

Electrochemical Detection of Phenol in Industrial Pollutant Absorbed Molecular Sieves by Electrochemically Activated Screen Printed Carbon Electrode

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An electrochemically activated screen printed carbon electrode (EASPCE) was used for the electrochemical detection of phenol in the industrial pollutant absorbed molecular sieves. GC-MS analysis had identified 15 organic compounds and found that phenol was the most abundant one among these identified organic compounds in the industrial pollutant absorbed molecular sieves. In addition, the phenol was also detected at modified electrodes by using the electrochemical methods such as cyclic voltammetry and differential pulse voltammetry. The surface morphology of the bare screen printed carbon electrode (SPCE) and EASPCE was investigated by scanning electron microscopy. The result of EASPCE showed a good oxidation peak response to phenol in the presence of industrial pollutant absorbed molecular sieves, while the bare SPCE showed a very weak response to phenol compared with EASPCE. The electrochemical behaviours of phenol implied that the oxidation of phenol is one electron and one proton transferred electrochemical reaction.

Keywords: Electrochemically activated screen printed carbon electrode; phenol; GC-MS; electro-oxidation; cyclic voltammetry; differential pulse voltammetry.

1. INTRODUCTION

Phenol is major by-product in various industries and has been mainly used for the conversion of precursors to products. It also involves in a range of functions in the plant growth, development, and

defense [1–3]. The phenol compound is listed as a one of the priority pollutant in many countries. It also can be easily absorbed and showed detrimental effects on animal health. Due to the high toxicity and impact in the environment, the detection of phenol in industrial pollutants is become more crucial. Recently, electrochemical methods have been widely employed for the detection of phenolic compounds due to their simplicity, high sensitivity along with portability compared with traditional chromatographic, capillary electrophoresis and spectrophotometric methods [4–7]. The electrodes modified with nanomaterials and biological molecules have been used for the sensing of phenol because of their high sensitivity and selectivity [8–11]. Since the bare electrodes are not suitable for the detection of phenol due to their poor sensitivity and fouling of signals by the oxidized products of phenol [12].

In recent years, electrochemically activated carbon electrodes such as glassy carbon and screen printed carbon electrode (SPCE) have been broadly used for the detection of various analytes [13–17]. The activated carbon electrodes have showed more surface area and high electrochemical conductivity than that of bare electrodes due to the presence of more surface defects on the electrode surface [17]. However, the electrochemically activated screen printed carbon electrode (EASPCE) has never been used for the detection of phenol in the industrial pollutants.

In this paper, we report an electrochemical detection of phenol in industrial pollutant absorbed molecular sieves by EASPCE. The fabricated EASPCE showed good electro-oxidation behaviour to phenol than that of bare SPCE. The electrochemical oxidation behaviour of phenol was investigated by cyclic voltammetry and the oxidation mechanism also been discussed in detail.

2. EXPERIMENTAL

2.1. Chemicals

Screen printed carbon electrode was purchased from Zensor R&D Co., Ltd., Taipei, Taiwan. The industrial pollutant absorbed molecular sieves were received from Taiwan Power Company (Republic of China). Phenol (99.0 %) was purchased from Kanto chemical Co. Inc. Tokyo, Japan. The supporting electrolyte pH 7 (PBS) was prepared by using 0.05 M Na_2HPO_4 and NaH_2PO_4 in doubly distilled water. All the chemicals used in this work were of analytical grade and all the solutions were prepared using doubly distilled water without any further purification.

2.2. Apparatus

Cyclic voltammetry and differential pulse voltammetry measurements were performed by the CHI 750a and CHI 400 electrochemical work station. Scanning electron microscopy (SEM) was performed using Hitachi S-3000 H electron microscope. Spectrofluorometry experiments were performed by the JASCO FP-8500 Series Spectrofluorometer. Conventional three-electrode system was used for the electrochemical experiments; the SPCE was used as a working electrode, a saturated Ag/AgCl as a reference electrode and a platinum electrode as the auxiliary electrode.

