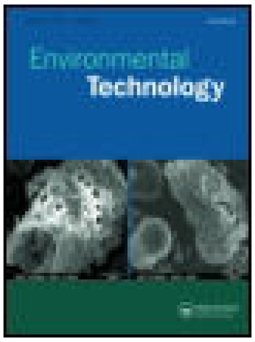

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Electrochemical degradation of psychoactive drug caffeine in aqueous solution using graphite electrode

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Abstract: In this study, the electrochemical degradation of caffeine (1, 3, 7-trimethylxanthine) in aqueous solution by a graphite electrode was investigated. Electrochemical degradation was tested by cyclic voltametry technique performed in the potential range of -1.0 to +1.0 V versus Ag/AgCl, which confirmed the electro-activity of the selected caffeine. The effects of the treatment process variables, such as initial pH, current density, electrolyte concentration and electrolysis time on the degradation of caffeine were explored. During the various stages of electrolysis, parameters such as COD, TOC were analysed. The maximum COD and TOC removal efficiency of 85% and 77% was achieved at neutral pH 7, operated at the current density of 5.1 mA/cm^2, electrolyte (Na_2SO_4) concentration of 0.1 M and at 240 min electrolysis time. From this study, it can be concluded that electrochemical treatment process could effectively reduce the COD and TOC from the caffeine in aqueous medium. The degradation of the caffeine were confirmed by UV spectra, IR Spectra and HPLC analysis.

Keywords: Caffeine, COD, TOC, Electrochemical degradation, Graphite electrode

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1. Introduction

Caffeine ($C_8H_{10}N_4O_2$) is an alkaloid belonging to methylxanthine family. In human, caffeine acts as a central nervous system (CNS) stimulant, temporarily warding off drowsiness and restoring alertness. This drug is highly consumed, for example, in high-developed countries, 90% of adults consume caffeine daily. Caffeine is the world's most widely consumed psychoactive substance [1].

Caffeine is ranked as the number one drug worldwide, with a massive production of hundreds of ton [2]. Usually employed as a stimulant, caffeine is commonly found in coffee, tea, chocolate, cocoa, and soft drinks. It is also a component of hundreds of prescription drugs, ranging from analgesics to cold medicines. Caffeine is therefore introduced continuously into the sewage system through many anthropogenic sources and is likely to persist in water because of its high solubility (21.7 g L^{-1}) and negligible volatility [3].

Despite the fact that it is high in nutrients, it cannot be used as animal feed due to the high levels of caffeine and other unwanted compounds [4]. Solvents commonly used to produce caffeine-free products are either very expensive to use or toxic [5]. However, a number of bacterial and fungal strains capable of biodegrading caffeine have been identified. There are various possible pathways depending on the genus, species and strain of organism biodegrading the caffeine. In the bacteria *Psuedomonas putida* and *Serratia marcescens*, the major pathway is through theobromine to 7-methylxanthine to Xanthine [6].

The biodegrading caffeine process major physical factors which affect microbial growth and degrading compounds are solutes and water activity, pH, temperature, oxygen level, pressure and radiation. Biodegradation can occur both aerobic and an-aerobic mode, still complete removal/degradation is not possible with conventional methods [7].even municipal wastewater treatment plants could not degrade caffeine completely [8].

Caffeine can be abated through advanced oxidation processes (AOPs) such as photo-Fenton process [9],catalytic degradation [10], ozone treatment [11],and electrochemical oxidation [12].Electrochemical oxidation is becoming a strong alternative for wastewater treatment because many industrial processes produce toxic wastewater, which are not easily biodegradable, and require costly physical or physiochemical pretreatments [13].On the other hand, the electrooxidation approach has been demonstrated to be a well established and an effective technology to destruct the biologically persistent organic pollutants in water or wastewater treatment [14].

A wide range of variables may influence the performance of wastewater treatment. In the case of electrooxidation, inorganic salts present in the medium can play an important role in the oxidation mechanisms of Persistent organic pollutant (POP) degradation [15-18].Compared with other methods for wastewater treatment, electrochemical technologies have many advantages they are convenient, highly efficient, and environmentally friendly [19].The electrochemical treatment of wastewater aims to mineralize organic contaminants to carbon dioxide or, at least, to transform them into more biodegradable and/or less toxic compounds [20].

This study aimed to degrade the caffeine contaminated wastewater under different operating variables, such as initial pH, applied current density, the supporting electrolyte concentration, and electrolysis time on the removal of chemical oxygen demand (COD) and total organic carbon (TOC) using electrooxidation technique.

2. Experimental

2.1 Chemicals

Analytical grade chemicals were used as received. Caffeine was purchased from Sigma-Aldrich (USA).The physiochemical property of caffeine is shown in Table 1. Sodium hydroxide, sodium sulphate, sulphuric acid, Ferrous ammonium sulphate, mercuric sulphate, silver sulphate, ferroin solution, dichloromethane were obtained from Hi media (Mumbai, India). All solutions were prepared in double distilled water and the pH value was adjusted by adding HCl (5%, v/v) and NaOH (5%, w/w). HPLC-grade Acetonitrile, water purchased from Sigma Aldrich without any further purification.

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2.2 Electrolytic system

The electrochemical treatments were performed using a glass reactor with a working volume of 250 mL.The experimental setup used for this study is shown in Figure 1. Having desired concentration of caffeine in the glass reactor was stirred continuously using magnetic stirrer. The graphite electrode with an effective surface area of 24 cm^2 (dimensions: 4×3 cm; thickness: 1 mm) was used as a working electrode. The electrode assembly was connected to DC power supply (Sri Sai Scientific, Coimbatore, India). The effect of the process variables, such as initial concentration of caffeine 20 mg/L, pH (5-7), current density (3.1-7.1 mA/cm^2), processing time (0-240 min), with supporting electrolyte concentration (0.02-0.1 M Na_2SO_4) were examined. During the process electrode distance was maintained at 2 mm to reduce the ohmic losses. The pH of solution were measured before and after treatment using the pH meter (Susima AP-1 Plus, Chennai, India). Electrolytic system was maintained at room temperature.

