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Removal of Pharmaceutical Waste Materials from Wastewater using Treated and Untreated Eggshells as Biosorbent

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Abstract **-** Pharmaceutical technology and industries are evolving and improving. However, the pharmaceutical wastewater that results from those industries has a complex composition, including high organic matter content, high salt content, microbial toxicity, and difficulty in biodegrading. Studies have shown that traces of dissolved organic matter and suspended solids remain even after secondary treatment. Additionally, the impact of pharmaceutical wastewater on environmental pollution is dramatically growing, resulting in the disposal of hazardous waste, an increase in microbial resistance, and adverse effects on marine life. Hence, this paper aims to investigate a method for the treatment of pharmaceutical wastewater effluent using a waste-to-treat-waste method. In the proposed methodology, eggshells are utilized as biosorbents for the removal of ciprofloxacin antibiotic, as a model of pharmaceutical wastewater. The preliminary results revealed a high potential for effective removal of this pharmaceutical from the aqueous solution using untreated eggshells. This study will consider factors affecting adsorption to further optimize experimental conditions and, thus, towards the maximum removal efficiency. It will also consider enhancing eggshell adsorption capability by its physical and chemical treatments.

Keywords**:** Pharmaceutical, Wastewater, Ciprofloxacin, Biosorbent, Eggshells

1. Introduction

advancements in the pharmaceutical sector have transformed healthcare by facilitating the creation of innovative drugs and therapies tailored to specific diseases and conditions, enhancing precision and efficacy. However, the pharmaceutical industry generates various types of wastewaters due to the diverse range of products and technological advancements. A significant portion of this wastewater comprises highly concentrated antibiotic residues, which are biologically toxic and environmentally harmful [1, 2]. Improper disposal or inadequate treatment of pharmaceutical waste can lead to contamination of water bodies, posing risks to aquatic ecosystems and human health. Additionally, it can disrupt ecosystems and adversely affect sensitive species, while also potentially causing long-term ecological damage. Exposure to pharmaceutical residues through contaminated water or food sources can have adverse effects on human health, including hormonal disruptions and antibiotic resistance [3, 4]. Therefore, proper disposal and effective treatment methods are crucial to minimize these negative impacts.

Conventional wastewater treatment techniques may not fully address the challenge posed by pharmaceutical waste, necessitating the exploration of alternative technologies [1, 4]. Options such as incineration and landfill disposal have drawbacks, including environmental emissions and long-term environmental impact. Wastewater treatment processes, while effective to some extent, may not eliminate all trace amounts of pharmaceutical compounds and can be costly [2].

One promising alternative for pharmaceutical waste treatment is adsorption using specific adsorbents. Eggshells possess characteristics that make them ideal candidates for biosorption. Composed mainly of calcium carbonate, eggshells offer a high surface area for adsorption due to their interconnected crystalline structure. Finely powdered eggshells have an even larger surface area, enhancing their adsorption capacity [5]. Their porous structure enables them to sorb and retain contaminants from aqueous solutions effectively. Moreover, eggshells are non-toxic, biodegradable, readily available, and cost-effective, making them environmentally friendly biosorbents [6]. They have demonstrated efficacy in removing heavy metals, dyes, and various organic and inorganic compounds, indicating their potential for pharmaceutical waste treatment and other environmental applications. Therefore, the main objective of this work is to use eggshells as biosorbents to remove pharmaceutical waste from wastewater. Ciprofloxacin (CIP) will be used as an antibiotic model in this study.

2. Materials and Methods

2.1. Preparation of Eggshells

Eggshells (ES) will be gathered from the kitchens and household trash. They will be cleaned multiple times with tap water and then rinsed with ultra-pure water to get rid of impurities and pollutants before being utilized. They will be then dried in an electric oven for 24 hours at 60°C to a constant weight. The eggshells will then ground in a mechanical grinder and sieved to create a powder with particles ranging in size from 200 to 800 μm. These eggshells will be kept in sterile polythene containers to be used as adsorbents later. The current study will consider use of eggshells as it is (inactivated sorbent), but there is a possibility to treat it chemically (activated eggshells) with a specific chemical agent to improve the performance of eggshells toward pharmaceutical removal from water. Thermally activated eggshells will be also considered where eggshells will be heated to 100-700 °C to see the effect of heat on removal efficiency of the eggshells.

2.2. Batch Sorption Tests

Batch adsorption tests will be carried out to evaluate the effects of pH, contact duration, concentration of ciprofloxacin, adsorbent dose, and operating temperature on the adsorption performance of eggshells. Batch tests have been performed to verify the removal efficiency of eggshell toward ciprofloxacin from aqueous solutions. In 250 mL flasks containing 40 mL of 50 μg/mL ciprofloxacin solution, various adsorbent doses, namely 5, 10, 15, and 20 g, were added to different flasks. The flasks were agitated using orbital shaker for 15 minutes at an agitation speed of 250 rpm. Other parameters were also varied, and batch tests were followed similarly. The suspensions were filtered using Whatman filter paper. Ciprofloxacin was measured in filtrate using UV spectrophotometer.

3. Results and Discussion

Maximum absorbance of the various aqueous standard solution of the ciprofloxacin was found to be 275 nm. Accordingly, a calibration curve has been plotted to check the linear range of ciprofloxacin in aqueous solution. The calibration curve was linear with R2 ≥ 0.99 for studied concentrations in the range 0.1-0.5 μg/mL and 1-5 μg/mL. This shows aqueous solution of ciprofloxacin is obeying the Beer law in the studied range of the concentration.

