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Electrochemical removal of metoprolol using graphite-polyvinyl chloride composite as anode

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Abstract. Metoprolol is one of pharmaceuticals that used for treatment of angina, heart failure, myocardial infarction, atrial fibrillation, atrial flutter and hypertension. It was frequently detected in wastewater samples. The application of graphite-PVC composite as anode was investigated for the degradation of metoprolol in the presence of strong electrolytes such as NaCl. The removal was strongly influenced by initial concentrations of metoprolol, NaCl and applied voltage. An initial concentration of 10 mg/L was eliminated more than 90% after 60 min under optimum conditions. The consumption energy of the electrochemical reaction was 0.665 Wh/mg while it was 2.717 Wh/mg for metoprolol in 0.5 g and 0.1 g NaCl, respectively at 5 V. The degradation results were monitored using liquid chromatography-time of flight/mass spectrometry.

1. Introduction

Over the last 20 years, pharmaceuticals have been receiving an increasing attention as potential bioactive organic compounds in the aquatic environment. They are considered as emerging pollutants in water bodies because they still remain unregulated or are currently undergoing a regularization process.

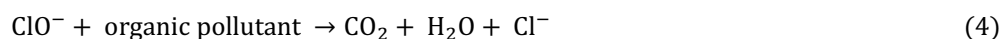
The occurrence of these compounds was observed in influent, effluent of sewage treatment plants and hospital, and surface water in Malaysia. Some studies have reported the abundance of drugs in groundwater, urban wastewater plants, rivers, hospital wastewater and lakes around the world. This frequent detection may be attributed to the fact that the conventional wastewater treatment plants are not sufficient to achieve this purpose [1,2]. Although, the concentration of these pollutants is low in the environment, these pharmaceuticals may pose adverse effects on the organisms and humans due to long-term exposure [3-5].

Various strategies were reported on the treatment of wastewater effluent including biological methods (enzymes and microorganisms), physical methods (filtration, flocculation, and adsorption), and oxidation methods (advanced oxidation and chemical oxidation) [6, 7]. However, today the use of electrochemical oxidation technique in wastewater treatment is getting more attention as this method does not involve the use of additional chemicals [8, 9]. Previous studies have shown that this technique provided high efficiency in the removal of organic and inorganic pollutants from the effluents [10,11]. According to Liu et al. (2019), this technique requires simple equipment, easy implementation, and on-site treatment in less space [12].



Anodic oxidation with conductive graphite-PVC composite anode has presented many advantages as compared to other known chemical and photochemical processes. Some papers have reported the anodic oxidation treatment with graphite anode of leachate and wastewater contaminated with drugs [13-15]. However, hypochlorite ClO^- can be the dominant and strong oxidizing agent which is responsible for the degradation of pharmaceuticals during the electrochemical process [12].

Electrochemical process is called anodic oxidation, where the direct and indirect oxidation process could be occurred on the surface of anode and/or at the bulk solution realising ClO^-/HOCl as an oxidizing agent [16]. Removal of pollutants depends on the active chlorine Cl_2/ClO^- which is strongly depend on the presence of NaCl as supporting electrolyte. This event can be explained by the primary transformation of Cl^- into Cl_2 then into ClO^-/HOCl [17].



In any degradation process, the most common question is “what is the fate of target compound and how to identify the by-products after treatment?”. In this report, the electrochemical treatment process for metoprolol was investigated using graphite-PVC as anode. Some of the aims of the study are as follow: (1) to investigate the efficiency of the electrochemical process for removal of metoprolol under different experimental parameters, (2) to evaluate the consumption energy during the electrochemical treatment profile.

2. Material and methods

2.1 Reagents

Metoprolol (Figure 1) was supplied by Sigma-Aldrich ($\geq 98\%$). Organic solvents and other chemicals used were HPLC-grade from Aldrich and J-baker. Graphite powder was obtained from University Kebangsaan Malaysia, Malaysia. All aqueous solutions were prepared with de-ionized water (DIW) with conductivity ≤ 18 S/cm at ambient temperature. NaCl was purchased from Merck with high purity $\geq 99.5\%$.

