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# Utilization of Polyethylenimine (PEI) Modified Carbon Black Adsorbent Derived from Tire Waste for the Removal of Aspirin

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**Abstract:** A new adsorbent was synthesized using polyethylenimine (PEI) on the carbon black to remove aspirin from an aqueous solution. In this study, adsorption performance of modified carbon black by polyethylenimine (PEI) on aspirin was investigated. Batch adsorption studies were performed to evaluate the effects of contact time, pH solution, temperature, and initial concentration on the adsorption of aspirin. For this study, the carbon black obtained from the pyrolysis of tire waste was used as a precursor for low-cost adsorbents. The carbon black was treated by 1 M of hydrochloric acid solution to remove ash and sulphur content. Then, the treated carbon black was modified by impregnation with PEI in one to one weight ratio within 24 hours at 65 ℃ and then cross linked with 1% (w/v) glutaraldehyde solution for one hour. The adsorption rate of aspirin by modified carbon black was rapid from 20 minutes to 60 minutes and reached equilibrium. Hence, the optimum contact time for this study is 60 minutes with 59.96% of aspirin removal and 29.98 mg/g adsorption capacity. The best performance for pH solution, temperature, and initial concentration was observed at pH 3 (26.1 mg/g), 30 ℃ (26.9 mg/g) and 20 ppm (40.96 mg/g) respectively.

**Key words:** Aspirin, adsorption, polyethylenimine, waste tire, modified adsorbent.

## 1. Introduction

Improper disposal of pharmaceutical waste might be hazardous and can contribute to the contamination of water supplies. Bbiomedical waste in Malaysia is expected to reach 33,000 tonnes per year by 2020 [1]. Many previous studies mentioned that traditional or conventional wastewater treatment methods are not sufficient as the pharmaceutical waste is not completely removed [2]. There are several advanced treatment methods that can be used to treat pharmaceutical waste such as autoclaving, ion-exchange, advanced oxidation process and biological treatment [3]. However, adsorption has become the most efficient method to treat pharmaceutical waste due to its cost effectiveness and simple design [4].

Disposal of tire waste becomes an issue because they are immune to biological degradation. In this study, tire waste has become the precursor of low-cost adsorbent. The pyrolysis of tire waste produces carbon black which is suitable for the low-cost adsorbent due to higher carbon content. At the same time, the usage of solid product as an adsorbent can overcome the problem of tire waste management.

The usage of current commercialized activated carbon is limited due to its high operating cost that consumes energy during the activation step. Due to this problem, this study was conducted to explore new adsorbents which are cheaper and environmentally-friendly. Tire waste is highly abundant in Malaysia and can be one of the potential sources for low-cost adsorbent. Hence, this study will explore the modification of carbon black by polyethylinimine (PEI) as the adsorbent on the adsorption of the pharmaceutical compound without any activation step.

Polyethylenimine (PEI) is a cationic molecule that

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has a large number of amine groups and is well known as the modification agent on the adsorbent surfaces in order to increase the performance of the adsorption. In this study, PEI is chemically bonded to the carbon black surfaces through the crosslinking agent of glutaraldehyde.

There are two objectives of this research which are to modify carbon black by PEI and to study the effect of various parameters on the adsorption of aspirin. The raw carbon black was treated by 1 M of hydrochloric acid and then modified by PEI using one to one weight ratio of carbon black to PEI. The adsorption studies were conducted on the effects of contact time, pH solution, temperature and initial concentration.

## 2. Method and Materials

Carbon black (CB) derived from tire waste was obtained from QCS Biotechnology Sdn Bhd at Senai, Johor. The tire waste underwent pryrolysis process in order to obtain the carbon black. Hydrochloric acid (HCl) used in this study was purchased from Acros Organics. For the pH adjustment, 0.1 M of HCl and sodium hydroxide (NaOH) were used. PEI and glutaraldehyde were purchased from Acros Organics.

