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Original Article

Simultaneous studies on solar energy storage by CO₂ reduction to HCOOH with Brilliant Green dye removal photoelectrochemicallyV.S.K. Yadav^{*}, M.K. Purkait

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ABSTRACT

The simultaneous study on photoelectrochemical CO₂ reduction with Brilliant Green (BG) dye removal was studied in the present work. Experimental studies were done in aqueous solutions of sodium and potassium based electrolytes using a cathode [Zinc (Zn) and Tin (Sn)] and a common cobalt oxide (Co₃O₄) anode electrocatalyst. The influence of reaction with electrolyte concentration for the both catalysts was shown clearly with respect to time. The selected electrocatalysts were able to reduce CO₂ to formic acid (HCOOH) along with high BG dye removal. With Sn as cathode, the maximum BG dye removal was obtained to be KHCO₃–[95.9% (10 min)–0.2 M], NaHCO₃–[98.6% (15 min)–0.6 M]. Similarly for Zn, KHCO₃–[99.8% (10 min)–0.4 M], NaHCO₃–[99.9% (20 min)–0.8 M] were observed respectively. Finally, the results have proven that higher efficiencies for BG dye removal were obtained along with HCOOH formation, which might be a better alternate for water purification and to decrease the atmospheric CO₂ concentrations.

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1. Introduction

Currently, the world is facing the problem of global warming effect due to the increase in atmospheric CO₂ concentrations by the combustion of fossil fuel during energy generation [1–3]. To resolve this problem, the major aim is to convert CO₂ to some valuable products which can be used as a fuel for our future generation [4,5]. Multiple processes using various electrocatalysts and electrolytes were reported for the CO₂ reduction with different applied conditions [6,7]. The removal of dye which generally comes from textile industries using various methods have been reported [8,9]. If the wastes dye solution can be used for proton generation in the CO₂ reduction process which might be another application. However, reduction of CO₂ photoelectrochemically is the finest method due to the usage of a free source of solar energy for converting CO₂ to fuel [10–13]. Different studies have been reported on photoelectrochemical process using various parameters like electrocatalyst [14–16], electrolytes [17–19] and their effect on CO₂ reduction for generating various products. However, studies on the photoelectrochemical CO₂ reduction were first reported in 1978

and exposed the effect of electrocatalysts towards various product formations [20]. A review for the CH₃OH production using a renewable energy source was reported on different materials in the designed photoelectrochemical cell [21]. Yuan et al. studied the photoelectrochemical process for the methanol formation using free solar energy on a fabricated copper indium alloy [22]. Peng et al. studied the CO₂ reduction photoelectrochemically on TiO₂ (anode) and copper (cathode) along with methyl orange dye removal. The studies reported the formation of different products like HCOOH, CH₃OH, HCHO, CH₄ and H₂ respectively [23]. The solar driven CO₂ reduction with azo-dye removal on Cu cathode and Pt anode electrocatalyst were reported in potassium based electrolyte solutions [24]. Adachi et al. studied the photo catalytic CO₂ reduction to different hydrocarbons like CH₄, C₂H₄ and C₂H₆ on Cu–TiO₂ electrocatalyst [25]. The lone HCOOH formation from CO₂ reduction was shown using Zn catalyst in various electrolyte solutions [26]. Jin et al. showed the solar driven CO₂ reduction on autocatalytic Zn electrocatalyst for HCOOH generation [27]. The photoelectrochemical reduction of CO₂ was reported using solar energy on different synthesized copper particles modifying with graphene oxide as efficient photo electrodes [28]. Similarly, the effect of Rubidium photo electrocatalyst was studied and effect of different electrolytes (Di methyl acetamide and dimethyl formamide) in reduction of CO₂ was shown [29]. The reported studies have shown the formation of multiple products during CO₂ reduction on

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different applied conditions which makes the system complex. The process becomes more feasible if CO₂ can be converted into a single product. For which, several studies were already reported for single product (HCOOH) on different synthesized electrocatalysts by electrochemical CO₂ reduction using Pt as anode [30–34].

