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Research Paper

Treatment of petroleum refinery wastewater by photo-anodic oxidation process with Gr /Bi-Ni-Sb-SnO2 rotating photo-anode: Performance and kinetic study

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ABSTRACT

This work explores the use of photoelectrocatalysis (PEC) as one of the most advanced oxidation processes (AOPs) for petroleum refinery wastewater (PRW) treatment. A photoelectrochemical reactor equipped with a $Gr/Bi-Ni-Sb-SnO_2$ photoanode and UVC irradiation was designed to enhance the degradation of pollutants. The effects of key operational parameters, including current density, pH, and anode rotation speed, on the treatment efficiency were systematically evaluated. The results confirmed that increasing the current density provided better chemical oxygen demand (COD) removal, while increasing pH above 5 results in a decrease in COD removal. In addition, increasing the anode rotation speed improved mass transfer and pollutant decomposition up to 200 rpm; after that, no significant improvement was observed, with a slight decrease in COD removal. According to the results, the best performance was achieved at a pH of 5, a current density of 6 mA/cm^2, and a rotation speed of 200 rpm, achieving a COD removal efficiency of 86.2% in 90 min with an energy consumption of 110.34 kWh/kg^{-1} COD. Kinetic studies confirmed that the degradation of COD over time exhibited pseudo-first-order kinetics, with an $R2$ of at least 0.999. Considering all factors, the results demonstrate that PEC technology, using $Gr/Bi-Ni-Sb-SnO_2$ Photoanode, offers a low-energy, sustainable, and facilitating method for the degradation of complex petroleum-derived pollutants. This study highlights the potential of PEC as a practical alternative to conventional industrial wastewater treatment methods.

1. Introduction

The wastewater resulting from power or oil production plants is considered one of the heavily polluted waters due to its content of organic compounds, aromatic pollutants, and chemical pollution that comes from days, heavy metals, and solvents [1, 2]. Recently, there has been an increase in the demand for oil production and energy production due to the increase in population density and the requirements for energy and oil. This has led to an increase in the number of factories that discharge wastewater significantly each year, threatening human consumption of water and especially aquatic creatures [3,4]. Through the enactment of laws to protect water and treat wastewater, there has been a development in the treatment of sewage in less energy-consuming ways, instead of traditional chemical processes that are ineffective due to their higher energy consumption. Thus, the trend has shifted towards oxidation in general to reduce energy consumption, as seen in wet oxidation and wet peroxide oxidation [5]. It is well known that the wastewater generated from power generation stations or others is characterized by containing large proportions of pollutants, damage, and negative effects on our health first and the environment second [6]. Ion exchange, flotation, chemical precipitation, and biological systems are traditional methods for eliminating pollution from wastewater. However, a number of disadvantages of these procedures, including their high energy consumption, low removal efficiency, and production of toxic sludge, restrict their widespread use [7, 8]. It has been widely noted that pollutants resistant to biological treatments are often defined by high chemical stability and/or significant challenges in achieving complete mineralization. In these instances, it is imperative to implement reactive systems that are far more efficient than those utilized in traditional purifying methods [9, 10]. Recently, with the advancement of technology, oxidation has also been improved to enhance the treatment process and facilitate the removal of difficult biological or relatively stable chemical pollutants, known as advanced oxidation processes(AOPs) [11, 12]. They work by producing powerful oxidizing agents, such as hydroxyl radicals (OH), which can quickly oxidize a variety of contaminants in a non-selective manner, turning them into CO2, water, and inorganic species [13, 14]. OH radicals are distinguished by their elevated standard oxidation potential (up to 2.80 V) and their rapid reaction rate relative to conventional oxidants such as chlorine, oxygen, ozone, H_2O_2, or potassium permanganate. As a result, both inorganic and organic solutes can react with OH to produce large rate constants [15]. There are several recognized AOPs, mostly categorized as UV–hydrogen peroxide (UV/H_2O_2), Fenton and photo-Fenton processes, ozone-based methods, photo-catalysis, physical techniques (such as son lysis, microwave and electron beam irradiation), and PEC [16, 17]. The polluting load of waste, which is typically stated as COD, is another factor pertaining to the potential for AOP use. These methods are only appropriate for treating wastes with comparatively low COD levels ≤ 5.0 (g/l), as greater COD concentrations require the use of excessively costly reacting substances. Wet oxidation or incineration are more practical methods for treating wastes with higher concentrations of contaminants [18]. PEC, a very effective kind of AOPs, has been examined as a highly effective method for the removal of recalcitrant organic contaminants [19–21]. Due to PEC sensing's many advantages, including its low background signal, ultra-high sensitivity, low cost, quick analytical time, and simple equipment, numerous researchers have focused on creating semiconductor materials with superior photo electrochemical performance [22, 23]. The photo-anode plays a major role in the collection of charges and the movement of photo-excited electrons from pollution to an external electrical circuit [24].

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Nomenclature

BOD	Biological oxygen demand (ppm or mg/L)	P	Lamp power (kW)
COD	Chemical oxygen demand (ppm or mg/L)	r	Rate of reaction ($mg/L.min$)
c	Concentration (ppm or mg/L)	RD	Relative difference (%)
E	Voltage of cell ($volt$)	RE	Removal efficiency (%)
E_a	Constant anode voltage ($volt$)	t	Time (h)
EE	Electrical Energy(kWh)	*Subscripts*	
EEC	Electrical energy consumption ($kWh/kg\ COD$)	i	Initial
HLT	Half-life time (min)	f	Final
I	Current (A)	app	Apparent
K	Pseudo-first-order kinetic constant (min^{-1})		

