface and therefore the production of weredecreased. Rate of degradation was decreased. The higher sulfanilamide concentration played an important role in the inhabitation of OH⁻ radicals producing.This phenomenon was the same as azo dyes and phenol. They were investigated the effect of electrochemical degradation on phenol. These experiments were performed an initial phenol concentration in the range of 0 to 300 mg/L at pH 7, reaction time 120 minute, distance between aluminium electrodes 2 cm, current density 19.3 mA/cm^2. At higher concentration, the efficiency started to lessen [21-22]. The EPC reactor reached the highest efficiency (100%) at pH 3, radiation time 15 minute, and aconcentration of 100 mg/L. Photocatalytic exposure time required for complete degradation (100 and 200 mg/L) were 15, and 45 min. This finding was in agreement with previously published data. These photocatalytic experiments were performed an initialC.I Reactive Black R 5 concentration in the range of 30 to 150 mg/L at acidic pH, titanium dioxide (TiO$_2$) 0.1 g/L, irradiation time 120 min, and radiation intensity of 260mW/cm^2[23]. At lower concentration, photocatalytic exposure time required for complete sulfanilamide degradation started to lessen. Degradation ofAzo Dye Acid Red-18 (A.R 18) using Methylene Blue immobilized resin Dowex-11 (MBIRD) photocatalystwas reported. They indicated that MBIRD photocatalyst nanoparticles degraded 40 mg/L A.R 18 in 160 minutes [24].
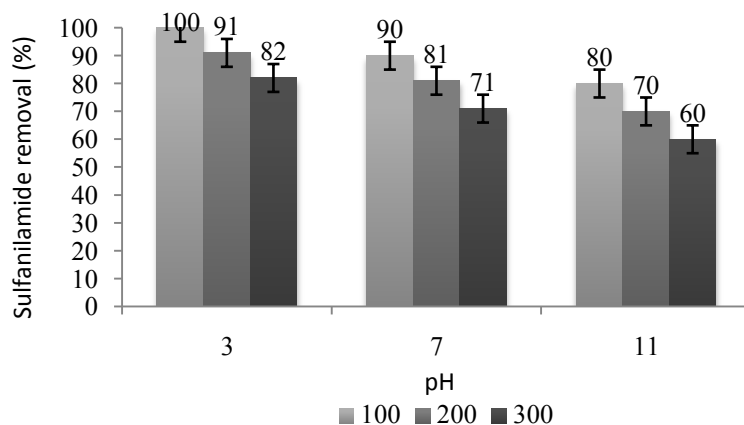

Fig. 2 Effect of the initial concentration of sulfanilamideand pH on efficiency of sulfanilamide removal (pH 3-11; Temperature 25°C; Radiation time 30 min; UV-A lamp intensity 600mW/cm^2; Initial concentration 100-300 mg/L; Current density 6 mA/cm^2; ZnOconcentration 10% wt)

Effect of pH

The pH was a significant operating variable affecting the performance of the EPC process. The degradation effect of this method was strongly dependent on pH, and was enhanced by a decrease in pH. In the EPC process, different