The present work shows the outcome of using low-cost Co₃O₄ as anode replacement with Pt and Zn, Sn as a cathode for CO₂ reduction along with BG dye removal using solar energy. The studies were done for the first time for simultaneous water purification by BG dye removal and HCOOH production in order to decrease atmospheric CO₂ concentrations. The process is very important because instead of using pure water as a reactant for oxidation reaction that can be replaced with dye water from textile industries for H⁺ generation. Similarly, the dye can be removed from the wastewater by oxidation at anode along with CO₂ reduction at the cathode [23,24]. The present studies show the use of cathode and anode combinations [Sn–Co₃O₄ and Zn–Co₃O₄] for simultaneous BG dye removal with HCOOH generation. A 2-electrode cell was used here to study the effect of catalysts in various electrolyte concentrations by the photoelectrochemical process and respective results were clearly explained. The studies give the future reference for water purification along with the CO₂ reduction using a free solar energy in order to develop a feasible process.

2. Experimental

2.1. Materials

Graphite plates (1.5 × 2.5) cm² and Solar panel [8.8 V 340 mA] were obtained from Sunrise Enterprises, Mumbai and Waare Energies Pvt. Ltd, Surat, India, respectively. NaHCO₃, KHCO₃, isopropyl alcohol and Brilliant Green dye [Merck, India]. Nafion (5 wt.%) was procured from DuPont, USA. All Chemicals without any further purification along with the deionized water used for all experimental studies.

2.2. Preparation of electrodes for anode and cathode

The electrodes were prepared by a catalyst ink coating on the graphite plates. The ink was made by adding 7.5 mg of synthesized catalysts to the 1:5 (nafion :iso propyl alcohol) binders of 200 μl solutions and further 30 min sonication to get the electrocatalyst ink. The ink was layered on a graphite plate and dried for 2hr (80 °C) to get an electrode loading of 2 mg/cm².

2.3. Photoelectrochemical studies for CO₂ reduction and BG dye removal

The studies were carried out in a 2-electrode cell for simultaneous BG dye removal and CO₂ reduction. The photoelectrochemical setup used in the present work was presented in Fig. 1.

For all experiments, 80 ml of solution along with 10 ppm dye electrolyte was bubbled for 50 min with the CO₂ to get CO₂ saturated solution. The prepared anode and cathode were connected to a solar panel by dipping in the CO₂ saturated solution. The reduction process was studied in different electrolyte concentrations of 0.2, 0.4, 0.6 and 0.8 M solutions for reaction times of 0–5, 10, 15, 20 and 25 min respectively.

2.4. Product analysis with BG dye analysis

Ultra-fast liquid chromatography <Shimadzu LC-20AD, UV-detector of deuterium lamp (SPD-20A)> at 205 nm using C-18 column (10 × 4 mm) was used for analyzing the reacted solution. 5 mM

(Tetrabutyl ammonium hydrogen sulfate) as the mobile phase at 1 ml/min flow rate was used. UV-Visible Spectrophotometer (Perkin Elmer, Model: Lambda 35) was used for BG dye removal analysis.

3. Results and discussion

3.1. CO₂ reduction photoelectrochemically and BG dye removal using Sn

The experiments were done using an anode (Co₃O₄/G) and cathode (Sn/G) electrodes for CO₂ reduction and BG dye removal. Different electrolyte concentrations of 0.2, 0.4, 0.6 and 0.8 M were used to study the reaction by varying reaction times was discussed in detail.