2.3. Fabrication of electrochemically activated SPCE

The EASPCE was prepared by according to our previous report [18]. Briefly, the SPCE was first pre-cleaned by ethanol and water solution. Next, the pre-cleaned SPCE was electrochemically activated at 0.2 V for 300 s in PBS containing 0.1 KCl solution. The fabricated electrochemically activated SPCE is denoted as EASPCE and used for further experiments. For the electrochemical experiments, the industrial pollutant absorbed molecular sieves were placed into the PBS at least for five minutes and the electrochemical experiments were performed by the different electrodes at room temperature.

2.4. Analysis of organic compounds in the industrial pollutant absorbed molecular sieves by GC-MS

The industrial pollutant absorbed molecular sieves was soaked with 20ml MeOH until GC-MS analysis (>12 hr). The prepared sample was separated on Rtx®-Wax capillary columns (30m x 0.25mm, film thickness 0.25 μ m; RESTEK, Pennsylvania, USA). Helium (5N5 grade) was used as the carrier gas, with a flow rate of 1.2 mL/min, and the split ratio was 50:1. Sample injection volume was 2 μ L and the injector temperature was 225°C. The column oven temperature was held at 60°C for 1 min, and then programmed to 70°C at 5°C/min and change the gradient to 200°C with 40°C/min. Finally, held at 200°C for 2 min and the total run time was 8.25 min. An electron ionization (EI) system with ionization energy of 70 eV was used for detection. The ion source temperature was set at 220°C, the interface temperature was 250°C, and the detector voltage was 2 kV. The mass spectrum was acquired in scan mode at a scan rate of 0.98 scan/sec within a mass range of 44–150 amu. The measurement was performed in duplicate for each sample. The data was processed by software provided by Agilent Technology (MSD ChemStation D.03.00.611). The compound identification was done by their MS data compared to the on-site NIST14 mass spectral library or on-line NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry/>).

3. RESULTS AND DISCUSSION

3.1. Characterization of bare and electrochemically activated SPCEs

Fig. 1A and 1B displays the SEM image of bare and electrochemically activated SPCEs. The bare SPCE shows its typical thin layer morphology associated with the graphitic layers, and the cracked morphology in the graphite surface of SPCE was etched by the electrochemical treatment at 2.0 V and observed in Fig. 1B. The result indicates that the surface morphology of the SPCE is greatly affected by the electrochemical activation. In addition, the impact of the surface enhancement for electrochemical activated SPCEs is higher than that of bare SPCE [18].