2.3 Analytical Method

The cyclic voltametry (CV) experiments were carried out by electrochemical workstation (Bio-Logic SP-50, France). The experiments were performed in the potential scan range between -1.0 and +1.0 versus three electrode cell was constructed using Pt wire as a counter electrode, Ag-AgCl as reference electrode and graphite electrode as working electrode respectively. Scan rate was set at 2 mV/s. During the electrochemical treatment, the sample were drawn at different time interval and the degradation of Caffeine molecule was recorded by UV-vis spectrophotometer (Shimadzu UV-160A, Japan).The standard method suggested by American Public Health Association was adopted for the analysis of COD (APHA 1998).

Caffeine degradation was analyzed using liquid chromatography (Waters, Milford, MA) equipped with the photodiode array detector (PDA), the data were processed with Empower software. The separation was achieved on symmetry® C18 column (4.6mm×250 mm, 5µm) using the mobile phase acetonitrile: water at a ratio of 60:40. The chromatographic conditions flow rate, temperature, wavelength and injection volume were set at 1.0 mL/min, 25ºC, 273 nm and 20µL, respectively**.**

The mineralization of caffeine was determined using TOC analyzer (Analytik Jena, Germany).The TOC removal ratio was estimated using the equation 1.

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TOC removal = (TOC_t/TOC_o) ×100% ... (Eq.1)

Where TOC_t is the value of TOC (mg/L) in aqueous solutions and TOC_o is the initial TOC value of caffeine (mg/L).

IR spectra were recorded using FT-IR spectrometer (Shimadzu 8201PC, Japan).

3. Results and Discussion

3.1 Cyclic voltammetric study of caffeine oxidation

Cyclic voltametry is usually performed as the first experiment in an electro analytical study. This technique was widely used for acquiring both qualitative and quantitative information on electrochemical reactions. Further, it offers a rapid location of oxidation and reduction potential of the electroactive species. In order to understand the redox behavior of caffeine on graphite electrode, experiments were conducted in a conventional, 3-electrode configuration with Ag/AgCl reference electrode and pt wire as the auxiliary electrodes and graphite electrode as working electrode using scan rate at 2 mV/s in 0.1 M Na_2SO_4 electrolyte. The experiments were conducted within a potential range from -1 to +1 V versus Ag/AgCl in 0.1 M Na_2SO_4 having concentration of the background electrolytes. Fig. 2 shows the cyclic voltammograms obtained for 0.1 M Na_2SO_4 solutions (supporting electrolyte) with and without 20 mg/L caffeine. Absence of caffeine in 0.1 M Na_2SO_4, a small shoulder was detected at about +1 V vs. Ag/AgCl. This is attributed to the oxidation of sulphate to per sulphate [21].When caffeine was added in the supporting electrolyte, clear oxidation peaks were observed at 0.5 V to 0.1 V vs. Ag/AgCl which is greater than that of background solution. It was mainly due to the contribution of caffeine oxidation. Moreover, aromatic intermediates might be formed during the oxidation process [22]. However, during the reverse scan from + 0.1. to − 0.1 V, corresponding reduction peak have not been identified, this findings reveals that the electrochemical oxidation of caffeine on graphite electrode was totally irreversible.

3.2 Effect of Initial pH

pH is an important factor for wastewater treatment. In anodic oxidation, there are many reports on the influence of solution pH, but the results are diverse and even contradictory due to different organic structures and employed electrode materials [23, 24]. To study the effect of pH

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on caffeine degradation experiments were carried out at different pH such as 5, 7 and 9 with an electrolyte concentration at 0.1M Na_2SO_4 with current density of 5.1 mA/cm^2. Results obtained from this study are presented in Figure 3. It showed that the caffeine degradation efficiency gradually increased from pH 5 to 9 and then upto the maximum removal of caffeine 90 % at pH 7, indicating that the degradation of caffeine more favorable in neutral environment, but, it showed slightly decreased at pH 5 and 9 were 83 % and 85%,respectively. It was found that the removal efficiency of caffeine, COD and TOC was higher in neutral pH than in acidic and alkaline conditions. It can be noticed that the maximum removal of COD and TOC were 85% and 77% observed at pH 7 respectively.

3.3 Effect of supporting electrolyte

The wastewater conductivity is an important factor for the electrochemical treatment processes. Electrolyte concentration is an important factor in electrochemical oxidation system [25, 26].In general, the larger the conductivity, the lower the ohmic-drop across the electrochemical cell, and the greater the efficiency of the process [27].In this experiment Na_2SO_4 was selected as the supporting electrolyte to avoid the production of toxic and carcinogenic chlorinated species [28].Commonly, adding Na_2SO_4 into the solution had positive influence on electrochemical oxidation efficiency. This could be attributed to the fact that good electro-conductivity leads to faster electron transfer and better degradation ratio. The insitu generation of sulphate radical ($S_2O_8^{2-}$) in the presence of Na_2SO_4 [29] during electrooxidation could be represented as, in Eq.2 to Eq.4.

