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Photoelectro-Fenton/photocatalytic process for decolorization of an organic compound by Ag:Cd-1,4-BDOAH₂ nano-photocatalyst: Response surface modeling and central composite design optimization

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Abstract

In the present research, the synthesis of the cadmium-benzene-1,4-dioxyacetic acid (Cd-1,4-BDOAH₂) was carried out by the assistance of ultrasound waves, and then it was loaded with the low amount of Ag nano-particles. Subsequently, the Ag:Cd-1,4-BDOAH₂ nano-photocatalyst was applied for photoelectro-Fenton/photocatalytic (PEF-PH) degradation of brilliant green (BG) in the existence of visible light in aqueous media. The synthesized composite was characterized by FTIR, SEM, EDX, TEM, XRD, DRS, and PL. The best operational conditions including time, initial BG concentration, pr1 amount of photocatalyst, current and amount of FeCl₃ on degradation efficienc () that and interactive) were as follows: 4 mg L⁻¹ of BG at pH of 5, 0.4 g L⁻¹ of Ag:Cd-1,-, BDOAH₂, 250 mA of current, and 0.3 mmol L⁻¹ of FeCl₃ obtained by central composite design. The PEF-PH degradation kinetic data of BG were successfully fitted to Langm in ¹⁴ inshelwood (L–H) model with the values of 1.16 mg L⁻¹ min⁻¹ and 0.018 Lmg⁻¹ f., the rate constant (k_r) and (K_A), respectively.

Keywords: Photoelectro-Fentor/ol.~'ocatalytic, Decolorization, Ag:Cd-1,4-BDOAH₂, Response surface methodology, Light-emitting diode irradiation.

1. Introduction

From past decades, organic pollutants such as dyes have caused a series of global environmental problems, while various industries have an ever-greater role in contaminating wastewaters [1-4]. In particular, the release of textile wastewater into the environment causes serious threat to human health; consequently, synthetic dyes removal from colored effluent is essential [5, 6]. Among all technologies for colored effluents treatment, advanced oxidation processes (AOPs) are reported as effective technologies to remove toxic species and improve water quality of industrial effluents [7-10]. The most popular Fenton's chemistry method is

based on treatment by advanced oxidation processes, and accordingly, Fenton reagents (Fe²⁺ and H₂O₂) have more ability to degrade organic pollutants based on the formation of hydroxyl radicals ('OH) [11]. The main properties of carbon based cathodes such as low toxicity, stability, and good conductivity caused them to be applied in the E-Fenton process [12-14] for the degradation of organic materials from aqueous solutions [15-18]. Photoelectro-Fenton (PEF) is based on simultaneous irradiation of solution with visible or ultra-violet (UV) light under PEF conditions, while accordingly light lead to acceleration in the photolysis of the complexes of Fe³⁺ and enhancement in the 'O'H and Fe²⁺ ions as product [19, 20]. The combination of PEF and heterogeneous protocatalysts is the integrated approach for efficient AOPs treatment.

In the past few years, the most popular photocatalysts are based on inorganic semiconductors such as TiO₂ and ZnO, which are w unique advantages. Nevertheless, their high and wide band gaps cause low efficiency, especially in the presence of visible light. These kinds of photocatalysts are also expensive and consume high energy sources, accordingly their usage are limited [2.1] Designing and synthesizing such photocatalysts have increased attentions in term of green heterogeneous catalysts. The combination of metal ions and the organic ligands leads to different ligand-to-metal charge-transfer (LMCT) transitions. This phenomenon plays a rundamental role in generating and manipulating band gaps that influences on photocatalytic degradation efficiency [22, 23]. Due to these reasons, metal organic photocatalysts have various functions, properties, and applications in electronics, optics, magnetism, sensors, catalysis, etc. [24, 25]. For instance, Cd-based metal organic materials are very promising candidates for photocatalytic application in terms of their relatively narrow band gaps, exposure of high-density active sites, large pore size, facile loading of highly dispersed heteroatoms, and high stability [26, 27].

The heterogeneous photocatalyst particle needs the necessary amount of light for activation under low operating costs and environmentally sustainable conditions, accordingly the light-emitting diode (LED) lamps are extremely better than UV lamps [28, 29]. As promising technology, photocatalysis has been widely studied for decomposition of very toxic contaminants; therefore, efficient visible-light photocatalysts have been synthesized via strategies such as doping and coupling with other semiconductors [30]. It is well known that Ag nano-particles have high conductivity properties, which quickly and effectively transfer photo-generated electron to inhibit recombination of electron belle pairs and improve the photocatalytic activity [31, 32]. The combination between inorganic and organic building blocks leads to the synthesis of metal organic materials with widely different compositions, morphologies, and sizes. An effective path to design and synthesis such materials is based on the application of metal-based ions/clusters with multidentate ligands (pre-designed or in situ generated) that contain N- or O-dono atoms. Usually, binding benzene multicarboxylate ligands with metal centers forms appropriate materials [33].

