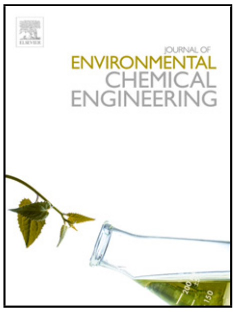

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Development of Diamond Composite Electrode for Anodic Oxidation of Organic Pollutants

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Abstract

Nano-diamond composite electrode was prepared and used as anode for anodic oxidation process for organic chemicals. Electrochemical techniques such as impedance and cyclic voltammetry have been used to characterize the diamond composite electrode properties. The oxidation power of the electrode was 0.8 V vs. Ag/AgCl, the charge transfer rate was 12.1 Ohm, and the double layer capacitance was less than 1 µF. The anodic oxidation behavior of p-benzoquinone, 2-chlorophenol, and phenol over diamond composite electrode were investigated by cyclic voltammetry in 0.1 M H_2SO_4 (pH 3) solution and 0.25 M Na_2SO_4 (pH 6.8) solution. Results marked that the electro-oxidation of p-benzoquinone was more active than phenol and 2-chlorophenol in the both solutions. The performance of the diamond composite electrode during incineration of 200 mg/L p-benzoquinone, 2-chlorophenol, phenol were investigated in an aqueous solution of pH 3 and pH 6.8 with 0.25 M Na_2SO_4 as the supporting electrolyte and applied current density of 40 mA/cm^2. Results showed that the degradation rate of benzoquinone was faster than 2-chlorophenol and phenol in both different pH solutions. Moreover, the benzoquinone degradation rate was enhanced at high pH solution, on the contrary of that of 2-chlorophenol and phenol were clearly favored in acid medium.

Keywords: Diamond particles, Anodic oxidation, composite electrode, Aromatic pollutant, Degradation.

1. Introduction

Most of the aromatic organic substrates are toxic materials and strong bio-refractory pollutant (high resistivity to biological treatment); thus, these compounds consider serious environmental contamination [1]. p-Benzoquinone (p-BQ), 2-Chlorophenol (2-Cph), and Phenol were classified as a dangerous chemicals by the Environmental Protection Agency [2]. There are many commercial uses for p-BQ, phenol, and 2-Cph such as in polymer industries, dyes, cellulose, pesticides, toners, and herbicides [1, 3, 4]. The bio-refractory nature and strong toxicity of these chemicals motivate researchers to improve suitable techniques that can mineralize these pollutants. Many techniques were investigated to treat aromatic chemicals in wastewater, including adsorption [5], photochemical degradation [6], electrocoagulation [7-9] and advanced oxidation processes [6, 10-13]. Among these techniques, electrochemical oxidation of bio-refractory toxic pollutant draw attention of the experts for many reasons such as high efficiency, amenability to automation, easy implementation, and environmental compatibility [14]. One of the most important parameter during electrochemical oxidation process is the electrode material nature [15]. Many conventional electrodes materials, such as SnO_2, platinum, and PbO_2 [16, 17], BDD [18, 19], Ti-based oxide [20, 21], Er-chitosan-PbO_2[22], have been investigated or developed as anodes for electrochemical incineration of organic pollutant. Most previous works have endeavored to suggest a suitable anode with stable electrochemical properties, low cost, and long service life. Aromatic oxidation process should be occur until the aromatic ring breaks, carboxylic acids form, and most acids are mineralized to CO_2, which requires generate a suitable amount of quasi-free hydroxyl radicals at the anode surface. Electrochemical properties of electrode are playing a significant role on the amount of hydroxyl radicals generated. In general, wide potential window electrodes present a suitable oxygen evolution potential which lead to produce huge amounts of OH^- and achieve high current efficiencies.

Diamond particles substrate is available within a suitable price range. Besides that, the inert surface and high corrosion resistance of diamond particles enhances the opportunity to develop an anode from this substrate for electrochemical oxidation process. However, previous researches have presented modified electrodes using diamond particles substrate for electrochemical sensor applications [23-26]. Lee et al. [27-29] have used detonation diamond particles to prepare a porous electrode with a wide electrochemical active area. A diamond composite electrode has an inert surface, and stable electrochemical properties hence it proposed in the present study for electrochemical oxidation of p-BQ, 2-Cph, and phenol. The effects pH is also investigated by cyclic voltammetry technique and electrolysis process.

2. Materials and methods

2.1. Electrode preparation

A disc of 3 cm diameter of diamond electrode was prepared from nano-diamond particles (Sigma-Aldrich, 98.3% purity and an average particle size 8 nanometer) by mixed 2 gram of nano-particles of diamond carefully with 0.4 gram of carbon black (Sigma-Aldrich, 97 % purity and an average particle size 15 nanometer). Powder mixture was mixed with suspension of 0.07 gram polytetrafluoroethylene (PTFE 60 wt% in water sigma-Aldrich) as the binder and 1,3-propanediol (98% purity, Sigma-Aldrich) and then dried as described in previous work [30].