3.1.1. CO₂ reduction and BG dye removal photoelectrochemically in KHCO₃ solution

The results for simultaneous studies in KHCO₃ solution was shown in Fig. 2a, c. The studies for methyl orange dye removal with a CO₂ reduction on copper electrocatalyst was reported in potassium based electrocatalyst [23]. For a reaction in 0.2 M, the HCOOH formation of 245.9, 102.3, 247.2, 231.5 and 193.5 μmol was obtained with BG dye removal of 95.4, 95.9, 95.06, 95.4 and 93.3% respectively. The improved reaction condition for the maximum HCOOH formation is 247.2 μmol for 15 min. Moles of HCOOH formation are varying with time, which is due to oxidation of formed product at Co₃O₄ anode [26]. For the case of photoelectrochemical studies in 0.4 M solution a mole of 397.2, 129, 219.1, 182.07 and 371.5 μmol (Fig. 2a), were obtained by BG removal in 93.7, 94.9, 95.02, 95.1 and 94.8%.

Moles of HCOOH (166.9, 431.9, 205.5, 245.4 and 217.3 μmol) and BG removal (92.8, 93.3, 93.7, 94.06 and 93.1%) were obtained in 0.6 M electrolyte solution. The maximum BG removal was observed in reaction time of 20 min with 94.06%. The concentration of product at different times was changing may be due to the conductivity of the electrolyte solution. The low product formation corresponds to the availability of more protons at the cathode surface leads to hydrogen evolution [32]. The studies for HCOOH formation using lead electrocatalyst was reported in KHCO₃ electrolyte solution without dye [36]. The reaction in 0.8 M shows the photoelectrochemical results of HCOOH (227.6, 126.3, 208.3, 210.8 and 212.3 μmol) with BG removal 92.4, 92.1, 90.4, 91.1 and 91.4% (Fig. 2c). Overall, maximum dye removal was observed irrespective of electrolyte concentrations with HCOOH formation.

3.1.2. Reduction of CO₂ and BG dye removal photoelectrochemically in NaHCO₃ solution

The results in NaHCO₃ electrolyte solution for simultaneous BG removal and HCOOH formation were given in Fig. 2b, d. The formation of HCOOH (289.1, 276.6, 137.4, 145.8 and 139.8 μmol) and BG dye removal (89.2, 95.6, 94.4, 96.8 and 98.2%) was obtained for a reaction in 0.2 M electrolyte solution. The optimized reaction condition for maximum formation is 289.1 μmol (5 min) and removal 98.2% (25 min) was observed. The effect of CO₂ reduction without dye has been studied using Sn as an electrocatalyst in KHCO₃ based solution for the HCOOH production [35]. Jin et al. studied the solar driven CO₂ reduction in sodium electrolyte-based solution on Zn catalyst for HCOOH generation [27]. For the reaction in a 0.4 M solution, a mole of HCOOH formed to be 107.5, 308.4, 163.2, 255.5 and 340.4 μmol (Fig. 2b) with BG dye removal (96.8, 98.07, 98.2, 98.06 and 98.4%) was obtained. The change in HCOOH formation with time corresponds to the oxidation of forming product at anode for the generation of hydrogen gas at anode [31]. Peng et al. studied on copper electrocatalyst using Pt anode for simultaneous methyl orange dye removal with CO₂