concentrations of OH$^{\cdot}$ radical from water were formed depending on the pH. These products played an important role in the removal of sulfanilamideconcentrations in the EPC process. This effect was attributed to an increase in the availability of OH^{-} anion at anacidic pH that generated more OH$^{\cdot}$ radicals due to decreasing ORP. This observation was consistent with other previously studies [25]. 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 reached the highest efficiency (100%) at pH 3, 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 600 mW/cm^2, current density 6 mA/cm^2, and a sulfanilamideconcentration of 100mg/L. The pH 3 needed lower current density, compared with the two other current densities. It was concluded that optimum pH for reaching to sulfanilamidestandard (0μg/L) was pH 3.The group -SO$_2$.NH$_2$.on the sulfanilamidecould be protonated and deprotonated depending on the pH of the sample.Sulfanilamide ionised with the release of a proton. The anion formed was stabilised by resonance. The pK$_a$ value for sulfanilamidewas 10.4. This finding was the same as photodegradationexperiments were performed using TiO$_2$ [26].
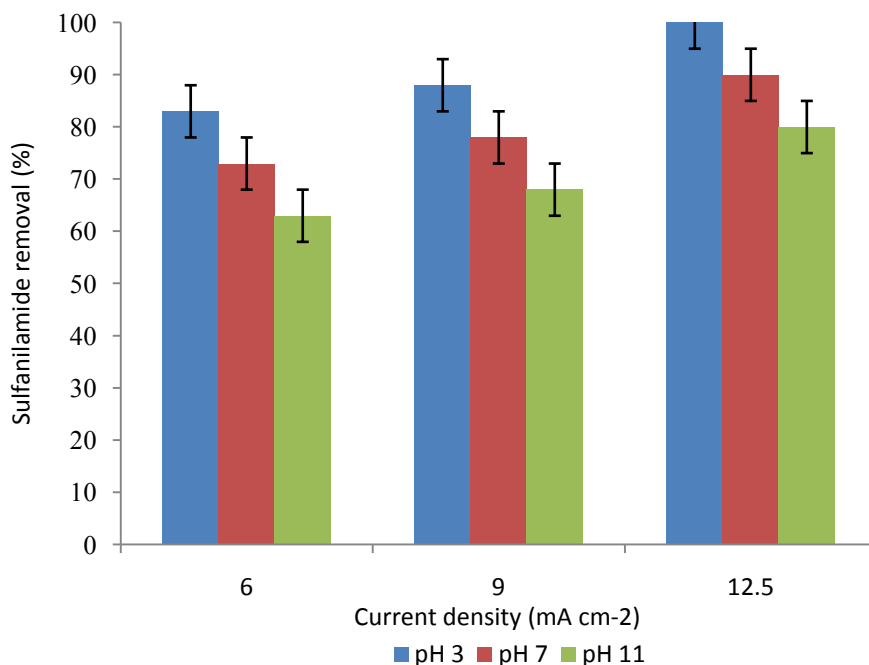

Fig. 3 Effect of the pH on efficiency of formaldehyde removal (pH 3-11; Temperature 25°C; Radiation time 45 min; UV-A lamp intensity 600mW/cm^2; Initial sulfanilamide concentration 300 mg/L; ZnO concentration 10% wt).

Effect of Lamp Intensity

The effect of the LED UV-A lamp intensity on the removal efficiency of the photoreactorprocess was shown in figure 4. The removal percentage for sulfanilamide concentration (300 mg/L) increased from 3% to 7% as the LED UV-A lamp intensity increased from 360 to 600 mW/cm^2, with 45 min of radiation, and pH 3. The removal efficiency of sulfanilamidewas 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 samples was exposed to UV irradiation, the concentration 50 mg/L of2,4-dichlorophenoxyacetic acid (2,4-D) decreased progressively from 49.5

