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Efficient Persulphate Mediated Electrooxidation of Substituted Benzyl Alcohols in Biphasic Media

A.ViniPriya, A.John Bosco, T. Maiyalagan, N. Xavier*, D. Vasudevan*

* Department of Chemistry, St.Joseph's College, Tiruchirapalli, Tamilnadu, India
Department of Chemistry, SRM University, Faculty of Science and Humanities,
Kattankulathur- 603 203, Chennai, India
* SRM Research Institute, Department of Chemistry, SRM University, Kattankulathur-603203,
Chennai, India
Electrodics Division, Central Electrochemical Research Institute, Karaikudi, Tamilnadu, India
* E-mail: maiyalagan@gmail.com

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This paper discusses the electro oxidative conversion of *p*-methoxybenzylalcohol (*p*-MBA) to *p*-anisaldehyde which was effected at a graphite anode in a biphasic media using persulphate as the mediator. Electrolysis conditions were optimized based on current density, electrode material, temperature, solvent, inorganic salt mediator and pH of the reaction system. The present investigation endowed with excellent yield of *p*-anisaldehyde (97%) under the best reaction conditions by tuning the electrolysis conditions along with a simple reaction set up .The optimized conditions were extended for the oxidation of other substituted benzyl alcohols and promising yields were obtained. A plausible mechanism for the oxidation of *p*-methoxy benzyl alcohol has been proposed.

Keywords: Selective oxidation, Biphasic media, Green Chemistry, Electro oxidation, Redox reaction *p*-methoxybenzyl alcohol

1. INTRODUCTION

Production of carbonyl compounds from alcohols is widely documented as one of the most important problems in organic synthesis as well as in process and medicinal chemistry. Carbonyl compounds are regarded as prominent intermediates to the assembly of a wide variety of natural products as well as bioactive molecules [1]. Nevertheless, the oxidation of alcohols to the corresponding carbonyl compounds is one of the most fundamental and important transformations in synthetic organic chemistry. They serve as crucial precursors of drugs, dyes and fine chemicals and hence this topic has attracted much attention in chemical research during the last few decades [2-3].

Most of the classically adopted methods for the alcohol oxidation have been perplexing from various constraints such as large reaction times, expensive toxic metals, stringent experimental conditions and solvent waste into the environment [4]. Most of the inorganic oxidants hitherto employed for alcohol oxidation produce large amount of spent reagent making the process not eco-friendly.

Although progress towards the catalytic oxidation of alcohols with the use of water soluble heame enzymes containing Rh(III), Fe(III), Mn (III) [5-7], and combination of transition metal salts with polyoxometallates have been reported earlier, but the success of these studies is attained less mildly [8-13].

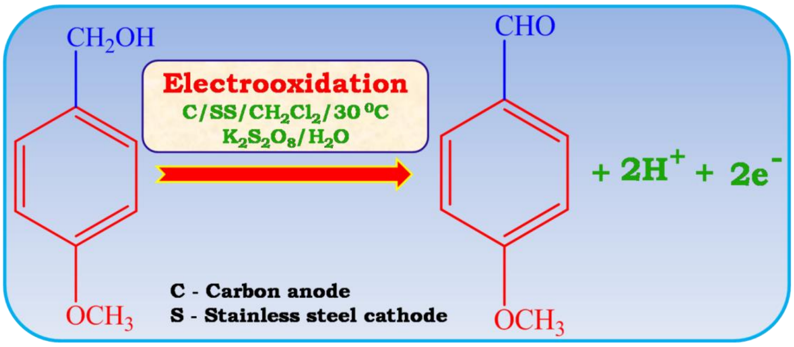
Recently, considerable attention has been focused on the development of efficient catalyst systems, both homogeneous (eg. Ru, Pd, Cu monometallic complexes, bi-metallic complex systems) and heterogeneous (eg. metal catalysts and supported catalyst, including mesoporous materials, zeolites etc), for alcohol oxidation [2-4, 14, 15]. At present, only a few reports are available related to environmentally benign reagents such as silica-supported reagents [16] and graphite-supported platinum catalysts [17] for the synthesis of aldehydes.

Although the use of *p*-methoxy benzylalcohol are versatile and powerful oxidant that have been extensively applied for the oxidative conversion reactions [18]. For example, O.Levent et al [19] reported that upon treatment with H_2O, *p*-methoxy benzylalcohol underwent photoelectrocatalytic selective conversion reactions. Employing the same concept, Jr.P.J. Bonitatibus et al [20] reported that the Iridium based functionalized *p*-methoxybenzyl alcohol gave a corresponding *p*-methoxy benzaldehyde as a conventional product.

Water soluble persulfate mediators are expected to show substantially excellent yield for the electro oxidation process. However, persulphate is a widely used oxidizing agent in organic chemistry [21]. Persulfate coated electrode [22] has been widely used as a mild and selective oxidizing agent and in *in-situ* oxidation of polychlorobiphenyls (PCBS) in low permeability soils using persulfate as an oxidant. Goyal et al [23] collectively, shows the use of persulfate mediated electrochemical oxidation of Indole-3-ethanol to the corresponding hydroxyl dimer.

Electrochemical synthesis provides an alternative greener technologies over regular homogenous processes in that they avoid the use of large quantities of noxious or corrosive reagents [24]. These methods offer numerous advantages over conventional methods; moreover the use of biphasic media offers several advantages in practical organic synthesis [25, 26]. Recent works by Christopher [27] and others [28 -29] have shown the electro oxidation of benzyl alcohols in biphasic media.