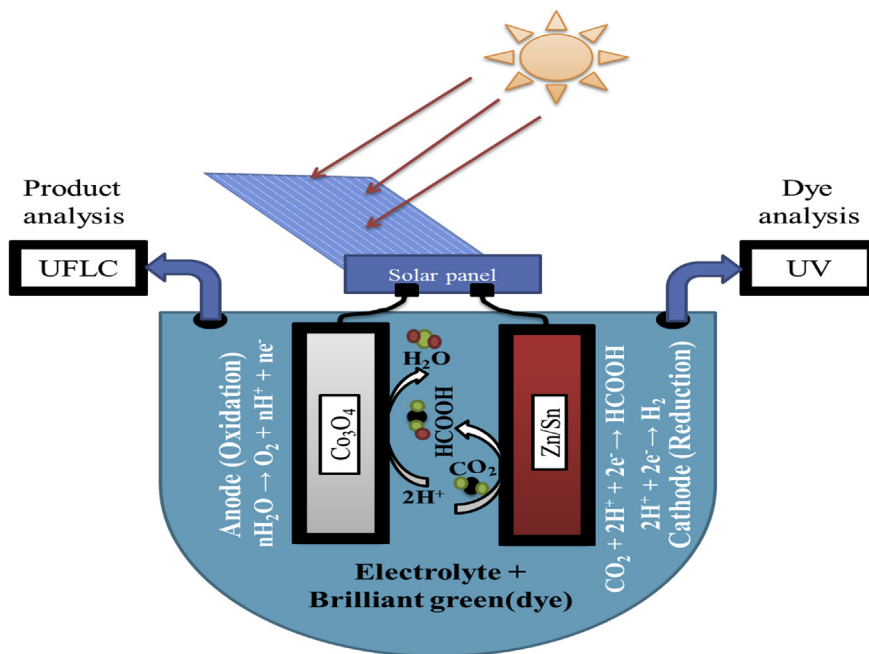


Fig. 1. Schematic setup for CO_2 reduction and BG dye removal photoelectrochemically.