mg/L to 30 mg/L as the UV-C lamp power increased from 100 to 400 W [27]. At higher lamp intensity, the exposure time, and current density started to lessen. Optimum UV-A lamp intensity for reaching to sulfanilamidestandard (10μg/L) was 600 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-}$). This phenomenon was attributed to the efficient separation of photogenerated holes and electrons and reducing their recombination by the application of an external electric bias. Consequently, more holes were available for the degradation of sulfanilamide and its intermediates; the photocatalytic process in the EPC process was more effective than the photoelectrochemical (PEC) process alone. This finding was consistent with photocatalytic experiments were performed using Ti/TiO$_2$ nanoparticle electrodes [28].The removal rate at the same reaction time in EPC process was larger than the sum of that in PEC and electrochemical (EC) process. Therefore, a synergetic effect was proved, which is consistent with the result in Fig. 4.
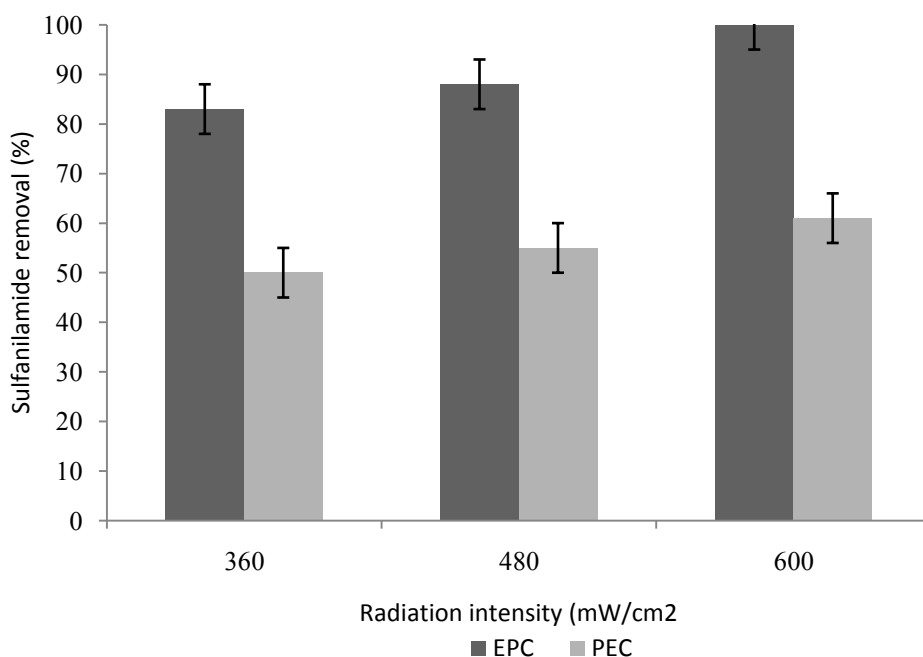

Fig. 4 Effect of the UV radiation and catalyst on efficiency of sulfanilamideremoval (pH 3; Temperature 25°C; Radiation time 45 min; UV-A lamp intensity 360-600mW/cm^2; Initial sulfanilamide concentration 300 mg/L; current density 6 mA/cm^2)

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 sulfanilamide concentrations dramatically increased in presence of ZnOphotocatalyst 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 sulfanilamide standard (0 μg/L) were 10% wt., and 600mW/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