Our ongoing interest in biphasic electrolysis [30,31], here in we wish to report an efficient persulphate mediated electrooxidation of *p*-methoxybenzyl alcohol to *p*-anisaldehyde in biphasic media at room temperature as shown in Scheme 1. No extra supporting electrolyte is required, thus this method simplifies the work-up, separation process and decrease in the waste product. The progressive work can be carried out in beaker type cell. To the best of our knowledge this is the first work with the electrochemical synthesis of the substituted benzylalcohol using persulfate as a redox mediator.



Scheme 1. Persulphate mediated electrooxidation of substituted benzyl alcohols

2. EXPERIMENTAL DETAILS

2.1. Chemicals and Materials

All the chemicals employed in this work were procured from Sigma Aldrich and S.D. Fine Chemicals Ltd for direct use without further purification. The chemical reagents were all analytical grade and directly used as supplied. All aqueous solutions were prepared with deionized water. The melting points were verified in capillary tubes measured with an Elchem lab melting point apparatus. (thin layer chromatography) TLC spots visualized in TLC plates were triggered by (Ultra violet) UV illumination, which were then exposed to iodine vapour.

2.2 Procedure for the oxidation of p-methoxy benzyl alcohol by Galvanostatic electrolysis

In an undivided cell (a 250 ml beaker), *p*-methoxybenzyl alcohol (1.53 g, 10 mmol) dissolved in 20 ml dichloromethane was taken. To this, 90 ml of aqueous potassium persulfate (6g, 25.1 mmol) having trivial sum of sulphuric acid was added. Graphite and stainless steel each of area 8 cm^2 were used as the anode and cathode respectively. They were carefully placed in the upper aqueous phase very close to the interphasial region. The aqueous phase acted as the supporting electrolyte. The lower organic phase was stirred with a magnetic pellet at a rate of 50 rpm. The organic layer did not touch the electrodes. Galvanostatic electrolysis was conducted in the current density range of 20 to 90 mA cm^{-2} at a temperature of 30± 1°C. Two faraday of charge per mole of *p*-methoxybenzyl alcohol was passed. The *in-situ* generated persulfate radical ion in the aqueous phase acted as the mediated electron carrier. After the theoretical time of electrolysis, the electrolysis was further continued till the yield reached a maximum value. At the completion of electrolysis, the magnetic stirring was stopped. The lower organic phase was carefully separated. The aqueous phase was extracted with chloroform (2×25 mL). The combined organic phase was extracted with water (2× 25 mL), dried over anhydrous sodium sulphate and the solvent was removed by distillation. HPLC analysis of the residue showed the presence of 97 % *p*-anisaldehyde (1.18 g). The product was isolated by column chromatography and characterized by NMR Spectroscopy. ^1H NMR (400 MHz, $CDCl_3$): δ 9.8 (s, **1H**), 7.77-7.75(d, **2H**), 6.94-6.92**(d, 2H)**, 3.80 (s, **3H)**. Silica was used as the adsorbent, and methanol (HPLC grade) was the eluent used for HPLC studies. The flow rate was 0.2 mL/min. Ultraviolet (254 nm) was used as detector. One microliter of the sample was injected into the coloumn.

2.3. Physical Characterisation.

Physical phases and compound formation were identified by ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ at 100 MHz or 125 MHz on Brucker-400 NMR spectrometer using TMS as internal standard. IR spectra were recorded on Perkin-Elmer100 Spectrochem series using KBr pellets. HPLC were performed on a SHIMADZU LC-8A pump (250 mm × 4.6 mm) as the stationary phase. The eluent consisted of acetonitrile / water (80:20). The flow rate was maintained at 1ml/min. Samples were analyzed at a wavelength of 254 nm with a UV detector. All the compounds were identified by comparison of their spectral data and physical properties with those of the authentic sample and all yields refer to isolated products. Deionized water was used for preparing potassium persulfate solution and supporting electrolyte.

3. RESULTS AND DISCUSSION

To understand the nature of the catalytic reaction and to optimize the reaction variables such as current density, charge passed, amount of catalyst, catalyst concentration, solvent, temperature and agitation, we started our investigation by using *p*-methoxy benzyl alcohol as a model substrate. The completion of the reaction was monitored through gas chromatography (GC). The results of the galvanostatic electrolysis of *p*-methoxybenzyl alcohol as functions of current density, organic phase solvent, electrode materials and temperature are discussed.

3.1 Effect of Current Density on the oxidation of p-methoxy benzyl alcohol

Table 1. Effect of current density on electrochemical synthesis of *p*-anisaldehyde at graphite anode in room temperature 30±5°C, Charge Passed: 2F/mol

S. No.	Current Density (mA cm^{-2})	Time (min)	Yield[†] (%)	Current efficiency (%)
1	20	116	83	83
2	30	77	74	74
3	45	52	67	67
4	60	39	69	69
5	75	31	64	64
6	90	26	62	62

Reaction Condition: *p*-methoxy benzyl alcohol (10 mmol), CH_2Cl_2 (20mL), $K_2S_2O_8$ (1.53g, 10 mmol), H_2O (90 mL).[†]Yield of *p*-anisaldehyde based on the amount of alcohol taken

Various current densities applied at anode, benzyl alcohol gets oxidized and form *p*-anisaldehyde which is tabulated in table1. The highest yield of *p*-anisaldehyde found at current density of 20 mAcm^{-2}. At higher current densities, the yield started to decrease substantially. This is probably due to the competing oxygen evolution reaction which becomes more predominant with increase the current density [Supplementary Figure 4]. Though the intial current density shows that higher in the yield of the product, higher is the current efficiency with minimum current density was applied, while the previous report shows that [28-29] decrease in the yield of the product with maximum current density. Thus the present work shows superior to the other works.