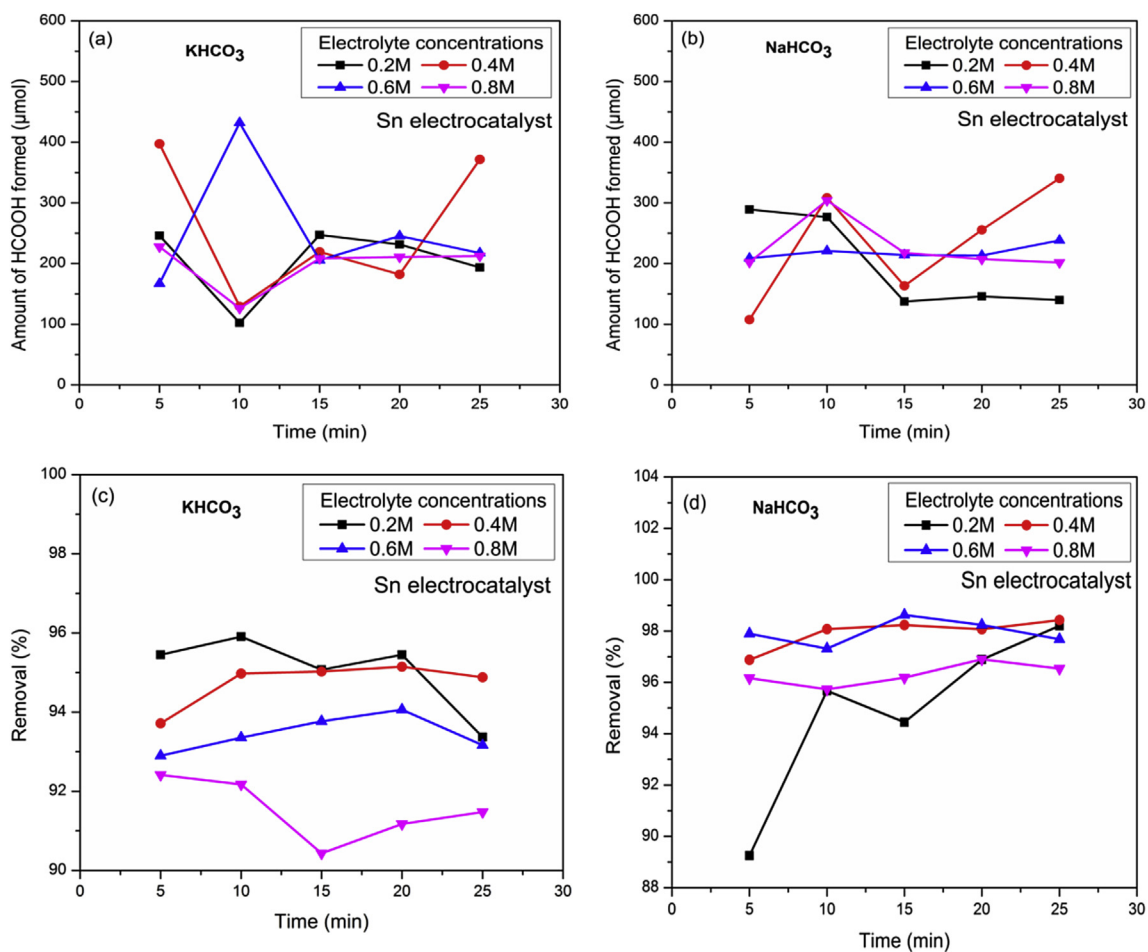


Fig. 2. Moles of HCOOH formed with time using (a) KHCO_3 (b) NaHCO_3 and BG dye removal (%) with Time in (c) KHCO_3 (d) NaHCO_3 on Sn electrocatalyst.

reduction [24]. The studies for solar driven CO_2 reduction to different products like methanol and formaldehyde were reported on copper electrocatalyst modified with graphene particles [28]. The photoelectrochemical studies in a 0.6 M solution were obtained to be HCOOH (208.7, 220.8, 214.2, 213.1 and 238.1 μmol) and BG dye removal of 97.8, 97.3, 98.6, 98.2 and 97.6% (Fig. 2d) respectively. The maximum dye removal of 98.6% was observed at 15 min reaction. The low product formation was due to the evolution of hydrogen on cathode by forming protons at anode [30]. HCOOH (202.1, 303.9, 217.6, 207.2 and 201.7 μmol), BG removal (96.1, 95.7, 96.1, 96.8 and 96.5%) were observed as experimental results for reaction in 0.8 M solution. The enhanced condition for the maximum HCOOH formation was 303.9 μmol for a reaction time of 5 min. The studies were shown the performance of using Sn as a cathode was shown in potassium and sodium based electrolytes with the Co_3O_4 anode for HCOOH generation.

3.2. Photoelectrochemical CO_2 reduction and BG removal on Zn

The effect of using Zn as a cathode and Co_3O_4 anode for simultaneous CO_2 reduction and BG dye removal was studied in KHCO_3 and NaHCO_3 electrolyte solutions. Formic acid was obtained as a product in all applied conditions with maximum BG dye removal.

3.2.1. Reduction of CO_2 and BG dye removal photoelectrochemically in KHCO_3 solution

The photoelectrochemical studies in different KHCO_3 electrolyte solutions were shown in Fig. 3a, c. In 0.2 M solution, 408.2, 372.7,

328.3, 281.1 and 151.5 μmol of HCOOH formation and BG dye removal (99.3, 99.72, 99.72, 99.6 and 99.3%) were obtained. The optimized reaction conditions for maximum HCOOH [408.2 μmol (5 min)] and the BG removal [99.7% (15 min)] were observed. The variation in product moles with time was due to HCOOH oxidation [26]. The studies on photoelectrochemical CO_2 reduction with methyl orange dye removal on copper electrocatalyst was reported [23]. HCOOH (94.2, 156.3, 175.09, 516.3 and 279.6 μmol) and BG dye removal (99.6, 99.8, 99.94, 99.97 and 99.9%) were obtained for a reaction in 0.4 M electrolyte solution. The photoelectrochemical studies in 0.6 M electrolyte solution were observed with HCOOH formation of 271.8, 279.6, 464.1, 203.4 and 218.5 μmol (Fig. 3a) along with BG removal (99.5, 99.6, 99.7, 99.7 and 99.6%) respectively. The maximum HCOOH formation of 464.1 μmol was happened after 15 min reaction.

The solar-driven process for methanol formation from a CO_2 reduction on copper based electrocatalyst was reported [22]. For a reaction in 0.8 M electrolyte solution low HCOOH formation (210.7, 312.4, 243.1, 299.02 and 222.5 μmol) with BG dye removal of 99.4, 99.6, 99.6, 99.5 and 99.5% (Fig. 3c) were obtained. Low product formation is due to the hydrogen formation at the cathode surface [28].

