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Adsorption of Rhodamine B by Egg Shell Hydroxyapatite

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Abstract

Agricultural waste has been severely reported as a low-cost and efficient adsorbent for the removal of pollutants including dyes from waste water and industrial effluents. This study investigates the optimum conditions for the efficient performance of chemically activated egg shell as an efficient biosorbent for the removal of Rhodamine B (RhB) from aqueous solutions. The adsorbent was characterized by Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). The optimum adsorption capacity of egg Shell hydroxyapatite was determined through batch adsorption experiments. The effects of initial RhB concentration, pH, contact time and temperature on the adsorption capacity were studied. Egg shell hydroxyapatite showed maximum adsorption capacity of 6.5 mg/g at an acidic pH of 3. The rate of Adsorption was found to increase with increase in temperature and contact time. The adsorption process followed pseudo-second-order kinetics, indicating chemisorption as the rate-limiting step. The adsorption isotherm data were well-fitted to the Langmuir isothern model, suggesting monolayer adsorption of RhB onto the egg shell hydroxyapatite surface. Overall, egg shell hydroxyapatite showed great potential as an effective and sustainable adsorbent for the removal of Rhodamine B from aqueous solutions.

Keyword: Adsorption, Agricultural waste, Egg shell hydroxyapatite, Rhodamine B.

1. Introduction

In recent years, the textile industries have been reported to be responsible for an extensive list of environmental impacts (Yaseen and Scholz, 2019). The main damages caused by the textile industry to the environment, however, are those resulting from the discharge of untreated effluents into the water bodies (Ardila-Leal *et al.*, 2021), which normally constitute 80% of the total emissions produced by this industry (Wang, 2016). Relatively high level of biochemical oxygen demand (BOD) and chemical oxygen demand (COD) has been reported in the composition of most of the residual waters of the textile industry (Wong *et al*., 2002). The textile dyes have also found to contain toxic, mutagenic and carcinogenic agents (Aquino *et al.*, 2014, Khatri *et al.*, 2018, Lellis *et al.*, 2019). These dyes persist as environmental pollutants across the entire food chains providing biomagnifications (Sandhya, 2010), such that organisms at higher trophic levels show higher levels of contamination compared to their prey (Newman, 2015). Therefore, the contamination of water bodies by synthetic dyes has become a significant environmental concern. Among these dyes, Rhodamine B, a widely used synthetic dye, has raised particular apprehension due to its carcinogenic and mutagenic properties.

Various methods have been employed to remove Rhodamine B from wastewater, with adsorption being one of the most promising and eco-friendly techniques. Adsorbents derived from agricultural waste such as coconut shell, rice husk, maize husk, egg shell etc., as emerged as a low-cost and efficient adsorbent for the removal of various pollutants from water, including dyes. The adsorption process involves the adherence of molecules or particles to the surface of a solid material, leading to the removal of contaminants from a liquid phase.

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The effectiveness of adsorption depends on several factors, such as the properties of the adsorbent and the adsorbate, as well as environmental conditions (Sana *et al.*, 2016). In this context, experimental studies play a crucial role in understanding the adsorption process.

This study investigates the adsorption behaviour of Rhodamine B onto egg shell hydroxyapatite (ESHA). The experiments will provide valuable insights into the optimal conditions, kinetics, and thermodynamics of the adsorption process.

2. Materials and Methods

2.1 Preparation of Poultry Egg Shell Hydroxyapaptite (PESHA) as the Adsorbent

Discarded eggshells were collected from local restaurants within Ilorin metropolis. To prevent decomposition, the eggshells were washed with tap water, dried at 105 ºC in a hot air oven for 2 hours. The membranes were separated from dried eggshells by hand. The dried eggshells and membranes were grounded separately using a blender. The powdered materials were sieved to obtain particles of various size ranges. The sieved materials were tested for their adsorbent qualities without further chemical or physical treatment.

2.2 Preparation of the Adsorbate

Rhodamine B Dye was obtained from the Laboratory. The dyes stock solution was prepared by dissolving accurate weight of it in deionised water to the concentration of 100 mg/L.

2.3 Adsorption Experiment

The chemicals used in this study were of analytical reagent grade and will be used without further purification. The working solution with different concentrations of the Rhodamine B will be prepared by appropriate dilution of the stock solution immediately prior to their use with deionized water. The stock solution was prepared by dissolving 0.025 g of Rhodamine B in 250 ml of deionized water in a 250 ml standard flask to obtain 100 mg/L aqueous solution of Rhodamine B. Standard solutions of varying concentrations were prepared by diluting appropriate amount of the dye solution to obtain each of the smaller concentrations (Reza and Ahmaruzzaman, 2014).