### *2.1 Preparation of the Adsorbent*

The CB was impregnated in 1 M of HCl solution (1 L) for 24 hours with 160 rpm at room temperature. The treated carbon black was filtered and washed using distilled water until a neutral pH was obtained. Next, 5 g of treated CB was impregnated in 5% (w/v) PEI/methanol solution (1:1 weight ratio of carbon black to PEI) within 24 hours in 65 ℃ at 160 rpm. Then, 100 mL of 1% (w/v) glutaraldehyde solution was added to the mixture for crosslinking reaction and agitated at 160 rpm, room temperature for 60 minutes. After that, the sample (PEI-CB) was filtered, washed and dried under 60 ℃ for 1 hour. The PEI-CB was then used for adsorption studies.

### *2.2 Adsorption Studies*

The effect of contact time on adsorption of aspirin was performed by adding 0.1 g of PEI-CB into 50 mL of 100 ppm of aspirin solution under pH 3, 30 ℃, and 160 rpm. The sample was collected for UV-Visible analysis at every 10 minutes for the first 30 minutes and for every 30 minutes for the rest of the experiment until equilibrium was reached. The optimum contact time was used for the next three parameters with a different condition. For the pH influence, the pH of aspirin solution was varied from pH 3 to pH 11 and the best pH was used for the temperature influence (30 ℃, 50 ℃ and 70 ℃). For the effect of initial concentration, the concentration of aspirin was varied from 10 ppm to 100 ppm.

The amount of aspirin adsorbed at equilibrium time, $Q_t$ was calculated using Eq. (1).

$$Q_t = (C_o - C_t)V/m \quad (1)$$

Where $C_o$ and $C_t$ are the initial and concentrations at any time of aspirin solution (mg/L), while $V$ is the total volume of the aspirin solution (L), and $m$ is the mass of adsorbent used (g).

## 3. Results and Discussions

The adsorption studies for aspirin removal by modified carbon black (PEI-CB) have been studied under different contact time, pH, temperature and initial concentration of aspirin.

### *3.1 Time-Dependent Adsorption Studies*

The effect of contact time was studied to investigate the equilibrium time for the removal of aspirin by PEI-CB. Based on Fig. 1, the adsorption of aspirin increased with increased contact time and achieved equilibrium contact time after 60 minutes with almost 30 mg/g adsorption capacity.

At initial stages, it is a large number of vacant sites on the surfaces of PEI-CB which lead to rapid and high adsorption rate. The adsorption has reached