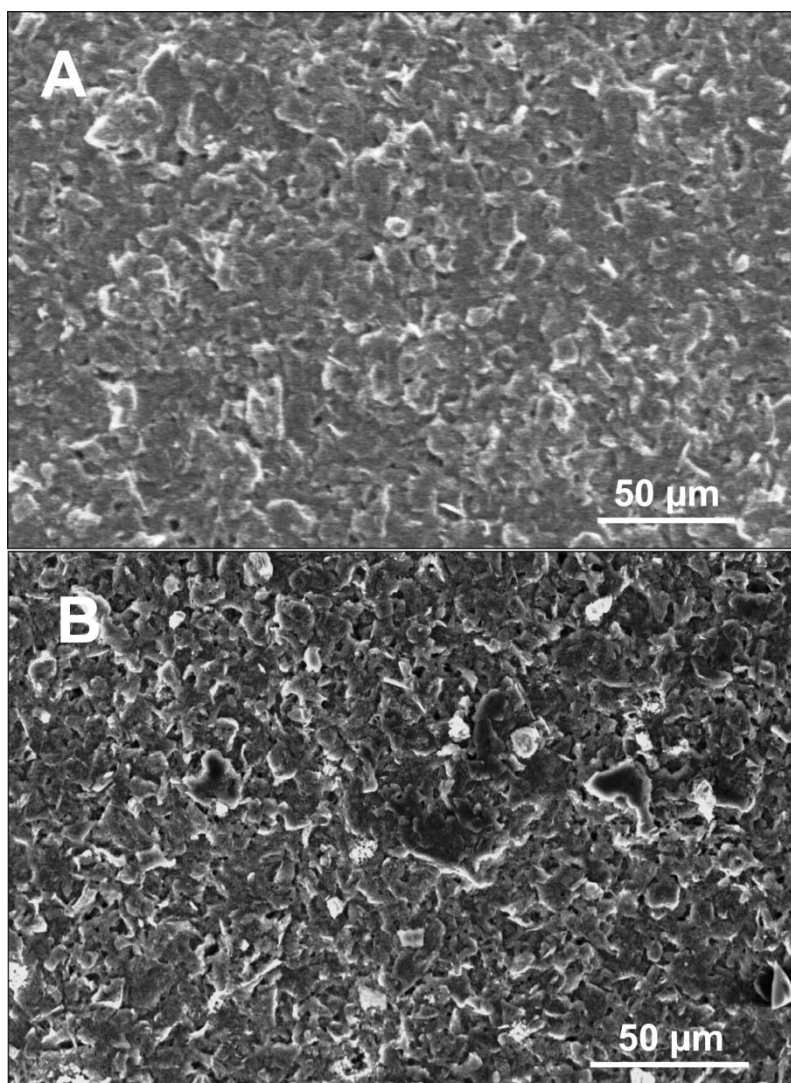
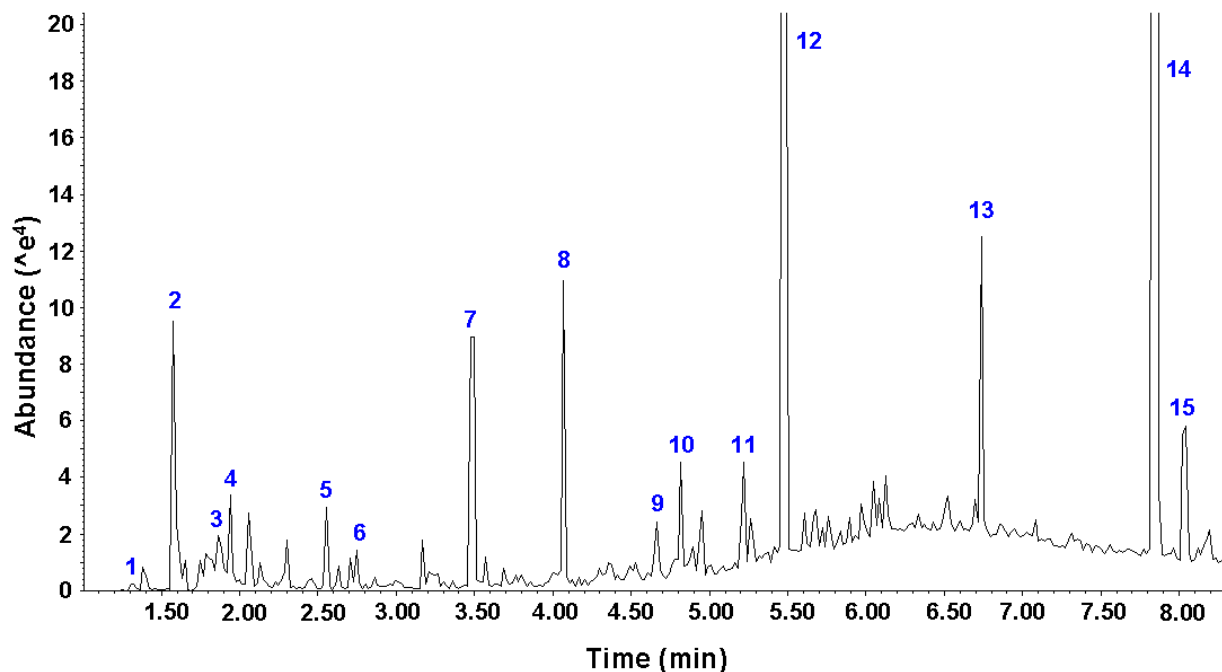


Figure 1. SEM image of (A) bare SPCE and (B) electrochemically activated SPCE.

3.2. Identification of organic compounds in industrial pollutant absorbed molecular sieves

Prior to the electrochemical experiments, the organic compounds in industrial pollutant absorbed molecular sieves were identified by GC-MS and the results are shown in Fig. 2. By matching the mass spectrum with database of the NIST14 library, 15 organic compounds present in the sample of industrial pollutant absorbed molecular sieves were observed and identified, and 12 of them are hydrocarbon compounds with cyclic or benzene group. The most three abundant compounds are phenol, 2,5-dimethylhydroxyquinone, and acetophenone shown in peaks 14, 12, 13 respectively. Furthermore, the fluorescence absorption and emission intensity were monitored by spectrofluorometer to validate the presence of phenol in industrial pollutant absorbed molecular sieves sample. Fig. 3 illustrates the 2D fluorescence spectra of pure (A) and the industrial pollutant absorbed molecular sieves (B). The corresponding 3D fluorescence spectrum of the industrial pollutant absorbed molecular sieves is shown in Fig. 3C. The pure molecular sieves does not show any absorption and emission intensity in the fluorescence spectra. Whereas, the industrial pollutant absorbed molecular sieves