3.2 Effect of Solvents on the oxidation of p-methoxy benzyl alcohol

Persulfate mediated oxidation of *p*-methoxy benzylalcohol has been conducted in various chlorinated hydrocarbons [Table 2]. Various solvents are used namely, dichloromethane, carbon tetrachloride and chloroform and the yield was obtained about 95, 84 and 89% respectively. Though the % of yield is almost same in all the solvents but current efficiency is more when dichloromethane is used as solvent. Dichloromethane may also be preferred for lesser degree of chlorination. However the reaction was studied in acetonitrile and ethanol solvents the converted yield is low as compared to the other solvents and also solubility difficult arose when acetonitrile was used as solvent.

M.Balaganesh et al studied [31] that, product became less when optimizing with the different solvents, this may be the formation of black polymer like slurries are passivated on the anode surface which block the electrode surface area and subsequently reduces the current efficiency, but in the present report there is no presence of polymer product on the electrode surface. This was the first attempt there is no passivation formation on the electrode surface, and this brought to the higher yield in the product.

Table 2. Effect of solvents on electrochemical synthesis of *p*-anisaldehyde at graphite anode in room temperature 30±5°C, Charge Passed: 2F/mol

S.No.	**Solvents**	**Time (min)**	**Yield† (%)**	**Current efficiency (%)**
1	$CHCl_3$	38	89	35
2	CH_2Cl_2	78	95	63
3	CCl_4	116	84	35

p- methoxy benzylalcohol (10 mmol), CH_2Cl_2 (20 mL), $K_2S_2O_8$ (1.53 g, 10 mmol), H_2O (90 mL).
†Yield of *p*-anisaldehyde based on the amount of alcohol taken.

3.3 Effect of electrodes on the oxidation of p-methoxy benzylalcohol

Table 3. Effect of Electrodes on electrochemical synthesis of *p*-anisaldehyde at graphite anode in room temperature 30±5^{o}C, Charge Passed: 2 F/mol

S. No.	**Electrodes**	**Time (min)**	**Yield**[†] **(%)**	**Current efficiency (%)**
1	[a] Pt/Ag	55	82	82
2	Pt/Pt	45	95	95
3	[b] Pt/SS	120	90	90
4	C/C	135	94	94
5	[c] C/Ag	70	93	93
6	[d] C/SS	75	97	97
7	Ag/Ag	80	94	94

[a] Pt /Ag = Platinum/Silver, [b] Pt /SS=Platinum/Stainless steel, [c] C/Ag = Graphite/Silver,
[d] C/SS = Graphite/Stainless steel .
p- methoxy benzylalcohol (10 mmol), CH_2Cl_2 (20 mL), $K_2S_2O_8$ (1.53 g, 10 mmol), H_2O (90 mL).
[†]Yield of *p*-anisaldehyde based on the amount of alcohol taken.

Electrode variation is another important parameter for the oxidation of *p*-methoxybenzyl alcohol. The effect of anode and cathode pair on the product yield were studied from [Table 3]. The yield of product varied slightly with the use of different pairs of anode and cathode materials such as Graphite/stainless steel, platinum/platinum, platinum/stainless steel, graphite/silver, silver/silver and graphite/graphite used for electrooxidation. Pt is expensive and so graphite is the preferred anode material. Stainless steel is cheap and so is the best cathode material for biphasic electrolysis.

In particular, the earlier report shows the benefits of platinum as an anodic material for the electrolytic conversion [32, 33], however platinum is very expensive material it has been found that yield is comparative less to the present investigation, when using carbon as an anodic material for the electrolytic conversion.

Employing the same concept, Daniel et al have been reported the use of glassy carbon as an anode [34] for the electrolytic conversion of benzoxole in NaI as a redox mediator using buffer system for improving the product, but the present work shows there is no further additional solvent to increase the yield, so from the above describe results we conclude that the optimal promising electrodes for the conversion of *p*-methoxybenzyl alcohol is carbon anode and stainless steel cathode.

3.4 Effect of Temperature on the oxidation of p-methoxy benzyl alcohol

With the view to increase the yield of the *p*-methoxybrenzaldehyde, the present study is expanded to one more temperature parameter. Table 4 shows the effect of temperature on the yield of the desired product. At 0-10°C the yield was around 57%.Maximum yield of *p*-anisaldehyde was observed when the temperature attained room temperature of 30–35°C. Above 40°C, the evaporation of organic solvent is more and also it does not favours the oxidation of substrate. The yield of *p*-anisaldehyde is maximum at 30-35°C.

R.Jegadeesan and co-workers [29] collectively studied the temprature based electroxidation of bromination in which increasing the higher temprature moderated yield was found , but in the present case the current efficiency and product yield are seems to be higher in room temprature and this methodology shows which is more greater than other electrocatalytic conversions.

Table 4. Effect of Temperature on electrochemical synthesis of *p*-anisaldehyde at graphite anode in room temperature 30±5°C, Charge Passed: 2 F/mol

S. No.	**Temperature**	**Time (min)**	**Yield [†] (%)**	**Current efficiency (%)**
1	0 -10°C	28	59	59
2	30–35°C	30	97	97
3	40- 60°C	35	50	50

p- methoxy benzylalcohol (10 mmol), CH_2Cl_2 (20 mL), $K_2S_2O_8$ (1.53g, 10 mmol), H_2O (90 mL).
[†]Yield of *p*-anisaldehyde based on the amount of alcohol taken.