Various batch tests were conducted, and results showed that with 50 μg/mL of ciprofloxacin and different eggshells, the absorbance drastically drops within 15 minutes. This indicates clearly that the eggshells is successfully removing ciprofloxacin from its aqueous solution.

3.1. Effect of concentration of CIP

The preliminary batch experiments aimed to assess the efficiency of eggshell powder in removing ciprofloxacin from aqueous solutions. In a series of 250 mL Erlenmeyer flasks, a solution containing 40 ml of CIP solution and 5 g of eggshell powder was blended with varying concentrations of ciprofloxacin, ranging from 10 to 90 μg/mL, over different contact time intervals. The evaluation of ciprofloxacin removal efficiency was carried out by determining the difference between the initial concentration and the concentration remaining in the solution after adsorption. The results depicted in the Figure 1 illustrate, as the concentration of ciprofloxacin (CIP) increases, the removal efficiency also increases across all contact time intervals (1 hour, 2 hours, and 24 hours). The concentrations of 60-90 μg/mL of ciprofloxacin exhibited over 90% removal efficiency after a 2-hour contact time, highlighting the promising potential of eggshell powder as an effective adsorbent for ciprofloxacin removal.

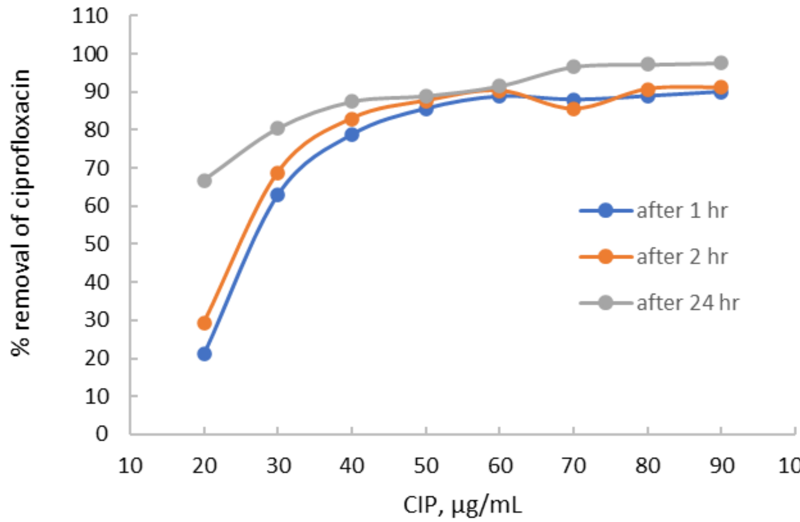

Fig. 1: Effect of ciprofloxacin dose on the removal of 40 mL ciprofloxacin using 5 g of eggshell at various time

3.2. Effect of dose of adsorbent

This study investigated the influence of the adsorbent dose, specifically eggshell, on ciprofloxacin removal. In 250 mL flasks, each containing 40 mL of solutions with a ciprofloxacin concentration of 50 µg/mL, varying doses of eggshell powder, ranging from 0.5 to 6 g, were introduced. The flasks were then subjected to agitation using an orbital shaker for a total duration of one hour, with an agitation speed set at 250 rpm. The results depicted in the Figure 3 indicate that an eggshell dose within the range of 5-6 g achieves a removal efficiency exceeding 90% after one hour, particularly when the initial ciprofloxacin concentration is 100 µg/mL. This study highlights the dose-dependent efficiency of eggshell in enhancing the removal of ciprofloxacin from aqueous solutions.

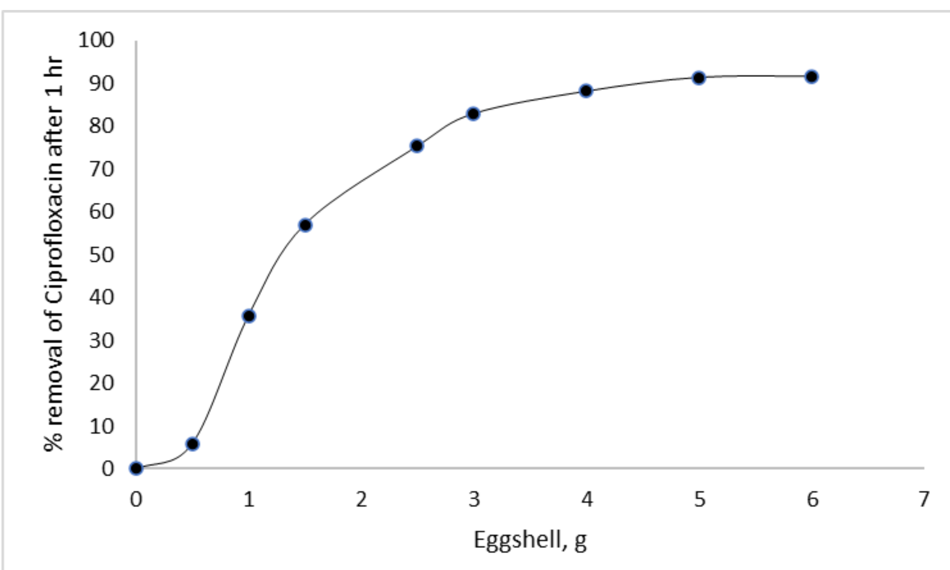

Fig. 2: Effect of eggshell dose on ciprofloxacin removal using 50 mL of 100 µg/mL CIP.

4. Conclusion

The findings from this study provide valuable insights for the development of sustainable and effective strategies for treating pharmaceutical wastewater and addressing the environmental impact of Ciprofloxacin contamination.

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