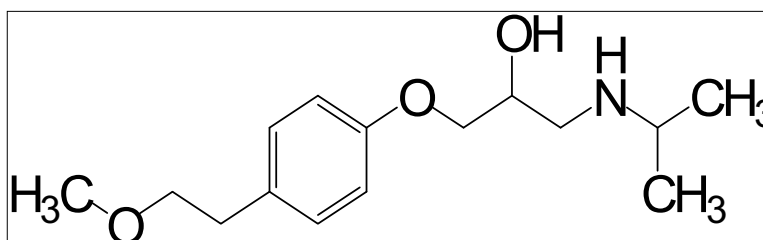


Figure 1. Chemical structure for metoprolol.

2.2. Preparation of a Graphite-polyvinyl Chloride Composite Electrode

The graphite-PVC composite electrode was prepared by mixing together a weighed portion of graphite powder (100 mesh in size and 99.9% purity, Aldrich chemical Company) and polyvinyl chloride (PVC) in 8 mL tetrahydrofuran (THF) solvent and swirled flatly to homogeneous followed by drying in an oven at 50 °C for 3 h. The mixture was then placed in 2 cm diameter stainless steel mould

and pressed at 10 ton/cm² using hydraulic machine (ATLAS auto touch HYDRAULIC). A typical pellet contained approximately 95% of graphite powder, and approximately 5% of PVC.

The total weighed of pellet obtained is approximately 2g. Graphite-PVC pellet connected to a silver wire with silver conducting paint and sealed to a glass rode. Subsequently, epoxy gum was applied to cover the silver wire connected surface as show in Figure 2.

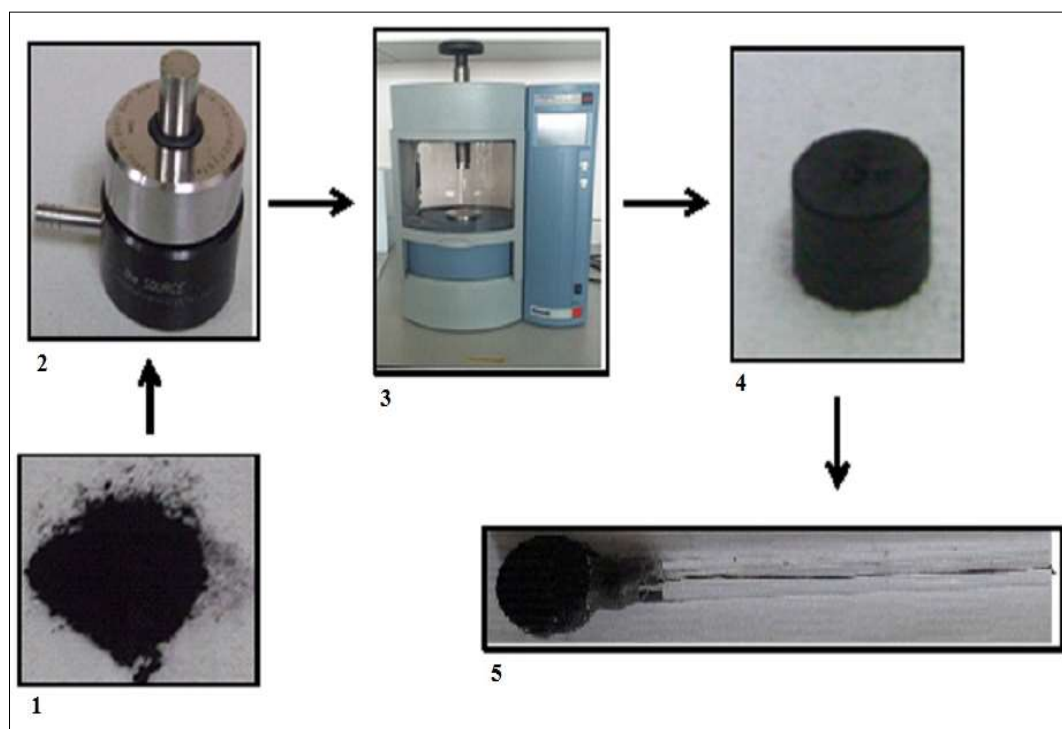


Figure 2.Steps of preparation of graphite-PVC electrode.