The amount of Rhodamine B adsorbed by the adsorbent will be calculated by using the following equation:

$$Q_e = \frac{v(C_o - C_e)}{M} \qquad \text{........ (1)}$$

Where Q_e is the quantity adsorbed (mg/g), C_o and C_e are the initial and final concentration of the Rhodamine B in solution at any time, t (mg/L), V is the total volume of the dye solution (Rhodamine B solution) in the flask (L), M is the mass of adsorbent used (g)
The percentage dye removal (%) was also calculated using the following equation:

$$\text{Percentage Dye Removal (\%)} = \frac{C_o - C_e}{C_e} \times 100 \qquad \text{....... (2)}$$

C_o and C_e are the initial and final dye concentrations (mg L^{-1}) respectively

3. Result and Discussion

3.1Adsorption Experiment Result

3.1.1 Effect of initial concentration

The Effect of initial concentration on adsorption of Rhodamine B dyes onto eggshell hydroxyapatite was determined by keeping adsorbent dose constant. In this study, the adsorption of these dyes was studied by varying concentration range from 2 to 20 mg/L. Figure 1 shows effect of initial concentration on adsorption of Rhodamine B by eggshell hydroxyapatite. This shows that adsorption decreases with increase in concentration of dyes. It was found that adsorption increases rapidly in the beginning and after that it decreases slowly. The percentage of dye removal decreases with an increase in the initial dye concentration, which is due to the saturation of adsorption sites on the adsorbent surface. At a low concentration there will be unoccupied active sites on the adsorbent surface, and when the initial dye concentration increases, the active sites required for adsorption of the dye molecules will lack unoccupied active sites thereby reducing the rate of adsorption.

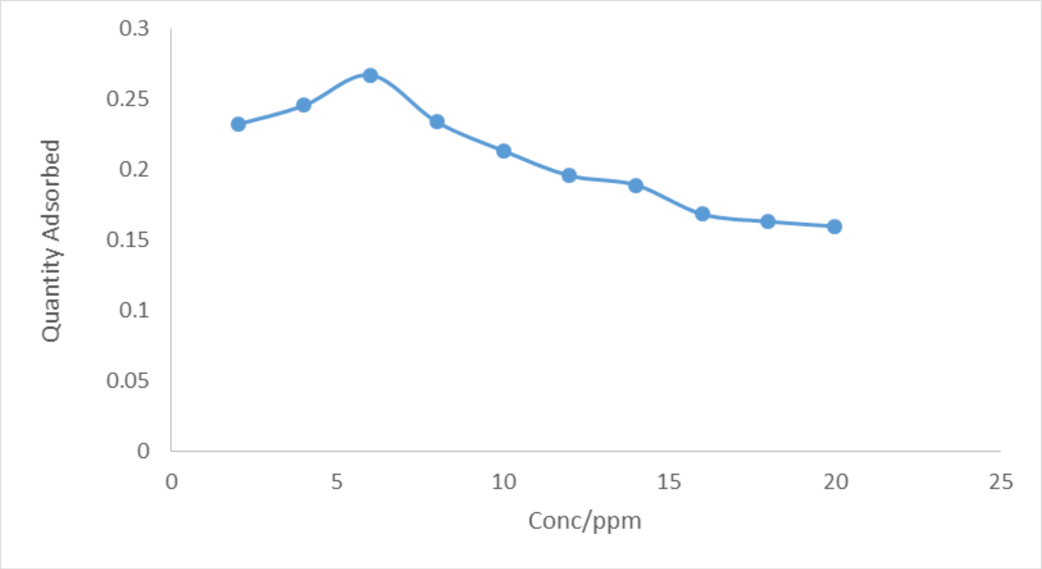

Figure 1 Effect of Concentration on Adsorption of Rhodamine B

3.1.2 Effect of pH

The surface charge of hydroxyapatite changes with pH. At lower pH levels, the surface tends to be positively charged, while at higher pH levels, it becomes negatively charged. Rhodamine B is a cationic dye, meaning it carries a positive charge in aqueous solutions. At lower pH the surface of HAP is positively charged, leading to repulsion between the positively charged Rhodamine B molecules and the HAP surface. Therefore, adsorption tends to be lower at acidic pH, at high pH The surface of HAP becomes negatively charged, which enhances the electrostatic attraction between the positively charged Rhodamine B molecules and the HAP surface, resulting in higher adsorption. From Figure 2, it is evident that the optimal pH for maximum adsorption of Rhodamine B onto HAP was found in the neutral to slightly basic (pH 8). This is where the balance between dye ionization and surface charge of HAP is most favourable for adsorption.