3.5 Effect of Agitation on the oxidation of p-methoxy benzyl alcohol

Agitation rate for the effective electro oxidation of *p*-methoxybenzyl alcohol was studied at different rpm level of 10-90rpm [Table 5]. To achieve higher yield Jing shan do et al adjusted to a rotating speed sufficiently high as 600 rpm for the electrolytic conversion of benzylalcohol by using tetrabutyl ammonium sulfate as a phase transfer catalyst [35], but the present work observed substantially higher yield at lower rotation speed (50 rpm) than normally is obtained under static conditions. Even at much lower rotation speed (10 rpm) moderate yield was observed whereas maximum yield is observed at optimum rotation speed of 50 rpm.

Table 5. Effect of agitation on electrochemical synthesis of *p*-anisaldehyde at graphite anode in room temperature 30±5°C, Charge Passed: 2 F/mol

S. No.	**Agitation (rpm)**	**Time (min)**	**Yield[†] (%)**	**Current Efficiency (%)**
1	10	25	75	75
2	30	36	88	88
3	50	40	86	86
4	70	45	95	95
5	90	65	89	89

p-methoxy benzyl alcohol (10 mmol), CH_2Cl_2 (20 mL), $K_2S_2O_8$ (1.53g, 10 mmol**)**, H_2O (90 mL).

[†] Yield of *p*-anisaldehyde based on the amount of alcohol taken.

3.6 Effect of medium pH and nature of the persulphate in biphasic electrolysis of p-methoxy benzyl alcohol

High yields of the product *p*-anisaldehyde (87%) were observed in neutral and alkaline media while it was relatively low in acidic media (74%) for the oxidation of *p*-methoxy benzyl alcohol in biphasic media [Table 6]. This is possibly due to better solubility of the persulphate in neutral and alkaline media.

Table 6. Effect of medium pH, nature of the persulphate on electrochemical synthesis of *p*- anisaldehyde at graphite anode in room temperature 30±5°C, Charge Passed: 2 F/mol

S. No.	**Medium**	**Time (min)**	**Yield[†] (%)**	**Current efficiency (%)**
1	[a] Acidic	38	74	74
2	[b] Basic	38	87	87
3	[c] Neutral	38	87	87

[a] Acidic - HCl [b] Basic - NaOH [c] Neutral -H_2O

p-methoxy benzyl alcohol (10 mmol), CH_2Cl_2 (20 mL), $K_2S_2O_8$ (1.53g, 10 mmol**)**, H_2O (90 mL).

[†] Yield of *p*-anisaldehyde based on the amount of alcohol taken.

3.7 Effect of Inorganic Persulfate salt Mediators

Various inorganic salt mediators were carried out in biphasic electrolysis among which, the use of potassium, ammonium or sodium persulphate gave almost similar yields of the product (89 %) but ammonium persulphate is preferred due to its low cost (Table 7).

Table 7. Effect of persulphate mediators on electrochemical synthesis of *p*- anisaldehyde at graphite anode in room temperature 30±5°C, Charge Passed: 2 F/mol

S. No.	**Inorganic Mediators**	**Time (min)**	**Yield[†] (%)**	**Current efficiency (%)**
1	$K_2S_2O_8$	38	89	89
2	$(NH_4)_2S_2O_8$	78	86	86
3	$Na_2S_2O_8$	116	80	80

[a]Acidic - HCl [b] Basic – NaOH [c] Neutral -H_2O

p-methoxy benzylalcohol (10 mmol), CH_2Cl_2 (20mL), $K_2S_2O_8$ (1.53g, 10mmol**)**, H_2O (90mL).

[†]Yield of *p*-anisaldehyde based on the amount of alcohol taken.

3.8 Reuse of persulfate catalyst

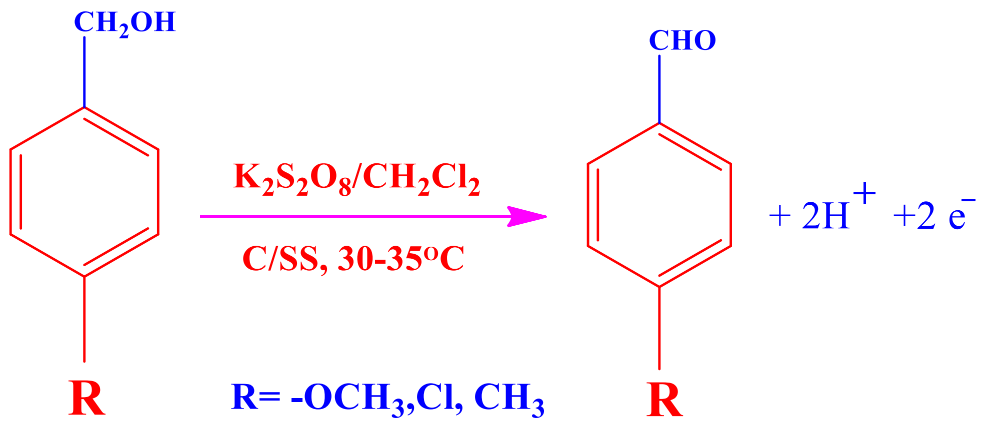
Table 8. Catalyst reuse on electrochemical synthesis of *p*- anisaldehyde at graphite anode in room temperature 30±5°C, Charge Passed: 2 F/mol

S. No.	**Reuse**	**Time (min)**	**Yield[†] (%)**	**Current efficiency (%)**
1	Fresh	38	97	97
2	1st Run	35	92	92
3	2nd Run	30	90	90
4	3rd Run	30	89	89

p- methoxy benzyl alcohol (10 mmol), CH_2Cl_2 (20mL), $K_2S_2O_8$ (1.53g, 10mmol), H_2O (90mL).

