Synthesis of Modified Spent Tea for Aspirin Adsorption in Aqueous Solution

Norfiona Rosli, Norzita Ngadi, Muhd Asyiq Azman,

Abstract*: This present study focuses on the synthesis of a new modified eco-friendly adsorbent, spent tea (ST, discarded Camellia sinensis leaves), and its application in the adsorption of Aspirin from aqueous solution by batch adsorption technique. This is an effort in shifting towards new substitutes that are both inexpensive and highly efficient, such as agricultural waste materials as an alternative of the commonly used adsorbent material, activated carbon. The ST will first undergo an acid treatment using phosphoric acid, and subsequently modified with Polyethyleneimine (PEI) using Glutaraldehyde (GA) as the cross-linker. Aspirin removal efficiency was compared between the untreated spent tea (ST) and new PEI modified acid treated spent tea (TA-PEI). Effects of ratio of acid treated spent tea (TA) and PEI (1:1, 1:2,1:3, 2:1,3:1), and GA concentration (0,0.5,1.0,2.0,3.0, and 4.0 v/v%) were investigated. The optimal conditions for the synthesis of the modified adsorbent, TA-PEI are TA: PEI ratio of 1:2, and 0.5(v/v %) of GA. Afterwards, the untreated ST and TA-PEI were tested to determine the effect of contact time on Aspirin adsorption. It was found that TA-PEI shows great removal effectiveness - up to 64.70% before reaching equilibrium after 30min of contact time. Nevertheless, ST only shows removal of 1% and after 15min, there is no appreciable adsorption. These results suggested that TA-PEI has high potential to be used as an effective adsorbent for Aspirin removal. In the future, TA-PEI will undergo further research to investigate the effects of different adsorbent dosage, solution pH, initial concentration, solution temperature, and contact time. Several analysis (FTIR, SEM, CHNS, BET and point of zero charge) has to be done as well to get a better understanding of its properties and the adsorption mechanisms

***Index Terms*: Adsorption, Aspirin removal, Spent tea.**

I. INTRODUCTION

Being extensively and escalating used in human and veterinary medicine, pharmaceuticals are now a major emerging environmental contaminants. It is composed of diverse group of compounds designed to hindered and treat diseases [1]. Treatment and removal of these wastes from the water is crucial in order to prevent the risks it may posed on the aquatic organisms. There are several advanced techniques that has been proposed by the researchers to tackle the issue of pharmaceutical waste contaminated water, such as, ion exchange method [2], membrane technology [3] and wet oxidation method [4]. Among the procedures that evolved, adsorption is the one most reassuring and applicable for removing organic and inorganic micro pollutants [5]

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Activated carbon is a prominent compound in waste water treatment as it shows effective adsorption potential. Large surface area, highly developed porosity, and high extent of surface reactivity makes activated carbon an effective adsorbent material [6]. Unfortunately, despite its high potential, the utilization of activated carbon is limited because it is costly [6], [7]. This leads to the interest in finding other substitutes that are cheaper, high adsorptions capacity and from wastes.

In recent years, attention has been shifted towards the materials which are byproducts of wastes from agricultural waste materials. Simple technique, less processes, free availability , and easily regenerate are some of the advantages of utilizing agricultural wastes [8]. This paper will focus on the screening process of new adsorbent from spent tea leaves (ST) modified with a surfactant, Polyethyleneimine (PEI) via a crosslinking method with Glutaraldehyde (GA) as the crosslinker. Effect of different ratio of ST with PEI and GA added that yield the optimum aspirin removal will be determined. Finally, the potential of new modified adsorbent will be compared to the untreated ST.

II. METHODOLOGY

A. Material

The spent tea will be collected from local households in Johor, Malaysia. In order to remove the adhesive dirt, the ST were washed with distilled water. Then, the ST were numerously boiled with distilled water until the filtrate turned into clear solution. The washed ST were then dried in oven overnight at 100°C and stored in air-tight container for further use.

B. Synthesis *of Modified TA-PEI*

The ST first undergo an acid treatment by immersing the ST in 0.1M H_3PO_4 for 1hr at room temperature. The acid treated spent tea (TA) was then washed thoroughly with distilled water until it reach pH7 and dried in the oven for 24 hrs. Next, the TA were mixed with PEI/methanol solution with ratio of 1:1 (TA: PEI) and soaked in water bath for 1hr at 65°C. Then, (1.0 % v/v) of Glutaraldehyde were used as the cross linker and added into the mixture solution under vigorous stirring at room temperature for 1 Hr. Once crosslinking reaction completed, the mixture were filtered, washed until pH neutral and dried overnight at 60°C. The modified sample is termed as TA-PEI in this work.