2.2. Electrochemical studies

Voltammetric experiments were conducted in one compartment of a 0.5 L cell at laboratory temperature to characterize the anode electrochemical properties. The electrolyte of 0.5M H_2SO_4 (98% Merck Pro Analysis) solution is used to investigate electrode oxidation power. Electrolyte of 0.5 M H_2SO_4 containing 0.5 mM of $K_4Fe(CN)_6$ was used as a redox prop to investigate the reactivity of the electrode. The electrochemical impedance spectroscopy experiments have been accomplished with potential amplitude of the AC signal was kept at 10 mV and the measured frequency range was $0.01–10^5$ Hz. Furthermore, the investigation of electrochemical oxidation behavior of p-BQ, 2-Cph, and phenol were performed same electrochemical cell. Three solutions were investigated 200 mg/L of p-BQ, 2-CP, and phenol (99.5% Merck Pro

Analysis), were prepared. Solutions were composed of 0.1 M H_2SO_4 for low pH (pH 3), and high pH solution was composed of 0.25 M Na_2SO_4 at pH 6.8. High resistivity double distillated water was used to prepare the electrolytes. A platinum wire was used as the counter electrode, and Ag/AgCl as the reference electrode. The electrochemical experiments were conducted by Gamry Reference 3000 potentiostat.

2.3. Electro-degradation Reaction

An Electro-oxidation reactor with 200 mL of 0.25 M Na_2SO_4 as the supporting electrolyte containing 200 mg/L p-BQ, 2-Cph, or phenol solution were used for electrochemical oxidation reaction experiments on the diamond composite anode. The experiments were conducted at applied current densities of 40 mA/cm^2 and pH 3 and 6.8 at 25 °C temperature.

2.4. Analysis method

The oxidation reactions of p-BQ, 2-Cph, and phenol during electrochemical oxidation process were observed by high performance liquid chromatography (HPLC) using an Agilent technology 1200 series. C18 column (4.6 mm × 250 mm × 5μm) at 20℃ was used as the separation column for aromatic compounds. A mixture of 60% acetonitrile with 39.9% water + 0.1% H_2PO_4 (v/v), was used as eluent. The injection volumes were 10 μL and mobile phase flow rate was 1 mL/min. The detection wavelength was set at 280 nm. A membrane filter with a 0.25 μmwas used to filtrate the samples.

3. Results and discussion

3.*1. Electrode Characterization*

SEM was used to investigate the morphology of diamond composite electrode. The scans were performed at high magnification (×50,000 times) with image resolution at 1.00 μm. The SEM image of diamond composite electrode Fig. 1 clearly shows that a uniform topography, unique structure, and no separated carbon layers could be observed. Furthermore, SEM micrograph shows an excellent dispersion of the nanoparticles of the diamond and carbon black in the binder matrix. Moreover, SEM micrograph shows a homogenous distribution of Carbone black particles in diamond particles

The electrochemical properties of diamond composite electrode were evaluated by cyclic voltammetry and electrochemical impedance techniques. Fig. 2 demonstrates the voltammogram of diamond composite electrode in aqueous solution of 0.5 M H_2SO_4. It is obvious; the background current was low and featureless between -0.4 to 1.95 V. According to the value of oxygen evolution potential showing in Fig. 2, the working potential window of this electrode is 2.35 vs. Ag/AgCl, which consider similar to that of low boron doped diamond and carbonaceous electrodes and its suitable for electro-oxidation process [31, 32]. The anodic oxidation process is dominated by the reaction step between hydroxyl radicals produced on anode surface and organic pollutant. Hydroxyl radicals are generated on electrode surface by water discharge (1.23 v/SHE under standard conditions). Moreover, there activity of produced hydroxyls radical is affected by the interaction force with electrode surface [33]. It is well known, that the diamond martials has an inert surface which leads to make the interaction force with the generated radicals is quasi-free[34].