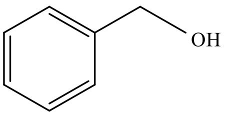
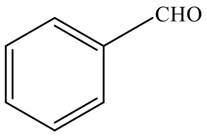
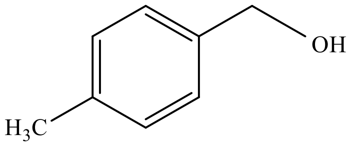
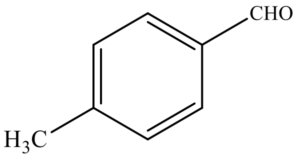
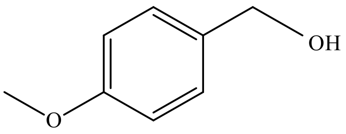
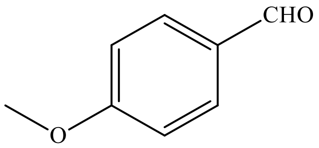
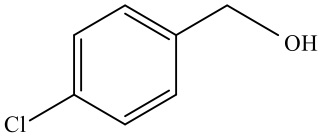
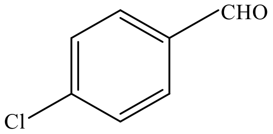
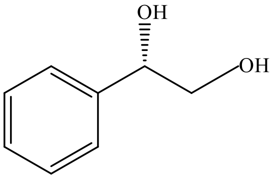
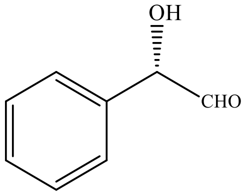
[†]Yield of *p*-anisaldehyde based on the amount of alcohol taken.

After successful screening of various parameters we end up our investigation with the reuse and recycling of the catalysts. Most attractive features in biphasic electrolysis is recycling ability of the catalyst, moreover it is also important for industrial applications.



Scheme 2. Persulfate mediated electro oxidation of various benzyl alcohols

Table 9. Optimization studies of various benzyl alcohols by biphasic electrolysis

Entry	Substrate	Product	Yield (%)	Faraday	Current Efficiency (%)
1			97	2F	97
2			96	2F	96
3			96	4F	95
4			96	4F	95
5			85	3F	81

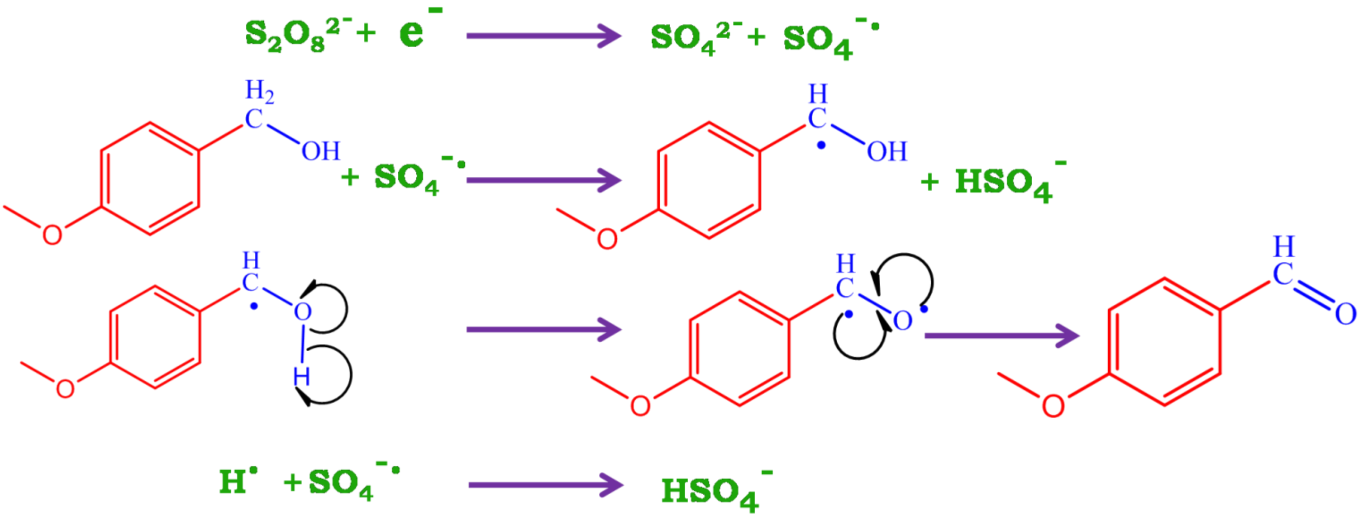
At the completion of the galvanostatic oxidation of *p*-methoxy benzyl alcohol, the aqueous layer was separated from the organic layer and washed with excess of chloroform. The oxidation reaction was carried out for additional 3 runs under identical conditions with the mediator $K_2S_2O_8$ being recycled as shown in [Table 8]. Even at the third run the yield of the product is 89%, indicating an excellent reusability and chemical stability of the catalyst. This suggests that the mediator can be successfully reused for 3 reuses. [Supplementary Figure 5].

To broaden the scope of the present catalytic reactions, we have examined the generality of the reaction conditions to a variety of alcohols. The results are summarized in [Table 9, entries 1-5]. In every case the corresponding aldehyde is the major product. Thus, benzylalcohol [entry1] was oxidized smoothly under optimized reaction condition to yield corresponding aldehydes only, without any noticeable further oxidation to acids. In a similar manner $-CH_3$, [entry 2] a + I effect causing group, also underwent excellent yield in the reaction. The present catalytic reaction was also successfully extended to (*S*)-(+)-1-Phenyl-1,2-ethanediol to scrutinize the generality of the reaction. The yields were quite high in the case of electron donating substituents with $-OCH_3$ and Cl groups [entries 3-4]. In case of (*S*)-(+)-1-Phenyl-1,2-ethanediol, [entry 5] the yield of the aldehyde was 85%. The reduction in yield was anticipated in this case due to steric effect due to the neighboring oxygen atom.