In PEC, the material of the anode plays a crucial role in the performance of the process; hence, many photoanodes were developed for treating wastewaters at high efficiency by enhancing the photo-conversion and electron transfer while reducing the combinations between holes and electrons [25–27]. These are nano-TiO_2 [28], $BiVO_4$-based photo-anodes [29, 30], Ni–PEG–PbO_2//Ti//TiO_2–Ag_2O [31], SnO_2/Mo: $BiVO_4$, and others [32]. Among them, photo anodes made by SnO_2 doped with bismuth or nickel are the most preferred in PEC due to their low cost, high efficiency, and oxygen overvoltage [33–37]. Yang et al. [33] found that doping SnO_2 anodes with nickel offered excellent properties and can drive both electrocatalysis and photocatalysis for the decomposition of phenol. Domingo-Torner et al. [37] found that Sb–SnO_2 ceramic anodes coated with $BiFeO_3$ showed high activity in the removal of norfloxacin as a result of the synergistic effect of Bi with SnO_2. Our previous work (Heba and Abbar, 2025), manuscript submitted for publication) showed Gr /Bi-Ni-Sb-SnO_2 (5:5:5:95) photo-anode has good activity for degrading tetracycline due to the combination effect of Ni and Bi on the structure of SnO_2, resulting in the formation of coherent deposits with the best photocatalytic activity. The present work aims to treat PRW by photo-anodic oxidation process using Gr /Bi-Ni-Sb-SnO_2 rotating photo-anode. Although many studies have used PEC for wastewater treatment, none have reported using Gr /Bi-Ni-Sb-SnO_2 for treating petroleum refinery wastewaters. The integration between Ni and Bi with SnO_2 is expected to improve electron mobility, reducing the recombination of electrons and holes generated by UV irradiation, and enhancing the catalytic stability. Applying rotation further improves via increasing mass transfer and light utilization. Accordingly, this study introduces a novel PEC approach that has not previously investigated for real, highly complex wastewater containing recalcitrant organic pollutants such as PRW. The effect of key parameters like current density, pH, and rotation speed on COD removal was investigated by determining the kinetics of degradation.

2. Materials and method

2.1 Characteristics of wastewater

In the present study, fifteen liters of wastewater from Al-Dora petroleum refinery in Iraq were obtained from the physical treatment unit's feeding collecting tank in the plant and stored at 4 °C until needed. The characteristics of treated effluent and untreated wastewater are shown in Table 1 according to the physical unit that the plant management gave.

Table 1. Characteristics of Al-Dora refinery plant wastewater.

Characteristic	Input	Output
Temperature, $°C$	32.00	28.00
pH	07.30	07.30
Turbidity, (NTU)	75.40	21.30
TDS, (mg/L)	938.0	1066.0
COD, (mg/L)	435.00	68.00
BOD, (mg/L)	176.00	16.00
Oil, (mg/L)	163.10	05.50
SO_4^{2-}, (mg/L)	340.00	380.00
Cl^-, (mg/L)	636.00	536.00
PO_4, (mg/L)	00.93	00.65

2.2 Materials and chemicals

$SnCl_2.2H_2O$, $SbCl_3$, Na_2SO_4, $NiCl_2$, $BiCl_3$, Isopropyl alcohol (IPA), 1,4-benzoquinone(p-BQ), ammonium oxalate monohydrate (AO), H_2SO_4, NaOH and citric acid were purchased from Merck. Analytical grade compounds were all utilized without additional purification. Every solution was made with deionized water.

2.3 Preparation of Gr /Bi-Ni-Sb-SnO_2 photo-anode

Gr /Bi-Ni-Sb-SnO_2 photo-anode was prepared according to a similar procedure mentioned in our previous work [38]. A graphite rod having a diameter of 20mm and a length of 50 mm was activated by soaking in a boiled water for 1h than, followed by putting in an electrochemical cell containing 1.44M sulfuric acid electrolyte in which the graphite rod act as anode and hollow cylinder graphite as cathode where current was applied at 14 mA/cm^2 for 30 min. The activated graphite rod was then used as a cathode in an electrochemical cell used to electrodeposited tin and other elements from their salts. In this case, an electrolytic solution containing the following composition was used: 67.5 (g/L) $SnCl_2 2H_2O$, 2.25 (g/L) $SbCl_3$, 3.56 (g/L) $NiCl_2$, 4.73 (g/L) $BiCl_3$, and 57.5 (g/L) citric acid. A current density of 10 mA/cm^2 was applied for 1h at 50 °C and 250 rpm as rotation for the cathode. The electroplated graphite was then rinsed in distilled water several times and dried at 100 °C for 1h followed by calcinating at 500 °C for 3h. the above procedure resulted in a photoanode called Gr /Bi-Ni-Sb-SnO_2 (5:5:5:95) based on the constituents of the plating solution.

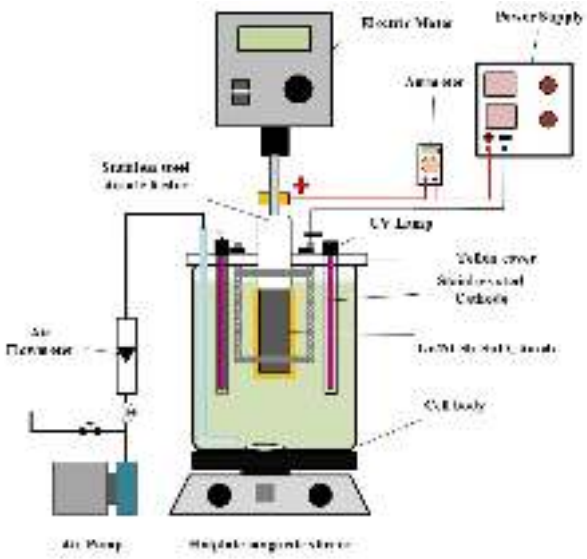


Figure 1. Photo-anodic oxidation system

2.4 Photo electrochemical system

The PEC system is composed of an electrochemical cell, an overhead electric motor (PHOEN RSO: 20D), an air compressor type-HAILEA/aco-280, a magnetic hot plate (ISO LAP), and a power supply type-UNI-T/UTP-3315TFL. The required current was monitored ammeter UNI-UT90A. While the flow rate of air was adjusted at 1 L/min via a control valve connected to an air flow meter, which has a range of 0.5-5 L/min. The PEC system is schematically depicted in Fig. 1. The photo-electro reactor was a Perspex cylindrical reactor that was 10 cm in diameter and 19.5 cm in length. A Perspex covering with an external diameter of 12 cm and a thickness of 1 cm was included. The cover had three holes drilled in it. The first is situated in the center and has a diameter of 2.5 cm for inclusion of the anode. The others are situated 2.5 from the center and have the same diameter (2 cm) for inclusion of two UVC lamps (Starlight R-CAN, Texas, USA, 10W, and λ of 253.7 nm). Based on López-Peñalver's work [39], UVC was chosen for this study. They discovered that utilizing UV with $\lambda = 254$ nm produced the optimum photo degradation of TC. UVC was used as a cause of irritation in other investigations as well [40]. The cathode

