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Preparation of Ti/TiO_2 Anode for Electrochemical Oxidation of Toxic Priority Pollutants

Asim Yaqub[1], Mohamed Hasnain Isa[2], Huma Ajab[3,*], and Muhammad Junaid[4]

[1]Department of Environmental Sciences, COMSATS Institute of Information Technology Abbottabad, KPK Pakistan
[2]Department of Civil and Environmental Engineering, Universiti Teknologi PETRONAS, Bandar Seri Iskandar 32610, Perak, Malaysia
[3]Department of Chemistry, COMSATS Institute of Information Technology Abbottabad, Pakistan
[4]Computer Sciences Department, University of Haripur, KPK Pakistan

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Abstract: *In present study, Ti/TiO_2 anodes were prepared in laboratory for degradation of polycyclic aromatic hydrocarbons. Polycyclic aromatic hydrocarbons considered as priority pollutants because of their carcinogenetic properties. PAHs were electrochemically oxidized under galvanostatic conditions using TiO_2 coated Ti anode. A synthetic solution containing 16 priority PAHs were prepared in the lab. Surface morphology showed cracked mud structure of coated Ti/TiO_2 surface. All the PAHs were efficiently oxidized and degraded from solution. About 96.87% of ΣPAHs were removed in five hours from the bulk solution. The results showed the potential of electrochemical process with Ti/TiO_2 anode as a possible and reliable technique for the degradation of PAHs in water.*

Keywords: Electrochemical; degradation; Ti-TiO_2; PAHs

1. INTRODUCTION

Polycyclic Aromatic hydrocarbons (PAHs) are present as pollutants in air, soil and water. They originate from two main sources natural (biogenic and geochemical) and anthropogenic. PAHs naturally occur in fossil fuels such as coal and petroleum, but are also formed during the incomplete combustion of organic materials such as coal, diesel, wood and vegetation [1, 2]. This results in airborne PAH contamination, which is the main route for PAH transport over long distances [3].

More than 160 PAHs have been characterized in nature, however only sixteen has been classified as priority pollutants by the USEPA due to their toxic properties [4]. Characteristics of the 16 priority pollutants are listed in Table 1.

It has long been known that PAHs can have serious deleterious effects on human health [5] with the physician John Hill first recognizing the link between the use of snuff and nasal cancer in 1761 [5]. Following this discovery, research into the toxic effects that PAHs have upon mammalian health has continued, with many PAHs displaying acute carcinogenic, mutagenic and teratogenic properties. Benzo[a]pyrene is recognized as a priority pollutant by the US Environmental Protection Agency [6] as this compound is known to be one of the most potently carcinogenic of all known PAHs [7].

PAHs are often resistant to biological degradation and are not efficiently removed. Therefore, carcinogenicity and toxicity is still a concern with regards to effluents treated by conventional methods. Aerobic biodegradation of low molecular weight PAHs by bacteria and microorganisms has been documented by various authors, but high-molecular weight PAHs (with five or six aromatic rings) have proven to be more recalcitrant to biological degradation [8].

Electrochemical oxidation is one of the advanced treatment systems that have drawn significant attention in wastewater treatment research because of its compatibility, small space requirement, and powerful oxidation ability [9, 10]. Electrochemistry offers different oxidation pathways; direct electrolysis, electrochemical oxygen transfer reaction and indirect mediated oxidation processes through formation of oxidants.

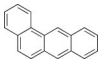
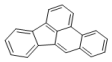
In the electrochemical treatment of wastewater containing or-

*To whom correspondence should be addressed: Email: humaajab@hotmail.com

ganic pollutants, the most important element is the anodic material [11]. The electrode material must have high electro-catalytic activity towards the electrochemical oxidation of organics to CO_2 and H_2O [12]. In addition, this process depends on the activity of coating materials on the electrodes. In recent studies transition metals oxides such as IrO_2 [13, 14], RuO_2 [15] and Ti/Pt [16] have shown good efficiency in electrochemical oxidation of organic pollutants.