In the present work, the Ag Cd-1,4-BDOAH₂ as a new nano-photpcatalyst was synthesized under green conditions, and its usage with blue LED irradiation for BG degradation was studied in docails. The central composite design (CCD) was utilized for optimizing and estimating the main variables that are efficient and interaction effects of the main variables (time, BG dye concentration, photocatalyst dosage, pH, current, and FeCl₃ dosage) in a batch mode. Additionally, the PEF-PH kinetic data of BG degradation in LED light/Ag:Cd-1,4-BDOAH₂ instrument were tested with L–H kinetic model.

2. Experimental

2.1. Materials and instruments

In this study, all chemicals and reagents such as hydroquinone, hydrochloric acid (37%), Iron (III) chloride, sodium sulfate anhydrous (99.0%), sodium hydroxide (97.0%), and BG (**Table 1**) were obtained from Merck. Cadmium nitrate dehydrate (Cd (NO₃)₂.2H₂O) was from Sigma-Aldrich. Dae-Jung chemicals and metals Co., LTD provided chloroacetic acid. The analytical grade of the reagents was used without further purification.

UV–Vis spectrophotometer model V-530, Jasco, Japan, was utilized for determining UV spectrum of BG. pH/Redox/Temperature meter model AL20 r^{4} (AQUALYTIC, Germany) was applied for measuring pH. For recording XRD pattern. Bruker AXS (D8, Advance) instrument was applied by the employment of Cu_{Kc} (1.34 Å) as the source of X-ray. The recordance of the FTIR spectra of the 1,4-BDO/H₂, Cd-1,4-BDOAH₂, and Ag:Cd-1,4-BDOAH₂ was carried out using a spectromet r r_{1} Crkin Elmer RX-IFTIR) over the range of 4000-500 cm⁻¹. The determination of the r_{1} range sizes of the of Cd-1,4-BDOAH₂ and Ag:Cd-1,4-BDOAH₂ and their morphologies were investigated by FESEM (ZEISS, model Sigma, Germany). Philips CM-10 TEM working at 100 kV was applied to further investigate the morphology and microstructure of the synthesized materials. The PL spectra of the samples were obtained by a Perkin r_{1} have.

<Table.1>

2.2. Photocatalyst synthesis

2.2.1. Synthesis of the 1,4-BDOAH₂ by ultrasound-assisted method

A mixture was prepared by 7.1 g of chloroacetic acid and 2.75 g of hydroquinone, and then NaOH (48 g in 97.5 mL water) was added dropwise to the prepared mixture and heated in an oil bath at the temperature of 80 °C. After 1.5 h sonication of the obtained mixture at this temperature, its temperature was decreased to 25 $^{\circ}$ C, and it was kept in an ice bath for 30 min.

To this mixture, hydrochloric acid was added dropwise until reaching neutral pH, and subsequently, the temperature of the flask was naturally increased to room temperature. The final white precipitates were filtered, washed with deionized water several times and finally recrystallized. Subsequently, it was identified by ¹HNMR and ¹³C NMR as follow: ¹H NMR (D₂O, 250 MHz): $\delta = 4.34$ (s, 4H), 6.81 (s, 4H). ¹³C NMR (D₂O, 62.9 MHz): $\delta = 67.24$, 115.42, 152.12, 147.7, 177.02.

2.2.2. Cd-1,4-BDOAH₂ synthesis by ultrasound-assisted method

Under sonication condition, 0.4 mmol of 1,4-BDOAH₂ was dispersed in 50 mL of distillated water, and then it was added to 50 mL of cadmium nitrate dehydrate solution (24 mmol). The mixture was sonicated at 25 °C for 30 min that led to the formation of white precipitates. The final product was filtered and washed with dei nitrate details water.

2.2.3. Ag:Cd-1,4-BDOAH₂ synthesis by ultrasound assisted method

The cadmium salt solution was $\operatorname{add} \operatorname{d}$ to 1,4-phenylenedioxy diacetic acid solution while sonicated at 25 °C for 10 min. Afterwards, the solution was thoroughly mixed with Ag(NO₃) (0.025 g). The sonication of the mixture was carried out for 10 min, which causes the reaction and mixing to be don, completely. Subsequently, the suspension was transferred to an autoclave at 100 °C for 24 h. After filtration of the obtained material, it was washed with deionized water several times and finally dried in an oven at 60 °C.