was a hollow stainless steel cylinder that measured 3.8 *cm* in diameter and 1 *mm* in thickness. It had holes evenly spaced over its lateral surface, each measuring 5 *mm* in diameter. The cathode was secured to the cover by two 5 *mm* diameter holes. The anode was composed of two sections, the first is a stainless steel current feeder measuring 0.7 *cm* in diameter and 17 *cm* in length, bounded by a Teflon shield at its lower section (9 *cm*) to prevent it from the corrosion while the second section is Gr /Bi-Ni-Sb-SnO_2 photo-anode. A copper ring that was placed around the anode feeder and connected to the power supply's positive pole allowed for the anode's electrical connection. The photoanodic oxidation was performed at room temperature. Firstly, 750 *ml* of wastewater was taken and put in a 1*L* beaker over a hotplate with magnetic stirrer, then Na_2SO_4 was added to make a concentration of 0.05*M* as a support electrolyte then allowed the mixture to homogenize under stirring for 15 *min*. After that, the solution was transferred to the cell, with supplying air to the solution for a further 15 *min* with switching on the UV lamps. The required current with a suitable current density was applied for a period of 90 *min*. Every 15 *min* sample was taken to measure its COD value.

2.5 Characterization and performance

The morphology of the photo-anode was identified by the SEM technique using SEM (FEI Company, Netherlands) operated at HV = 25 kV, spot = 8.0, bias = 1400 V. The crystalline structure of the photo-anode was recognized by X-ray diffractometer (XRD 6000/Shimadzu/Japan) with CuKα radiation of 1.5405 Å and operated at 40 kV, 30 *mA*, step size of 0.2°, and scan step time of 1.2s. The testing was performed in the range of 2θ between 20 and 80°. COD was determined by digesting the sample with potassium permanganate at 150°C for 2*h* using a thermo reactor (RD125, Lovibond). The sample was allowed to cool, and its COD value was obtained by putting the digested sample in a spectrophotometer (MD200, Lovibond). The oil content was measured by HORIBA OCMA-350, while turbidity was measured using Lovibond TurbDirect /serial number12/1805. Cl- concentration was determined by Photo Flex. Series (WTW model no 14541, Germany). The removal efficiency(RE%) of COD was evaluated by Eq. 1 [41].

$$RE\ (\%) = \frac{COD_i - COD_f}{COD_i} \times 100 \tag{1}$$

RE (%) stands for the COD removal efficiency, COD_i for the initial COD (mg/L), and COD_f for the final COD (mg/L) in the computation. The total amount of energy necessary to digest one kilogram of COD is known as EEC. EEC ($kWh/kg\ COD$) can be calculated using Eqs. 2 and 3 [41].

$$EEC = \frac{EE_{total} \times 1000}{COD_i - COD_f} \times v \tag{2}$$

$$EE_{total} = (P + E \times I) \times t \tag{3}$$

In this case, P is lamp power in watts, I stands for current in amperes, E for applied cell potential in volts, and t for electrolysis period (*hour*). Phenol concentration was identified using Hach Company/Hach Lange GmbH, USA's Method 8047, whereas chloride ion concentration was measured using the Photo Flex Series (WTW, model number 14541, Germany). Multiple replications were performed for each run, and the mean value in this study was taken after verifying the accuracy of the experimental results by assessing the relative difference (RD) using Eq. 4, which must be less than 10% [42]:

$$RD = \frac{(C_1 - C_2) \times 100\%}{(C_1 + C_2)/2} \tag{4}$$

3. Results and discussion

3.1 Characterization of photoanode

Figure 2 shows XRD results for Gr /Bi-Ni-Sb-SnO_2(5:5:5:95) where strong peaks for tetragonal rutile SnO_2 were observed at 2θ = 26.45°(110), 33.85°(101), 37.95°(200), 51.65°(211), 54.45°(220), 59.55°(002) , 61.85°(310), 64.55°(112), and 65.85°(301) (PDF no. 41-1445) [43]. Furthermore, strong peaks were observed at 2θ=28.4°, 30.1°, 34.6 and 48.7 corresponding to Sb_2O_5 [44–46]. Peaks at 2θ= 26.45°(002), 42.4°(111), 44.5°(101), 54.45°(004) and 77.4°(006) are belong to graphite [47]. Peaks of α-Bi_2O_3 were observed at 2θ= (27.4°(120), 33.3°(200), 46.3°(041)) which belong to monoclinic Bi_2O_3 crystal structure (JCPDS Card No.01-072-0398) [48, 49]. Peaks at 2θ=37.20°(111), 43.095°(200), 62.86°(220), and 75.20°(311) were observed, which corresponds to the cubic NiO crystal structure (JCPDS Card No: 78-0643) [50–52]. Furthermore, a single peak at 2θ= 56.3°was observed, which corresponds to Ni_2O_3 [53]. The results of XRD confirm the successful doping of B_i and N_i within the structure of SnO2 forming Gr /Bi-Ni-Sb-SnO_2 photoanode. Figure 3 shows the SEM of Gr/ Bi-Ni-Sb-SnO_2 (5:5:5:95) photo-anode at two magnifications (1000× and 2000×). Adding N_i and B_i resulted in a bale yellow structure proposing successful formation of the composite NiO and Bi_2O_3 [49,52]. The shape of the deposits turns sharp edges aggregates. No cracks were detected, which could result in an improvement in the stability and lifespan of the electrode [54]. Figure 4 shows the EDS of Gr/ Bi-Ni-Sb-SnO_2 (5:5:5:95) anode, which confirms the existence of O, Sn, Sb, B_i,and N_i within the structure of film deposited on Gr. Oxygen evolution potential (OEP) is one of the most important parameters that gives an indication of the catalytic activity of an anode, where higher values represent the best catalytic activity in which few side reactions could be happened with OH generation [55].