Fig. 3 demonstrates the electrochemical reactivity of diamond electrode in 0.5 M H_2SO_4 solution containing 0.5 mM of $[Fe(CN)6]^{4-/3-}$ and 100 mV scan rate. It is obviously the reaction was quasi-reversible with, the anodic and cathodic separation potential peak 428 mV. The anodic-cathodic potential peak on diamond composite is considered high with compare to that registered on platinum, glass carbon, and boron doped diamond electrodes. The low electron transfer rate of diamond composite electrode is attributed to the presence of PTFE particles in electrode composition. It’s well known; the reactivity of electrode is reduced by the presence of the nonconductive particles on electrode surface and the type or the amount of binder has crucial effect on electrode reactivity [35-37]. Electrochemical impedance is an efficient technique may use to investigate the electrode/electrolyte parameters [38]. Potassium ferrocyanide of 5mM in 0.5 M H_2SO_4 has been selected to use as redox prop with potential of zero V vs. Ag/AgCl and frequency range is $0.1–10^5$ Hz to evaluate diamond composite electrode. The Inset of Fig. 3 shows the Nyquist plot of diamond electrode has semicircle at high frequencies and straight line with a unit slope at low frequencies reveal the kinetic and mass transfer control respectively [39]. The best fit for diamond composite electrode impedance spectra was the Randles equivalent circuit. The electrode charge transfer resistance is represented by the diameter of semicircle and is value 12.1 Ω. The double layer capacitance of diamond composite electrode was similar to that of boron doped diamond within 1 μF cm^{-2} which it is ten times lower than glassy carbon electrode capacitance [40, 41].

3.1. Anodic oxidation behavior

Prior to the electrolysis study, cyclic voltammeter technique was use d to investigate the electrochemical oxidation trend of 200mg/L of p-BQ, 2-Cph, and phenol on diamond composite electrode. Fig. 4 shows the cyclic voltammogram of the anodic oxidation peak potentials were 1.1, 1.29, and 1.36V in electrolyte of 0.1 M H_2SO_4 (pH 3) for phenol, 2-Cph, and p-BQ respectively. Fig. 5 shows the cyclic voltammogram of anodic oxidation peak in neutral solution of 0.25 M Na_2SO_4 (pH 6.8) were 0.95, 1.15, and 1.36 V for phenol, 2-Cph, and p-BQ respectively. Several researches reported that anodic peak potentials shift toward more negative values with increasing solution pH [42, 43]. Electrochemical oxidation of phenol and 2-Cph on diamond composite electrode are clearly favored in acid medium as represented in the voltammogram of Fig. 5. In contrast, the anodic oxidation of p-BQ was more active at medium solution. The 2-Cph and phenol anodic peak currents in the 0.1 M H_2SO_4 (pH 3) solution was 5.7 and 3.2 mA, higher than that registered in the 0.25M Na_2SO_4 (pH 6.8; 3.1 and 2.0 mA). Moreover, it is obvious the anodic oxidation of p-benzoquinone were more active than 2-chlorophenol and phenol in both different pH solutions.

3.2. Electro-degradation process

Fig. 6 shows the electro-degradation trend of 200 mg/L of 2-Ch, phenol, and p-BQ in 0.25 M Na_2SO_4 as the supporting electrolyte on the diamond composite electrode at 40 mA /cm^2 and 25 °C. It is obvious the degradation rate of p-BQ was higher than that of 2-Cph and phenol. After 3 hour of electrolysis time the degradation rates were 97%, 82%, and 38.5% for p-BQ, 2-Cph, and phenol respectively. It is well known, Quinone and p-BQ are the first products of phenolic substrates electro-oxidation. High amount of current is consumed to covert aromatic substrates from phenolic phase to p-BQ that may explain partially why p-BQ degradation rate was faster than that of 2-Cph and phenol. Furthermore, the electrode passivation considers a significant parameter during electrochemical process. Phenolic substrates oxidation reactions have aside reaction produced the dimers, which react together and produce the oligomer [44, 45]. The dimer and oligomer generation reaction leads to the extensive high amount of current and reduces the reaction rate of phenolic substrates, while also causing fouling of electrode. On the other hand, p-BQ anodic oxidation reactions haven’t suffer from passivation phenomenon compared to that registered for phenols substrates as reported by many studies[18, 22]. Moreover, the different degradation rate between phenol and 2-Cphon diamond composite electrode is also marked. The prime factor lead to that is the different between 2-Cph and phenol in the molecules mass transfer rate (adsorption) from the solution bulk to the electrode surface.

3.2.1. pH effect

Solution pH considers a significant parameter during anodic oxidation process of organic pollutants. However, the role of pH is largely depending on the nature of the organic substrates, anode materials, supporting electrolyte [46]. In addition to the investigated value of pH (3) that demonstrated in Fig.6. Another pH (6.8) was selected to study the pH solution effect on the electro-degradation rate of 200 mg/L p-BQ, phenol, and 2-Chp with 0.25 M Na_2SO_4 and 40mA/cm^2. Fig. 7 shows the degradation rate of p-BQ, 2-Chp, and phenol at pH 6.8 after one hour of reaction were 98%, 45%, and 15%, respectively. Electro-degradation of p-BQ is clearly favored the higher pH medium as shown in Fig.7. The increase of p-BQ degradation rate at higher pH value is attributed to exist of p-BQ at alkaline medium in the form of anion that was easier to be adsorbed on the surface of the electrode by electric attraction, which could enhance p-BQ degradation [20, 22, 42]. On the contrary, result show the electro-degradation of phenol and 2-Cph favors acid medium. However, most of the reported studies that using different anodes materials for degradation of phenolic substrates registered the anodes performance are more efficient in acidic solutions than in neutral or alkaline solutions [47-50]. This trend may be attributed to many reasons. First, the passivation phenomenon during phenolic electro-oxidation process in acid medium is less than that in neutral or basic solutions [51-53]. As well, the anode current efficiency in low pH solutions is higher than that in high pH solutions [51], also the electron transfer rate is more active at acid solution than that at neutral or basic solutions [50]. Moreover, the hydroxyl radicals potential oxidation is increases as pH decreases [54-56], that could justify the high degradation rate of phenol and 2-Cph which marked at low pH solution.