degradation of sulfanilamideconcentrations. This finding was consistent with photocatalytic experiments were performed using TiO_2 thin films. They concluded that the decay rate constants of red sulphonyl 3BL were proportional to the film thickness. The decay rate constants enhanced with increasing film thickness. However, a limiting value was observed at thick films due to an increase in opacity and light scattering leading to a decrease in the passage of irradiation through the film [29]. At higher catalyst loadings (i.e. more than two layers) the removal efficiency ofsulfanilamidestarted 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 ZnOphotocatalyst nanoparticles and UV-A was led to increasing the removal efficiency ofsulfanilamidedue to the generation of OH˙ radicals. This finding was consistent with photocatalytic experiments were carried out using ZnO and UV-A LED for degradation of phenol [30]. OH˙ radicals led to oxidising of sulfanilamide. O_2˙‾, hydro peroxyl radical and hydrogen peroxide, generated by the reduction of dissolved oxygen in anode, could also feed into the photocatalyticdegradation mechanism. These species were responsible for degrading thesulfanilamide. The photocatalyticdegradation of congo red in water had been reported [31].
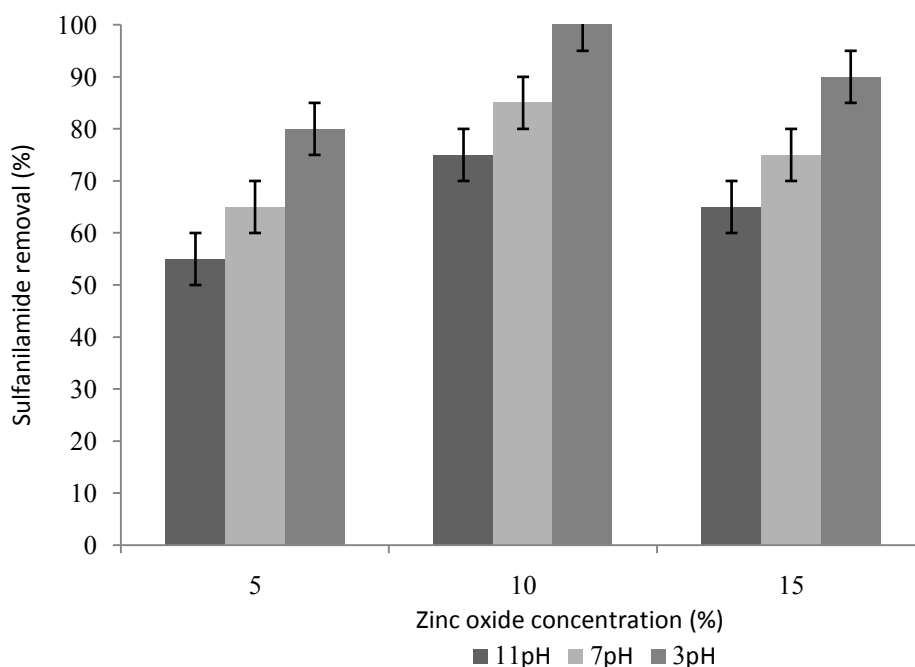

Fig. 5 Effect of the catalyst layer on efficiency of sulfanilamide removal (pH 3-11; Temperature 25°C; Radiation time 30 min; UV-A lamp intensity 600 mW/cm^2; Initial formaldehyde concentration 300 mg/L; current density 12.5 mA/cm^2)

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 sulfanilamidestarted to lessen. On the other hand, at higher current density, the radiation time started to lessen. The optimum current density for reaching to sulfanilamidestandard (0 μg/L)was 12.5 mA/cm^2. At lower initial concentration loadings, the photocatalytic treatment time required for complete degradation 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 degradation 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 degradation 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 sulfanilamidetowards the electrode. This finding was the same as photocatalytic experiments were carried out using graphite-supported TiO_2[32]. The experimental results showed that the more intensity the radiation penetrating the photocatalytic electrode was, the faster the formaldehyde degradation progressed. As expected, for the current density and exposure time was enhanced, accordingly the removal efficiency ofsulfanilamidewas enhanced as shown in Figure 3. This finding was the same as UVA photoelectro-Fenton degradation experiments were carried out using the BDDreactor [33]. The increase in current density, and exposure time led to faster generation of electrolysis products such as OH^- anion in cathode electrode. This product was responsible forsulfanilamide degradation. Increased current density led to an increased drift force on electrode surface, which was the main factor in electrochemical processes. The applied current density controlled the amounts of generated OH˙ radicals acting as oxidizing agents. This finding was the same as experiments were performed using electrode [34]. The oxygen produced in anode electrode led to higher degradation effect againstsulfanilamide, because oxygen molecule played an important role in photocatalysis stage, and transformed toO_2˙¯ radical in capacity bond of ZnOphotocatalyst nanoparticles. This finding was the same as photocatalytic experiments were performed using ZnO [35].
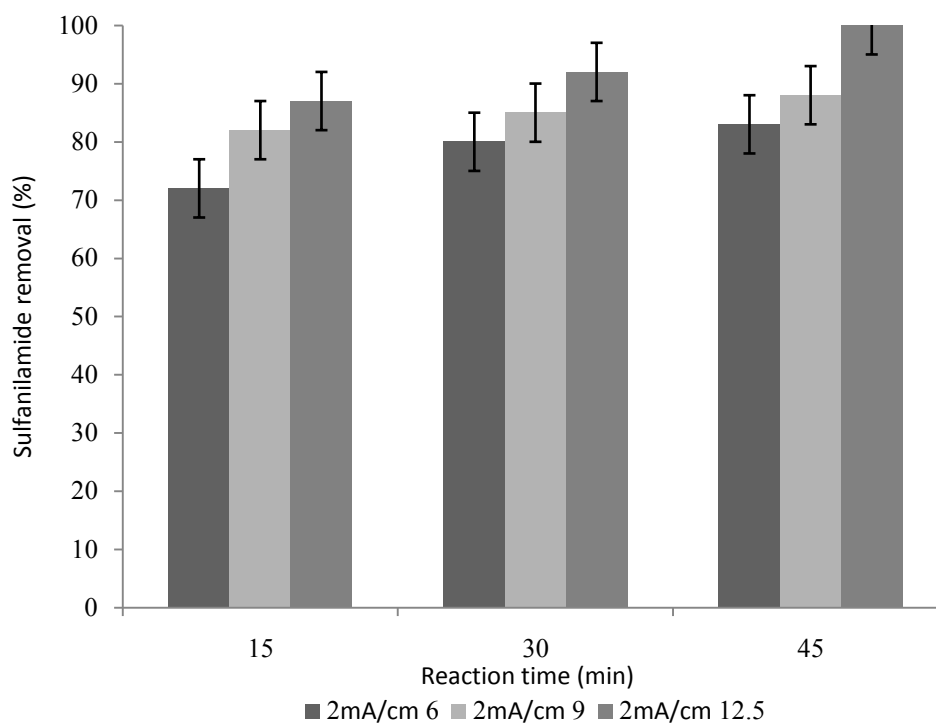