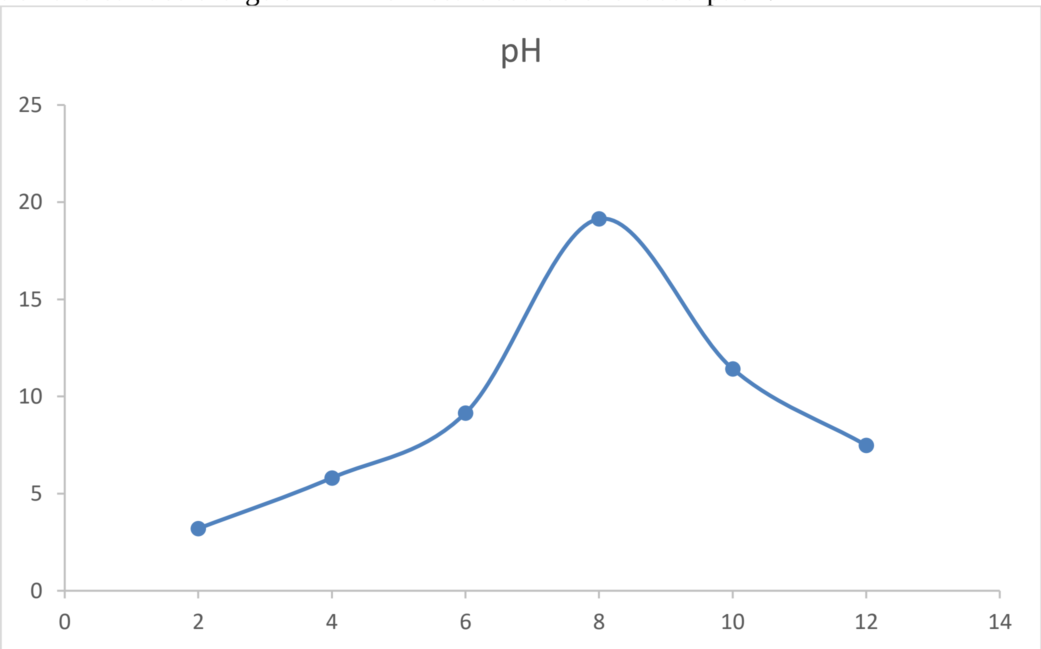

Figure 2 Effect of pH on Adsorption of Rhodamine B

3.1.3 Effect of contact time

The effect of contact time on adsorption of Rhodamine B, dyes onto eggshell powder was determined by keeping initial concentration, adsorbent dose constant. In this study, the adsorption process of Rhodamine B dyes was studied for various time including 5, 10, 15, 30, 45-, 60-, 90- and 120-min. Figure 3 shows effect of contact time on adsorption of Rhodamine B, dyes by eggshell powder. This shows that adsorption increases with increase in contact time as for adsorption more sites are available. It was found that adsorption increases rapidly in the beginning and after that it remains constant. The equilibrium time was found to be 90 min for 2 mg/L dyes concentration at pH 5