Conclusion

The working potential window of diamond composite electrode was 2.35 vs. Ag/AgCl. Moreover, the value of peak potential separation on diamond composite reaction was 428 mV and the double layer capacitance was 1 µF cm^{-2}. The electrochemical behavior of p-BQ, 2-Chp and phenol oxidation on diamond composite electrode has been investigated. The voltammogram current peak of the p-BQ in neutral solution was higher than that in acid solution, which reveals that p-BQ anodic oxidation is easier to accomplish at high pH than that at low pH solution. Conversely, 2-Cph and phenol anodic oxidation peaks were higher at acid solution than that at neutral solution.

p-BQ electro-degradation rates were higher than that of 2-Chp and phenol in both different pH solutions. The p-BQ, 2Chp, and phenol removal efficiencies after 3 h of the process were 97% and 82%, and 38.5% respectively.

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Figures captions

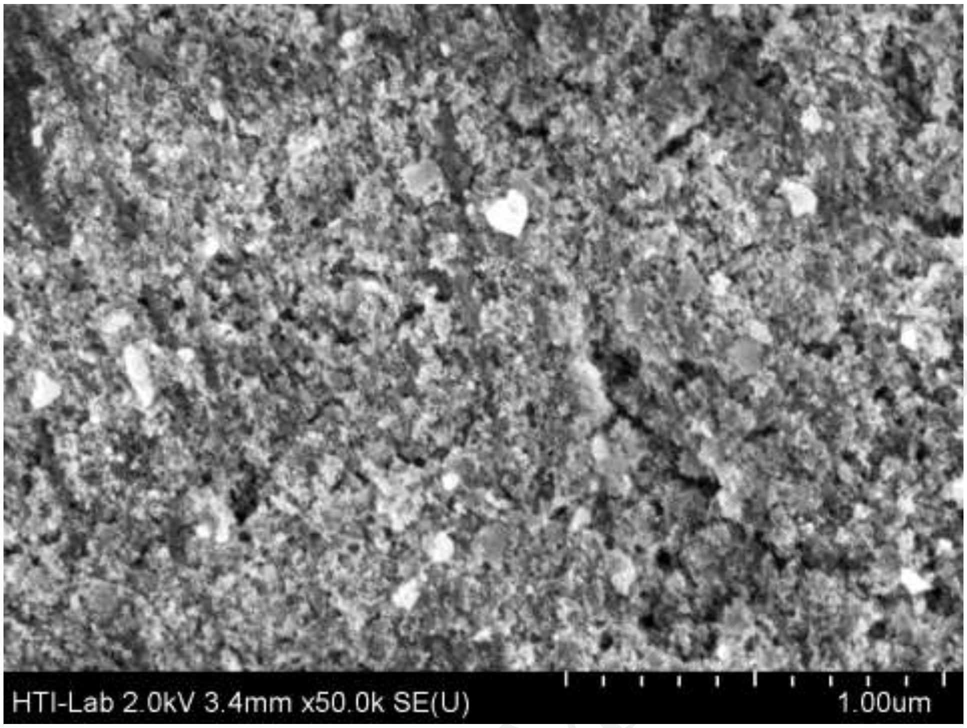

Figure 1. Scanning electron microscopy (SEM) image for diamond composite electrode. The scan was performed at high magnification (×50,000 times) with image resolution at 1.00 μm.

