International Journal of Recent Technology and Engineering (IJRTE)
ISSN: 2277-3878 (Online), Volume-10 Issue-5, January 2022

Synthesis of Magnetic Eggshell Modified with Polyethyleneimine for Aspirin Removal

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***Abstract**: The application of domestic waste as an economical and eco-friendly adsorbent has emerged among the most promising options for pharmaceutical remediation due to its high performance. Nonetheless, one of the most significant challenges of modified adsorbents is the difficulty in their recovery process, which includes separating adsorbents from cleaned water. This study synthesized and investigated a magnetic adsorbent derived from chicken eggshell (CE) modified with polyethyleneimine (PEI) for aspirin removal to address this issue. The chosen variables for the adsorbent synthesized were the ratio of CE:PEI (1:1, 1:2, 2:1, 2:0.5), the ratio of CE-PEI: magnet powder (2:1:2, 2:1:1, 2:1:0.5, 2:1:0.25). Adsorption studies were carried out to remove 0.1 g/l of aspirin. The results indicated that the optimal synthesis conditions for the magnetic chicken eggshell modified with polyethyleneimine (MCEP) are 2:1 for CE: PEI ratio, 2:1:1 ratio for CE-PEI to magnet particles and 120 minutes of crosslinking time.*

Keywords: Adsorption, Polyethyleneimine, Chicken Eggshell, Aspirin, Pharmaceutical Waste.

I. INTRODUCTION

Following the current outbreak of Coronavirus disease, a plentiful supply of medicines or drugs has been increasing vigorously in their production during the past two years. Millions of individuals worldwide were reported infected with Coronavirus, necessitating treatment and prevention for this sporadic virus. Many facilities, including healthcare and quarantine centres, have been developed and inadvertently contribute to a large volume of clinical waste, including medicines and pharmaceutical waste increasing production. According to the Department of Statistics Malaysia, clinical waste production has increased by 20% during this COVID-19 pandemic in 2020. In Malaysia, all clinical wastes must be collected, managed, and disposed of appropriately according to the laws and guidelines outlined in the Environmental Quality (Scheduled Waste) Regulations, 2005. Nonetheless, many other activities in the hospitals and health facilities include cleaning, diagnostic, research, and excretion from the human body that causes the drugs or medicines, classified as pharmaceutical waste, to be released into the sewage system without proper treatment.

Pharmaceutical waste is an emerging contaminant in water systems due to its complex molecular structure, high persistence, and low biodegradability, which potentially have harmful effects on humans and aquatic systems. Among all pharmaceutical products, aspirin (acetylsalicylic acid), a non-steroidal anti-inflammatory drug, is commonly consumed as an effective painkiller due to its low price and is easily accessible over the counter at any pharmacy or drugstore. A study has been conducted to determine the toxicity of acetylsalicylic acid (ASA) towards crustaceans. The ASA has caused several biological defects such as eye regeneration, DNA destruction, and passive behaviour [1]. Besides, other effects were also found for zebrafish embryos, such as death rate increase and delay in the hatching process. Meanwhile, long-period exposure has altered zebrafish sex differentiation [2]. Although the concentrations of ASA found in wastewater are currently low, the prolonged existence of these active compounds can lead to bioaccumulation. Thus, irreversible effects on living organisms and further consequences may threaten the human body health.

In the past decades, several technologies have been developed and studied concerning removing pharmaceutical waste from wastewater, including biological treatments, membrane technology [3], adsorption [4], and advanced oxidation processes [5]. Biological treatments and advanced oxidation processes have been used to remove pharmaceutical waste. Still, they are cost-ineffective and challenging treatments because of intermediate products generated during the degradation process with high toxicity to the environment and human health. Among these various removal applications, adsorption is a favourable treatment and efficient in removing pharmaceuticals from the water stream due to its simple operational scheme, low operational cost, comprehensive alternatives of eco-friendly adsorbents, and the reusability of the adsorbents.

Many adsorbent materials such as activated carbon, biochars, iron oxides, graphene oxides, and chitosan have received significant attention.

Manuscript received on January 19, 2022.
Revised Manuscript received on January 24, 2022.
Manuscript published on January 30, 2022.
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Commercial activated carbon often promises excellent results in pharmaceutical waste removal; however, it suffers from a high temperature and energy applied, poor results in regeneration, and a deficiency in which the activating agents used during the synthesis process are leached into solution [6].

Many economical materials such as biomass, industrial waste, and domestic waste have been explored and studied to be utilized as alternative adsorbents with the simple operational procedure involved. Recently, considered common domestic waste, chicken eggshells have received extra attention for their outstanding properties in numerous applications.

Calcium carbonate, as the main component in chicken eggshells, contributes to its utilization such as hydroxyapatite preparation in bone tissue replacement [7], in dentistry applications to provide better protection for tooth enamel [8], and effective adsorbents for heavy metals and dyes in wastewater [9, 10].