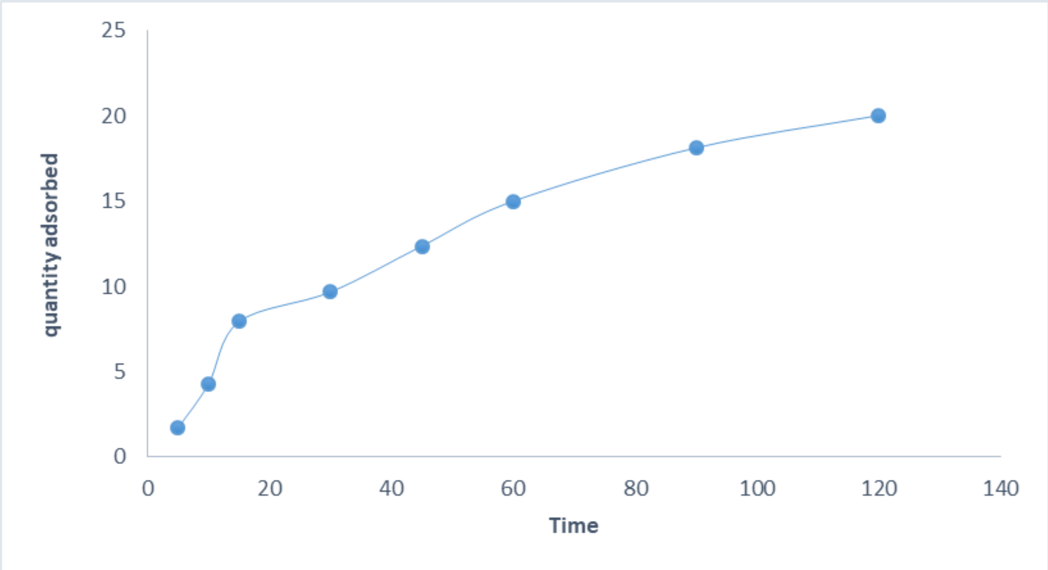

Figure 3 Effect of Contact time on Adsorption of Rhodamine B

3.1.4 Effect of Temperature

The adsorption capacity of the Egg Shell Hydroxyapatite increases with increasing temperature (Figure 4) indicating that the adsorption process is an endothermic process. This may be due to increasing the mobility of the dye molecules and an increase in the number of active sites for the adsorption with increasing temperature. This effect depends mainly on the movement of dye molecules of Rhodamine B Dye.

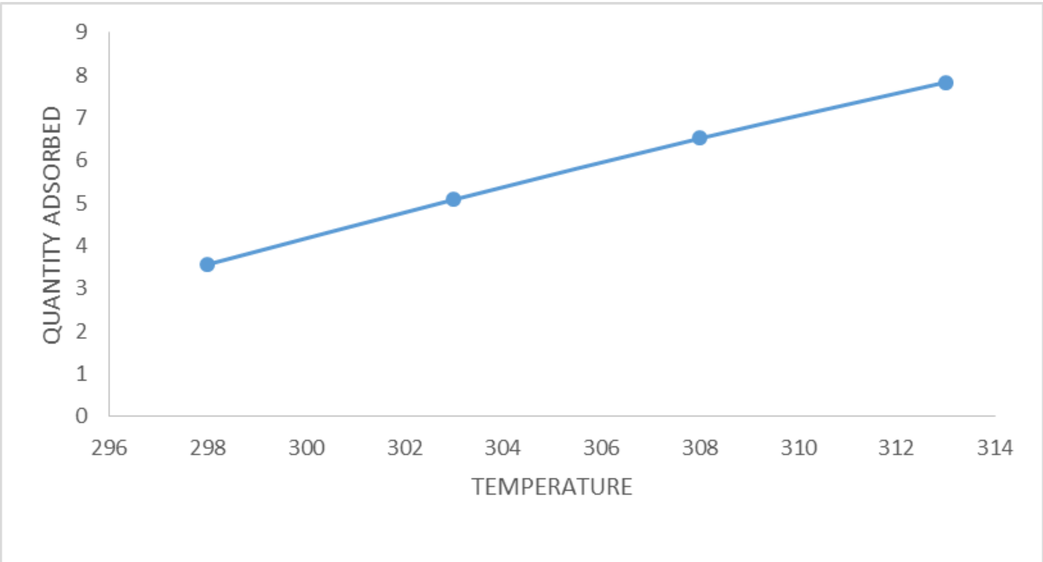

Figure 4 Effect of Temperature on Adsorption of Rhodamine B

3.2 Adsorption isotherm models

To optimize the design of adsorption system to remove dye from aqueous solution, kinetic profiling of rhodamine B dye adsorption were carried out to determine the rate controlling mechanisms involved in adsorption process using Langmuir (Choy *et al.*, 2000) and Freundlich (Sheindof etal., 1981) isotherm models.