Titanium was selected as the base material/substrate for making the electrodes in the present study. Titanium is a metal with unique features such as high strength and durability, anticorrosion, high conductivity and easiness for treatment. It is the most reliable and widely used support metal of electrodes for semi-conductive metal oxide coating. Ti-based electrodes are commonly employed in electrochemical applications, including water and wastewater treatment [17, 18]. High over-potential metal oxides anodes for oxygen evolution are relatively cheap and easy to manufacture. Nanostruc-

Table 1. Characteristics of PAHs [13].

PAHs	Nomenclature	Chemical formula	Mol. Wt	Structure	No. of Benzene rings	Solubility (μMoles /L)	MCL* (μMoles /L)
Naphthalene	Nph	$C_{10}H_8$	128.1		2	247.65	-
Acenaphthylene	Acy	$C_{12}H_8$	152.2		3	25.85	-
Acenaphthene	Ace	$C_{12}H_{10}$	154.2		3	12.53	-
Fluorene	Flr	$C_{13}H_{10}$	166.2		3	11.02	-
Phenanthrene	Phn	$C_{14}H_{10}$	178.2		3	6.74	-
Anthracene	Ant	$C_{14}H_{10}$	178.2		3	0.42	-
Fluoranthene	Fln	$C_{16}H_{10}$	202.2		4	1.14	-
Pyrene	Pyr	$C_{16}H_{10}$	202.2		4	0.38	-
Benz(a)anthracene	BaA	$C_{18}H_{12}$	228.2		4	0.04	0.44×10^{-3}
Chrysene	CHR	$C_{18}H_{12}$	228.2		4	0.008	0.87×10^{-3}
Benzo(b)fluoranthene	B*b*F	$C_{20}H_{12}$	252.3		5	0.006	0.79×10^{-3}
Benzo(k) fluoranthene	B*k*F	$C_{20}H_{12}$	252.3		5	0.006	0.79×10^{-3}
Benzo(a)pyrene	B*a*P	$C_{20}H_{12}$	252.3		5	0.0063	0.79×10^{-3}
Indeno(1,2,3-cd) pyrene	INP	$C_{22}H_{12}$	276.3		6	0.224	0.14×10^{-3}
Dibenz (a,h) anthracene	dBA	$C_{22}H_{14}$	278.3		5	0.002	0.11×10^{-3}
Benzo (g,h,i) perylene	B*ghi*P	$C_{22}H_{12}$	276.3		6	0.001	-

*Maximum Contaminant Level: US EPA. Standards and Regulations for Polycyclic Aromatic Hydrocarbons (PAHs)