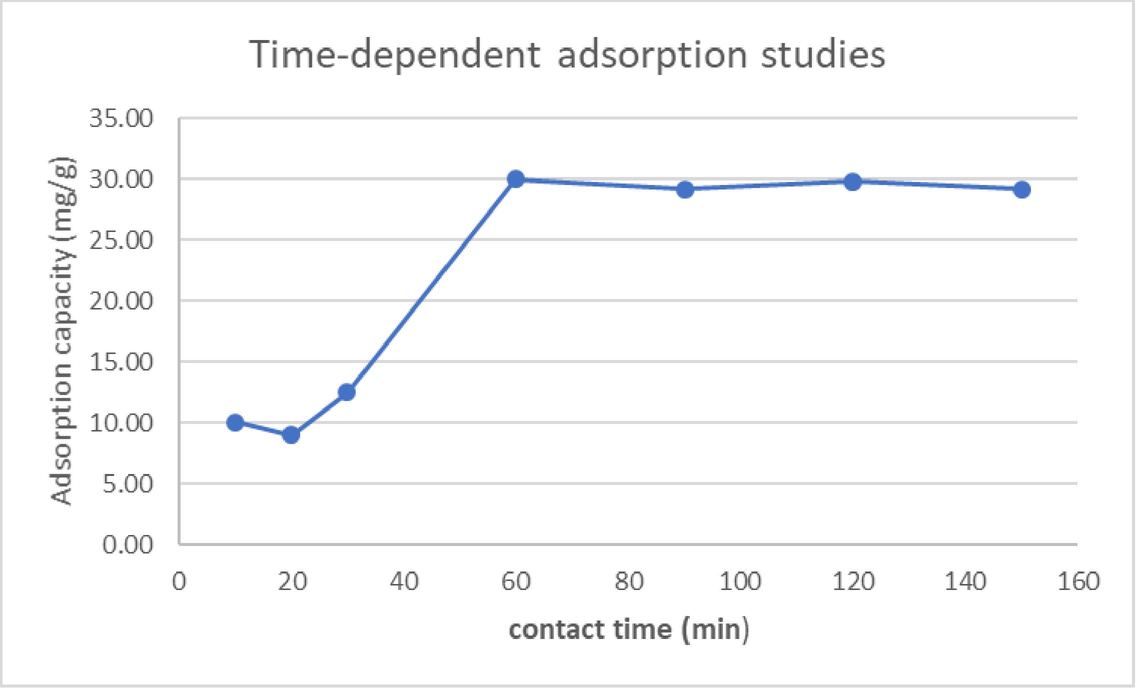


**Fig. 1 Time-dependent of aspirin adsorption by PEI-CB.**

equilibrium due to the occupied vacant sites with aspirin molecule. The same trend was shown in the previous study using rice hull activated carbon for the removal of aspirin [5]. Hence, for this study, the steady state for adsorption process is approximately at 60 minutes.

*3.2 Effect of pH on Adsorption Studies*

The effect of pH solution on the adsorption of aspirin was studied by varying the pH values (3, 5, 7, 9 and 11). The adsorption capacity of aspirin was significantly reduced from pH 3 to pH 7 and there was no adsorption occurring at higher pH (pH 9 and pH 11). This might be due to the competition of $OH^-$ molecules and aspirin solution to attach on the cationic adsorbent surfaces. The highest adsorption capacity for aspirin was at pH 3 with 24.81 mg/g as shown in Fig. 2. The adsorption of aspirin by N-CNT/-CD and Fe/N-CNT/-CD from the previous study shows the same trend in which the highest adsorption occurred at low pH and unfavorable adsorption occurred at high pH [6].

*3.3 Effect of Temperature on Adsorption Studies*

Fig. 3 shows the performance of aspirin removal with three different temperatures. The performance indicates unfavorable reaction when the temperature increases. This phenomenon contributes to exothermic process [7]. In this study, the efficient temperature for adsorption of aspirin is below 30 ℃ with 24 mg/g. The assumption has been made when the temperature rises, the interaction between adsorbate and the adsorbent becomes weaker which means physisorption process. This behavior has also been reported in a previous study [8].

*3.4 Effect of Initial Concentration on Adsorption Studies*

Fig. 4 shows the effect of initial concentration on the adsorption of aspirin by PEI-CB. The graph shows that the removal of aspirin decreased with increased concentration from 20 mg/L to 80 mg/L. At higher concentration of aspirin, the number of solute molecule was higher than the number of sites available