2.3. Setup of experiment

General schematic of the experimental setup shown in **Fig. 1** was used for BG degradation in aqueous solution. As can be seen in the schematic, it includes power supply, graphite cylindrical cathode (with 20 cm length and 9 mm diameter), platinum wire anode (76×1 mm

dimensions), LED (light strip flexible SMD 5050 RGB, 14.4 W/m²), sparger (diffuser), power source, and oxygen cylinder. The anode and cathode electrodes were plunged in the aqueous solution. The constant electric current between a platinum anode and graphite cathode is produced using a DC power supply for the electrochemical process. Around the outer cylindrical pipe, a flexible RGB LED light strip is wrapped. The LED lamp is located in a glass tube and put in the central of Pyrex (Simax, Czech) cylindrical photo reactor with the volume of 3 L. A box covering with aluminum foil for the avoidance of light dispersion is used to seal all parts of the system. In the present operation, the Texible RGB LED strip is used to provide a blue light, and the spectral distribution of the light with the wavelength of irradiation in the range of 465–470 nm. The working volume of the photo reactor is 1 L solution consisting photocatalyst. To supply oxygen derivand and solution mixing, an oxygen diffuser is used.

<'.'ig.1 >

2.4. Experimental procedure

The PEF-PH process for BG degredation was conducted in a batch reactor at the temperature of 25 °C. Before each experiment run, the reactor glass and the tube glass of LED lamp were filled with deionized water. According to CCD, specific amounts of FeCl₃ and BG were added to the aqueous setup containing 0.05 M Na₂SO₄ as the supporting electrolyte and well mixed for carrying out each experiment run. The solution pH in the range of 3.0-11 was adjusted by adding HCl and/or NaOH, and it was transferred to the photo reactor equipped with the lamp of LED with glass tube at its middle while the distribution of oxygen in aqueous media was at a certain flow rate. After putting the solution of the reactor in a dark condition for 20 min for the complete establishment of adsorption and desorption equilibrium of BG dye over the surface area of the photocatalyst, the DC power supply, oxygen distribution and LED irradiation were switched. At a specific time in each experiment run,

the sample was brought out, and then centrifugation was done at 2000 rpm for 2 min for the separation of the photocatalyst particles. Analyzing the sample was performed using a UV-Vis spectrophotometer for determining the PEF-PH degradation of BG. The calculation of degradation efficiency (R%) was done by Eq. 1 as following [34, 35]:

$$R\%_{BG} = \frac{\left(C_0 - C_t\right)}{C_0} \times 100 \tag{1}$$

Where $C_0 \pmod{L^{-1}}$ is the concentration of target at initial under and $C_t \pmod{L^{-1}}$ is the concentration of target at time t. The typical changes in the absorption spectra of UV–Vis during the degradation by PEF-PH is shown in **Fig. 2**

<Fi7,.` >

2.5. Response surface methodology

For the evaluation of experimental model and recognition of the main factors that are effective on the process and their interactions with the least number of experimental runs, and also the optimization of multiple variables by a suitable model, response surface methodology (RSM) and experiments, response surface modeling by regression, and optimization. It is used to evaluate the coefficients in a second order (quadratic) mathematical model [38, 39]. In the present work, CCD was applied for modeling the understudy PEF-PH degradation process (**Table 2**). The effective factors including time (X₁), BG concentration (X₂), pH (X₃), photocatalyst dosage (X₄), current (X₅) and amount of FeCl₃ (X₆) were designed by STATISTICA (version. 10.0) (**Table 2**). Based on the method of small CCD experiments, 33 individual experimental runs were proposed, and a quadratic polynomial equation was

applied for the approximation of the mathematical relationship between the independent parameters as follows [40]:

$$R\% = \beta_0 + \sum_{i=1}^6 \beta_i X_i + \sum_{i=1}^6 \sum_{j=1}^6 \beta_{ij} X_i X_j + \sum_{i=1}^6 \beta_{ii} X_i^2 + \varepsilon$$
(2)

Where R% is the response predicted by the model (degradation efficiency of BG), and the X_i and X_j are known independent variables for each experiment 1 run. β_0 parameter is the constant of the model, and β_i , β_{ii} , and β_{ij} are respective γ_j the linear coefficient, quadratic coefficient, and the coefficient of cross-product [41]. The fitted model quality can be evaluated by analysis of variance (ANOVA) that is miable. The determination of model significance is based on the values of P-value and F-value obtained by ANOVA, while the best optimum levels for each factor, to attain maximum degradation efficiency are determined by desirability function (DF) with value between 0.0 and 1.0 (low and high desirability, respectively) [42].