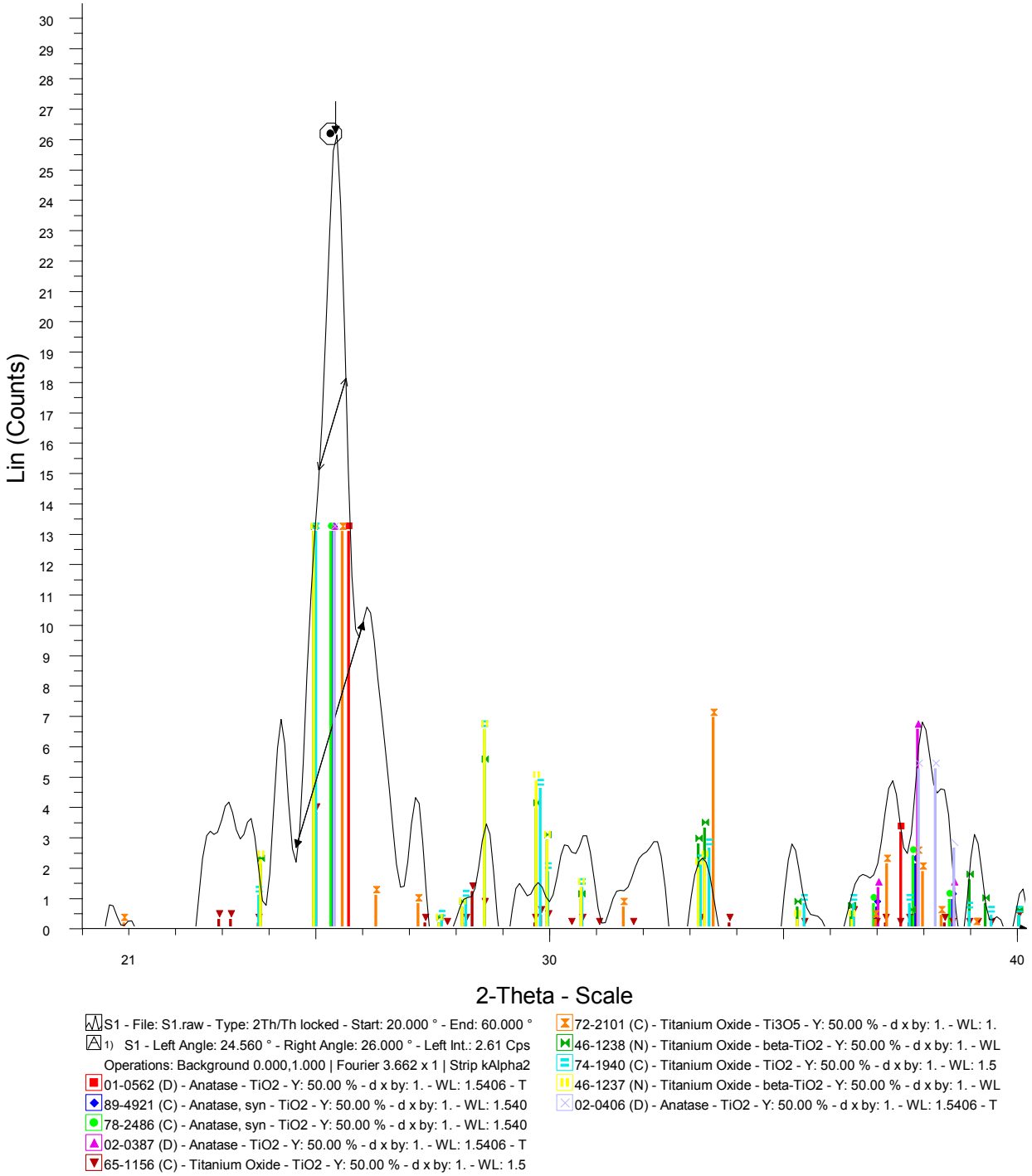


Figure 1. XRD spectra of coated Ti/TiO$_2$ anode.

Table 2. Experimental conditions for Electrochemical oxidation of PAHs.

Surface Area of Anode	Electrodes Distance	Current	Time	pH
(Units)				
cm^2	cm	mA/cm^2	hours	
6	2	4	5	3

ture semiconductor thin-film electrodes of Ti/TiO$_2$ are characterized by electrochemical stability and large internal surface areas which results in higher efficiency during degradation of organic compounds [19].

Ti/TiO$_2$ anode is used for the time in this study for PAHs degradation. No literature or study was found on the subject previously using Ti/TiO$_2$ anode.