Fig. 6 Effect of the current density on efficiency of sulfanilamide removal (pH 3; Temperature 25°C; Radiation time 15-45 min; UV-A lamp intensity 600 mW/cm^2; Initial sulfanilamide concentration 300 mg/L; current density 6-12.5 mA/cm^2; ZnO concentration 10% wt)

Kinetic Studies

The results of sulfanilamideremoval efficiency by Taguchi model showed that reaction time is the most important variable. This finding was not consistent with experiments were performed using iron electrodes [36]. Sulfanilamide could be oxidized by $OH^{\cdot}$ radical. This electrophotocatalytic mechanism was illustrated in the following equations:

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

$$O_2 + H_2O \dashrightarrow O_3 + 2H^+ + 2e^- \tag{5}$$

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

$$O_{2ads}^{\cdot -} + H^{+} \dashrightarrow HO_{2ads}^{\cdot -} \tag{7}$$

$$HO_{2ads}^{\cdot -} \dashrightarrow O_2 + H_2O_2 \tag{8}$$

$$H_2O_2 + h\nu \dashrightarrow 2\ OH^{\cdot} \tag{9}$$

$$h^{+}_{(VB)} + OH^{-} \dashrightarrow OH^{\cdot} \tag{10}$$

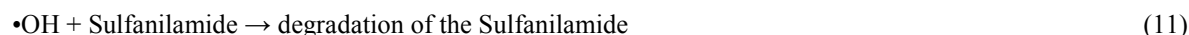$$\bullet OH + Sulfanilamide \rightarrow degradation\ of\ the\ Sulfanilamide \tag{11}$$