<Table.2>

3. Result and discussion

3.1. Photocatalyst ch. "a. "crization

The FTIR spectrum in **Fig. 3** for 1,4-BDOAH₂, Cd-1,4-BDOAH₂, and Ag:Cd-1,4-BDOAH₂ recorded from 4000 to 500 cm⁻¹ indicates a large broad band in the range of 2000-3400 cm⁻¹, attributing to the acidic O-H group stretching vibrations. The band at 1604 cm⁻¹ assigns to the groups of carboxylate (C=O), and the observed band at 1220 cm⁻¹ relates to the C-O stretching vibrations. In addition, the bands shown at 1058 cm⁻¹ is related to the symmetric and asymmetric stretching vibrations of O-C=O and the stretching vibration of C-O, as well. The bending of aromatic C-H is observed at 684 and 813 cm⁻¹ [43]. A large shift in the FTIR spectra of the Cd-1,4-BDOAH₂ and Ag:Cd-1,4-BDOAH₂ is assigned to the O-H, C=O and

O-C=O groups transmittance as compared with the free ligand, showing the interaction possibility of Cd^{2+} ion with the OH group of free ligand. The peak observed at 1600 cm⁻¹ for the benzene ring skeleton stretching of 1,4-BDOAH₂ can be seen at the same wavenumber for the Cd-1,4-BDOAH₂ and Ag:Cd-1,4-BDOAH₂, proving the successful synthesis of the materials.

<Fig.3>

The analysis of the surface morphology for the Cd-1,4-BDOAH₂ and Ag:Cd-1,4-BDOAH₂ was examined using SEM in **Figs. 4 (a-c)** and (**d-f**), respectively. As it is observed, the Cd-1,4-BDOAH₂ is a nano-powder with the typical needle shope of the particles.

<Fig.4>

The EDX spectrum (**Fig. 5a**) clearly shows the existence of O, C, and Cd in the sample, and the changes observed in the chemical composition. of the sample (**Fig. 5b**) containing Ag clearly shows the incorporation of Ag in Λg Cd-1,4-BDOAH₂. The A% of the elements in the obtained samples is in good agreement with the compositions, indicating the favorable synthesis of understudy materials

<Fig.5>

The Cd-1,4-BDOAH₂ and A_{E} Cd-1,4-BDOAH₂ in terms of shape and size are respectively shown in **Fig. 6 (a)** and **(b)**. The approximate size of the Cd-1,4-BDOAH₂ particles is about 100 nm and Ag nano-particles in the Ag:Cd-1,4-BDOAH₂ are in the range of 30-80 nm (**Fig. 6b**). The TEM results are in agreement with those of SEM.

<Fig.6>

The XRD patterns of the samples were applied to determine their crystalline structures. **Fig. 7** (a) reveals the absence of CdO and CdO₂. The XRD peaks prove that the Cd-1,4-BDOAH₂ is successfully synthesized [44, 45]. Comparing the XRD patterns of the Cd-1,4-BDOAH₂ and

Ag:Cd-1,4-BDOAH₂ indicates no extra peaks corresponding to secondary phases, while the absence of silver and silver oxide peaks in the synthesized photocatalysts is probably due to the low amount of the loaded Ag [46]. According to the XRD, the average particle size is 80 nm using Debye-Scherrer equation.

<Fig.7>

In general, photocatalytic efficiency can be seriously influenced by rapid recombination rate of the photo-generated charge carriers. The direct measurement of the electron-hole recombination rate is done by photoluminescence (PL) intentity and accordingly increasing in intensity of spectrum denotes faster recombination The samples were investigated by PL spectra and the results in **Fig. 8** for the Cd-1,4-BDCAre and Ag:Cd-1,4-BDOAH₂ (using an excitation wavelength of 360 nm) denote a lower intensity of fluorescence emission for the Ag:Cd-1,4-BDOAH₂, implying a lower rate of electron-hole recombination and higher photocatalytic activity in comparison with the Cd-1,4-BDOAH₂.

<Fig.8>

3.2. Comparison of photocalclytic activity of the Cd-1,4-BDOAH₂ and Ag:Cd-1,4 BDOAH₂

The degradation efficiency of BG using the Cd-1,4-BDOAH₂ and Ag:Cd-1,4 BDOAH₂ (**Fig. 9**) reveals higher degradation efficiency using the Ag:Cd-1,4 BDOAH₂ in comparison with the Cd-1,4-BDOAH₂, which prove that the incorporation of Ag leads to enhance in the PEF-PH activity.