A 100 mL of metoprolol solution was electrochemically treated at different intervals (0, 10, 20, 30, 40, 50, 60, 70 and 80). However, consumption energy was investigated at different values of applied voltages and sodium chloride during the electrochemical oxidation process to ensure that the present study is preferred for this purpose. Metoprolol was tested without switching on power as a control test to confirm that the removal of metoprolol is not due to the adsorption to the electrodes.

2.3. Preparation of metoprolol solution

Metoprolol (0.01 g) dissolve in 10 mL of methanol to prepare a stock solution of 1000 mg/L. Subsequent concentrations 2, 5 and 10 mg/L were prepared after diluting in de-ionized water.

2.4. Set up of electrochemical oxidation

The schematic experimental setup is as shown in Figure 3. The reaction was carried out using 100 mL pyrex glass. The glass pyrex electrochemical cell (reactor) was placed on magnetic stirring block in order to keep its contents well mixed during the experiment. Graphite-PVC pellet and Pt plate were used parallel as anode and cathode, respectively. The distant between the electrodes was 4 cm. The electrodes were then connected to a direct current (DC) power supply (CPX200 DUAL, 35V 10A PSU).



Figure 3. The schematic diagram of the electrochemical process

2.5. Energy consumption (EC)

Energy consumption was considered in this study during electrochemical oxidation process of metoprolol, it was calculated based on Eq.(5) [18].

$$EC = \frac{VI\Delta t}{\Delta(m)} \quad (5)$$

Where EC is energy consumption in watt hour per milligram of compound reduced in the process (Wh/mg compound); V is the applied voltage in volt (V), I is the current in Amper (A), t is the electrolysis time in hours and $\Delta(m)$ is the amount of compound reduced in mg.

2.6. Liquid chromatography-time of flight/mass spectrometry

Separation of the studied pharmaceuticals was performed on the dionex Ultimate 3000/LC 09115047 (USA) system equipped with a vacuum degasser, a quaternary pump, and an auto-sampler. Sample aliquots of 30 μ L were injected to Gemini 5 μ m NX 110A C18 column (2 mm x 150 mm, Phenomenex). Electrospray ionization (ESI) source was utilized as ionization source. Metoprolol was analysed in positive ionization mode ESI (+). The elution off the column was achieved with a mobile phase consisting of (A) 0.1% FA in DIW and (B) ACN-MeOH (3:1, v/v) at 0.3 mL/min. the gradient elution is as follow:

5% B (0 min) $\rightarrow$ 60% B (linear increased in 3 min) $\rightarrow$ 97% B (linear increased in 3 min) $\rightarrow$ 97% B (hold 5 min) $\rightarrow$ 5% B (linear decreased in 0.1 min) $\rightarrow$ 5% B (hold 5 min).

Mass spectrometry was performed on ESI-TOF instrument (Bruker/Germany). The results were obtained with the following settings: MS capillary voltages, 4000/3500 [ESI (+)]; drying gas flow rate, 8.0 L/min; drying gas temperature, 190 $^{\circ}$ C; and nebulizer pressure, 4.0 bar. Two molecular ions, $[M+H]^+$, was observed for ESI (+) analysis. All analytes were acquired using an independent reference spray via the LockSpray interference to ensure accuracy and reproducibility. A mixture of sodium

hydroxide and formic acid (FA) was used as the lock mass m/z 90.9766 to 974.8132. The accurate mass was calculated using Daltonics Data Analysis software incorporated in the instrument.

3. Results and Discussion

Removal of metoprolol was investigated using electrochemical treatment process under different conditions such as initial concentration, applied voltage and sodium chloride. It was observed that the efficiency of electrochemical process was impacted by rate of generation the oxidizing agent ClO^- which is the most effective oxidizing agent for the removal of pollutants such as metoprolol.