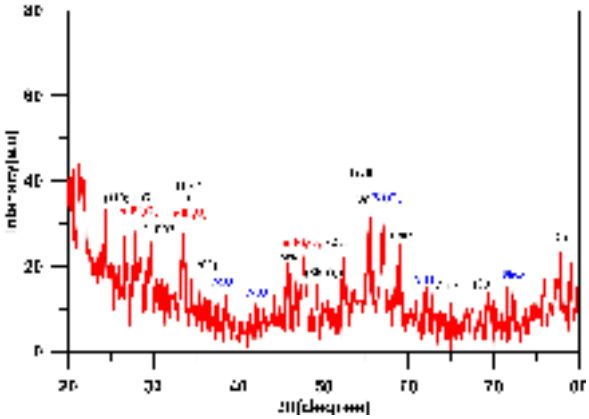
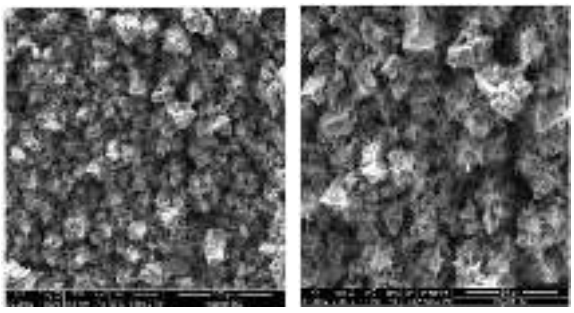


Figure 2. XRfor Gr/ Bi-Ni-Sb-SnO2 (5:5:5:95) photo anode



(a) Magnification of 1000x (b) Magnification of 2000x

Figure 3. SEM of Gr/ Bi-Ni-Sb-SnO2 (5:5:5:95).

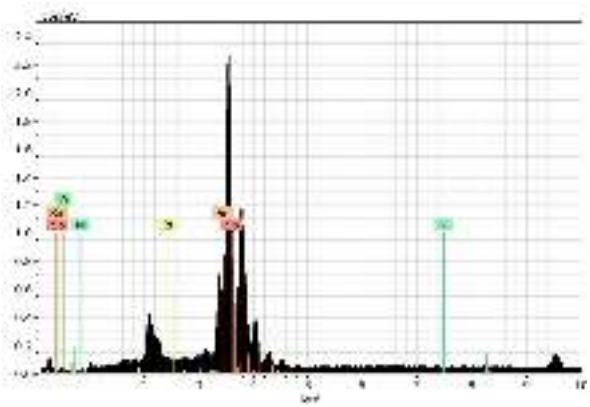


Figure 4. EDS for Gr/ Bi-Ni-Sb-SnO2 (5:5:5:95) anode

Figure 5 displays LSV for Gr/ Bi-Ni-Sb-SnO_2 (5:5:5:95) anode compared with no doping case (Gr/ Sb-SnO_2) in sodium sulfate solution (0.1 M) at a scan rate

of 10 mVs^{-1}. Results confirmed the present photoanode has good catalytic activity with OEP of 2.14 V (vs. Ag/AgCl), which is higher than SnO_2 alone and other related SnO_2 anodes prepared by thermal decomposition methods [56,57]. Furthermore, the present photoanode could be considered cheap in comparison with the expensive boron-doped diamond anode, non-toxic in comparison with the PbO_2 anode, and easy to scale-up [58].

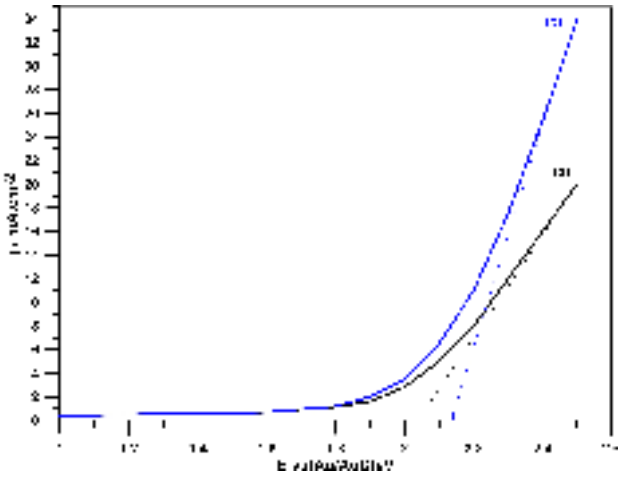


Figure 5. LSV for Gr/ Bi-Ni-Sb-SnO2 (5:5:5:95)(a) compared with Gr/ Sb-SnO2 anode(b).

3.2 Effect of operating variables

3.2.1 Effect of current density

In PEC, current density plays a vital role in the performance of oxidation in this process [59]. Figure 6 shows the impact of current density on the COD removal efficiency at different values under an initial pH of 5 and a rotation speed of 200 *rpm*. It was observed that the RE% increases with increasing current density up to 6 mA/cm^2 beyond which a decrease in RE% occurs.

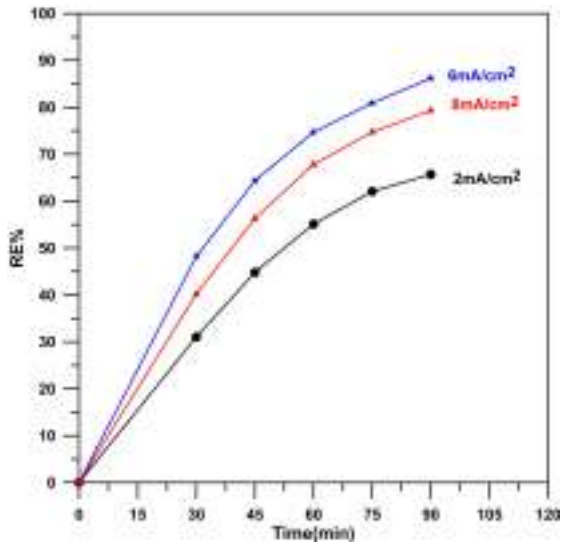


Figure 6. Impact of current density on RE%. pH=5, 200 rpm.