In adsorption practice, the cellulosic structure that gives the high surface area, porosity, and amino groups from the chicken eggshells is a significant contributor to removing heavy metals, dyes, and phenolic compounds from wastewater. However, the effectiveness of pure chicken eggshells as an adsorbent is still limited due to the low availability of amino groups required to remove chosen contaminants effectively. Thus, increasing the quantity of amino and hydroxyl groups in the backbone of chicken eggshells can improve their effectiveness as adsorbents for specific contaminants. Due to its many amino groups, polyethyleneimine (PEI) has become a great potential of amino-functionalized reagents in adsorption studies. It can be used to capture potentially pharmaceutical compounds such as diclofenac sodium [11] and clofibric acid [12].

Additionally, an ideal adsorbent needs to be economically practical in actual application varied from the preparation to separation. Thus, the incorporation of magnetic nanoparticles has been extensively studied in previous works to aid in the adsorption separation process following desorption and regeneration. Magnetic nanoparticles are gaining more attention and recognition due to their superior segregation capabilities. A magnetic field was employed to ease the magnetic extraction of absorbents from liquid samples, and the used adsorbents may be regenerated and reused, resulting in low capital expenses. However, many recent studies have neglected to consider the best condition of the magnetic adsorbent throughout its preparation, which is critical for developing an economically viable and effective adsorbent.

Meanwhile, to solve these limitations mentioned, this work will focus on identifying the ideal combination ratio during synthesis between raw chicken eggshells and Polyethyleneimine (PEI) and magnetic nanoparticles to generate an economical adsorbent. The magnetic chicken eggshell-PEI (MCEP) performance will be measured using aspirin adsorption to determine the best parameters.

II. METHODOLOGY

A. Preparation and Screening of MCEP Adsorbent

Chicken eggshells (CE) were obtained from local residences in Johor Bahru, Johor, as raw materials to prepare MCEP. The CE was immersed thoroughly in boiled distilled water to remove any residual's impurities. After that, the washed CE was oven-dried at 80°C overnight before being ground and sieved with a 300 µm sieve for further utilization.

The MCEP adsorbent was synthesized via a crosslinking technique with glutaraldehyde (GD) as the cross-linker. Firstly, a specified amount of CE was weighed and then homogenized with PEI in various ratios (1:1, 1:2, 2:1, 2:0.5, 2:0.25) and magnetic nanoparticles with CE-PEI: magnet powder ratio (2:1:2, 2:1:1, 2:1:0.5, 2:1:0.25) at room temperature by using horizontal shaker at 200 rpm for 30 minutes. Following that, a precise volume of GD was added to the mixture in droplets for crosslinking reasons. After shaking for a specified time (30, 60, 120, 240, 360, 480 minutes), the MCEP adsorbent was filtered, washed until pH neutral and dried at 100°C until it reached constant weight.

B. Batch Adsorption Experiments

Aspirin stock solutions (100 mg L-1) were made by dissolving a known amount of aspirin powder in distilled water. Aspirin elimination was performed in sample bottles containing 50 ml of stock solutions and 0.3g of MCEP. The batch adsorption studies were then carried out at a constant room temperature using a horizontal shaker with a 180 rpm rotational speed. After 2 hours of adsorption, the MCEP was separated, and the solutions were filtered. The concentrations of aspirin were determined using a UV-Vis Spectrophotometer with a wavelength of 282.5nm.

The amount of aspirin adsorbed by MCEP (q_t, mg g^{-1}) was calculated as follows:

$$q_t = \frac{V\,(C_O - C_e)}{m}$$

Where Co (mg L-1) represents the starting concentration of aspirin; Ce (mg L-1) represents the aqueous concentration of aspirin at equilibrium time; V (l) represents the volume of aspirin solution, and m (g) represents the quantity of MCEP utilized.

III. RESULTS AND FINDINGS

A. Effect of Ratio CE: PEI

This study explored the CE to PEI ratio considering the adsorbent's cost-effective and excellent performance. Figure 1 shows the percentage removal for aspirin with a different ratio of chicken eggshell and PEI at an initial concentration of 100 mg/L of aspirin. As can be seen, the optimum ratio for modified chicken eggshells was 2:1 of CE onto PEI solution. The adsorbent with CE to PEI ratio of 2:1, 2:0.5, and 2:0.25 have higher removal percentage than that of 1:1 and 1:2.

The result obtained is similar to the study done by Nordin et al. (2021) in their adsorbent preparation of cellulose modified with PEI that found 2:1 ratio is the best for dye removal [13].

This observation happens because the amino-functionalized PEI's reagent is sufficient to cover the active sites of the surface of the chicken eggshell.

Retrieval Number: 100.1/ijrte.E67810110522
DOI: 10.35940/ijrte.E6781.0110522
Journal Website: www.ijrte.org

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However, if the CE amount is inadequate, it may cause the excessive PEI to mobilize in the solution thus, leading to poor adsorption performance. It is a remarkable finding that the amount of PEI required is only half of the chicken eggshells to achieve outstanding adsorption performance towards aspirin.