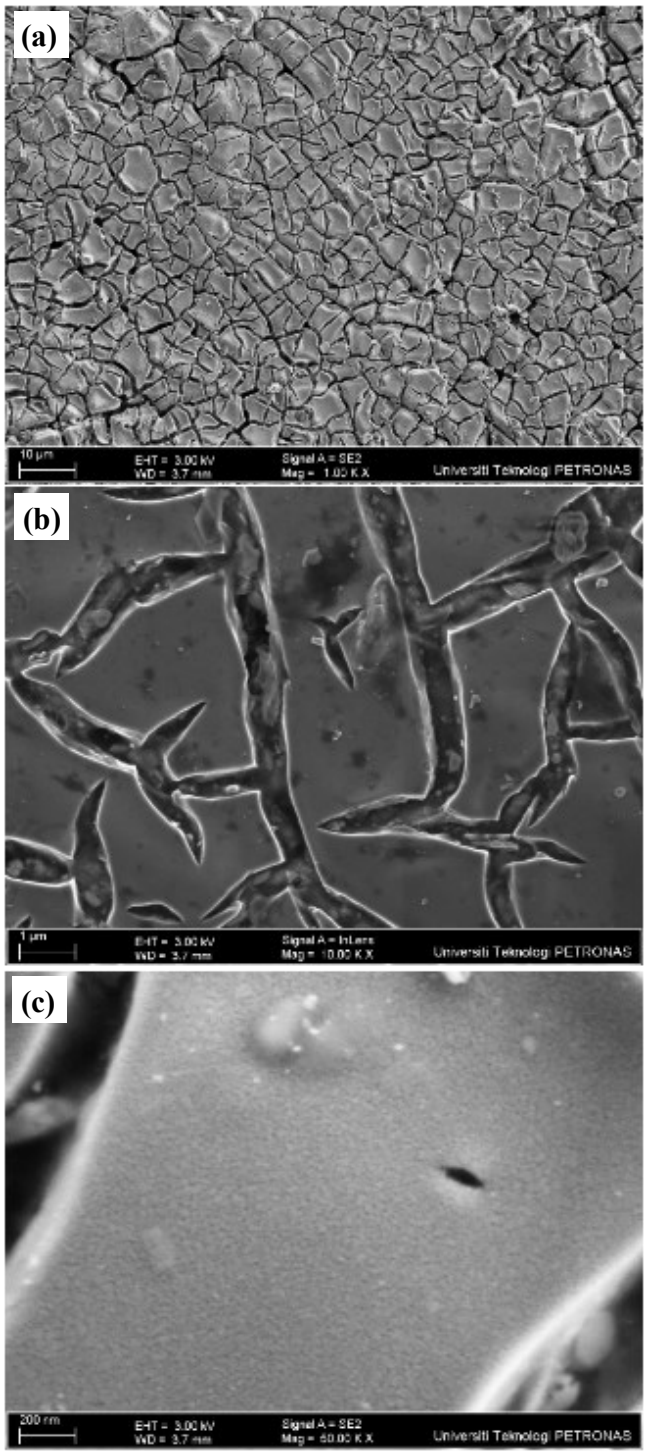


Figure 2. FESEM images of Ti/TiO_2 anode surface at different magnifications (a) 1.00 KX, (b) 10.00 KX and (c) 50.00 KX.

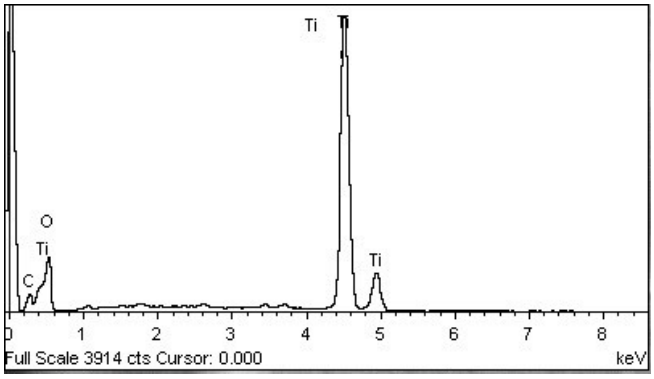


Figure 3. EDAX Spectra for elemental composition of Ti/TiO_2 anode surface.

2. MATERIALS AND METHODS

2.1. Electrochemical Cell

All experiments were performed in an electrochemical cell under galvanostatic conditions. The electrochemical cell consisted of 100 ml beaker, one anode (Ti/TiO_2) and one cathode (Titanium Plate) connected to DC power supply. Synthetic solution of PAHs was used in all experiments. The experimental conditions are given in Table 2.

2.2. Anode coating

Coating or precursor solution was prepared from the analytical grade reagents: acetic acid (AA), ethylene-glycol (EG), Titanium (IV) chloride $TiCl_4$ purchased from Merck. $TiCl_4$ was dissolved in AA and EG in ratios of AA: EG: $TiCl_4$ (2mL: 10mL: 2mL). Rectangular Ti plates (80 mm × 10 mm × 2 mm) were used for TiO_2 coating. The Ti plates were smoothened with 320-grit sandpaper and washed with distilled water. To remove oxides from the surface, the Ti plates were etched in 18 % HCl for 30 min at 80 °C followed by a thorough washing with deionized water [15].

2.3. Analysis

Variable Pressure Field Emission Scanning Electron Microscopy (VP-FESEM) was used for surface morphology recognition and EDAX (Energy Dispersive Analysis of X Rays) of coating material. X-Ray Diffraction pattern was used for the crystalline structure identification of the coated surface. GC-MS was used for the detection and quantification of PAHs. Analysis was performed using Gas Chromatography Mass Spectroscopy. Column used for GC-MS analysis having length of 30 m and 0.25 µm film thickness was used. The oven temperature was increased from 60 to 175˚C at 6˚C/min, further increased at a rate of 3˚C/min until 240˚C and finally held at 300˚C for 7 min. Injector and transfer line temperatures were 280 and 300˚C, respectively [13, 14].