Figure 7 showedthe plots of the kinetics first, and second order reaction models fitted with the sulfanilamide removal experimental data in batch EPCreactor. The experimental data fitted better to the first order reaction. This finding was consistent with photochemical experiments were performed using UV lamp. They concluded that the degradation of the herbicide 2,4-D under UV light follows first-order kinetics [27].
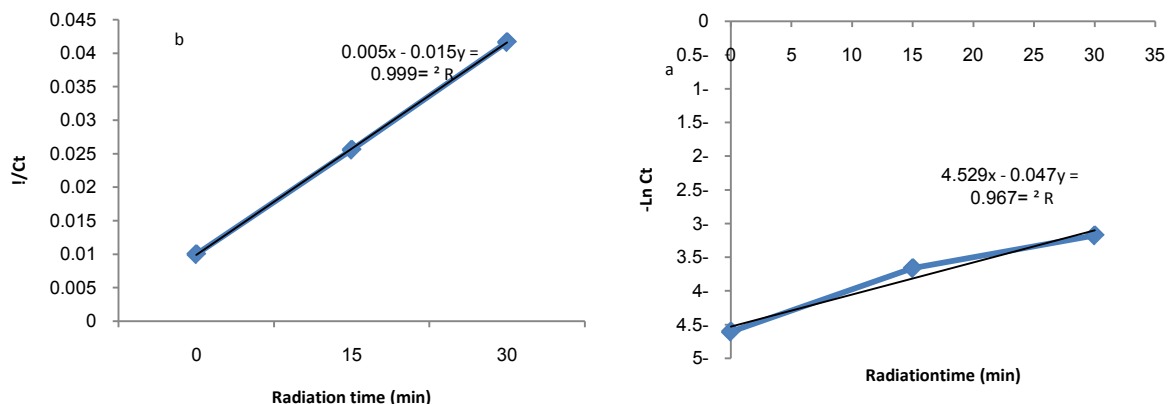

Fig. 7 The plots of first, and second order reaction models fitted with the sulfanilamideremoval experimental data in batch EPCreactor (experimental conditions: 25 ºC, pH: 3, reaction time: 0-15 min)
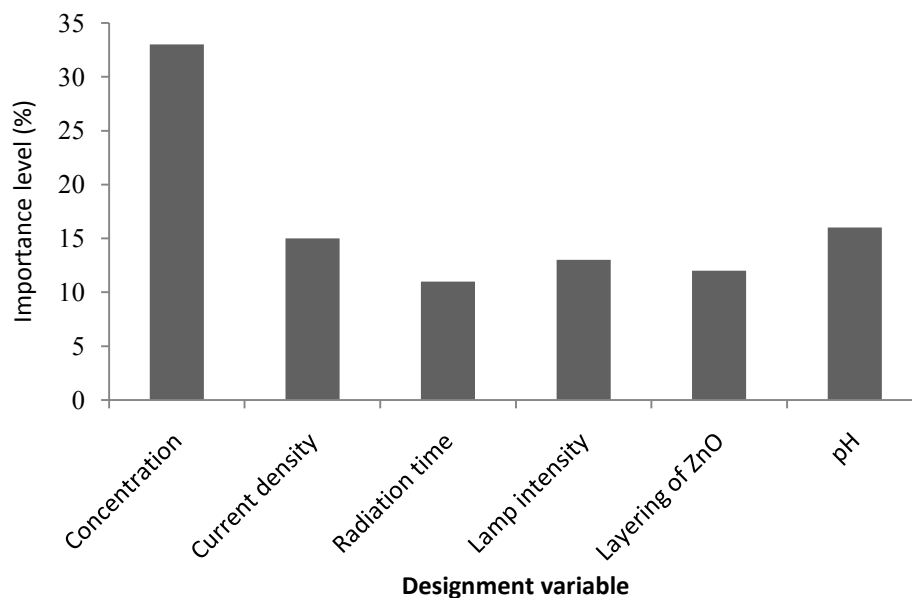
Fig. 8 The Taguchi model

4. Conclusion

The experimental results suggested that ZnO thin layer nanoparticles immobilized on Zn in an EPC process was a promising method for the sulfanilamidedegradation was affected by pH, the concentration of sulfanilamide, the lamp intensity, radiation time, the number of layers ZnO nanoparticles catalyst, and current density. The EPC treatments were capable ofsulfanilamideremoval at the pH value (3) investigated, with a radiation time less than 45 min. Enhancedsulfanilamideremoval was obtained with an increase in the lamp intensity, radiation time, and current density.

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