$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^-$ … (Eq.2)

$^{\bullet}OH + 2SO_4^{2-} \rightarrow SO4^{-\bullet} + OH^-$ ... (Eq.3)

$SO_4^{-\bullet} + SO4^{-\bullet} \rightarrow S_2O_8^{2-}$ ... (Eq.4)

To study the effect of electrolyte concentration on caffeine degradation were carried out at different electrolyte concentration such as 0.02, 0.05 and 0.01 M Na_2SO_4. The experiments were carried out using a current density of 5.1 mA/cm^2 for graphite electrode at pH 7, respectively and results obtained are presented in Figure 4. The caffeine degradation efficiency increased significantly with the 0.02 to 0.1 M Na_2SO_4. After 240 min degradation, the relative removal rate

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was 51%, 70% and 90% at electrolyte concentration of 0.02, 0.05 and 0.1 M Na_2SO_4 respectively. At the same experimental conditions COD removal were 42%, 58% and 85%, respectively.

3.4 Effect of current density

Current density is an important parameter on pollutant removal in electrochemical process. Some research indicated that high current density could cause an increase of electrode material decomposition while it could also lead to side reactions including oxygen evolution at the same time [30].To study the influence of different current density on degradation of caffeine, it was varied at 3.1, 5.1 and 7.1 mA/cm^2. The initial concentration of caffeine at 20 mg/L, electrolyte concentration of 0.1 M Na_2SO_4 at pH 7 maintained for all experiments.

The results obtained are shown in Figure 5. The caffeine concentration and COD removal were observed at 71%, 90%, 99% and 60%, 85%, 93% with a current density 3.1, 5.1 and 7.1 mA/cm^2 respectively. This was primarily, higher current density could produce large amount of hydroxyl radicals [31].which resulted in higher degradation removal efficiency of caffeine. It was noted that the rate of degradation increased significantly when the applied current density increased. High voltage attributed to high current density inducing of oxygen evolution as shows in equation 5 and 6 [32, 33].

$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ … (Eq.5)

$2^{\bullet}HO \rightarrow O_2 + 2H^+ + 2e^-$ … (Eq.6)

High current could lead a part of electric energy transfer to thermal energy and result in a larger invalid consumption of the giving charge. In addition, much higher current density also leads to more energy dissipation and shorten the life of electrode [34]. Hence from above suggestion, a current density of 5.1 mA/cm^2 was chosen for the further studies.

3.5 Effect of electrolysis time

The effects of electrolysis time on caffeine degradation were carried out at different electrolysis time such as 0, 30, 60,120,180, and 240 min. The Experiments were performed at a constant

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current density of 5.1 mA/cm^2, electrolyte (Na_2SO_4) concentration of 0.1M and optimum pH 7 Results obtained are presented in Figure 6. The maximum removal efficiency caffeine concentration, COD and TOC increases with electrolysis time. It was noted that the caffeine concentration, COD and TOC removal were 90 %, 85 % and 77% respectively.

3.6 UV spectra studies

To confirm the degradation, samples are collected at different time interval and their corresponding UV spectra were recorded and are presented in Figure 7. It can be seen that a maximum absorbance peak occurs at 273 nm, representing the caffeine, which disappear gradually during the electrochemical oxidation process with increasing treatment time. It can be concluded that the caffeine degradation was increased with increasing time.

3.7 FT-IR analysis of caffeine

In order to know the functional group changes during electrooxidation of caffeine, FT-IR Spectra was recorded the samples obtained after 240 min of treatment. Spectra obtained are presented in Figure 8. The peaks at 3337.21 cm^{-1} supports for H- C-H stretching in methane group. The peak at 3108.69 cm^{-1} and 2952.48 cm^{-1}corresponds to aromatic -CH stretching vibrations. The peak at 2570.65 cm^{-1} indicates -CH stretch. The peaks at 1653.66 and 1477.21 cm^{-1} corresponds to C=C and C-C stretches respectively. The other peaks at 1546.63 cm^{-1} and below 1477.21 cm^{-1} represents C-N stretches.

FT-IR spectra of after 240 min degradation products showed different peaks at 3330.46 cm^{-1} for the presence of N–H stretching. Characteristic of this functional group is observed along with the broad OH stretching band at 3434.6 cm^{-1}. Overtone combination bands appear at 2030.68 cm^{-1}.Absence of peaks at 3108.69 and 2952.48 cm^{-1} indicated the demethylation of caffeine. No C=O band due to a carboxylic acid is observed but very weak bands are observed around 1637.27 cm^{-1} which indicate the presence of some carboxylate salts in the sample. In addition, a very broad N-H out of plane band is observed at 508.151 cm^{-1}. Signals due to C-H and C-H strectch band along with C-C=H out of plane bending bands is still observed in the sample. The FT-IR spectra data supported the functional group changes of caffeine during electrooxidation process.

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3.8 HPLC studies

Further to confirm the degradation of caffeine during electrooxidation process, samples were analysed using HPLC. The spectra obtained are presented in Figure 9. The retention time of caffeine at 2.8 min. After 240 min the peak has been decreased due to the oxidation of caffeine molecules. However the other peaks were observed which indicated the formation of by-products such as 1-Methylxanthine. It was calculated based on area found that 92% caffeine reduction has been occurred.

4. Conclusion

Electrochemical degradation of caffeine was carried out to optimize the influencing variables such as initial pH, current density, electrolyte concentration were evaluated. The degradation efficiency of caffeine was achieved 90%, COD and TOC removal were 85% and 77% respectively after 240 min electrolysis under optimal condition with 0.1 M Na_2SO_4 with neutral pH 7.0 respectively. Neutral pH 7 has shown maximum reduction of caffeine, COD and TOC compared with acidic and alkaline pH. The supporting electrolyte sodium sulphate was found to be for effective maximum removal of caffeine. An increase in current density, electrolysis time resulted in increase caffeine, COD removal. The cyclic voltametric studies have revealed that the caffeine is oxidized at + 0.5 to 1.0 V by direct electron transfer. UV-vis spectra confirmed the caffeine degradation pattern. FT-IR spectra confirmed the functional group changes before and after electrolysis of caffeine. HPLC studies revealed the byproduct formation. The results obtained in this study shows that the electrochemical degradation a efficient method for removal of psychoactive drug caffeine in aqueous medium.