C. Screening *of Modified TA-PEI Adsorbent*

Synthesis steps were repeated with different TA: PEI ratio (1:1, 1:2, 1:3, 2:2, and 3:1) and the adsorbents were tested with Aspirin removal ability. The optimum TA: PEI ratio were determined based on the highest percentage removal of aspirin. Next, effect of different amount of GA (0, 0.5, 1.0, 2.0, 3.0, and 4.0 % v/v) used in the synthesis steps were investigated.

D. Batch Adsorption Studies

The adsorbate used in this study is Aspirin. The stock solution was prepared by dissolving 0.1g of aspirin in 1000 mL of distilled water. The test solutions were prepared by diluting stock solution to the desired concentrations. The absorbance of the sample were measured by UV-Vis Spectrophotometer (Aquamate, v4.60) with the Aspirin wavelength used is 300nm. Standard calibration curve of Aspirin were used to determine the concentration of aspirin before and after the adsorption process. The adsorption capacity, q_e (mg/g) and percentage removal (%) were calculated by using equation (1) and (2) respectively [9].

$$q_e = \frac{(C_o - C_e)V}{m} \quad (1)$$

$$\%Removal = \frac{C_o - C_f}{C_o} X\ 100 \quad (2)$$

Where,
C_o (mg/L): Initial concentration of Aspirin
C_e (mg/L): Equilibrium concentration of Aspirin
V (L) : Volume of solution used
m (g) : Adsorbent mass

The batch test was performed by contacting 50ml of aspirin solution of initial concentration of 100mg/L with 0.1g of adsorbent at room temperature. The mixture was agitated on the rotary shaker for 30 mins with speed of 200rpm. The solution were then filtered, and analyzed by the Uv-Vis.The adsorption study was conducted to analyse the effects of different TA: PEI ratio and amount of GA used. Finally, aspirin removal efficiency was compared between the untreated spent tea (ST) and new PEI modified acid treated spent tea (TA-PEI).

III. RESULTS AND FINDINGS

A. Effect of TA to PEI ratio

Based on Figure 1, TA: PEI ratio of 1:2 and 1:3 shows the highest percentage removal of aspirin which is 65% for both compared to 55% for the equal amount of TA and PEI with the ratio of 1:1. It can be seen that PEI added increased the removal ability as it works as the surfactant on the TA which contained a massive amount of nitrogen-containing functional group and its abundant functional groups improved the adsorption properties of the supporting material [10].

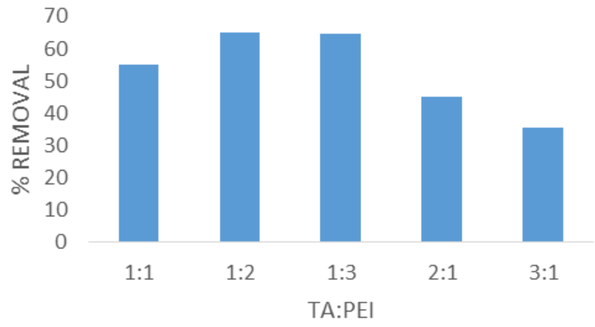

Figure 1: The effect of TA: PEI ratio on aspirin adsorption (GA concentration (1%v/v), pH 3, 30°, 100 mg/L initial aspirin concentration, 0.1 adsorbent dosage)

Due to the high water solubility of PEI, it requires support materials in order to be further utilized in adsorption process [11] , in which in this synthesis process, the PEI molecules will attached to the TA surface to form the active sites where the adsorption of aspirin will takes place. The best TA: PEI ratio chosen is 1:2 since increasing the ratio up to 1:3 brings no significance difference. Excessive amount of PEI compared to the TA will not yield higher aspirin removal as there is insufficient surface for the attachment of the PEI onto the TA and it will not aid in the adsorption performance. However, it is great to discover that small amount of PEI usage portrayed a promising adsorption performance.

In the other hand, the higher the TA amount compared to PEI, the percentage removal of aspirin were further reduced as it can be seen in the TA: PEI ratio of 2:1 and 3:1 in which the percentage removal are 45% and 35% respectively. This is due to limited active sites with the PEI attached, available for the adsorption process to takes place. As TA mostly acts as the support material for the adsorbent, PEI content is the main concern in determining the removal efficiency.

B. Effect of GA Concentration

In this synthesis process, GA were used as the crosslinker to introduce intermolecular bridges between the TA and PEI molecules. Figure 2 shows that the GA addition in the impregnation of TA and PEI increased the percentage removal up to 25%. This proved that utilization of GA as the crosslinker aid in the adsorption performance. In addition, GA are prominent crosslinker with the roles of ensuring high adsorption capacity and good stability [12].