3.2.2. CO_2 reduction and BG dye removal photoelectrochemically in NaHCO_3 solution

The results in NaHCO_3 solution using Zn as a cathode was shown in Fig. 3b, d. Solar-driven studies on CO_2 reduction in NaHCO_3 electrolyte on Zn catalyst was shown for HCOOH generation [27]. The photoelectrochemical studies in 0.2 M electrolyte solution for

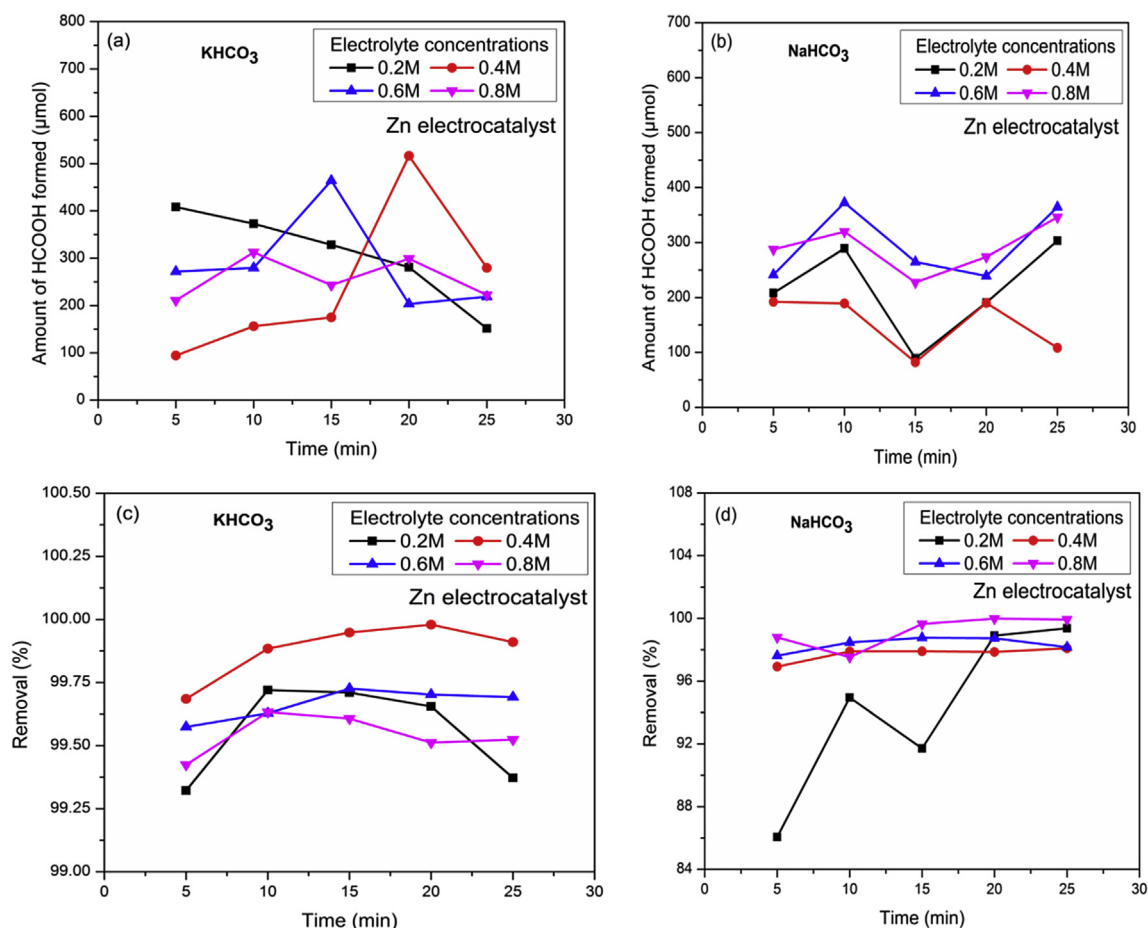


Fig. 3. Moles of HCOOH formed with time using (a) KHCO_3 (b) NaHCO_3 and BG dye removal (%) with Time in (c) KHCO_3 (d) NaHCO_3 on Zn electrocatalyst.