Consequently, a current density of 6 mA/cm^2 is recommended. The increase in COD removal with increasing current density up to 6 mA/cm^2 can be explained as more hydroxyl radicals are generated with increasing current. Moreover, increasing the current can cause a decrease in the recombination rate of electrons and holes generated by UV irradiation, and thus, more radicals are generated on the photoanode [60]. With increasing current density, a large number of oxygen bubbles are formed, which results in a loss of current towards O_2 evolution rather than OH radicals generation [61]. Ahdour et al. [62] found a similar behavior in the degradation of tetracycline using $BaHPO_4$/SSA photoanode, where the optimum current density was 10.56 mA/cm^2 within a range of 4–12 mA/cm^2. Orimolade et al. [63] found a similar effect of current density in the degradation of paracetamol using a FTO-$BiVO_4$/BiOI photoanode, where the degradation rate increased with increasing current density from 5 to 15 mA/cm^2 and then decreased at 20 mA/cm^2. Similar behaviors have been reported by other works using different photoanodes and contaminants [35,47,64]. In support of our results, most previous studies have confirmed the existence of an optimum value of current density or voltage that achieved maximum generation of OH and thus the highest degradation rate, beyond which no improvement or decrease in the removal rate occurs because OH is no longer dominant [59,65,66]. Furthermore, the improvement in the performance of the present photoanode could be linked to the effect of N_i and B_i addition. Pirsaheb et al. [67] found that excellent humic acid removal occurred when using $NiTiO_2$-NT photoanode due to the presence of N_i, which narrows the band gap leading to enhanced electron transfer rate and reduced recombination of electrons and holes.

3.2.2 Effect of pH

The pH of the solution plays a fundamental role in the oxidation mechanism during PEC and thus affects the degradation rate of contaminants. pH influences the formation of reactive species such as OH, the formation rate of which increases under acidic conditions [68]. pH also affects the surface charge of the photoanode, its stability, and corrosion phenomena [69]. Furthermore, pH affects the band bending of the semiconductors that make up the photoanode, as high band bending can occur on the semiconductor surface under acidic conditions due to the adsorption of more organic contaminants, thus increasing the oxidation process, and vice versa under alkaline conditions [61,70]. Figure 7 shows the effect of pH on the COD removal rate in terms of RE% under 6 mA/cm^2 and 200 rpm. It can be seen that the COD removal is almost constant with a slight increase as the pH moves from 3 to 5, reaching 86.2%. However, it starts to decrease with further increase in pH and reaches 74.7% at pH 9. Zhou et al. [71] found that pH 2 is more favorable for the degradation of landfill leachate by PEC using TiO_2/Ti photoanode than alkaline conditions. Umukoro et al. [64] found that the best ciprofloxacin removal occurred at pH 5.4 and decreased when pH became 4 or 8 using PEC with MoS_2-SnO_2/EG nanocomposite photoanode. Similar results were found in previous works [72,73]. However, operation at neutral conditions also yielded good COD removal of 81.6% at a COD level of 80 mg/L below the standard limit for discharge of PRW to the environment. These results confirmed the good activity of the Gr/Bi-Ni-Sb-SnO_2 photoanode in treating one of the most hazardous wastewaters generated by industry.

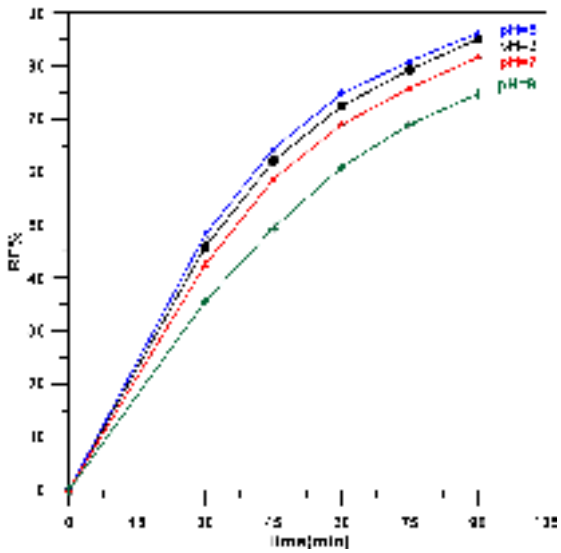


Figure 7. Impact of pH on RE% . 6 mA/cm^2, 200 rpm.

3.2.3 Effect of anodic rotation speed

Rotation speed is an essential operating parameter in PEC used for wastewater treatment. It has a direct impact on mass transfer, hydrodynamics, and light utilization efficiency. The photoanode's rotational motion (as in a spinning disc or rotating electrode system) improves the diffusion of pollutants and dissolved oxygen towards the photoactive surface by decreasing the thickness of the boundary layer around the photoanode [26]. Light penetration and effective charge separation at the photo anode surface are enhanced by increasing turbulence at the electrode–solution interface caused by an increase in the rotation speed

[74]. High speed prevents deactivation of the photo anode and reduces fouling [75]. Figure 8 illustrates the effect of photoanode rotation speed on the removal rate of COD under 6 mA/cm^2 and pH=5. It can be seen that increasing rotation speed up to 200 rpm gives higher removal of COD, while further increase in rotation speed has no significant effect on COD removal and causes a slight decrease in RE% due to the effect of turbulence and mechanical stress resulting from vibration of the anode that could cause destabilizing the intermediates [26]. Similar results were found by Cho et al. [74] in the removal of methylene blue using rotating TiO_2 nanotubes photo anode. The rotation speed of 90 rpm is the best in the removal of methylene blue, while a higher speed resulted in a decrease in methylene blue removal. Xu et al. [76] found that a rotation speed of 90 rpm is the best for the removal of Rhodamine B using TiO_2 rotating disk photoanode.