GA concentration of 0.5 and 1%v/v yielded similar percentage removal of 65% and increasing the GA concentration to higher amount resulted in deterioration of the removal efficiency. The same pattern was observed in the research by Zhou et al. (2014) where the growth of the adsorption capacities slowed after certain limit of GA concentration where in the research was 0.5ml/L as GA has become saturated and less quaternary structure was formed hence less adsorption capacities of the adsorbent. Furthermore, resulted from vast crosslinking between GA and PEI amino groups due to

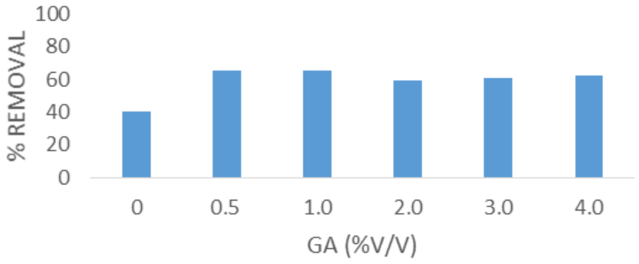

Fig 2 : The effect of GA concentration (TA: PEI of 1:2, pH 3, 30°, 100 mg/L initial aspirin concentration, 0.1 adsorbent dosage)

the excessive GA amount than the required volume elicited to the loss of amino binding sites for adsorption [13]. Hence, the adsorption performance declined as these functional groups are deficient for adsorption to occur. In a nutshell, 0.5%v/v of GA are chosen as the best concentration for the TA: PEI synthesis as increasing it to 1%v/v shows indistinguishable removal percentage.

C. Equilibrium Study of ST and modified TA-PEI

The potential of the newly synthesized adsorbent, TA-PEI with the optimum TA: PEI ratio and GA concentration of 1:2 and 0.5(%v/v) and the untreated ST were compared based on the equilibrium study by investigating the adsorption performance in certain period of time until both reached equilibrium. It can clearly be seen that TA-PEI shown a magnificent adsorption performance compared to ST.

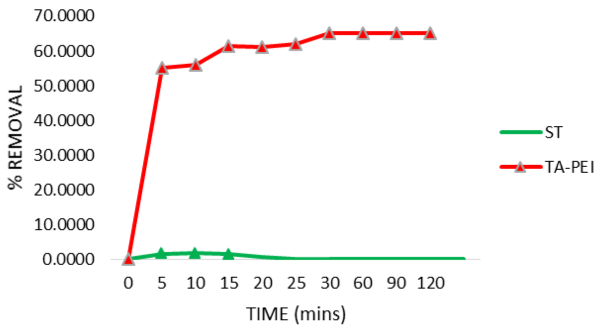

Fig 3: Comparison of adsorption process between ST and TA-PEI (TA:PEI of 1:2, GA concentration: 0.5%v/v, pH 3, 30°, 100 mg/L initial aspirin concentration, 0.1 adsorbent dosage)

Figure 3 shows the trend of the removal over the period of time. It was observed that the aspirin adsorption escalated swiftly for the first 5 minutes where the percentage removal rose up significantly to 55% and then proceeds slowly until it reach equilibrium at 30minutes with 65% of removal. The same trend was observed in the research by Azman et al. (2019) in his study of aspirin adsorption by waste tire adsorbent. This was due to the high concentration gradient of aspirin and massive unoccupied active sites for aspirin adsorption to takes place initially. However, as time goes by and more aspirin were adsorbed and attached to the TA: PEI surface, both these factor depreciates. In the other hand, the untreated ST shows bad adsorption performance where ST only shows removal of 1% and after 15min, there is no appreciable adsorption.

IV. CONCLUSION

In this study, a new modified TA-PEI adsorbent was synthesized with the optimum TA: PEI ratio of 1:2 and GA concentration of 0.5(%v/v) and were tested for the adsorption performance of aspirin. The batch adsorption studies shows that the new modified TA-PEI has a great potential to be utilized in aspirin removal with the encouraging result of percentage removal up to 65% compared to the untreated ST. This shows that spent tea, as the easily available waste source, of low cost and easy processing has great tendency as its role as the adsorbents. Furthermore, these finding could fill the gap of the limited and narrow studies on the utilization of spent tea based adsorbent studies in the removal of aspirin in aqueous solution. However, further studies has to be done in the future on the TA-PEI adsorbent to investigate the effects of initial concentration of aspirin, initial pH, temperature, and adsorbent dosage to determine the optimum conditions that will yield its utmost performance. The TA-PEI will also undergo few analysis to understand its characteristic and mechanisms.

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