References

[1] Lovett R, Coffee Demon drink. New Sci.2005; 187:38-4.

[2] Gardinali P. R, Zhao X.Trace determination of caffeine in surface water samples by liquid chromatography--atmospheric pressure chemical ionization--mass spectrometry (LC-APCI-MS). Environ. Int.2002; 28:521-528.

[3] Seiler R. L, Zaugg S. D, Thomas J. M, Howcroft D. L, et al. Caffeine and pharmaceuticals as indicators of waste water contamination in wells. Groundwater.1999; 37: 405-410.

ACCEPTED MANUSCRIPT

[4] Pandey A, Soccol CR, Nigam P, Brand D, Mohan R, Roussos S, et al. Biotechnological potential of coffee pulp and coffee husk for bioprocesses. Biochem Eng J. 2000; 1; 6(2):153-162.

[5] Dash SS, Gummadi SN. Catabolic pathways and biotechnological applications of microbial caffeine degradation. Biotechnol Lett. 2006; 28(24):1993-2002

[6] Mazzafera P,Catabolism of caffeine in plants and microorganisms.Front Biosci. 2004;1; 9:1348-59.

[7] Salihu Ibrahim,Mohd Yunus Shukor,Mohd Arif Syed,Nor Arina Ab Rahman,Khalilah Abdul Khalil,Ariff Khalid and Siti Aqlima Ahmad,et al.Bacterial Degradation of Caffeine: A Review Asian Journal of Plant Biology.2014;2,(1):18-27.

[8] María J. Martín de Vidales, María Millán, Cristina Sáez, , José F. Pérez, Manuel A. Rodrigo, Pablo Cañizares,et al. Conductive diamond electrochemical oxidation of caffeine-intensified biologically treated urban wastewater.Chemosphere.2015;136: 281–288

[9] Trovó A.G, Silva T.F.S, Gomes O. Jr, Machado A.E.H, Neto W.B, Muller P.S.Jr, Daniel D,et al.Degradation of caffeine by photo-Fenton process: Optimization of treatment conditions using experimental design.Chemosphere.2013;90:170−175,10.

[10] Qi F, Chu W, Xu B,et al.Catalytic degradation of caffeine in aqueous solutions by cobalt-MCM41 activation of peroxymonosulfate. Appl. Catal. B: Environ. 2013; 134−135,324−332, 11.

[11] Rosal R, Rodríguez A, Perdigón-Melón J.A, Petre A, García-Calvo E, Gómez M.J, Agüera A, FernándezAlba A.R, et al.Degradation of caffeine and identification of the transformation products generated by ozonation. Chemosphere.2003; 74:825−831, 12.

[12] Indermuhle C, de Vidales M.J.M, Sáez S, Robles J, Cañizares P, García-Reyes J.F, Molina-Díaz A, Comninellis C, Rodrigo M.A,et al.Degradation of caffeine by conductive diamond electrochemical oxidation.Chemosphere.2013;93:1720−1725.

[13] Pulgarin C, Adler N, Peringer P, Comninellis C,et al. Electrochemical detoxification of a 1,4-benzoquinone solution in wastewater treatment. Water Res.1994; 28 (4): 887.

ACCEPTED MANUSCRIPT

[14] Chen G.Electrochemical technologies in wastewater treatment. Sep. Purif. Technol.2004; 38: 11−41.

[15] Serrano K, Michaud P.A, Comninellis C, Savall A, et al. Electrochemical preparation of peroxodisulfuric acid using boron doped diamond thin film electrodes. Electrochim. Acta.2002; 48:431-436.

[16] Wang J, Farrell J. Electrochemical Inactivation of Triclosan with Boron Doped Diamond Film Electrodes. Environ. Sci. Technol.2004; 38:5232-5237.

[17] Murata M, Ivandini T.A, Shibata M, Nomura S, Fujishima A, Einaga Y,et al. Electrochemical detection of free chlorine at highly boron-doped diamond electrodes. Electroanal. Chem.2008; 612:29-36

[18] Polcaro A.M, Vacca A, Mascia M, Ferrara F,et al. Product and by-product formation in electrolysis of dilute chloride solutions. J.Appl. Electrochem .2008; 38:979-984.

[19] Bergmann M.E.H, Rollin J, Iourtchouk T,et al, The occurrence of perchlorate during drinking water electrolysis using BDD anodes. Electrochim. Acta.2009; 54:2102-2107

[20] Zhang X.D, Li W.S, Huang Y.J, Peng H.Y,et al. Promotion of oxygen reduction of oxygen reduction reaction on vitreous carbon electrode by DTAB. Acta. Phys.-Chim. Sin.2008; 24 (4): 691.

[21] Martínez-Huitle C.A, Quiroz M.A, Comninellis C, Ferro S, Battisti A.D,et al. Electrochemical incineration of chloranilic acid using Ti/IrO2, Pb/PbO2 and Si/BDD electrodes. Electrochim. Acta .2004; 50:949–956

[22] Martínez-Huitle C.A, Brillas, E. Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods: A general review. Applied.2009; 87:105-145.

[23] Brinzila C.I, Pacheco M.J, Ciríaco L, Ciobanu R.C, Lopes A, et al. Electrodegradation of tetracycline on BDD anode. Chemical Engineering Journal.2012; 209:54-61.