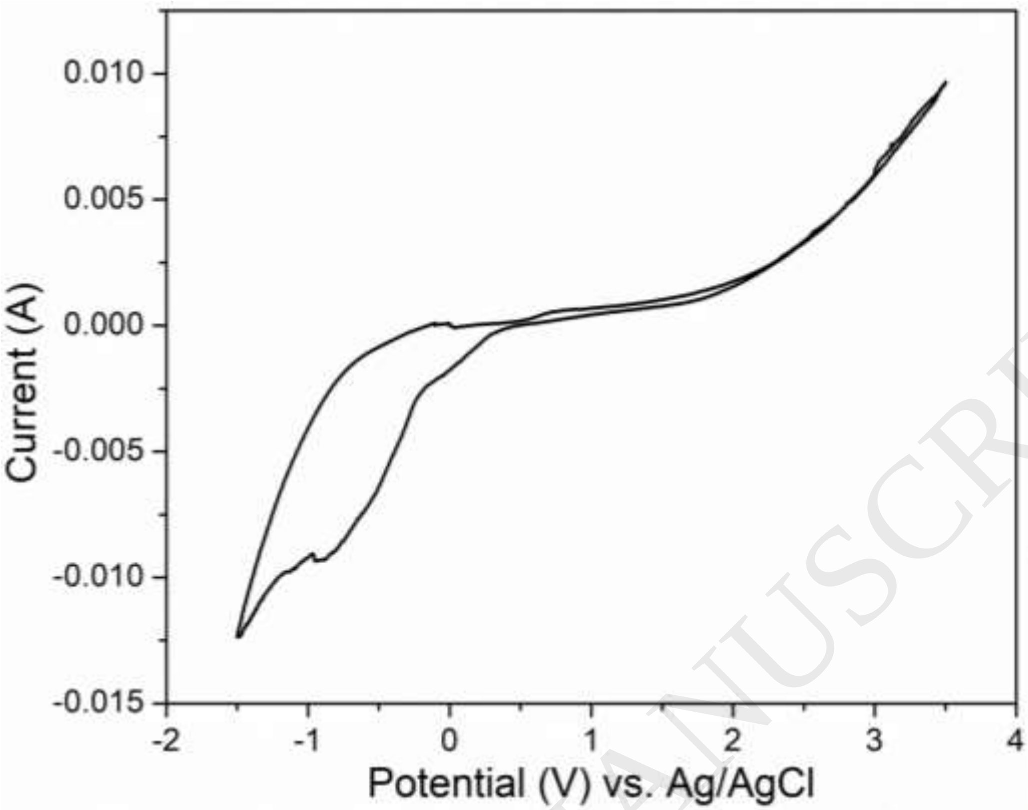

Figure 2. Cyclic voltammetry of diamond composite electrodes in an aqueous solution of 0.25 M H_2SO_4. Scan rate 100 mV/s and 25 ^oC temperature.