3.1. Effect of initial concentration

Figure 4 shows the removal% of metoprolol for each initial concentration (2, 5 and 10 mg/L). Experimental results showed that all trends of removal% have different profile which means decreased as the initial concentration increased. By comparing initial concentration of 10, 5 and 2 mg/L, their removal% are 62, 82 and 97%, respectively after 30 min. It was observed that low removal% was accompanied with high initial concentration (10 mg/L) whilst high removal% was found with low initial concentration (2 mg/L). The reason may be attributed to the fact that the number of moles of metoprolol at high initial concentration is more than its number at low initial concentration.

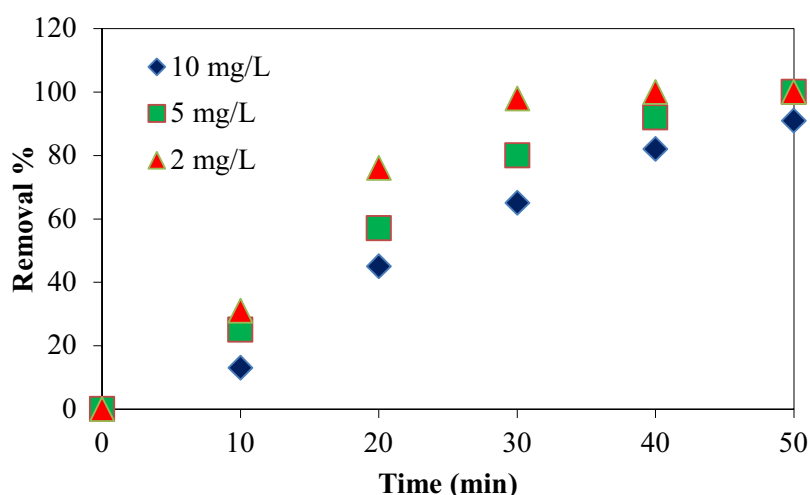


Figure 4. Effect of initial concentration on the removal% of metoprolol

3.2. Effect of NaCl amount

Several experiments were conducted to study the removal behavior under various amounts of NaCl (0.1, 0.3 and 0.5 g). Experimental results showed that most metoprolol was eliminated very effectively using graphite-PVC anode using 0.5 g NaCl, the removal of metoprolol reduced sharply at low amount of NaCl (0.1 and 0.3 g) as shown in **Figure 5**. Almost no removal was found for the lowest amount of 0.1 g of NaCl. The effect of amount NaCl on the removal of metoprolol from aqueous solution by electrochemical treatment process using graphite-PVC anode can be discussed as presented in equations 1-4, by the considering the formation of active oxidizing agent (ClO^-). In electrochemical treatment process, low consumption energy is preferred for this type of treatment unless the removal% is high. From **Table 1**, it was observed that the highest consumption energy was ranged between 1.812 Wh/mg and 2.804 Wh/mg using 0.1 g NaCl during the electrochemical treatment process. Average energy consumption values of the electrochemical process measured are mostly similar between 0.3 and 0.5 g NaCl. From the results, 0.5 g NaCl was the best choice for further experiments.