3.9 Galvanostatic Electrolysis conditions for various benzyl and substituted benzyl alcohols:

Organic Phase: *p*-methoxy benzylalcohol (10 mmol), dissolved in CH_2Cl_2 (20 mL); Aqueous Phase: 1.53 g, (10 mmol); $K_2S_2O_8$ + 90 mL Deionised water; Charge Passed: 2 F/mol; Temperature: 30-35°C; Stirring Rate: 50 rpm

3.10. Proposed Mechanism



Scheme 3. Proposed mechanism for the persulfate mediated electro oxidation of substituted benzylalcohols

A possible reaction mechanism for the present investigation is proposed in [Scheme 3]. After passing the current 2F for theoretical time, per sulfate ion undergoes a one-electron oxidation to form persulphate radical which reacts with *p*-methoxy benzyl alcohol to form an *in-situ* generated persulfate radical as an effective intermediate which is known to be a factual hydrogen abstractor. Finally, the *p*-methoxy benzyl alcohol yields the corresponding *p*-methoxy benzaldehyde on further oxidation [25-30].

4. CONCLUSIONS

In conclusion we have developed the simple, cheap and economically approachable persulphate mediated electrochemical oxidation of benzyl and substituted benzyl alcohols in biphasic media to the corresponding aldehydes in good to excellent yields. In addition, we have also successfully optimized the reaction conditions to obtain best yields of the product based on current density, temperature and nature of electrode material. The mediator in the aqueous phase can be reused to three additional runs without significant change in the yield. The process is cheaper compared to chemical methods wherein costly catalysts are employed. Moreover, it has several benefits such as metal free catalyst, atom utility, absence of secondary and by-products, low cost of production, selective oxidation, high current efficiency, high yield and recycling of spent mediator. Thus it seems that this scheme is amenable for scale up as a pollution free and environmentally benign process.

SUPPLEMENTARY DATA

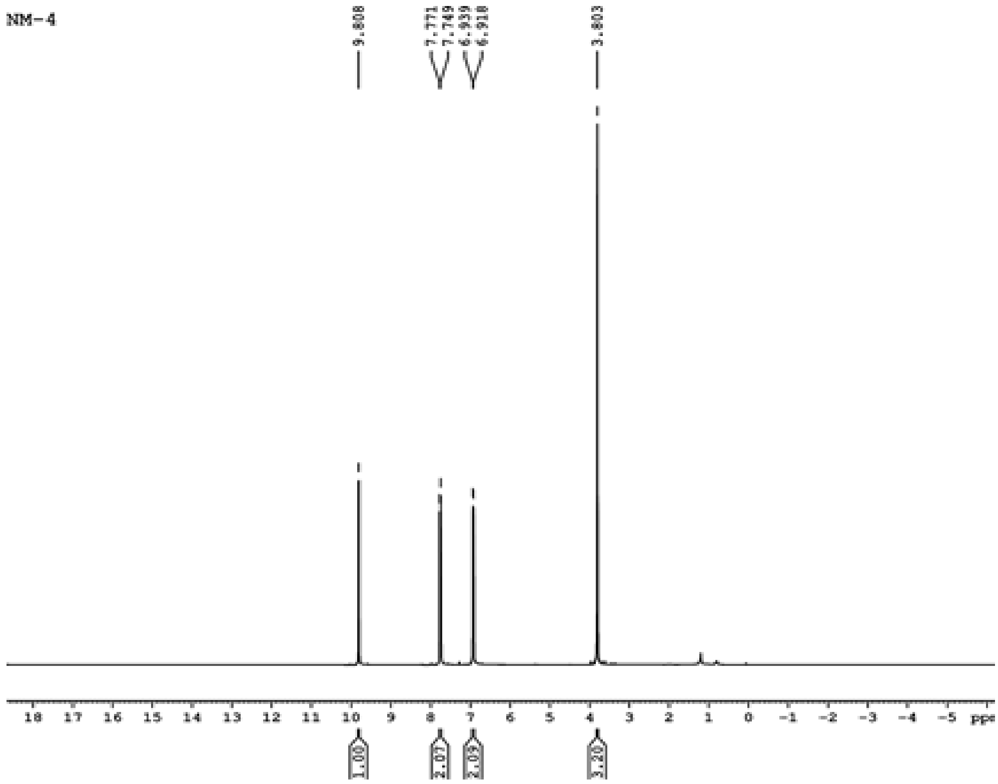
Experimental section

All the reagents used were of chemically pure or analar grade. Commercial grade solvents were distilled according to standard procedures and dried over molecular sieves before use. All other chemicals were purchased from Aldrich and were used without further purification. GC analysis was carried out in Shimadzu GC-2010 chromatograph equipped with Restek-5 (60 m × 0.25 mm I.D.) capillary column.