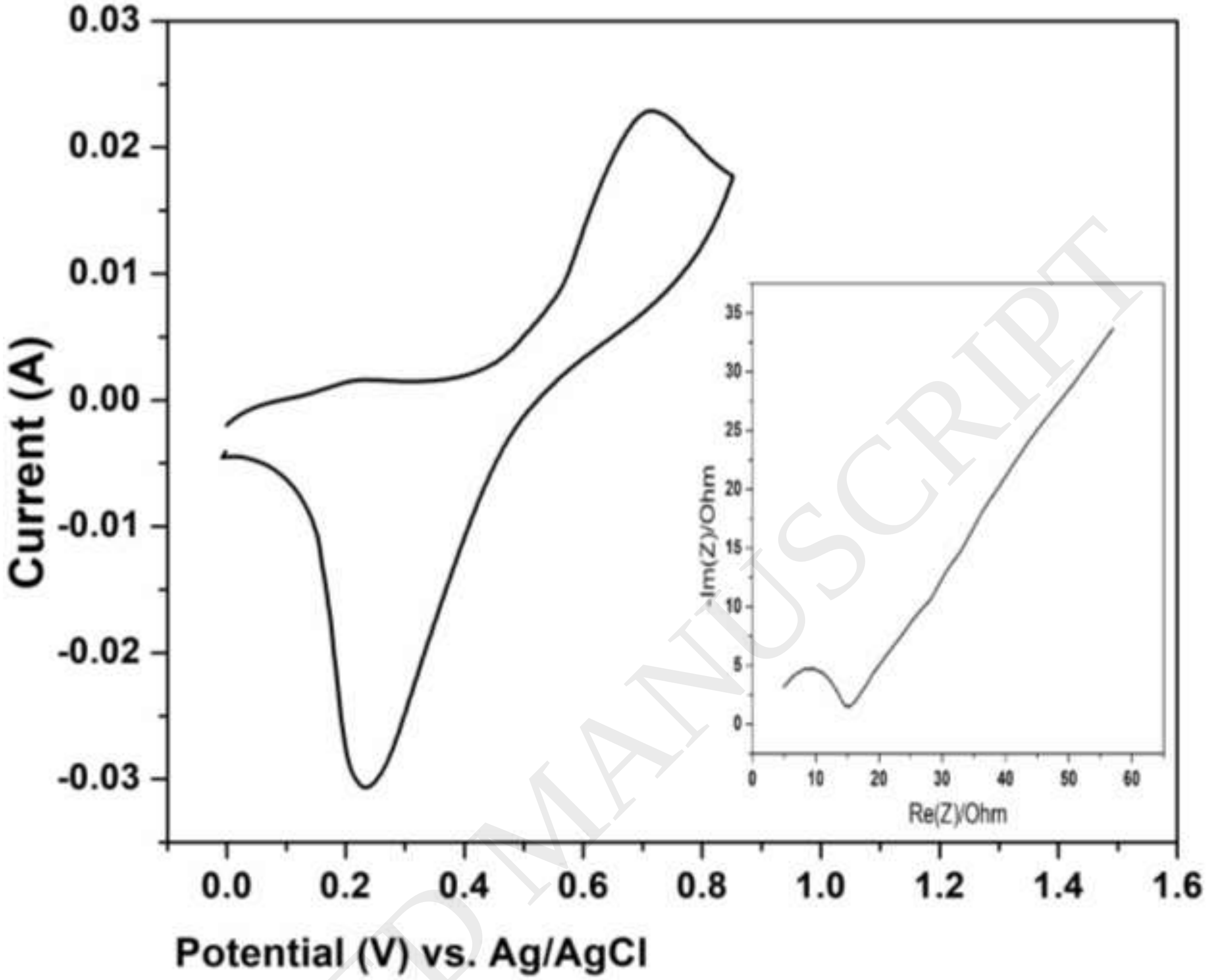

Figure 3. Cyclic voltammogram of diamond composite electrode in aqueous solution of 0.25 M H_2SO_4 containing 5 mM $K_4Fe(CN)_6$ at 100 mV/s scan rate and 25 °C. Inset is the Nyquist plot of the electrode in same aqueous solution at zero potential vs. Ag/AgCl.

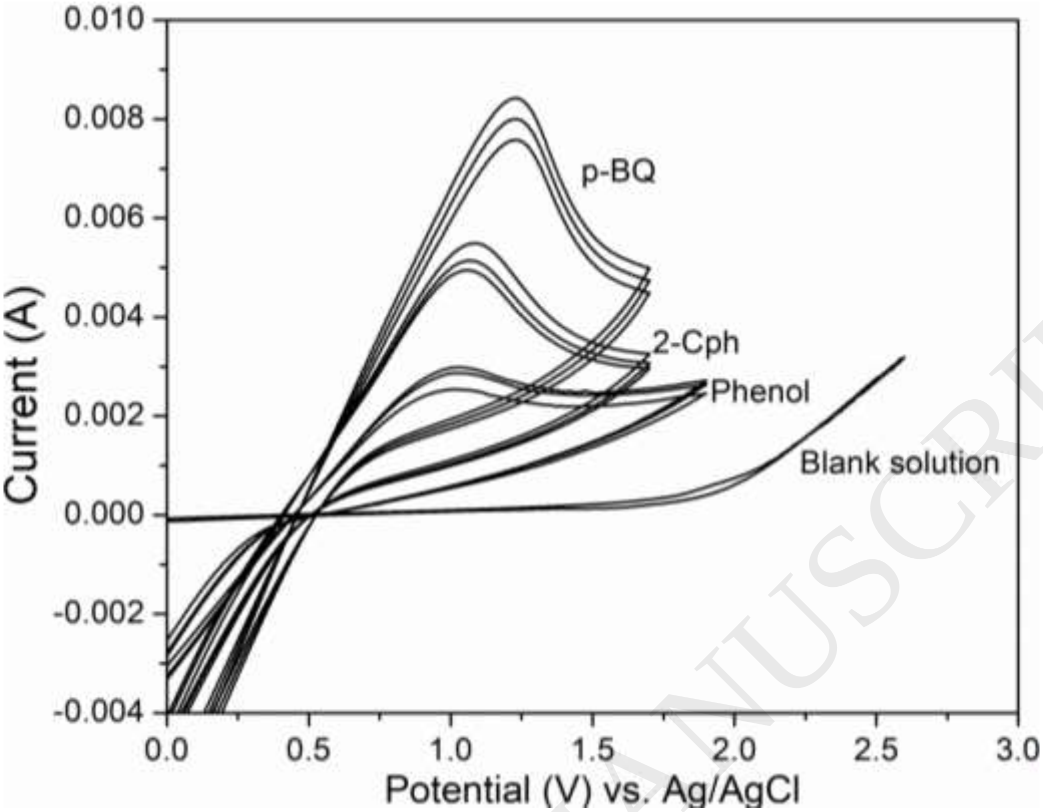

Figure 4. Cyclic voltammograms of diamond composite electrodes in an aqueous solution of 0.1 M sulfuric acid containing 200 mg/L p-BQ, 2-Cph or phenol. Scan rate 100 m V/s and 25 ^{o}C temperature and pH 3