ACCEPTED MANUSCRIPT

[24] Hachami F, Salghi R, Errami M, Bazzi L, Hormatallah A, Chakir A, Hammouti B,et al. Electrochemical oxidation of methidathion organophosphorous pesticide, I.J .Phys. Chem. News.2010;52:106.

[25] Errami M, El Mouden O.I.D, Salghi R, Zougagh M, Zarrouk A, Hammouti B, Chakir A, Al-Deyab S.S, Bouri M,et al. Detoxification of bupirimate pesticide in aqueous solutions by electrochemical oxidation. I.J. Der Pharm. Chem.2012; 4:297.

[26] Abaci S, Pekmez K, Yildiz A,et al. The influence of nonstoichiometry on the electrocatalytic activity of PbO_2 for oxygen evolution in acidic media. Electrochem. Commun.2005; 7:328.

[27] Low C.T.J, Pletcher D, Walsh F.C, et al. The electrodeposition of highly reflective lead dioxide coatings. Electrochem. Commun.2009; 11:1301.

[28] Malpass G.R.P, Miwa D.W, Mortari D.A, Machado S.A.S, Motheo A.J,et al. Decolorisation of real textile waste using electrochemical techniques: Effect of the chloride concentration. Water Res .2007; 41:13, 2969.

[29] Guenfoud F, Mokhtari M, Akrout H, et al. Electrochemical degradation of Malachite Green with BDD electrodes: Effect of electrochemical parameters. Diam, Relat.Mater.2014; 46: 8-14.

[30] Marselli B, Garcia-Gomez J, Michaud P.A, Rodrigo M. A, Comninellis Ch,et al. Electrogeneration of Hydroxyl Radicals on Boron-Doped Diamond Electrodes, Electrochem. Soc.2003;150:3,D79-D83

[31] Kobya M, Demirbas M, Bayramoglu M, et al. Treatment of the textile wastewater by combined electrocoagulation. Chemosphere.2006; 132,183.

[32] Panizza M, Cerisola G. Influence of anode material on the electrochemical oxidation of 2-naphthol: Part 2. Bulk electrolysis experiments. Electrochemica.Acta.2004; 49:3221-3226.

[33] Samet Y, Agengui L, Abdelhedi R,et al.Electrochemical degradation of chlorpyrifos pesticide in aqueous solutions by anodic oxidation at boron-doped diamond electrodes. Chem Eng J.2010; 161:167-172.

ACCEPTED MANUSCRIPT

[34] Niu J, Li Y, Shang E, Xu Z, Liu J,et al. Electrochemical oxidation of perfluorinated compounds in water. Chemosphere.2016; 146:526-538.

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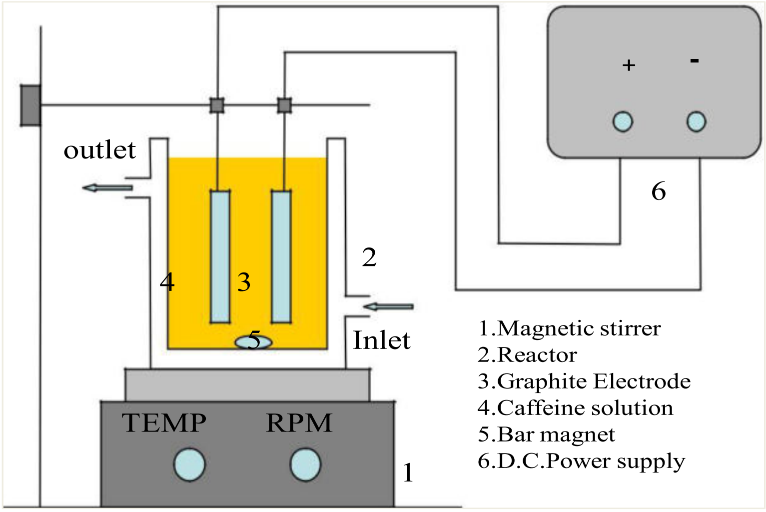

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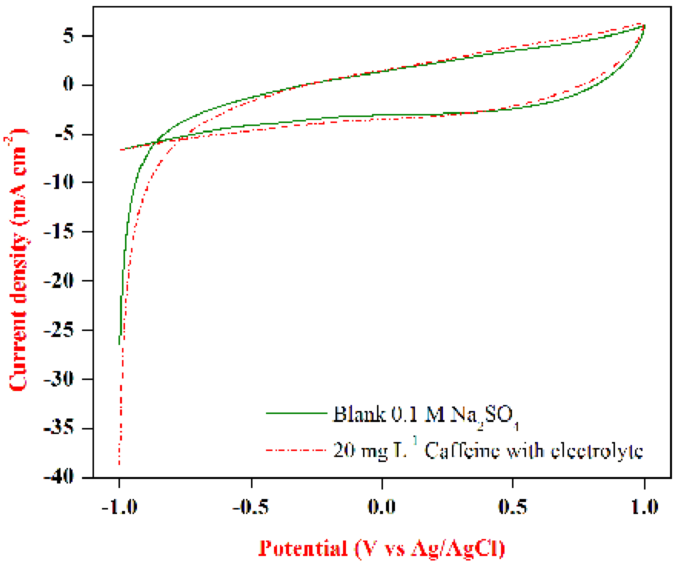