<Fig.9>

3.3. Analysis of central composite design

ANOVA analysis for CCD is applied to find the best operational conditions and construct mathematical equation, which are applicable to correlate signal to effective terms. The error functions were applied to fit the model to empirical data for calculating the significance of each term based on the comparison of the calculated F-value and P-value [47, 48]. The results represented in **Table 3** for BG degradation by the Ag:Cd-1,4-BDOAH₂ reveals the F-value of 81.57 obtained by the model. The lack-of-fit (LOF) of the proposed model with the amount of 0.0502 for BG photo degradation by the Ag:Cd-1,4-BDOAH₂ is not significant, and "Lack of Fit F-value" is 6.15. The reduced model equation in terms of the coded factors was given as follows:

$$R\%_{BG} = +65.4 + 16.8 X_{1} - 4.0 X_{2} - 5.1 X_{3} + 5.6 X_{4} + .1.5 X_{5} + 8.7 X_{6} + 1.9 X_{1} X_{2} + 6.8 X_{1} X_{3} + 7.3 X_{1} X_{4} + 5.0 X_{1} X_{5} + 0.9 X_{1} X_{6} + 8.5 X_{2} Y_{3} + 2.5 X_{2} X_{4} + 7.9 X_{2} X_{6} - (3)$$

$$3.3 X_{3} X_{4} + 5.7 X_{4} X_{5} + 1.0 X_{5} X_{6} - 0.6 X_{1}^{2} < 6 X_{2}^{2} + 1.5 X_{4}^{2} + 1.4 X_{5}^{2} + 4.1 X_{6}^{2}$$

<Table. 3>

3.4. Response surface plots

3D RSM plots were applied to indicate the combined effects and main interactions between the factors on PEF-PU of BG by the Ag:Cd-1,4-BDOAH₂ (**Fig. 10a-c**). The fitted response surface plots (R%) vertues the main variables (**Fig. 10a**) shows the presence of interaction between reaction time and BG concentration on the PEF-PH degradation efficiency. Increasing BG degradation efficiency of BG with raising time is due to higher contact time between the Ag:Cd-1,4-BDOAH₂ and BG. Increasing initial dye concentration leads to reduce in degradation efficiency. Lower BG concentration is proportional with higher ratio of reaction sites to BG concentration, which causes an increase in degradation efficiency of the understudy system. The effects of pH and photocatalyst dosage on PEF-PH degradation efficiency and their interactions are shown in **Fig. 10(b**). The reactor probably enhances the

production of H^+ ion species at lower range of pH, which mainly causes an increase in degradation efficiency. In addition, PEF-PH degradation efficiency increases by the production of •OH ion species due to increase in pH value. An enhance in degradation efficiency of BG is observed when photocatalyst dosage raised due to the higher specific surface of photocatalyst at higher dosage. The results show that current and the amount of FeCl₃ have a positive effect on PEF-PH degradation efficiency (**Fig. 10b**). The higher value of current and FeCl₃ amount cause an increase in PEF rate in the aqueous solution.

<Fig. 10>

3.5. Optimization condition study

The present study used a desirability function (DF) approach based on CCD model for the optimization of the parameters in the PEF-PH process [38, 39]. The predicated values and DF for the PEF-PH degradation of BG dyeby the Ag:Cd-1,4-BDOAH₂ is displayed in **Fig. 11**. The maximum degradation efficiency processents the desired conditions while desirability is close to 1. The desirability profile represents the maximum PEF-PH degradation of 100% (DF = 1) for BG using the Ag.Cd-1,4-BDOAH₂. The optimum conditions for this percentage are the process time (X₁) on 5C (min), BG concentration (X₂) of 4 (mg L⁻¹), pH (X₃) of 5, Ag:Cd-1,4-BDOAH₂ (a) uosage of 0.4 (g L⁻¹), current (X₅) of 250 (mA), and FeCl₃ amount (X₆) of 0.3 (mmol L⁻¹).

<Fig.11>

3.6. Kinetic effect study

To design a PEF-PH reactor, the degradation rate assigning to the studies of kinetic is considered as an important stage. The degradation kinetic in aqueous solutions can be expressed by first-order kinetic model by the bellowing equation:

$$\ln\left(\frac{C_0}{C_t}\right) = kt \tag{4}$$

All parameters corresponding to this equation have been described elsewhere [9, 42]. Fig. 12(a) shows the fitness of the experimental data by pseudo-first order model with a high order of linearity. The L–H model was employed to analyze the degradation kinetic of BG [49-51]. By using the definition of surface coverage factor (θ), the reaction between the interface of solid-liquid with the photocatalyst and FeCl₃ for BG degradation was described by L-H kinetic model:

$$R = -\frac{dC}{dt} = k_r \theta = k_r \frac{KC_0}{1 + KC_0 + K_s C_s}$$
(5)

All parameters corresponding to this equation have been described elsewhere [9, 42]. The final form of the kinetic rate is as follows:

$$\frac{1}{R} = \frac{1}{k_r K_A C_0} + \frac{1}{k_r}$$
(6)

Where K_A is defined by $K_A=K/(1-T-C_s)$. The result in **Fig. 12(b)** shows a straight line formed by the plot of 1/R vertus $1/C_0$ according to L–H model with the coefficient of determination value of 0.998. The plot gives the intercept of $1/k_r$ and slope of $1/k_rK_A$. The rate constant values of PEF-PH degradation were calculated to be $k_r=1.164$ mg L⁻¹ min⁻¹ and $K_A=0.0181$ Lmg⁻¹.