Table 1
Maximum HCOOH formation in different electrolytes.

Molarity (M)	Moles of HCOOH							
	Sn				Zn			
	KHCO ₃		NaHCO ₃		KHCO ₃		NaHCO ₃	
	μmol	(min)	μmol	(min)	μmol	(min)	μmol	(min)
0.2	247.2	15	589.1	5	408.2	5	303.2	25
0.4	397.2	5	340.4	25	516.3	20	192.1	5
0.6	431.9	10	238.1	25	464.1	15	364.2	25
0.8	227.6	5	303.9	10	312.4	10	345.9	25

Table 2
Maximum BG dye removal in different electrolytes.

Molarity (M)	BG dye removal (time)							
	Sn				Zn			
	KHCO ₃		NaHCO ₃		KHCO ₃		NaHCO ₃	
	(%)	(min)	(%)	(min)	(%)	(min)	(%)	(min)
0.2	95.9	10	98.2	25	99.72	10	99.3	25
0.4	95.1	20	98.4	25	99.97	20	98.08	25
0.6	94	20	98.6	15	99.72	15	98.76	15
0.8	92.4	5	96.8	20	99.63	10	99.98	20

BG dye removal (86.06, 94.9, 91.7, 98.9 and 99.3%) and HCOOH (208.05, 289.1, 89.08, 190.7 and 303.2 μmol) were obtained. The optimized reaction conditions for HCOOH formation is 289.1 μmol for a reaction time of 10 min. The sudden decrease in HCOOH formation after 15 min reaction is due to forming product oxidation at anode [31]. HCOOH (192.1, 189.2, 82.2, 190.1 and 108.4 μmol) (Fig. 3b), BG dye removal (96.9, 97.89, 97.89, 97.86, 98.08%) were obtained respectively. The optimized reaction conditions for maximum dye removal of 98.08% (25 min) and HCOOH formation of 192.1 μmol (5 min) were observed. The effect of CO₂ reduction to HCOOH electrochemically was studied without dye solution using Zn electrocatalyst in sodium-based electrolyte solution [26]. In the case of 0.6 M electrolyte solution, HCOOH formation of 241.3, 372.4, 264.7, 239.2 and 364.2 μmol and BG dye removal (97.6, 98.4, 98.76, 98.73 and 94.1%) were obtained. In 0.8 M electrolyte concentration, the BG dye removal and HCOOH formation were observed to be (287.2, 319.5, 227.3, 273.9 and 345.9 μmol), (98.7, 97.5, 99.6, 99.98 and 99.92%) (Fig. 3d). Low product formation is due to the hydrogen formation at cathode [34]. The effect of electrocatalysts was studied for HCOOH formation with maximum BG dye removal within a short span of time. The maximum HCOOH formation and BG dye removal using different electrocatalyst of Sn, Zn as a cathode to C₃O₄ anode in sodium and potassium based solutions were given in Tables 1 and 2 respectively.

4. Conclusion

A new approach has been studied for simultaneous water purification by BG dye removal along CO₂ reduction to HCOOH photoelectrochemically. Maximum BG dye removal was obtained in all different electrolyte concentrations in fewer spans of reaction with HCOOH formation. The studies were clearly proved that the selected electrocatalysts can be used for CO₂ reduction along with BG dye removal. The maximum HCOOH formation was obtained with KHCO₃–[431.9 μmol (10 min)–0.6 M], NaHCO₃–[340.4 μmol (25 min)–0.4 M] using Sn as an electrocatalyst. In the case of Zn electrocatalyst, KHCO₃–[516.3 μmol (20 min)–0.4 M], NaHCO₃–[364.2 μmol (20 min)–0.6 M] were obtained. The present

study shows the way to proceed for a simultaneous higher BG dye removal rate with HCOOH formation using a free source of solar energy.

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