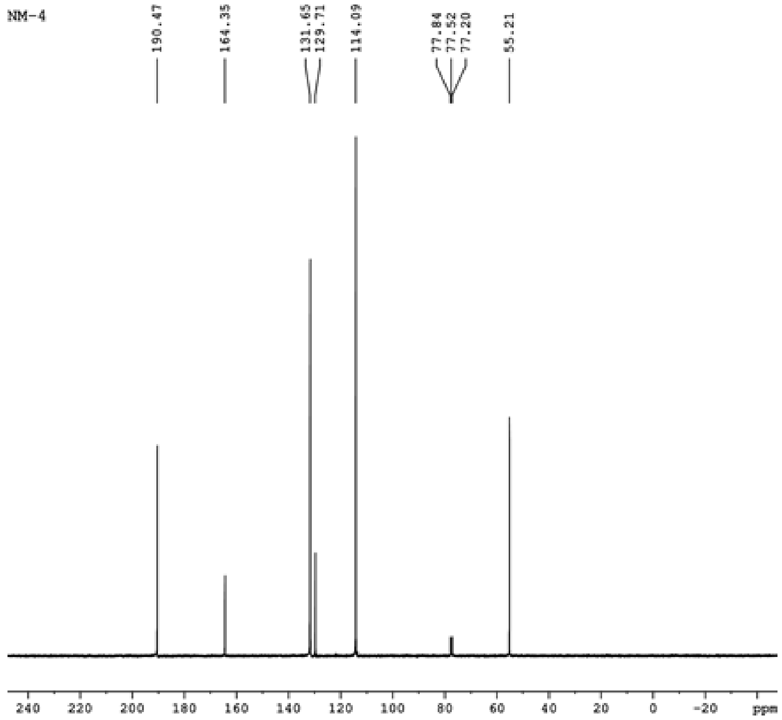
Characterization of p-methoxy benzaldehyde

NMR spectra of representative products

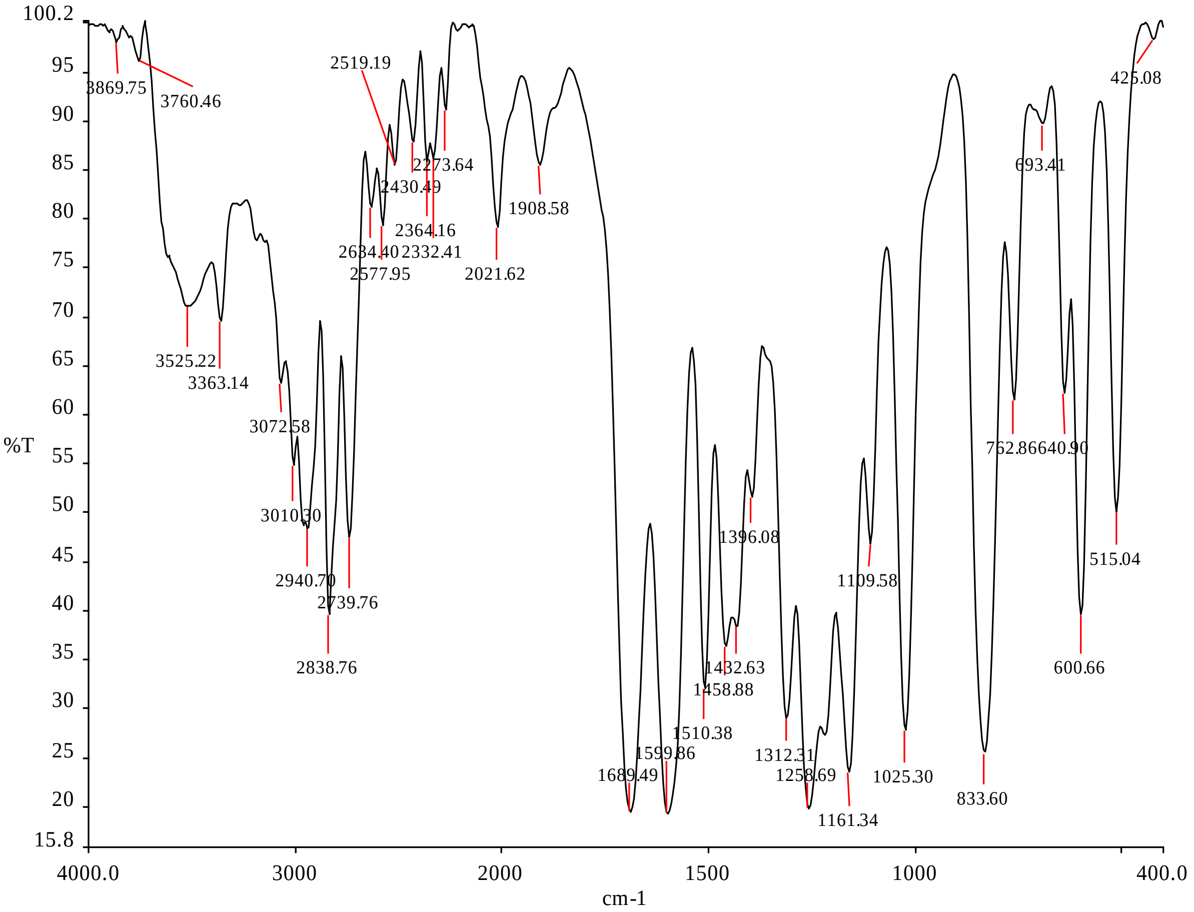
^{1}H NMR and ^{13}C NMR spectra were recorded using approximately 0.05 M solutions in $CDCl_3$ at 100 MHz or 125 MHz on Brucker-400 NMR spectrometer using TMS as internal standard.



Supplementary Figure 1 ^{1}H NMR spectra of *p*-methoxy benzaldehyde (Yield**:** 1.03g, 97%.)
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.8 (S, 1H, J= 10 Hz, CH_3), δ 7.77-7.75 (d, 2H) CH of Phenyl rings, δ 6.94-6.92 (d, 2H) CH of Phenyl rings, δ3.80 (S, 3H, J= 8Hz).