<Fig.12>

3.7. Effect of procedure on the treatment efficiency

To evaluate the performance of individual and combinational procedures, different treatment processes including catalysis (adsorption), photolysis (light irradiation without catalyst), photocatalysis (light irradiation + catalyst), Fenton (electro Fenton + catalyst), and

photoelectro-Fenton (electro Fenton + light irradiation + catalyst) were investigated (**Fig. 13a**). The experimental results indicate the treatment percentages of 6.74, 19.22, 32.22, 58.54, and 76.45% using adsorption, photolysis, photocatalyst, Fenton, and photoelectro-Fenton, respectively. The contribution of Fenton and photocatalytic processes leads to an increase in BG degradation efficiency due to the generation of the hydroxyl radicals. **Fig. 13b** indicates the reusability of the photoelectron Fenton for the degradation of BG in three cycles under visible-light (LED) irradiation, and the experimental results reveal that the photocatalyst can be reused three times, indicating the good stability of understudy photoelectron Fenton.

<Fig.13 >

3.8. Proposed mechanism of BG degradation up the PEF-PH process

The mechanism of PEF-PH degradation using the synthesized photocatalyst under the irradiation of blue LED is illustrated in **Fig. 14**. Since the blue LED provides energy higher than the energy band gap of the synthesized photocatalyst, it can be excited by light energy, leading to the formation of electron-hole pairs. The valence holes (h_{VB}^+) are strong oxidants and are able to oxidize verticus contaminants and form hydroxyl radicals, while the conduction band electrons (e_{CB}^-) are good reductants and can reduce the dissolved oxygen to O₂-[52, 53].

Ag:Cd-1,4-BDOAH₂ + h
$$\nu \rightarrow$$
 Ag:Cd-1,4-BDOAH₂ ($e^- + h^+$) (7)

$$H_2O + h^+ \to OH^{-}$$
(8)

$$O_2 + e^- \to O_2^{--} \tag{9}$$

On the other hand, iron is added as a Fe^{3+} salt and H_2O_2 is produced by reduction of oxygen at the cathode.

$$\mathrm{Fe}^{3+} + \mathrm{e}^{-} \to \mathrm{Fe}^{2+} \tag{10}$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{11}$$

In the presence of light, the photo-Fenton process can be more efficient by the photo reduction of Fe^{3+} to Fe^{2+} and the generation of additional hydroxyl radicals.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^-$$
(12)

$$Fe^{3+} + H_2O_2 \to Fe^{2+} + H^+ + OOH^-$$
 (13)

In both processes, a large number of O_2^{-} and OH^{+} is produced that can act as strong oxidants and play an efficient role in BG degradation.

<Fig.14 >

3.9. Comparison of the PEF-PH with other systems

BG degradation efficiency by the PEF-PH was convarid with formerly reported photocatalyst, and the results is represented in **Table 4.** The esu's indicate that the PEF for Ag:Cd-1,4-BDOAH₂ is suitable and shows reasonable degradation performance for BG.

<Table. 4>

4. Conclusion

In this work, the synthesis of a photocatalyst (Cd-1,4-BDOAH₂) with a low band gap was performed without using any toxic and expensive solvents. By loading this photocatalyst with Ag, a better photocatalyst, namely Ag:Cd-1,4-BDOAH₂, was synthesized with a lower band gap that showed higher efficiency in PEF-PH degradation of BG under blue LED irradiation. The combination of photoelectro-Fenton and photocatalytic processes showed an efficient approach for degradation of BG dye. The optimum values to reach the maximum degradation efficiency using the Ag:Cd-1,4-BDOAH₂ were obtained at 50 min of time, 4 mg L⁻¹ of BG concentration, 5 of pH, 0.4 g L⁻¹ of the Ag:Cd-1,4-BDOAH₂, 250 mA of current, and 0.3

mmol L^{-1} of FeCl₃. At these conditions, the maximum degradation efficiency of BG by the PEF-PH was obtained (100%). The treatment percentages of 6.74, 19.22, 32.22, 58.54, and 76.45% obtained by adsorption, photolysis, photocatalyst, Fenton, and photoelectro-Fenton, respectively. All hypotheses about the applicability of the PEF-PH were achieved, and it showed to be high efficient. As a result, it could be considered as a promising approach for the treatment of dye wastewater.