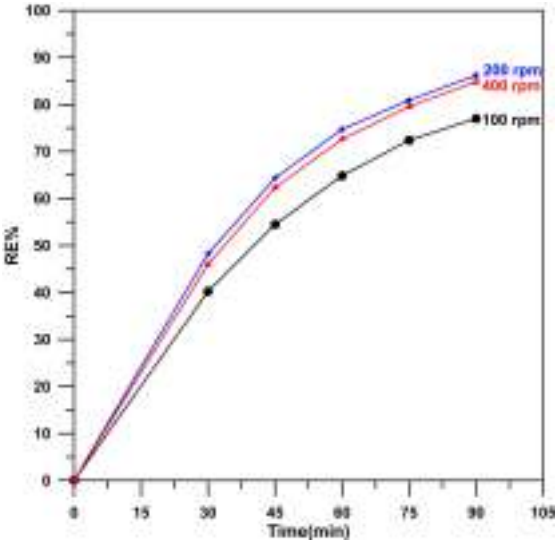


Figure 8. Impact of rotation speed on RE%. 6 mA/cm^2, pH=5

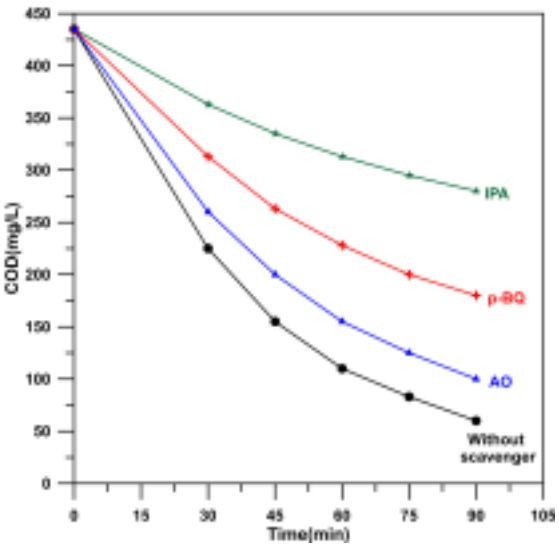


Figure 9. Effect of various scavengers on the COD removal by PEC process. 6 mA/cm^2, pH=5, 200rpm.

3.3 Free Radical Recognition

To determine the role of free radicals (OH, O_2^-, and h^+) that can be generated in PEC, three known scavengers (IPA, p-BQ, and AO) were used at a concentration of 5 mM [38]. They were added to a PEC operating at 6 mA/cm^2, pH 5, and 200 rpm, as shown in Fig. 9. It was observed that COD degradation was suppressed upon the addition of the scavengers. The addition of IPA resulted in a decrease in RE% from 86.2% to 35.6%, confirming that OH is the dominant radical in COD degradation. The addition of p-BQ resulted in a decrease in RE% to 58.6%, confirming an important role for O_2^- during PEC, which shares its effect with OH. h^+ has a minor effect on COD removal. Ahdor et al. [62] reported that O_2^- is the major radical in the PEC of tetracycline using the $BaHPO_4$/SSA photoanode, with a minor role for OH and h^+. Kang and Kim [32] reported similar behavior during the PEC treatment of tetracycline hydrochloride using the SnO_2/Mo:$BiVO_4$ photoanode. The discrepancy with other work may be due to the catalytic activity of the photoanode used in the degradation process.

3.4 Reusability of PEC

From an industrial application perspective, the long-term efficiency and stability of PECs are key factors in evaluating their performance. In this study, the stability of the photoanode in a PEC was verified by sequentially running the system through multiple cycles. In each cycle, the anode was cleaned with distilled water and ethanol and then used in the next cycle. Figure 10 shows the RE% at different cycles operated at 6 mA/cm^2, pH 5, and 200 rpm. A decrease in RE% was observed from 86.2% to 79.5% after 5 cycles, confirming the photoanode's effectiveness in removing COD from PRW.

3.5 Kinetic studies

Studying PEC kinetics has several benefits including determining the optimal PEC based on high removal efficiency with low energy consumption, providing insight into the rate of contaminant oxidation, providing a basis for calculating reactor size, operating time and electrode surface area when scaling up to industrial scale, and preventing overtreatment by stopping the process at the point of diminishing returns [77]. For PEC process, the degradation rate of COD can be fitted to a pseudo-first order kinetic model as follows Eq. 5 [64, 78, 79]:

$$r = \frac{dCOD}{dt} = k_{app}\, COD \tag{5}$$

where k_{app} represents a pseudo-first-order kinetic constant.

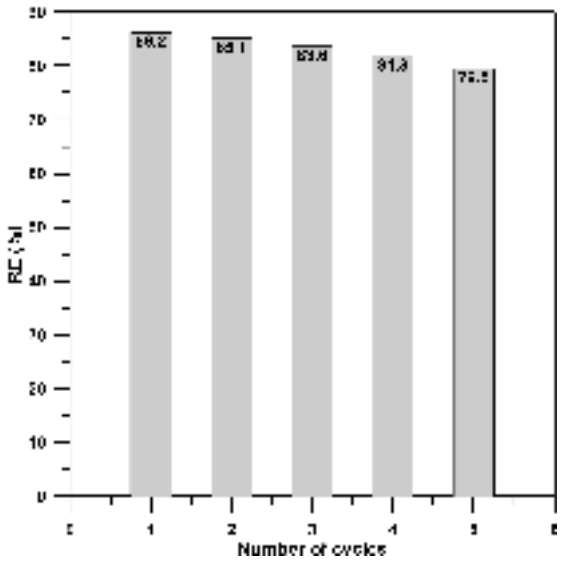
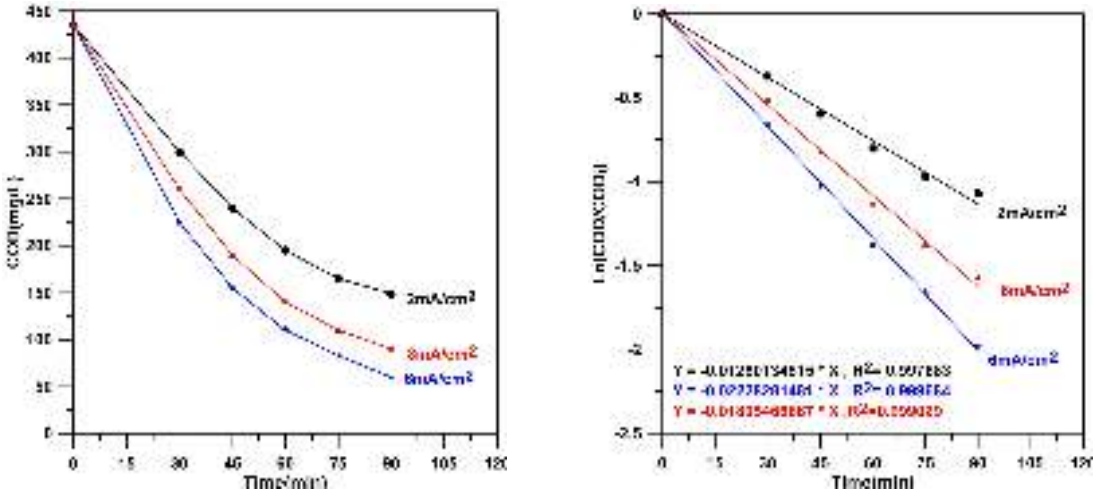


Figure 10. Reusability of Gr/ Bi-Ni-Sb-SnO2 (5:5:5:95) photo-anode.