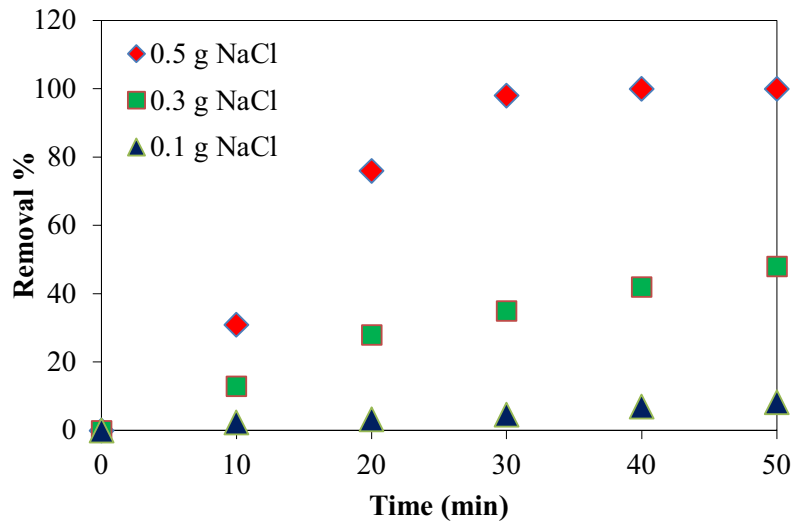


Figure 5.Effect of NaCl amount on the removal% of metoprolol

3.3. Effect of applied voltage

The effect of applied voltage on the electrochemical treatment of metoprolol was also investigated through the determination of removal% and consumption energy. **Figure 6** shows that the removal% are in range of 6 to 55%, 27 to 92% and 67 to 97% at 3, 5 and 7 V, respectively. Normally, a greater removal of metoprolol is associated with a greater value of applied voltage. Comparing the removal% of 3, 5 and 7V, it is obvious that the efficiency of electrochemical treatment at 7 V was greater than that of 3 V as also reported previously [18].

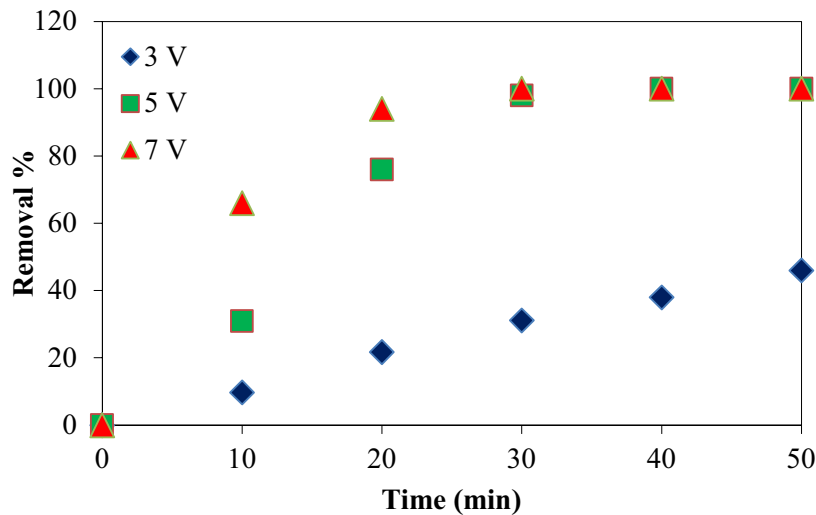


Figure 6.Effect of applied voltage on the removal% of metoprolol

It is well known that high applied voltage may mean high consumption energy so this concept was considered in this study. From **Table 1**, consumption energy was very high at 7 V comparing to 5 V. On the other hand, removal% was not too much different between 7 and 5 V under same conditions. It could be concluded that the removal% at 5 V is more preferred compared to 7 V since the

consumption energy is much lower 0.665 and 1.117 Wh/mg, respectively. On the other hand, although energy consumption at 5 and 3 V is almost similar, 5 V was selected due to high removal% was gained >95% compared to 3 V (38%) after 30 min.

Table 1. Energy consumption under different values of NaCl amount and applied voltage

Time (min)	Energy consumption (Wh/mg)/ NaCl amount (g)			Energy consumption (Wh/mg)/Applied voltage (V)		
	0.1	0.3	0.5	3	5	7
10	1.812	0.641	0.548	0.510	0.548	0.795
20	2.525	0.595	0.595	0.459	0.595	1.117
30	2.717	0.714	0.665	0.481	0.665	-
40	2.451	0.794	-	0.526	-	-
50	2.541	0.868	-	0.543	-	-

4. Conclusion

In this research work, metoprolol was treated using electrochemical oxidation process. The electrochemical process showed that metoprolol was eliminated within 30 min at 0.5 g NaCl and 5 V using graphite-PVC composite electrode. It was observed that increasing of initial concentration resulting in decreasing of removal%. Energy consumption was studied and it was very impacted by NaCl amount and applied voltage. However, at low amount of NaCl the consumption energy was high compared to 0.3 and 0.5 g NaCl.

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