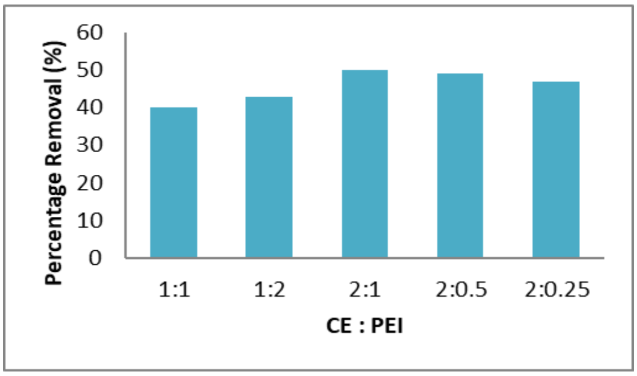

Fig. 1: The effect of ratio CE: PEI towards aspirin removal (Conditions: initial concentration of aspirin: 100 mg/L, GD volume: 3ml, 25°C, 120 minutes)

B. Effect of Ratio CE-PEI to Magnetic Powder

The magnetic powder was used to modify the adsorbent in this study to exhibit magnetic properties and be separated easily. It is crucial to study the perfect ratio needed to avoid any accumulated or leaching iron oxide that may affect adsorption.

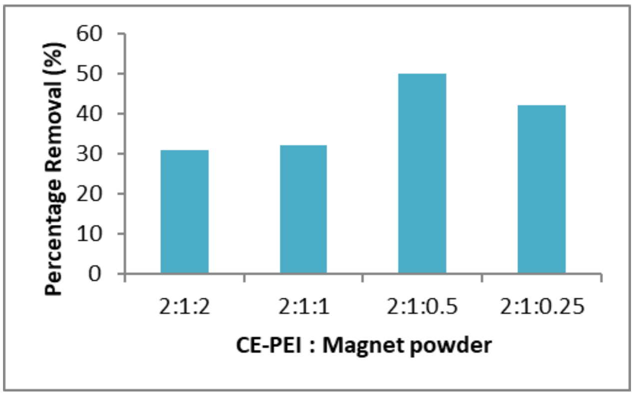

Fig. 2: The effect of ratio CE-PEI: magnetic powder towards aspirin removal (Conditions: initial concentration of aspirin: 100 mg/L, GD volume: 3ml, 25°C, 120 minutes)

In studying the ratio of CE-PEI to magnetic powder, the PEI concentration is constant at (2% v/v). The amount of magnetic powder varies from 2.0 g until 0.25g at room temperature for 2 hours of impregnation time. The CE-PEI to magnetic powder ratio on aspirin adsorption is shown in Figure 2. Based on the findings, applying an excessive amount of magnetic material reduces the percentage of aspirin removed. The exceeding magnetic nanoparticles attached to the CE-PEI have a high tendency for the nanoparticles clusters to occur, thus hindering the magnetic nanoparticles from achieving stability and resulting in poor adsorption performance [14]. From this study, the best ratio of CE-PEI to magnet powder is 2:1:0.5, with the best removal percentage of aspirin at 50%.

C. Effect of Crosslinking Time

The crosslinking time for CE-PEI and magnetic powder was varied from 30 minutes to 360 minutes at room temperature. Figure 3 shows the results of aspirin removal with different crosslinking times. From the first 120 minutes, the removal percentage of aspirin increases then decreases until 360 minutes. The lowest elimination of aspirin was found at minute 30 because most of the CE and PEI were not entirely building a copolymer chain with the cross-linker at that time. The decrease in performance after minute 120 is undoubtedly related to the PEI molecule detaching from the CE surface. Furthermore, this may be because the active site of CE was completely occupied by PEI molecules, resulting in adsorption limitation. As a result, it can be determined that the optimal time for crosslinking was 120 minutes. At this point, the CE and PEI were completely polymerized with GD to create a copolymer chain, which improved aspirin removal.

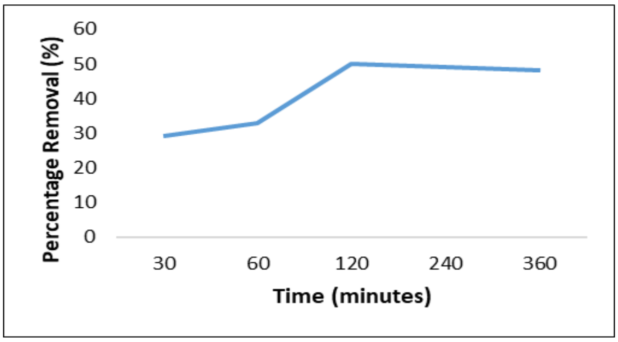

Fig. 3: The effect of crosslinking times towards aspirin removal (Conditions: initial concentration of aspirin: 100 mg/L, GD volume: 3ml, 25°C, 120 minutes)

IV. CONCLUSION

The synthesis condition of MCEP towards the removal of aspirin was presented and discussed. This work establishes that the modification of chicken eggshells with PEI and magnetic powder has been successfully manufactured and applied to treat pharmaceutical waste with a 50% elimination rate. This finding was also able to fill the study gap of the necessary condition that needed to be determined to combine chicken eggshell, PEI, and magnetic nanoparticles. For future works, detailed studies on adsorption conditions such as the pH, concentration, adsorption time, temperature, and adsorbent dosage must be performed.

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