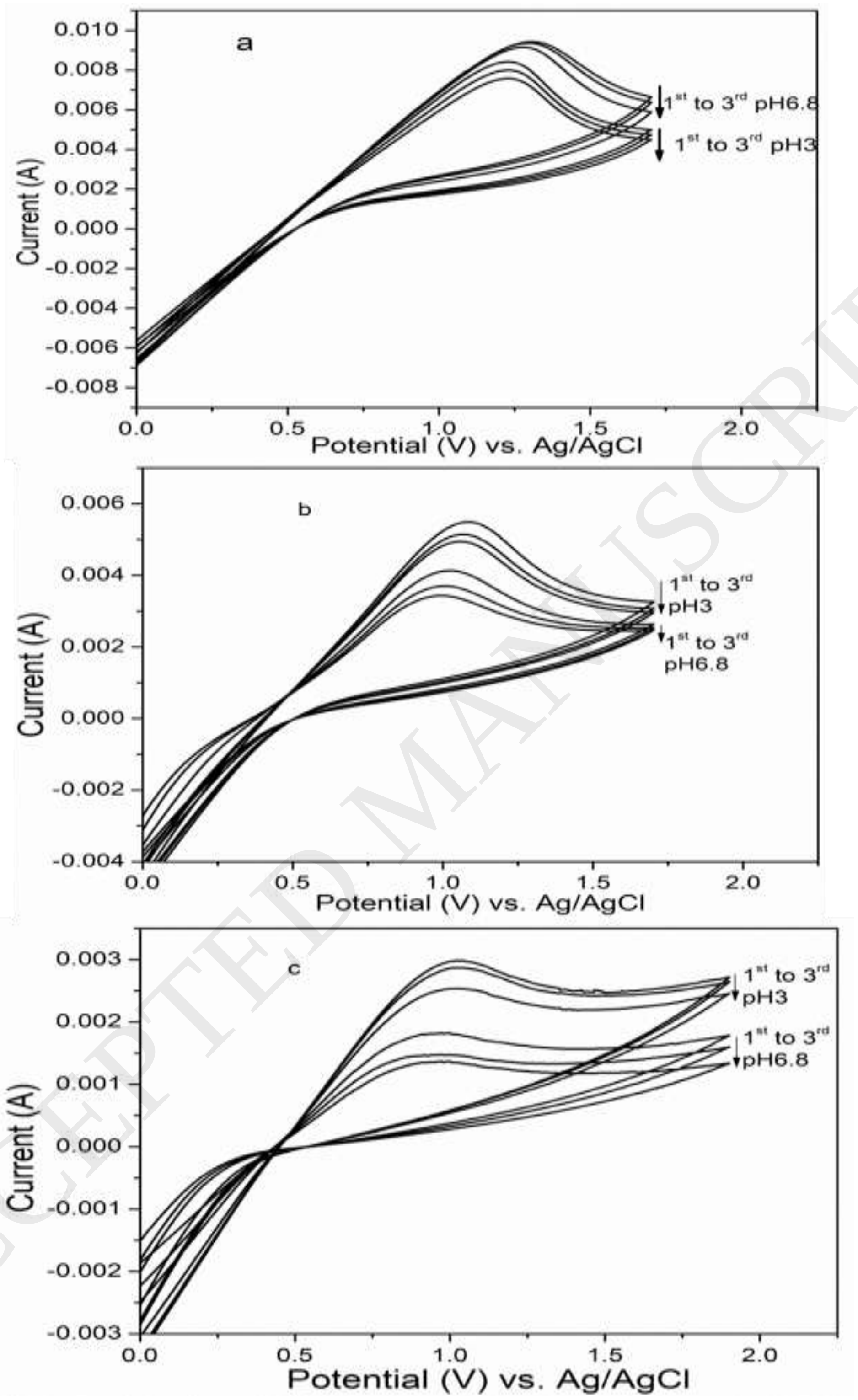

Figure 5. Cyclic voltemmograms recorded for 200 mg/L p-BQ, 2-Cph or phenol in an aqueous solution of (a) 0.1 M H_2SO_4 at pH 3 and in (b) an aqueous solution of 0.25 M Na_2SO_4 at pH 6.8. Scan rate 100 mV/s and 25 ^oC temperature.