The integration of Eq. 5 subject to the initial conditions COD=COD_i at t=0 leads to the following Eq. 6:

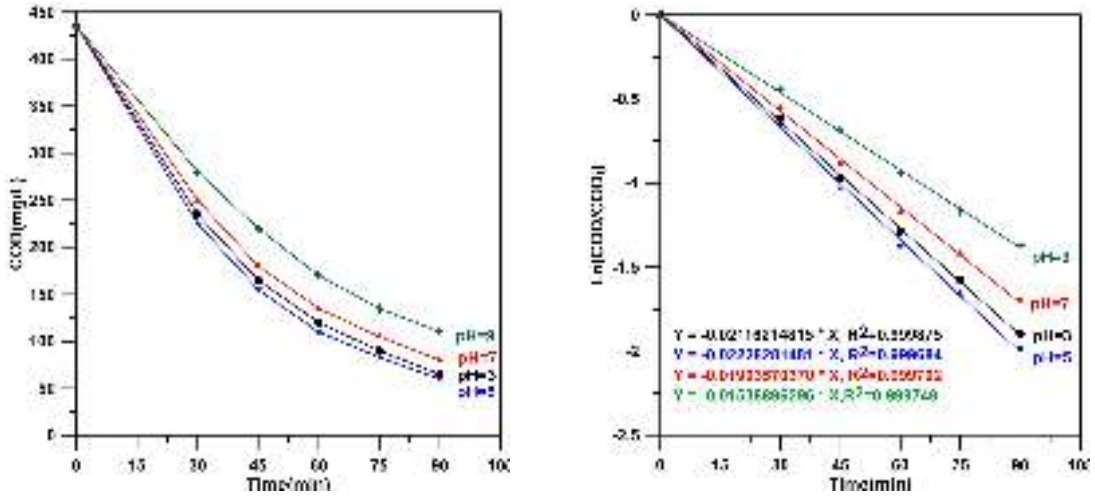
$$ln\frac{COD}{COD_i} = k_{app}\, t \tag{6}$$

Figures 11, 12, and 13 illustrate the COD degradation over time for different operating variables with the relevant plot of $ln(COD/COD_i)$ versus time. Table 2 shows the k_{app} values with the respective R^2 and the half-life time (HLT) calculated as $(ln(2)/k_{app})$. It can be seen that all decays of COD with time follow pseudo-order behaviour, driven by OH attack on aromatic contaminants, which is consistent with most works in PEC. Furthermore, current density has the greatest influence on k_{app} than other variables, confirming that the current controls the oxidation rate. It is observed that k_{app} increases with increasing current density up to an optimum value after which it starts to decrease with increasing current Table 2.



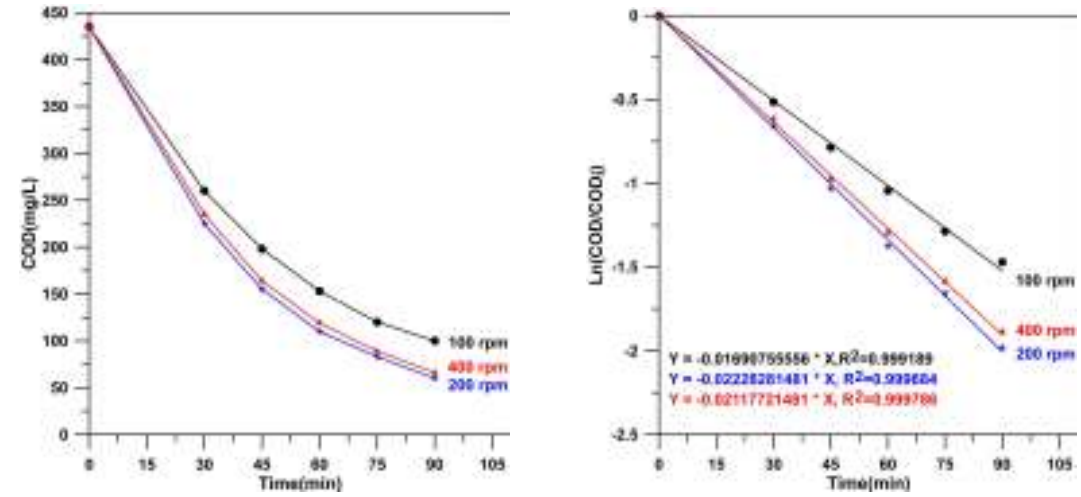
(a) COD decay with time. (b) ln(COD/CODi)versus time.

Figure 11**.** kinetic results for effect of current density.



(a) COD decay with time. (b) ln(COD/CODi)versus time.

Figure 12**.** kinetic results for effect of pH.



(a) COD decay with time. (b) ln(COD/CODi)versus time.

Figure 13**.** kinetic results for effect of rotation speed.

Table 2. Pseudo-first order rate constant at different operating variables.