shows a sharp fluorescence emission intensity at 485 nm is due to the fluorescence quenching of phenol in the impure molecular sieves. The presence of phenol in industrial pollutant absorbed molecular sieves was further confirmed by UV-visible spectra and shown in Fig. 4. A shoulder peak was appeared at 281 nm, and the observed peak is appeared at higher wavelength than pure phenol (270 nm). This is possibly due to strong interaction between phenolic -OH group and other impurities in the industrial pollutant absorbed molecular sieves. The result also further confirms the presence of phenol in industrial pollutant absorbed molecular sieves.



No.	RT (min)	m/z	Formula	Candidate
1	1.30	146.0	SF ₆	Sulfur hexafluoride
2	1.58	120.1	C ₄ H ₁₂ O ₂ Si	Dimethoxydimethylsilane
3	1.86	111.0	CH ₅ NO ₃ S	Aminomethanesulfonic acid
4	1.94	98.0	C ₂ H ₆ O	Dimethyl ether
5	2.30	75.0	C ₂ H ₅ NS	Ethanethioamide
6	2.55	88.1	C ₄ H ₈ O ₂	1,4-Dioxane
7	2.71	156.2	C ₁₁ H ₂₄	2,4,6-Trimethyl-octane
8	3.48	120.0	C ₄ H ₈ O ₄	p-Dioxane-2,3-diol
9	4.07	222.2	C ₁₅ H ₂₆ O	Viridiflorol
10	4.67	222.2	C ₁₅ H ₂₆ O	4-Methyl-1-(1,2,2-trimethylcyclopentyl)cyclohex-3-enol
11	4.82	242.2	C ₁₇ H ₂₂ O	(5E,8E)-3-phenylundeca-5,8,10-trien-3-ol
12	5.22	138.1	C ₈ H ₁₀ O ₂	2,5-dimethylhydroquinone
13	5.47	120.1	C ₈ H ₈ O	Acetophenone
14	6.74	94.0	C ₆ H ₆ O	Phenol
15	7.85	143.1	C ₁₀ H ₉ N	2-Methylquinoline

Figure 2. Industrial pollutant absorbed molecular sieves sample analysis by GC-MS. Total ion chromatography (TIC) and NIST library matched compound list table.