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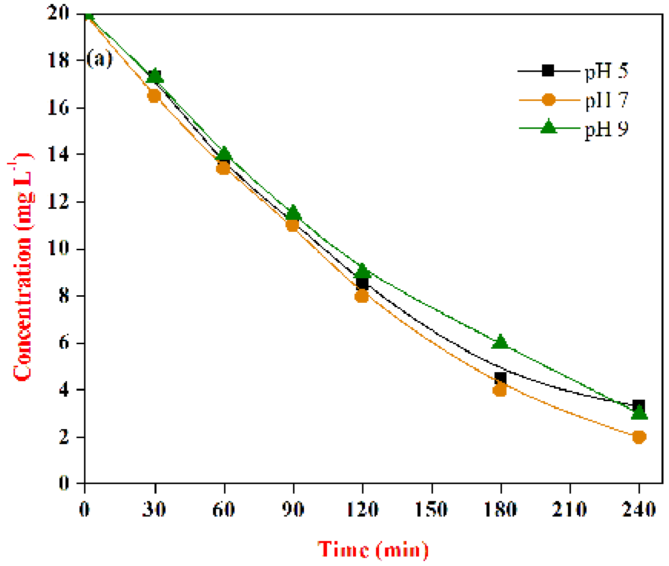

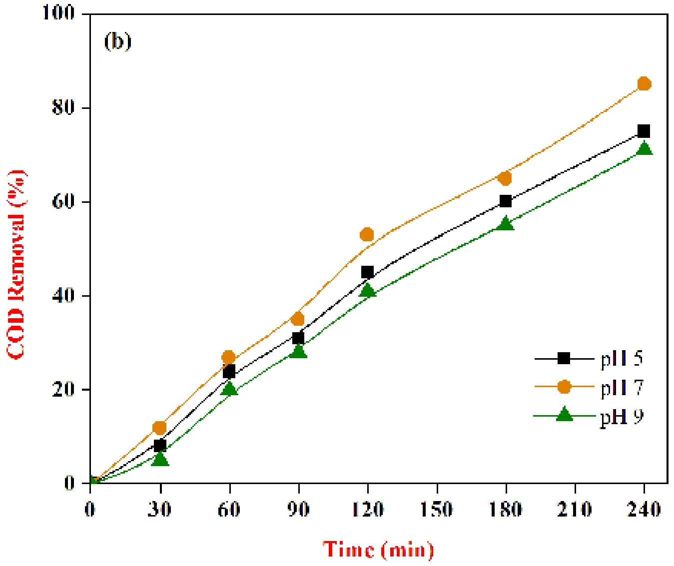

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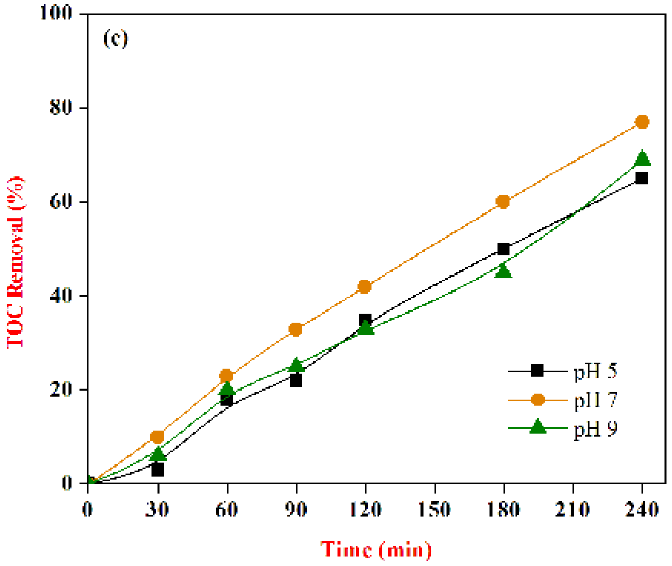

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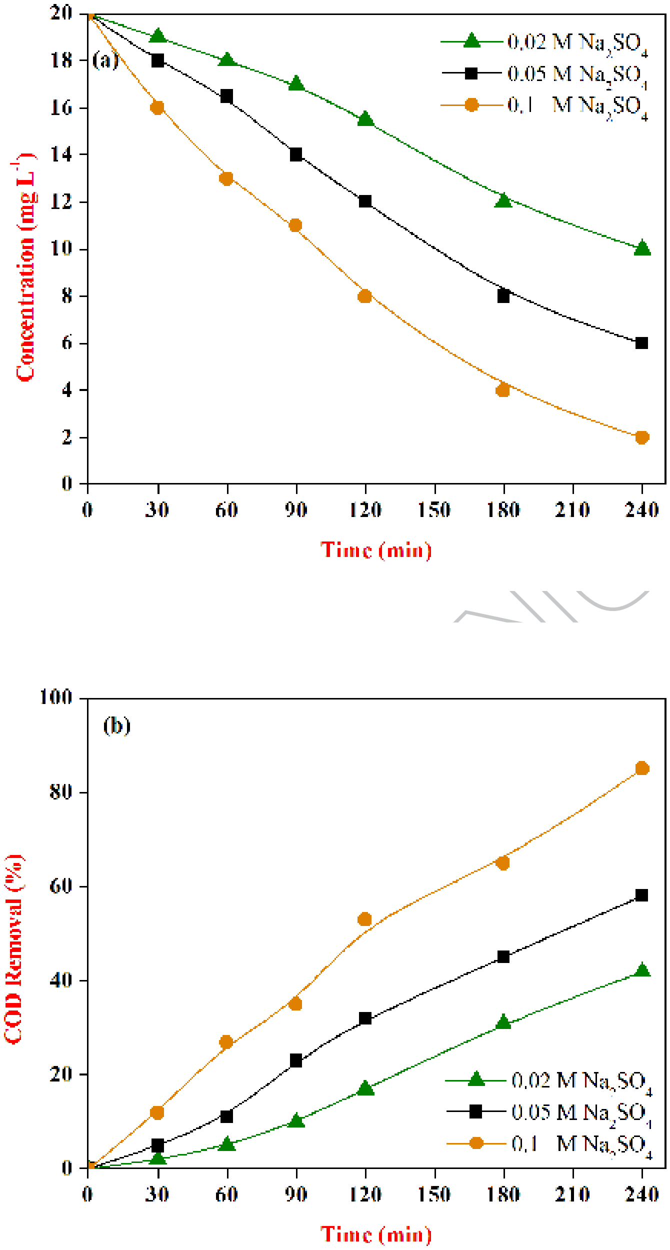