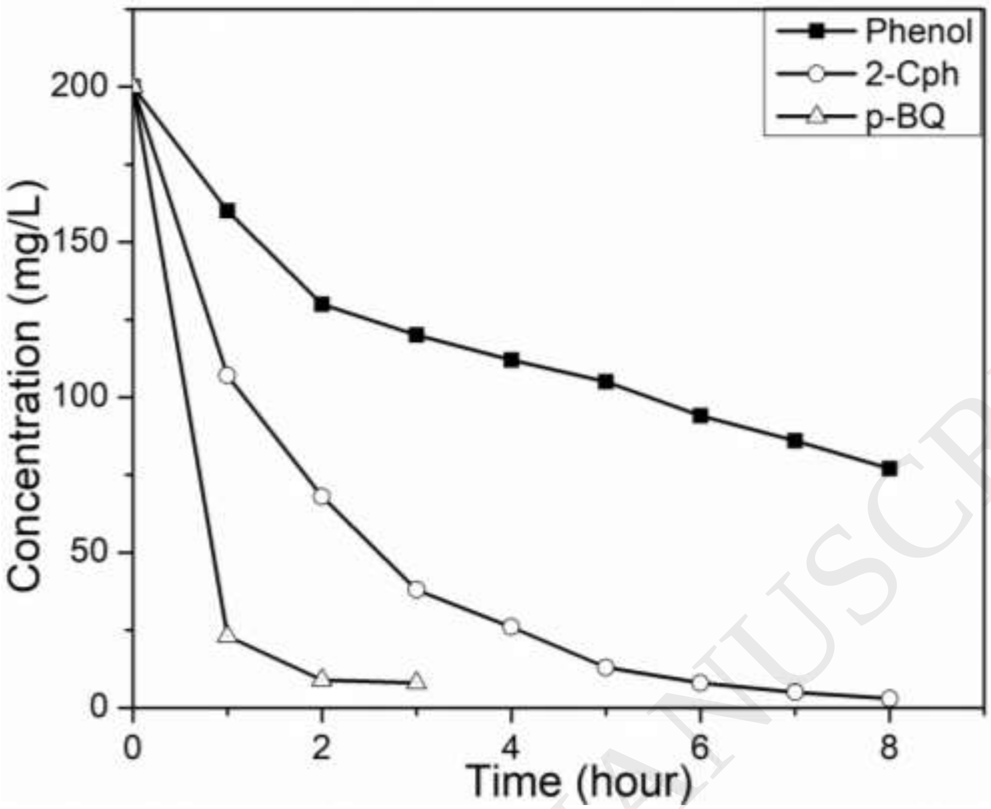

Figure 6. Electrochemical degradation of 200 mg/L p-BQ, 2-Cph, and phenol in aqueous solution of 0.25 M Na_2SO_4 as supporting electrolyte at pH 3 and 25 ºC temperature.

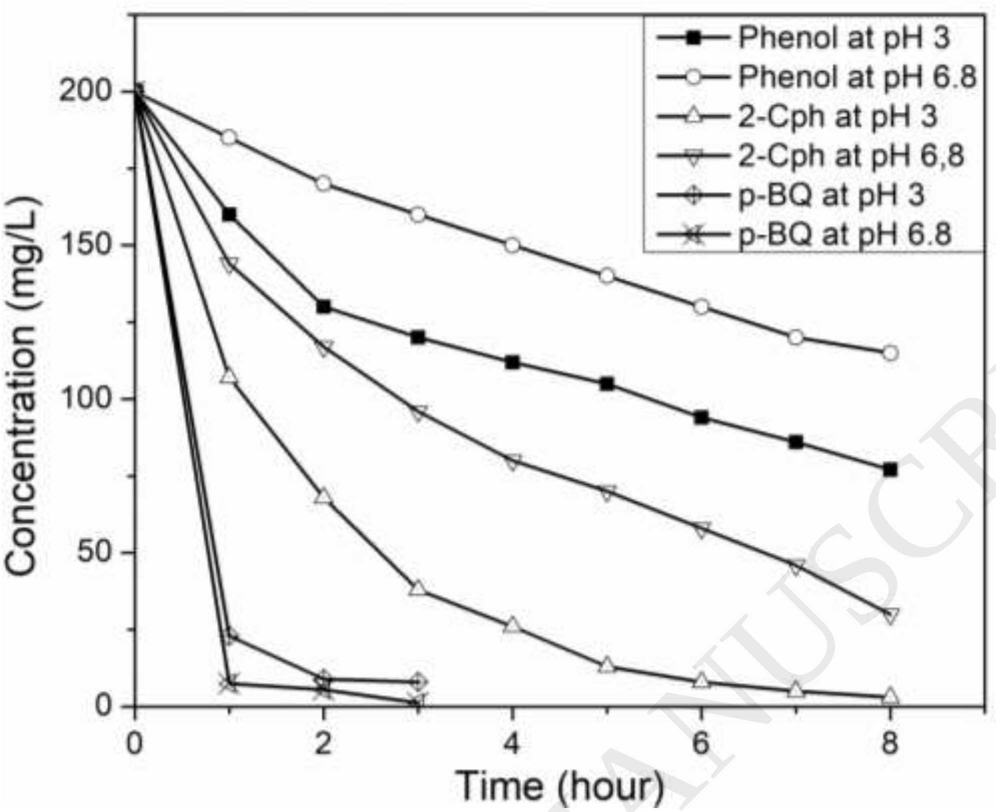

Figure 7. Electrochemical degradation of 200 mg/L of p-BQ, 2-Cph, and phenol in different pH solutions (pH 3 and pH 6.8) with 0.25 M Na_2SO_4 as supporting electrolyte and 25 ^oC temperature.