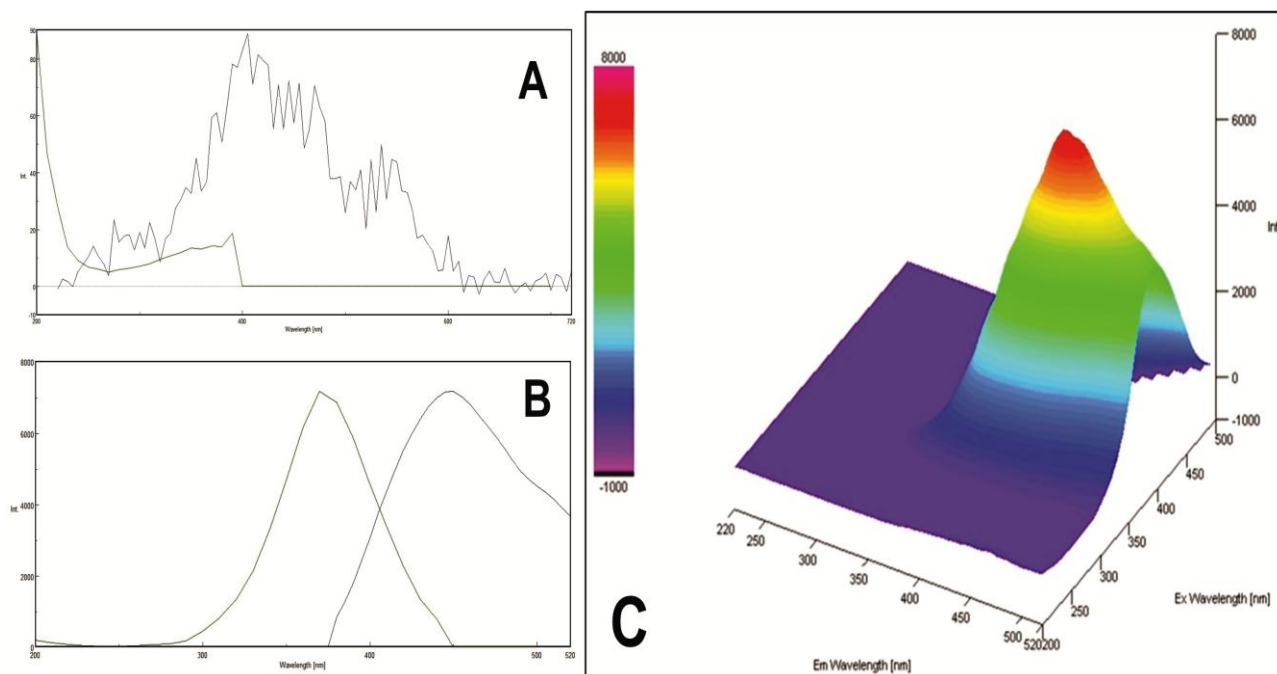


Figure 3. 2D fluorescence spectra of pure (A) and industrial pollutant absorbed molecular sieves (B). (C) 3D fluorescence spectrum of industrial pollutant absorbed molecular sieves.