Figure 4

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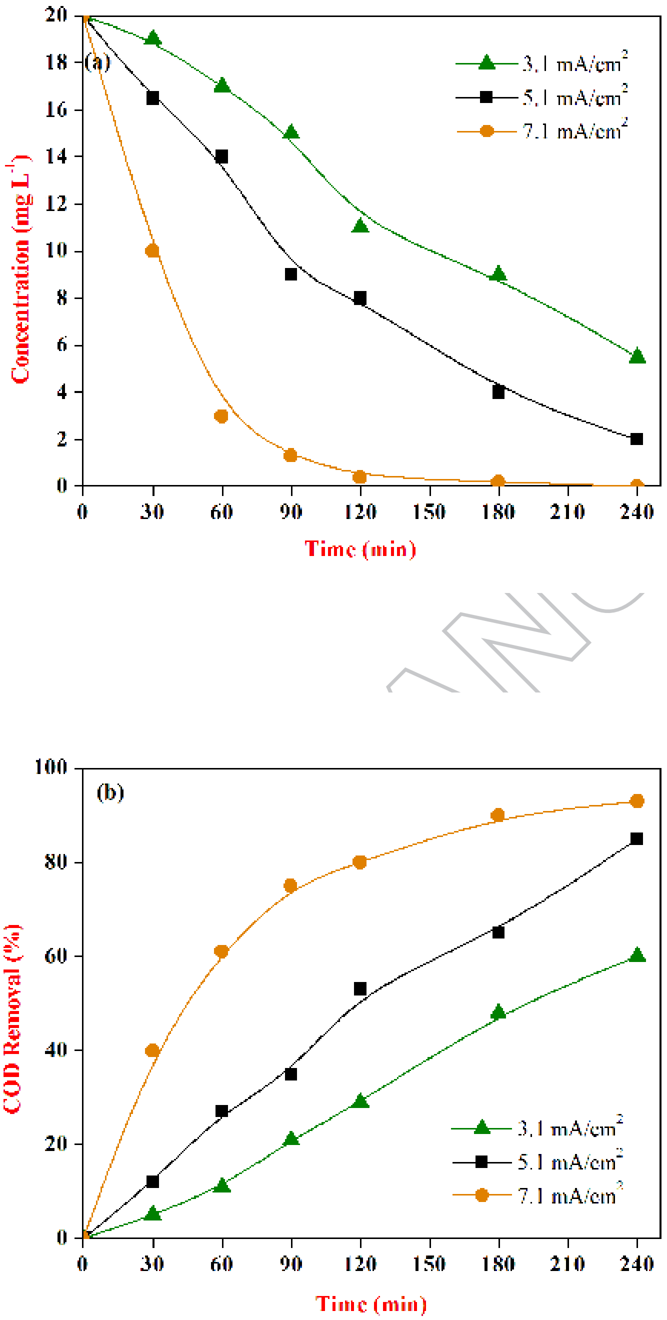

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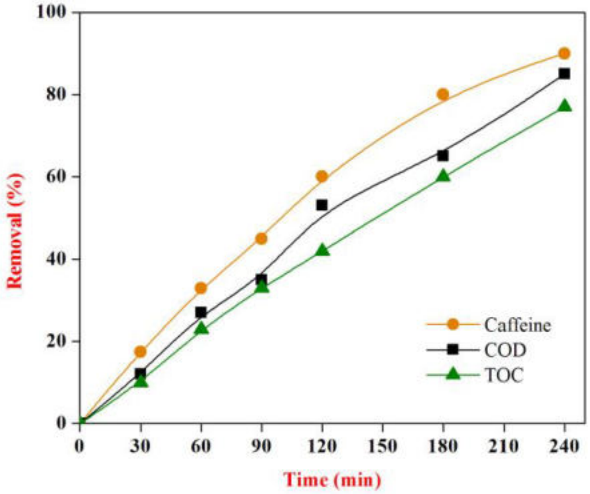

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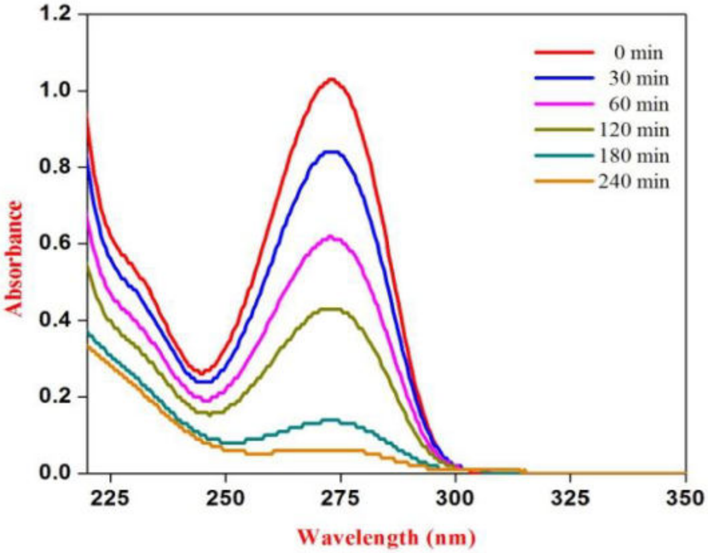