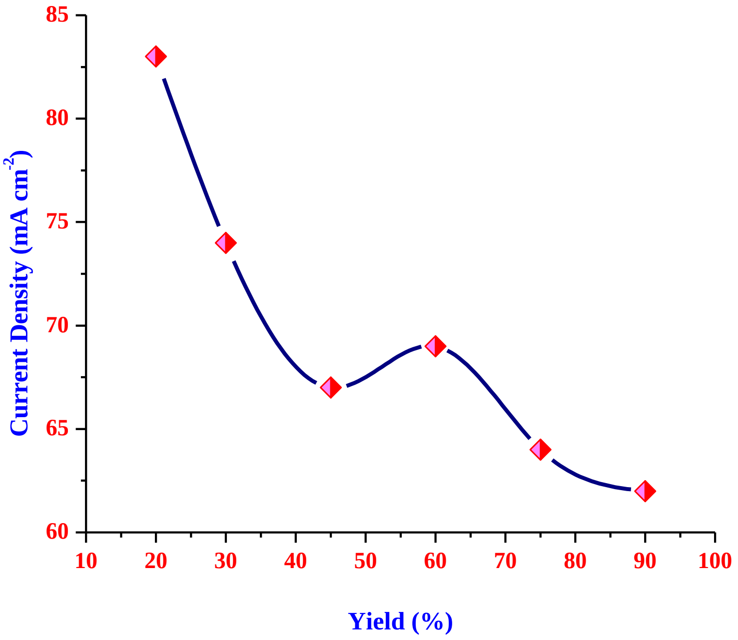


Supplementary Figure 2 ^{13}C NMR spectra of *p*-methoxy benzaldehyde
^{13}C NMR (100 MHz, $CDCl_3$): δ 190.47 (CHO), δ 164.35 (-OCH_3), δ 128, 129, 134 and 138 (CH of phenyl rings), δ 77.8-77.82 ($CDCl_3$)

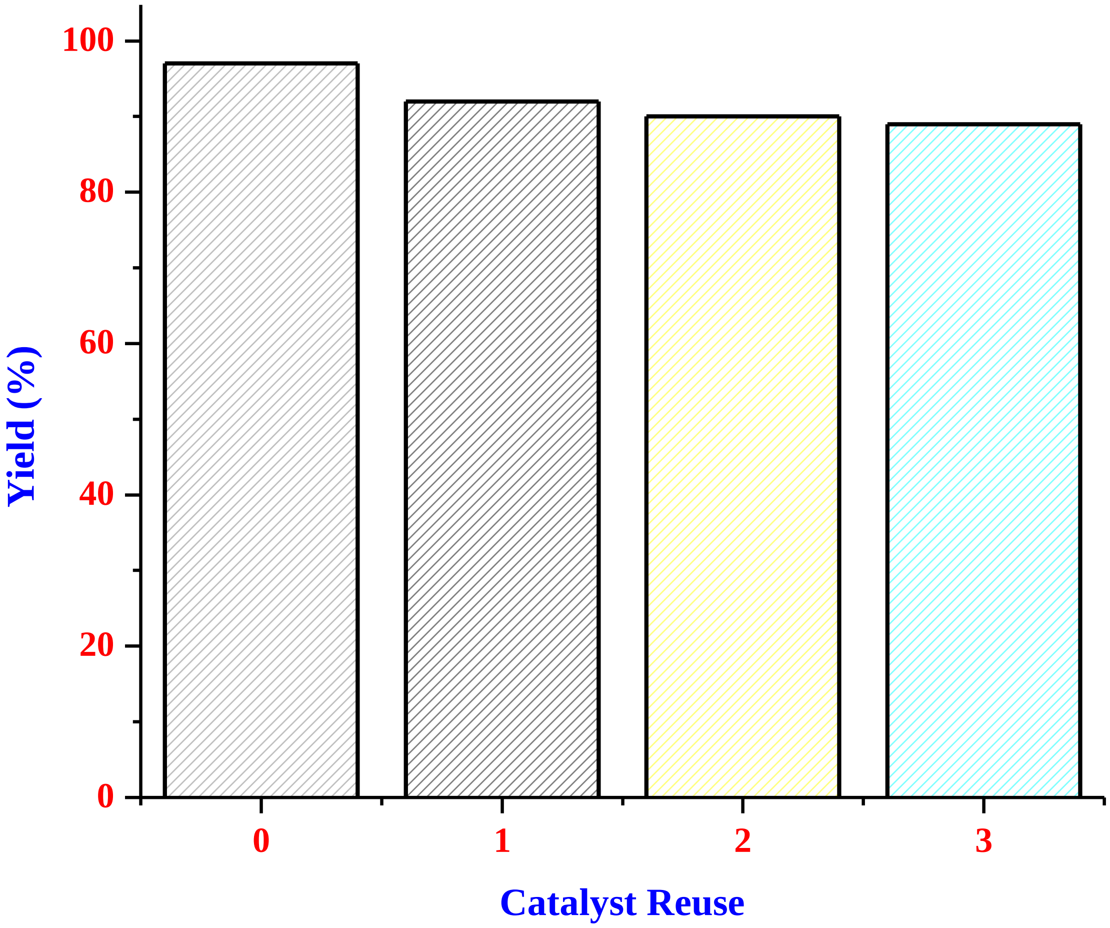


Supplementary Figure 3 FT-IR spectra of *p*-methoxy benzaldehyde

FT-IR (KBr, cm^{-1}): 1599 υ (aromatic CH), 3072 υ (aromatic CH stretching), 1689 υ (aldehyde-C=O), 1360-1355 υ (methoxy –COCH$_3$), 1432 υ (aliphatic –CH bending vibrations).



Supplementary Figure 4 Correlation between Current Density and Yield of *p*-anisaldehyde



Supplementary Figure 5 Reusability of $K_2S_2O_8$ for the electrooxidation of *p*-methoxybenzyl alcohol

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