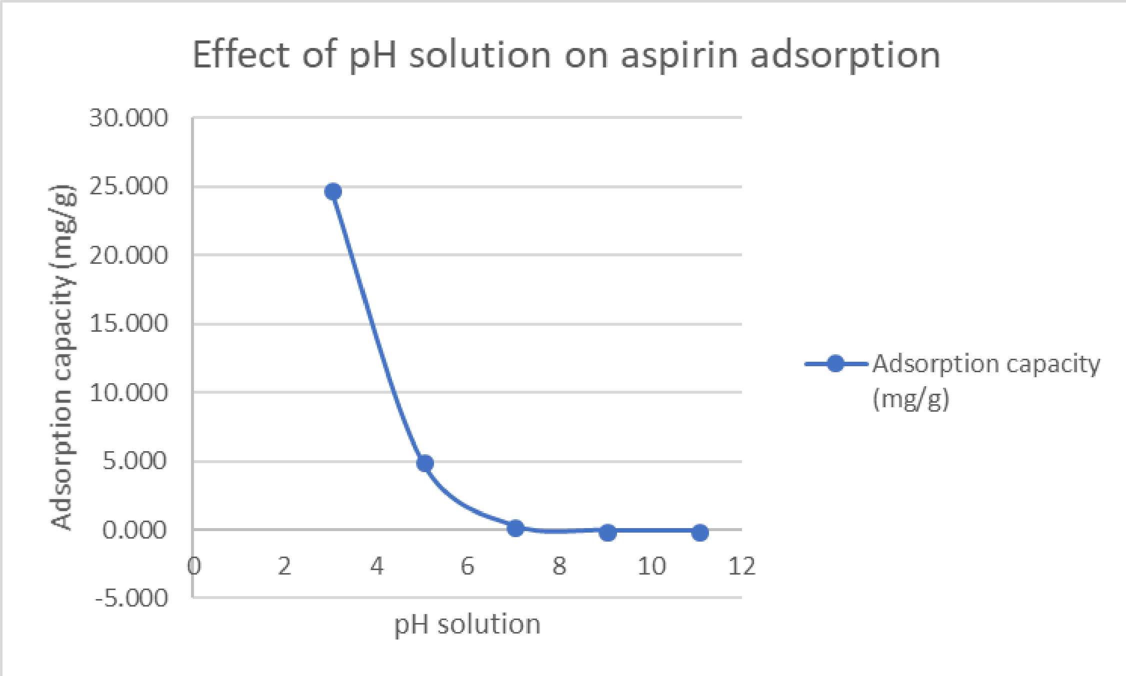


**Fig. 2** **Effect of pH solution on aspirin adsorption by PEI-CB.**

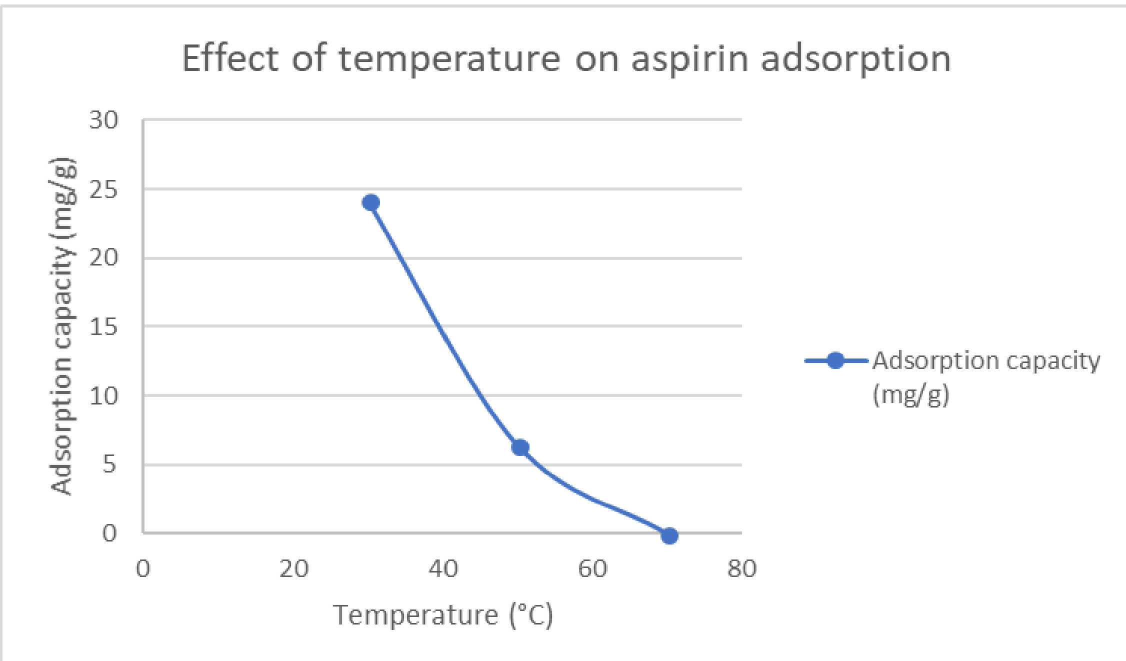


**Fig. 3** **Effect of temperature on aspirin adsorption by PEI-CB.**

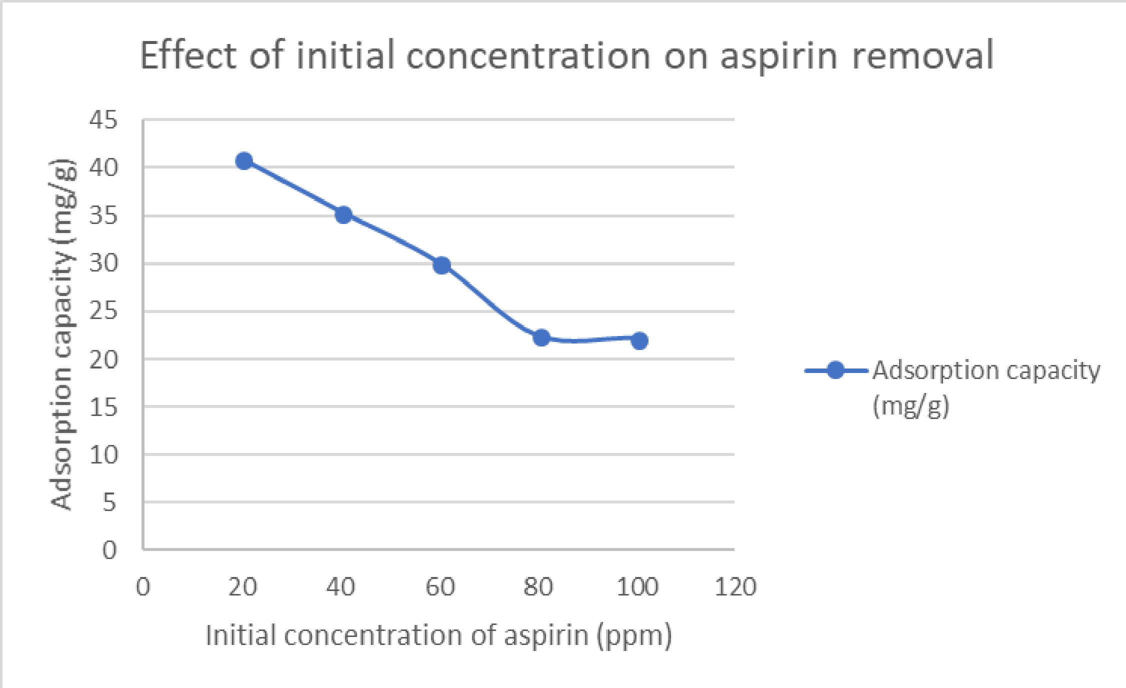


**Fig. 4 Effect of initial concentration on aspirin adsorption by PEI-CB.**

on the adsorbent surfaces. Therefore, lower removal of aspirin at a higher concentration as shown in Fig. 4 was due to the saturation limit achieved on the surfaces of the adsorbent.

## 4. Conclusions

The removal of aspirin as one of the pharmaceutical compounds from wastewater has been investigated. The effect of different parameters such as contact time, pH solution, temperature, and initial concentration of aspirin on the adsorption process has been studied. From the results obtained in this study, the following conclusions may be revealed:

(1) The PEI-CB used in this study has a potential to remove aspirin within 60 minutes with almost 30 mg/g of adsorption capacity.

(2) pH solution can also influence the adsorption process whereby higher pH leads to lower performance of aspirin removal. The best pH for adsorption of aspirin is in the acidic region (pH 3).

(3) The temperature of the solution can also affect the adsorption of aspirin whereby the adsorption capacity of aspirin decreases when temperature increases. The best condition for adsorption process is at 30 ℃.

(4) The performance of adsorption process decreases with the increase in of initial concentration.

(5) A study on the existence of pharmaceutical waste in the environment is crucial for the understanding of the risk of their presence to the environment and wastewater.

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