3.2.1 Frieundlich Adsorption Isotherm

From the plot of Log Q_e and Log C_e showed in figure 5, the correlation coefficient R^2 was found to be 0.987. The value of n is greater than 1, hence the process of adsorption is endothermic. The values of K_f and 1/n were calculated to be 3.13 and 0.746. From the values of in 1/n, it can be interpreted that the adsorption is more heterogeneous nature

Table 3.1 Freundlich Isotherm

1/n	K_f	R^2
0.746	3.13	0.987

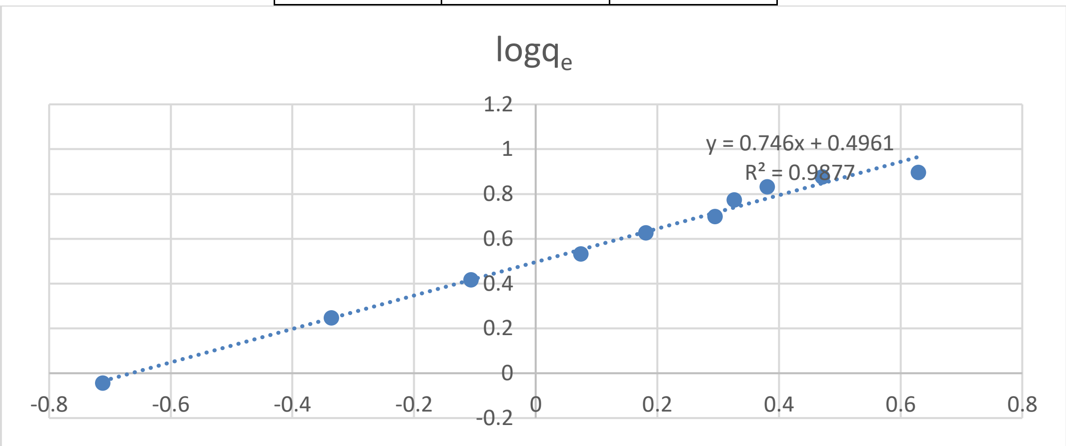

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Figure 5: Frieundlich Isotherm Behaviour

3.2.2 Lagmiur Adsorption Isotherm

The Langmuir constants, Q_m and K_L were determined to be 15.15 and 4.3 from the intercept and the slope of the straight line obtained by plotting C_e/Q_e versus C_e. The correlation coefficient R^2 was found to be 0.888 and the adsorption was less favorable.

Table 3.2 Lagmiur Isotherm

Q_m (mg.g^{-1})	K_L(L.mg^{-1})	R^2
15.15	4.3	0.888

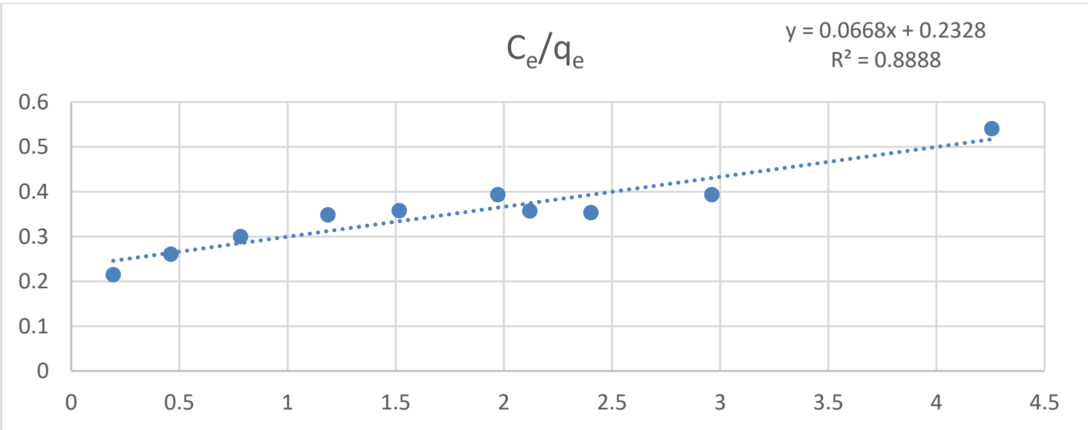

Figure 6: Lagmiur Isotherm Behaviour

4. Conclusion

The hydroxyapatite (HAp) derived from egg shells demonstrated a significant adsorption capacity for Rhodamine B (RhB), highlighting its potential as an effective adsorbent for removing dye from aqueous solutions.The adsorption kinetics followed a pseudo-second-order model, suggesting that chemisorption might be the rate-limiting step. The adsorption isotherms fitted well with the *Freudlich* model, suggesting heterogeneous adsorption of RhB on ESHA. The maximum adsorption capacity obtained from the Fruedlich model was found to be 6 mg/g.The adsorption of RhB was highly dependent on the pH of the solution, with optimal adsorption occurring at a pH of 8. This can be attributed to the ionization state of RhB and the surface charge of Hap. The thermodynamic parameters (ΔG°, ΔH°, and ΔS°) indicated that the adsorption process was spontaneous and endothermic in nature.

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