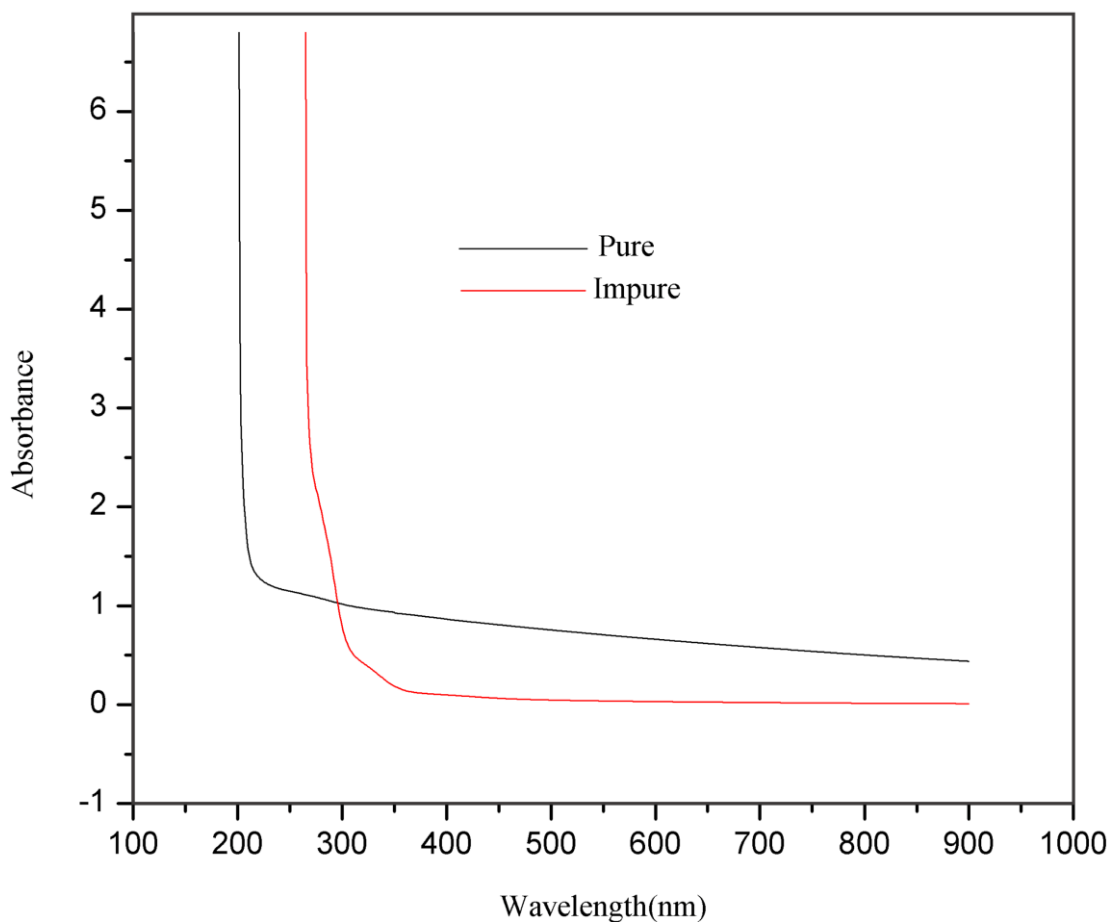


Figure 4. UV-Vis spectra of pure (black color) and industrial pollutant absorbed molecular sieves (red color).

3.3. Electrochemical behavior of industrial pollutant absorbed molecular sieves

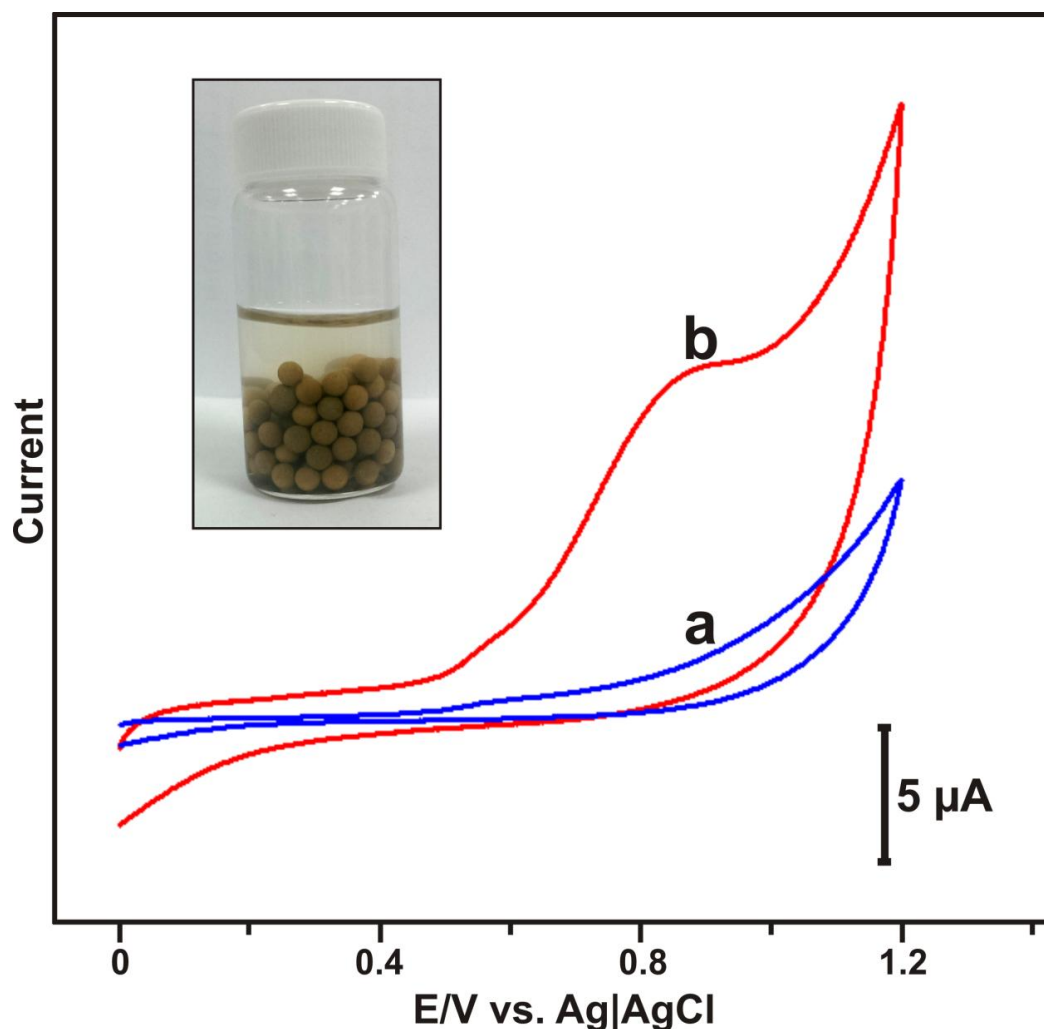


Figure 5. Cyclic voltammety response of bare SPCE (a) and EASPCE (b) in PBS containing industrial pollutant absorbed molecular sieves at a scan rate of 50 mVs^{-1} . Inset shows the digital photographs of industrial pollutant absorbed molecular sieves in PBS.