Operating variables		K_{app}	R^2	HLT	RE	EEC
Parameter	Value	(min^{-1})		(min)	(%)	(kWh/kg)
Current density (mA/cm^2)	2	0.0126	0.997683	55.01	65.7	1.302
	6	0.0223	0.999684	31.08	86.2	3.648
	8	0.0181	0.999029	38.29	79.31	6.08
pH	3	0.0212	0.999875	32.69	85.05	3.406
	5	0.0223	0.999684	31.08	86.2	3.648
	7	0.0190	0.999702	36.48	81.6	3.854
	9	0.0154	0.999749	45.01	74.7	4.321
Rotation (rpm)	100	0.0169	0.999189	41.01	77	4.18
	200	0.0223	0.999684	31.08	86.2	3.648
	400	0.0212	0.999786	32.69	84.827	3.415

A similar observation was made by Brillas et al. [80] in their work on the degradation of dyes by PEC. The lowest HLT value of about 31 (min) is achieved at 6 mA/cm^2, pH 5, and 200 rpm, which is within the general range in PEC systems (3-70 min) depending on the type of pollutants, light source (solar or UV), photoanode material and current density [81]. Table 3 shows the characteristics of the wastewater after treatment. It can be seen that in addition to removing COD and reducing its value to 60 (mg/L), TDS was also reduced by 28.57%, BOD was lowered to below the standard limit (40 (mg/L), and turbidity was significantly reduced by 92.9%, as was oil content (97.85%). SO_4^{2-} increased due to the use of a supporting electrolyte, while Cl^- decreased due to the indirect oxidation of Cl^- to Cl_2 at the anode surface, which reacts with water to form ClO^-, which attacks organic compounds and converts them to CO_2 and H_2O. Therefore, the chlorine ions present in the PEC process have other advantages.

Table 3. Characteristics of the treated wastewater.

Characteristic	Initial	Final(after treatment)
pH	07.30	05.00
Turbidity, (NTU)	75.40	05.34
TDS, (mg/L)	938.0	670
COD, (mg/L)	435.00	60.00
BOD, (mg/L)	176.00	26.00
Oil, (mg/L)	163.10	03.50
SO_4^{2-}, (mg/L)	340.00	680.0
Cl^-, (mg/L)	636.00	336.00

3.6 Comparison with related works

Table 4 shows a comparison between the present work and other related works on PEC using different photoanodes and various pollutants. Most of these works focus on the removal of a single pollutant, and a few on real wastewater using either constant current density or constant anode voltage (Ea). Based on previous works, the present work yields better results in terms of pollutant removal from complex wastewater (PRW) in a short time, with low lamp power, and easy photoanode fabrication. Furthermore, to estimate the electrical energy consumption in the present work, the system was operated under optimal conditions (6 mA/cm^2, pH = 3, and 200 rpm) with a constant current of 0.18 A applied for 90 minutes, while the cell voltage was recorded in the range of 3.6–4.0 V. The calculated EEC was 110.34 $kWh/kg\ COD$, which is relatively low compared to those reported in previous studies using PEC, where the power consumption range was limited to 30–300 $kWh/kg\ COD$ [81], making the present work more feasible for industrial applications. It is important to note that the application of rotation leads to a lower applied voltage required for PEC and thus lower energy consumption.

Table 4. PEC applied to different types of pollutants in comparison with present work.

Photo anode / Fabrication method	Cathode	Pollutant	Operational conditions	RE%	Ref.
Gr /Bi-Ni-Sb-SnO_2 Electrochemical deposition	SS	PRW	6 mA/cm^2, pH=5, time=90 min, UVC(20W)	86.2	This work
TiO_2/BDD Sol-gel/Spin-coating	Graphite	Glyphosate	3 mA/cm^2, pH=4, time=300 min, UVC(9W)	99.5	[59]
TiO_2/BDD Electrophoretic Deposition	Platinum	Diclofenac	2.2 mA/cm^2, pH=5.5, time=120 min, UVC(25W)	98.5	[82]
N-rGO-TiO_2/SS Sol-gel method/dip-coating	SS	Phenol	Ea=0.8V, pH=1, time=180 min, UV-VIS (150 W)	45.0	[83]
FTO/$BiVO_4$/BiOI Electrochemical deposition	Platinum	Paracetamol	Ea=1.5V, pH=5.9, time=120 min, UV-VIS (100 W)	68.0	[84]
Sn_3O_4/TiO_2/Ti Spin-coating	DSA	Azo acid yellow 17	Ea=0.5V, pH=2.0, time=60 min, UV-VIS (125 W)	95.0	[85]
Ti/TiO_2(NT) Electrochemical anodization	Graphite	Real oil-produced water	Ea=2.5 V, time=120 min, UVC(36W)	73.0	[86]
TiO_2/Ti sol–gel	Titanium	Oil Field wastewater	Ea=30V, pH=2.0, time=240 min, UVC(50 W)	47.4	[87]
$BiVO_4$/FTO Electrochemical deposition	Hemin / Cu Carbon felt	Tetracycline	Ea=0.8V, pH=5.9, time=120 min, xenon lamp	60.6	[88]

4. Conclusion

The results of this study demonstrate that the PEC system is an efficient and environmentally friendly technology for treating industrial wastewater from petroleum refineries. RE% was found to be strongly influenced by three operating factors: current density, pH, and anodic rotation speed. The best results were obtained at a current density of 6 mA/cm^2, pH 5, and a rotation speed of 200 rpm, where an RE% of 86.2% was achieved. The anode rotation speed plays a significant role in the degradation efficiency due to improved mass transfer; however, very high speeds have a minimal effect and are associated with increased energy consumption. The kinetic study showed that COD followed a pseudo-first-order model for all parameter conditions, indicating that the degradation rate depends on the COD concentration, while the concentration of the reactive reagents is assumed to be constant during PEC. The scavengers test revealed that OH is the dominant radical in COD degradation, indicating that the oxidation process is controlled by OH. The Gr/Bi-Ni-Sb-SnO_2 photoanode demonstrated excellent reusability after five cycles, indicating its robust structural stability and resistance to deactivation. The adoption of concentric configuration of the electrode with rotation of anode makes the present system more feasible to scale-up as the rotation effect improves current and voltage distribution uniformly with ensuring good light absorption with minimal fouling. Overall, this study demonstrates that PEC technology, utilizing advanced photoanodes such as Gr/Bi-Ni-Sb-SnO_2, effectively removes organic and petroleum pollutants with lower energy consumption and a reduced negative environmental impact. Therefore, this technology can be considered a promising approach for industrial wastewater treatment and promoting more sustainable water resource management.

Authors' contribution

All authors contributed equally to the preparation of this article.

Declaration of competing interest

The authors declare no conflicts of interest.

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Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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