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Conflict of Interest Statement

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Fig. 1. Schematic diagram of the reactor setup for electrolytic–photocatalytic process: (1) power supply, (2) the reaction flask, (3) Pt aloce, (4) graphite cathode, (5) LED lamp, (6) sparger (diffuser), (7) power source, (8) flow meter, and (9) oxygen cylinder.



Fig. 2. UV–Vis absorption spectra of photoelectro-Fenton/photocatalytic degradation of BG.



Fig. 3. FT-IR spectra of 1 4 BDUAH₂, Cd-1,4-BDOAH₂, and Ag:Cd-1,4-BDOAH₂.



Fig. 4. SEM images of (a-c) Cd-1,4-BDOAH₂ and (d-f) Ag:Cd-1,4-BDOAH₂.



Fig. 5. EDX spectra of the prepared (a) Cd-1,4-BDOAH₂ and (b) Ag:Cd-1,4-BDOAH₂.



Fig. 6. TEM images of (a) Cd-1,4-BDOAH₂ and (b) Ag:Cd-1,4-BDOAH₂.



Fig. 7. XRD p. tterns of (a) Cd-1,4-BDOAH₂ and (b) Ag:Cd-1,4-BDOAH₂.



Fig. 8. Photoluminescence (PL) specur of Cd-1,4-BDOAH₂ and Ag:Cd-1,4 BDOAH₂.



Fig. 9. Comparison of the photocatalytic activity of Cd-1,4-BDOAH₂ and Ag:Cd-1,4 BDOAH₂.

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Fig. 10. Response surface plots for (a) X_1X_2 , (b) X_3X_4 , and (c) X_5X_6 for PEF-PH degradation of BG.



Fig. 11. Profiles of predicated value *a*¹, ¹ desirability functions for PEF-PH degradation of BG.



Fig. 12. Plots of the kinetin models, typically for BG degradation using Ag:Cd-1,4-BDOAH₂: (a) first-order and (b) L–H.



Fig. 13. (a) Comparison of the obtained efficiency using different treatment methods and (b) Reusability of Ag:Cd-1,4 BDOAH₂ for PEF-PH degradation of BG.



Fig. 14. Proposed mechanism for PEF-PH degradation of BG.

Table 1. Characteristics of Brilliant C	Green dye.
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Name	BG
Chemical formula	$C_{27}H_{33}N_2.HO_4S$
Molecular weight	$482.64 \text{ g mol}^{-1}$
Molecular structure	HSO4

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Factor				Levels							
			Low (-1)		Central (0)		High (+1)	-α	+α		
X ₁ : Time	1: Time (min) 30			50		70	10	90			
X_2 : Dye concentration (mg L ⁻¹)		¹)	3		4		5	2	6		
X ₃ : pH			5		7		9	3	11		
X ₄ : Photo	ocatalyst d	losage (g L	-1)	0.02		0.03	0.03 0		0.01	0.05	
X ₅ : Curre	ent (mA)			150		200	250		100	300	
X ₆ : Fecl ₃	(mmol L	¹)		0.2		0.3		0.4	0.1	0.6	
Run	Block	X ₁	X	2	X ₃	X ₄		\mathbf{X}_{5}	X ₆	P%	
1	1	90	4		7	0.03		200	0.30	94.61	
2	1	50	4		11 0.03		200	0.30	79.60		
3	1	30	5		9	0.04		250	0.20	46.22	
4	1	50	4		7	0.03		2)0	0.30	65.35	
5	1	50	4		7	0.01		200	0.30	58.32	
6	1	50	4		7	0.03	\mathbf{T}	200	0.30	66.83	
7	1	30	3		5	0.24		250	0.20	99.67	
8	1	70	3		5	6.72		250	0.20	98.80	
9	1	70	5		9	0.02		250	0.20	82.93	
10	1	70	3		9	- <u>().04</u>	$\frac{2}{4}$ 150		0.40	76.28	
11	1	50	4		7	-0.03		300	0.30	91.71	
12	1	30	5			0.02		150	0.20	39.98	
13	1	50	4			0.03		200	0.10	62.74	
14	1	50	4	L	7	0.05	0.05 200		0.30	80.73	
15	1	70	5		$\overline{)}$	0.04		150	0.20	78.49	
16	1	30	5	- +	$\overline{5}$	0.02		150	0.40	71.30	
17	1	50	2	-+	7	0.03		200	0.30	72.73	
18	1	50	4		7	0.03		100	0.30	46.52	
19	1	50	-4		7	0.03		200	0.30	64.90	
20	1	30	$\overline{3}$		5	0.02		150	0.20	89.16	
21	1	50	4		7	0.03		200	0.30	67.84	
22	1	30	3		9	0.02		150	0.40	54.06	
23	1	50	4		7	0.03		200	0.30	67.52	
24	1	70	3		5	0.04		150	0.20	95.85	
25	1	50	6		7	0.03		200	0.30	56.54	
26	1	70	3		9	0.02		250	0.40	98.90	
27	1	70	5		5	0.04		150	0.40	97.03	
28	1	10	4		7	0.03	0.03 200		0.30	27.62	
29	1	50	4		7	0.03	0.03 200		0.50	97.37	
30	1	50	4		3	0.03		200	0.30	100.0	
31	1	70	5		5	0.02		250	0.40	94.10	
32	1	30	3		9	0.04		250	0.40	53.67	
33	1	30	5		5	0.04		250	0.40	91.76	

Table 2. CCD matrix and responses for the PEF-PH degradation of BG.