Data acquisition was carried out in the selected ion monitoring (SIM) mode. Each PAH was separately quantified using a five-point calibration of mixed standard solutions in the range from 1×10^{-2} to 10×10^{-2} µMoles/L. PAHs were extracted by Liquid-Liquid Extraction Gas Chromatography Mass Spectroscopy Method.

3. RESULTS AND DISCUSSION

3.1. Surface Morphology of Ti/TiO_2

The Ti plate was coated by painting a precursor solution containing $TiCl_4$, ethylene glycol and acetic acid. After multiple applica-

tion of precursor solution the coated anode is then heat-treated in the presence of oxygen at moderate temperature (100 ˚C) to drive out excess solvent and finally at higher temperature (550 ˚C) to calcinate the coating. Continuous heating oxidized $TiCl_4$ was to TiO_2. In Fig 1, XRD spectra confirms the generation of TiO_2 oxide on anode surface. Tensions were built in causing the coating to crack called the "cracked-mud" structure. The cracks are probably formed during the stage of solvent evaporation. Fig. 2 shows FESEM images at different magnifications (low to high) for the surface of coated Ti/TiO_2 anodes. In Fig. 2a, low magnifications shows clear cracked-mud structure appearing and Fig. 2b, high magnification shows an island with flat area. It can be seen in Fig. 2c, flat area contains nano-scale dots with the diameter of up to10 nm that could provide more active sites for adsorption of OH ions and PAHs. Fig. 3 shows EDAX spectra of Ti/TiO_2 surface confirming the presence of oxygen with titanium elements. EDAX spectra also give the weight % and atomic % of elements present on the Ti/TiO_2 surface, are shown in the Table 3.

3.2. Electrochemical Oxidation

Electrochemical oxidation experiments of synthetic solutions of 16 PAHs were performed at current density of 4 mA/cm^2 and pH 3. Decrease in concentrations and removal % of each PAH are shown in Table 4. Removal of two and three rings PAHs were considerably faster than those with more rings. About 37.18, 66.85, 79.91, 88.27 and 96.87% of total PAHs removal were obtained at each hour from the bulk solution. Low removal efficiency was observed during startup of experiment. As reaction time was increased to two hour 66.85% removal of PAH was achieved. This indicated that during start of experiment only direct oxidation was mechanism of PAH degradation, PAHs closer to Ti/TiO_2 surface was oxidized only. In direct oxidation OH radicals readily react with the organic molecules adsorbed on or in the vicinity of anode to cause the oxidation reaction. Hydroxyl (OH) radicals adsorbed on the surface of anode which favors the oxidation of organic compounds [20, 21]. With the passage of time direct and indirect oxidation mechanism both encounter the PAHs. It is confirmed that TiO_2 coated Ti anode producing greater number of OH radicals in the bulk solution which participate in indirect oxidation organic compounds. Reaction (1) and (2) suggest a summation of electrolytic formation of hydroxyl radicals on Ti/TiO_2 surface.

$$H_2O + TiO_2/Ti \rightarrow TiO_2/Ti\,[OH] + H+ + e- \quad (1)$$

$$R + TiO_2/Ti[OH] \rightarrow TiO_2/Ti + RO + H+ + e- \quad (2)$$

3.3. Intermediates generation and reaction pathway

During 1 and 2 hour of reaction time electrolytic PAHs oxidized to phenolic compounds. GC-MS scan results shows *Phenol, 2, 4-bis (1, 1-dimethylethyl)* as immediate detected at retention time 12.17 min. On the basis of GC-MS results following reaction take place during first two hours of reaction time.

$$C_xH_{y2} + OH \rightarrow C_xH_yO + H_2O \quad (3)$$

Table 3: Elemental compositions of Ti/TiO_2 anode surface

Element	Weight %	Atomic %
C K	8.60	15.87
O K	43.83	61.38
Ti K	47.67	22.75
Totals	100.00	

Table 4: Concentration of PAHs at each hour of electrochemical treatment.