Figure 7

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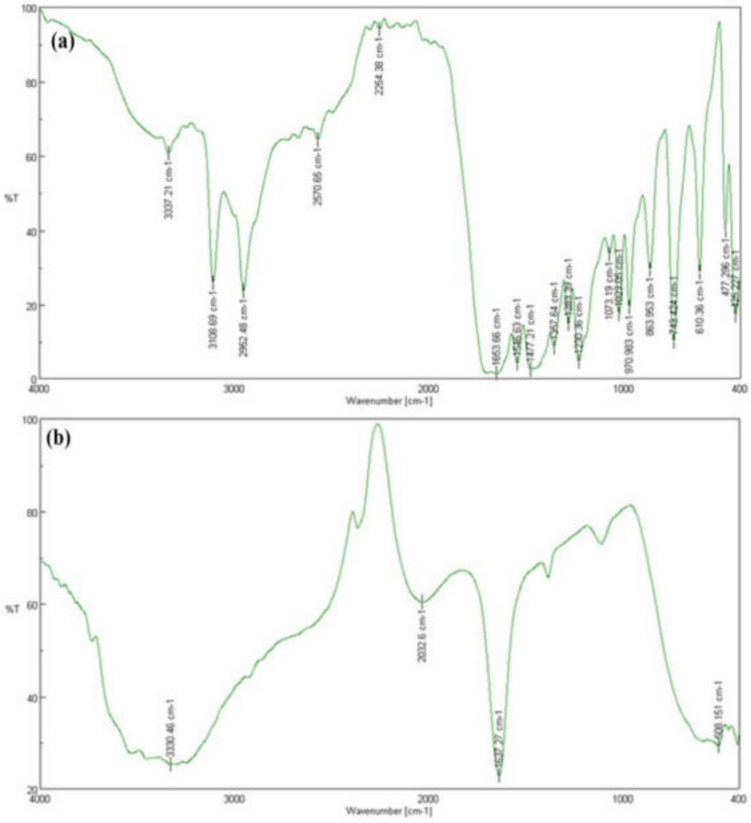

Figure 8

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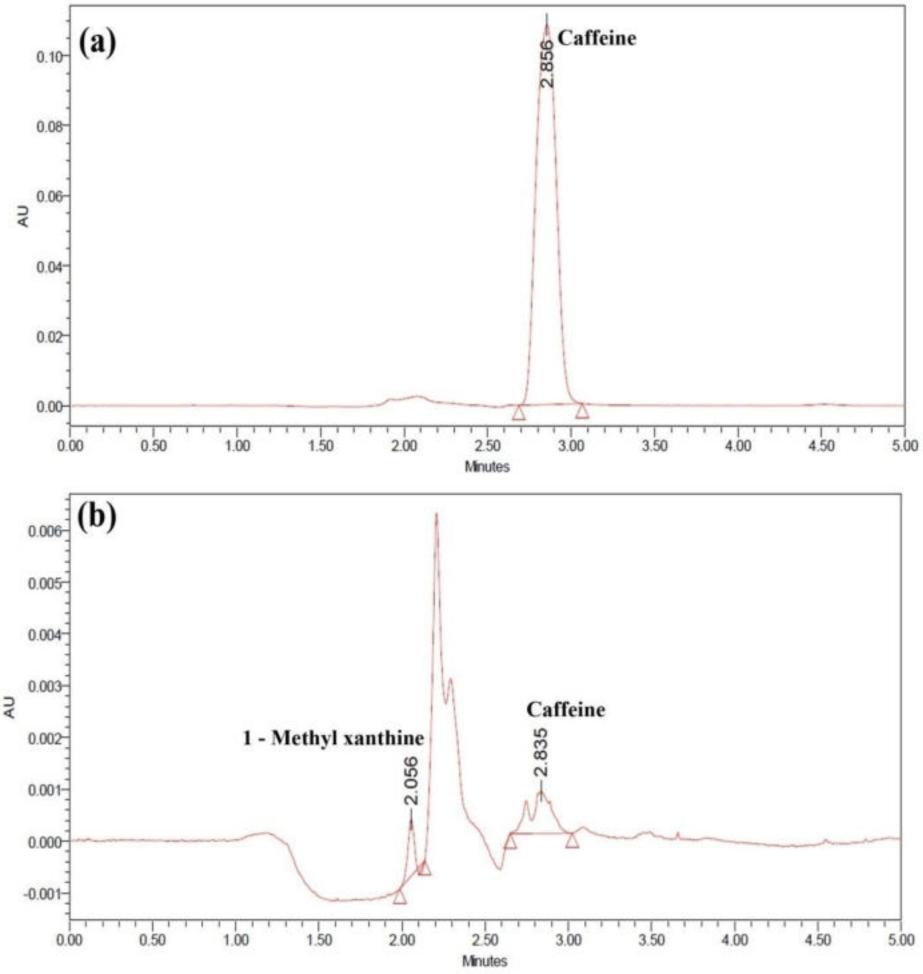

Figure 9

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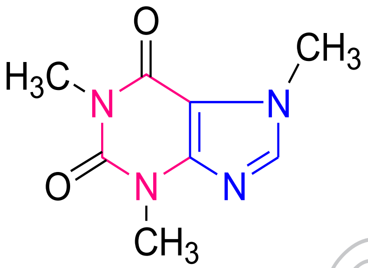
Table 1. Physiochemical properties of Caffeine

Properties	**Caffeine**
Chemical structure	
Generic name	1,3,7-Trimethylpurine,2,6-dione
Trade name	Guaranine , Methyltheobromine,1,3,7,Trimethyl Xanthine,Theine
Molecular formula	$C_8H_{10}N_4O_2$
Molecular weight	194.19 g/mol
Melting point(^{O}C)	238
CAS number	58-08-2

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