In order to confirm the presence of phenol, the electrochemical behaviour of industrial pollutant absorbed molecular sieves in PBS (Fig. 3 inset) was investigated at SPCEs by using CV. Fig. 5 shows the CV response of bare SPCE (a) and EASPCE (b) PBS containing industrial pollutant absorbed molecular sieves at a scan rate of 50 mV s^{-1} . In the presence of industrial pollutant absorbed molecular sieves in PBS, the bare SPCE does not show any peak response at the potential scanning from 0 to 1.2 V. The result indicates that the bare SPCE is not suitable electrode for identification of phenol in industrial pollutant absorbed molecular sieves. On the other hand, EASPCE shows a good anodic peak at a potential of 0.866 V and very small anodic peak at 0.561 V for the industrial pollutant absorbed molecular sieves in PBS. The observed anodic peak at 0.866 V is due to the oxidation of phenol in the industrial pollutant absorbed molecular sieves [19]. It can be seen from Fig. 5 curve b, a sharp oxidation peak is observed at 0.866 V due to the oxidation of phenol to phenoxy radical and the peak at 0.561 V is due to the formation of benzoquinone [19]. The similar results were reported earlier

for the electrochemical detection phenol. The electro-oxidation mechanism of phenol at EASPCE can be explained by the Fig. 6 [19].

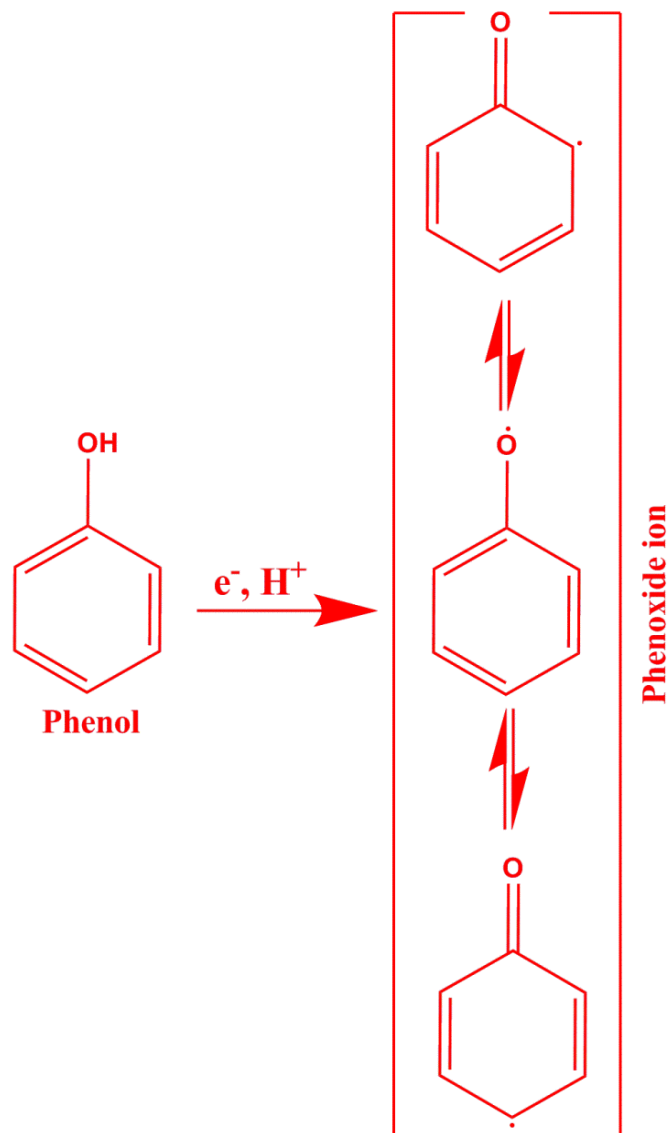


Figure 6. Typical electro-oxidation mechanism of phenol at EASPCE.