PAHs	RT(min)	Concentration (μMoles per Liter) × 10^{-2}					
		0 h	1 h	2 h	3 h	4 h	5 h
Nph	7.57	22.10	5.85	0	0	0	0
Acy	11.19	16.70	0.65	0	0	0	0
Ace	11.61	15.60	8.44	2.21	0	0	0
Flr	12.84	16.10	8.43	3.43	0	0	0
Phn	15.12	13.50	7.92	2.41	0.23	0	0
Ant	15.13	15.60	7.97	2.35	0.62	0	0
Fln	17.96	14.30	6.98	3.36	1.38	0.12	0
Pyr	18.48	13.80	7.03	3.11	1.23	0.10	0
BaA	21.38	10.60	9.38	5.31	2.50	1.14	0
CHR	21.46	11.90	10.3	5.65	4.69	3.72	1.10
B*b*F	23.77	10.10	8.41	5.0	3.61	2.10	0.65
B*k*F	23.83	10.90	9.80	5.0	4.44	3.01	2.12
B*a*P	24.45	10.10	8.21	4.21	3.41	1.86	0
INP	27.28	10.40	7.53	6.34	4.81	3.41	2.11
dBA	27.40	9.01	7.26	4.96	3.27	1.83	0
B*ghi*P	28.05	9.40	7.68	6.34	3.81	2.21	0.21

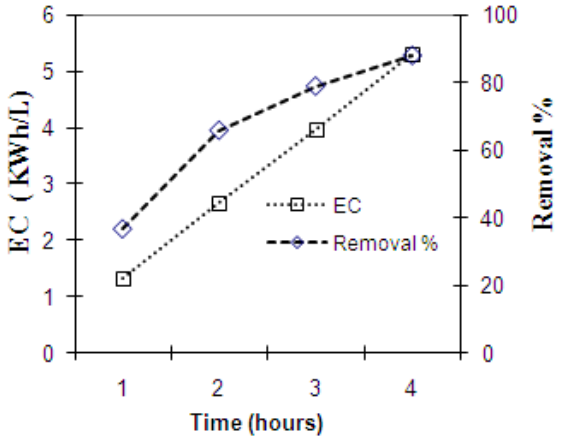


Figure 4. PAH removal efficiency and Energy Consumption during electrochemical oxidation of PAHs.

It is generally believed that phenols are oxidized to benzoquinone [22]. In the later steps, benzoquinone can be degraded with ring breakage to various carboxylic acids. Several mechanisms have been proposed for benzoquinone degradation. If benzoquinone is adsorbed onto the anode surface and gives up an electron, then the carbon that is double-bonded with the oxygen will be attacked by a neighboring hydroxyl radical generated from water electrolysis [23]. With continuous electrolysis benzoquinone would be broken down into small volatile fatty acid such as carboxylic and acetic acid and then finally to converted to CO_2 [23, 24].

3.4. Energy Consumption

Fig. 4 shows the Energy Consumption (EC) during the electrochemical oxidation of PAHs. EC was increases with rate of 1.33 KWh/L in each hour. TiO_2 is a semiconductor and due to high over potential high EC was observed during the electrochemical process. Energy Consumption EC was measured by eq. 4: I is current, ΔV is Change in voltage from eq. 5, t is time and v is volume of solution in liters L.

$$EC = \frac{I\,\Delta V t}{v} \tag{4}$$

$$\Delta V = (Vf - Vi)\left(1 - \frac{1}{e^{\frac{t}{\tau}}}\right) \tag{5}$$

ΔV is Change in voltage, Vf is final Voltage, Vi is initial voltage, t is time in seconds, τ is time constant for circuit in seconds (τ = 1 sec) and e is *e constant* or *Euler's number* is a mathematical constant. The e constant is real and irrational number (e = 2.718281828459….).

4. CONCLUSIONS

Ti/TiO_2 anode is a favorable electro-catalyst for PAHs degradation in aqueous solution. Ti/TiO_2 anode was capable for complete removal of 2-4 rings PAHs and gave maximum removal of 5 and 6 rings to acceptable discharge limit. EDAX and XRD results confirm the presence TiO_2 oxide on anode surface. Cracked mud structure supported the organic degradation.

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