Source	BG							
variation	SS ^a	DF ^b	MS ^c	F-value	P-value			
Model	12522.94	22	569.22	81.57	< 0.0001			
X ₁	2243.83	1	2243.83	321.56	< 0.0001			
X_2	391.72	1	391.72	56.14	< 0.0001			
X ₃	208.08	1	208.08	29.82	0.0003			
X_4	251.10	1	251.10	35.98	0.0001			
X_5	1021.07	1	1021.07	146.33	< 0.0001			
X ₆	599.62	1	599.62	85.93	< 0.0001			
X_1X_2	56.33	1	56.33	8.07	0.0175			
X_1X_3	739.57	1	739.57	105.99	< 0.0001			
X_1X_4	284.51	1	284.51	40.77	< 0.0001			
X_1X_5	133.00	1	133.00	19.06	0.0014			
X_1X_6	13.10	1	13.10	1.88	0.2005			
X_2X_3	365.87	1	365.87	52.43	< 0.0001			
X_2X_4	103.23	1	103.25	14.79	0.0032			
X_2X_6	328.34	1	328.2+	47.05	< 0.0001			
X_3X_4	170.04	1	170.04	24.37	0.0006			
X_4X_5	174.04	1	174.04	24.94	0.0005			
X_5X_6	15.25	1	15.25	2.19	0.1701			
X_1^2	11.61	1	11.61	1.66	0.2261			
X_{3}^{2}	1297.19		1297.19	185.90	< 0.0001			
X_4^2	66.44		66.44	9.52	0.0115			
X_5^2	57.57		57.57	8.25	0.0166			
X_6^2	511.81	1	511.81	73.35	< 0.0001			
Residual	69.78	10	6.98					
Lack of Fit	62.95	6	10.49	6.15	0.0502			
Pure Error	682	4	1.71					
Cor Total	12: 92. 2	32						

Table 3. Results of ANOVA for the response surface quadratic model for the PEF-PH degradation of BG.

^a Sum of Square ^b Degree of freedom ^c Mean of Square

Photocataly st (dispersed)	Anode	Cathode	Dye	Tim e (min)	Eliminatio n (%)	Sourc e of light	Ref.
TiO ₂	Boron- doped diamon d	Carbon felt	Reactive yellow 17	30	99.0	UV	[54]
TiO ₂	Pt sheets	Carbon nanotube– polytetrafluoroethyle ne	Basic Red 46	360	98.8	UV	[52]
TiO ₂	Pt sheet	Carbon nanotube- polytetrafluoroethyle ne	Acid Red 17	36	96.4	UV	[55]
TiO ₂	Pt sheet	Graphite felt	Acid Blue 9	2	98.0	UV	[21]
TiO ₂	Platinu m	Carbon felt	Reactive Red 120	91	99.5	UV	[56]
-	TiO ₂ – Ti mesh	Pt sheet	Orange-C	300	96.8	UV	[57]
-	WO ₃ /W	$\begin{array}{ll} Fe@Fe_2O_3 & /carbon \\ felt & \end{array}$	Methyl slue	90	91.6	UV	[58]
-	Pt plate	Reducedgrapheneoxide(RGO)-Ce/WO3nanoshe .ts(RCW)	^{••} iprofloxac in	60	100.0	UV	[59]
Ag:Cd-1,4- BDOAH ₂	Platinu m	Graphite	BG	50	~99.9	LED	Presen t study

Table 4. Performance comparison of different degradation systems for degradation of some pollutants.

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1. Highlights

- 1) Cadmium-benzene-1,4-dioxyacetic acid photocatalyst synthesis by ultrasonication.
- Doping Cd-1,4-BDOAH₂ with Ag to produce Ag:Cd-1,4-BDOAH₂ with a low band gap.
- 3) Photoelectro-Fenton degradation of BG at various time of blue LED irradiation.
- 4) The degradation kinetic data of BG were successfully fitted to L–H model.





Figure 2



avenumber (cm⁻)



Figure 4



Figure 5





Figure 7



Figure 8



Figure 9



Figure 10



Figure 11



Figure 12



Figure 13



Figure 14