3.4. Electrochemical detection of phenol in industrial pollutant absorbed molecular sieves by DPV

The electrochemical detection of phenol in industrial pollutant absorbed molecular sieves was done at EASPCE by DPV, since DPV is a more sensitive method for the detection of phenol than CV. Fig. 7A shows the DPV response of the EASPCE in PBS containing industrial pollutant absorbed molecular sieves. A good oxidation peak response of phenol was observed at the EASPCE at a potential of 0.808 V. Moreover, another one oxidation peak was also observed at 0.536 V. The oxidation peak at 0.808 and 0.536 V is due to the formation of phenoxy radical and benzoquinone, respectively. In order to further verify the oxidation behaviour of phenol in EASPCE, DPV was performed in PBS containing 200 μ M pure phenol and shown in Fig. 7B. It can be seen that the

observed response at pure phenol and phenol containing industrial pollutant absorbed molecular sieves are close each other. The result further confirms that the presence of phenol in industrial pollutant absorbed molecular sieves.

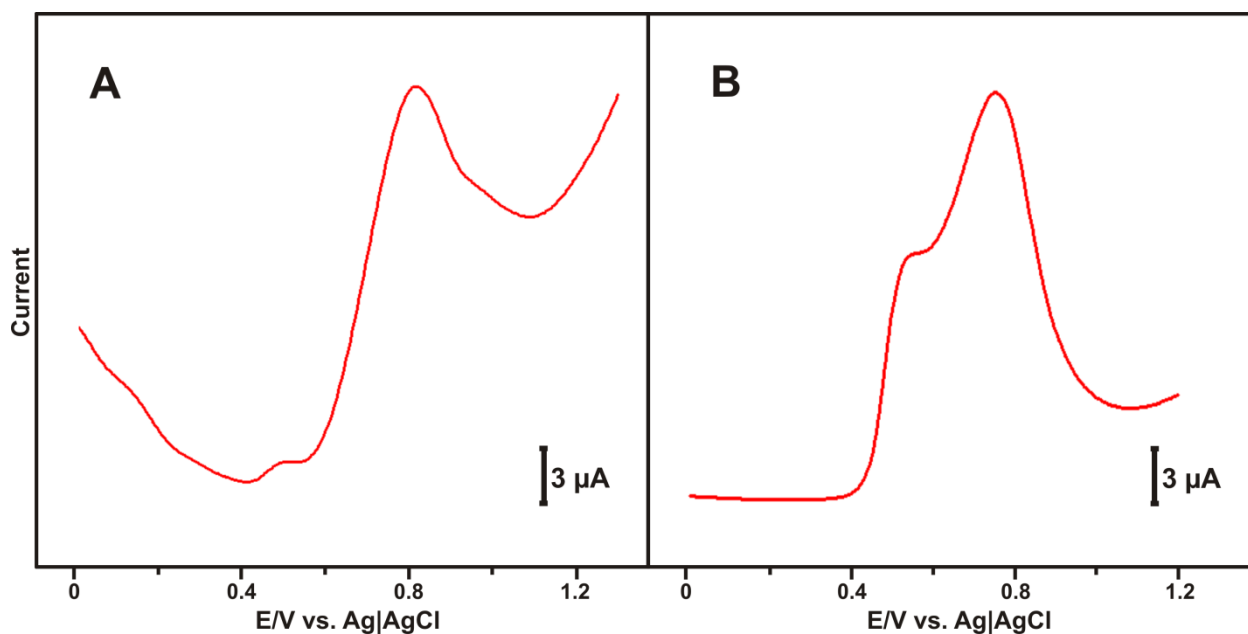


Figure 7. A) DPV response of EASPCE in the presence of industrial pollutant absorbed molecular sieves in PBS. B) In same conditions, DPV response of EASPCE in the presence of 200 μM phenol in PBS.

4. CONCLUSIONS

In conclusion, GC-MS and electrochemically activated SPCE can be applied for the identification and detection of phenol in industrial pollutant absorbed molecular sieves. Compared to SPCE, the EASPCE exhibited a better ability of electro-oxidation for phenol. The electrochemical oxidation behaviour of phenol containing industrial pollutant absorbed molecular sieves at EASPCE was in good agreement with those observed in the pure phenol sample. As a future perspective, the fabricated EASPCE could be used as an advanced electrode material for detection of phenol in the industrial industrial pollutant absorbed samples.

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