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Comparative Assessment of Adsorption Capacities of Periwinkle, Snail, and Egg Shell Biomass for the Decontamination of Cadmium (II) Ion from Textile Effluent

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ABSTRACT

Pollution of the environment with toxic metals is a global concern in the era of industrial evolution. Biosorption type of metal adsorption process is an economical alternative tool in waste water treatment compares to high cost conventional methods like precipitation and reverse osmosis. The study examined the comparison of the adsorption capacities of Snail, Periwinkle and egg shell powder adsorbents developed from agricultural by-product for the removal of Cd (II) ion from textile effluent. The procedure involved the performance of these adsorbents with each other by initial metal ion concentrations and contact time. The binding capacities for Cd (II) ion are 1.26 to 11.87 mg/kg for Periwinkle shell, 1.18 to 10.31 mg/kg for Snail shell and 1.02 to 7.10 mg/kg for egg shell adsorbent compare with the capacities on activated charcoal of 1.30 to 11.98 mg/kg. The optimum contact time for all the adsorbents is 3 hours. Adsorption isotherms patterns of the adsorbents were modeled using Langmuir and Freundlich isotherms. Based on correlation coefficient (R2) values, equilibrium data found fitted well to both the Langmuir and Freundlich isotherms. The kinetic characteristics using the pseudo-first-order Langergren and pseudo-second-order Ho model was evaluated and the result was best fitted into the pseudo-second-order kinetic model. It is concluded that these adsorbents can be used as an effective adsorbent for removal of toxic Cd (II) ion from waste water, but Periwinkle shell has a greater potential over snail and egg shells.

Keywords:
Adsorption, Cadmium, Adsorbents, Isotherm, Kinetic.

1. INTRODUCTION

Environmental pollution is of great concern due to its global risk and its effects on society Removal of heavy metal from industrial waste water is of primary importance. Waste water contamination by heavy metal is a serious environmental problem because of indiscriminate discharge by small and medium scale industries [1,2].

Heavy metals like Chromium (Cr), Nickel (Ni), Cadmium (Cd), Lead (Pb), Copper (Cu), Zinc (Zn), etc are not biodegradable, unlike organic pollutants which are biodegradable [3]. Their increasing concentration in the environment is detrimental to a variety of living species [4].

Cadmium is one of the heavy metals that have been classified by the World Health Organisation (WHO) to be a serious health concern [5]. In fact, this metal together with Pb and Hg are referred to as "the big three" because of their significant negative impact on the environment [6]. It also causes cancer and genetic changes [5].

Several conventional methods have been employed for eliminating these cations from water systems such as chemical precipitation, solvent extraction, vacuum evaporation, membrane technologies, adsorption, membrane separation, reverse osmosis, ion exchange, and ultra-filtration [7]. However, these methods have their own restrictions such as low efficiency, sensitive working environments, and the production of toxic slurry [8,9]. Hence, there is an urgent need for more practical and environment-friendly technologies. Bio-sorption is now considered among the most effective, economic, and selective methods for water treatment and analysis purposes [10,7]. Also, adsorption is preferred because of the ease of application and high removal efficiencies [11]. However, in large scale industrial applications, the cost of the process is as important as the cost of remediation. When evaluated in this context, interest in economic and environmental wastewater treatment methods based on adsorption is increasing with the use of economically unstable initiators in the preparation of adsorbents [12].

2. MATERIALS AND METHODS

Distilled water, 0.1 M NaOH. Activated carbon all of analytical grade. Periwinkle, snail and egg shells, conical flasks, pipette, measuring cylinder,1000 ml standard flask, glass funnel, beaker, sieve, stirring rod, air tight containers, 30 ml sample bottles, grinding machine, air dried oven, hot plate, atomic absorption spectrophotometer (AAS) and mechanical shaker (G 10 GYROTORY SHAKER)

2.1. Sorbents

The adsorbents used in this study were Periwinkle, Snail, and Egg shell adsorbents and compare with the activated carbon adsorbent as control. These were prepared by collecting periwinkle, snail and egg shells from local market area in Lagos State Southern Western Nigeria, washed in distilled water, dried in open air for two days. The prepared adsorbents were further dried in an oven at 105°C for two hours. Then the adsorbents were grounded separately and the resulting powders were sieved by the standard test sieve of 150µm mesh size for the adsorption study.

2.2. Sorbates

Preparation of Real Sample Effluent at discharge point from Textile Industry (which is a private industry in Lagos, Southern Western Nigeria) was collected. To study the capacities of the adsorbents for the removal of Cd (ll) ion from the effluent which had pH 5.6 and 50 mgL^{-1} initial Cd (ll) ion concentration, 20 mL of effluent was measured and added into 50 mL conical flasks and the pH was adjusted to pH 7 by dropwise addition of 0.1 M NaOH. The solutions were shaken under the same conditions, filtered and prepared for analysis using AAS. The initial cadmium concentration in the effluent was very high (2006 mg L^{-1}) and was beyond the calibration curve limit and hence was determined after dilution of 100 µL of the real sample in to 50 mL (300-fold dilution).

2.3. Adsorption Experiments

The adsorption capacity studies were conducted by batch experiment under different conditions at neutral pH value and 25ºC. This was done by weighing 0.5 g of each of the adsorbents into the conical flasks containing 30 mL of 20 mg L^{-1} of the Cd (ll) ion solutions and agitated using a mechanical shaker at a speed of 150rpm for 20, 40, 60, 120, 180, 210, 240, 270 and 300 mins. After the time of adsorption was completed, the solution was filtered using Whatman filter paper. The final concentration of cadmium left in the filtrates was analyzed using Atomic Absorption Spectroscopy (AAS) [13].

2.4. Statistical Analysis

The average of triplicate AAS measurements was considered during the determination of Cd (II) ion using multi point external standardization method by AAS. The curve-fitting tests for data points for isotherm and kinetic studies were determined from the coefficient of determination from each graph. Then the adsorption capacity the amount of Cd(II) adsorbed at equilibrium, Qe (mg L^{-1})and at time t(min), were calculated according to the equations [13]. The adsorption capacity was calculated as:

$$Q_e = \frac{(C_o - C_t)V}{m} \quad (1)$$

where m = mass of adsorbent (g)
C_o = initial concentration of metal ion (mg/L) in solution
C_t = concentration at any time (mg/L),
V = Volume of solution (L)
Q_e= Adsorption capacity or metal ion uptake capacity (mg/g biomass) at equilibrium..
Ce = Concentration of heavy metal at equilibrium (mg/L) [13].

3. RESULTS AND DISCUSSION

The adsorbents (periwinkle, Snail, egg shells and control (activated carbon) depicted in fig. 1.1 and the impact of contact duration on the cadmium (11) ion uptake rate. Cadmium was absorbed into the adsorbents in two stages: Adsorption capacities initially increased at the start of the cadmium removal process due to continuously diffusion of cadmium ions onto the surface of the adsorbents [14]. However, after 180 minutes regardless of the adsorbents, adsorption remained constant i.e after reaching equilibrium. The wide surface area for the sorption of cadmium ions on the binding sites may affect the nature of the adsorbent and its accessible sorption sites. All cadmium (II) ions required 180 minutes of optimum equilibration time indicating that physisorption was the main process. This agrees with the work Eruola on he kinetic study of the sorption of cadmium, lead manganese from aqueous solution using cocoa shell. These encourage easy removal of the adsorbed heavy metals. The graph unequivocally demonstrates that, in terms of maximum cadmium adsorption capacity apart from the activated carbon (control), periwinkle shell performed better than snail shell. Egg shell has the least adsorption capacity.

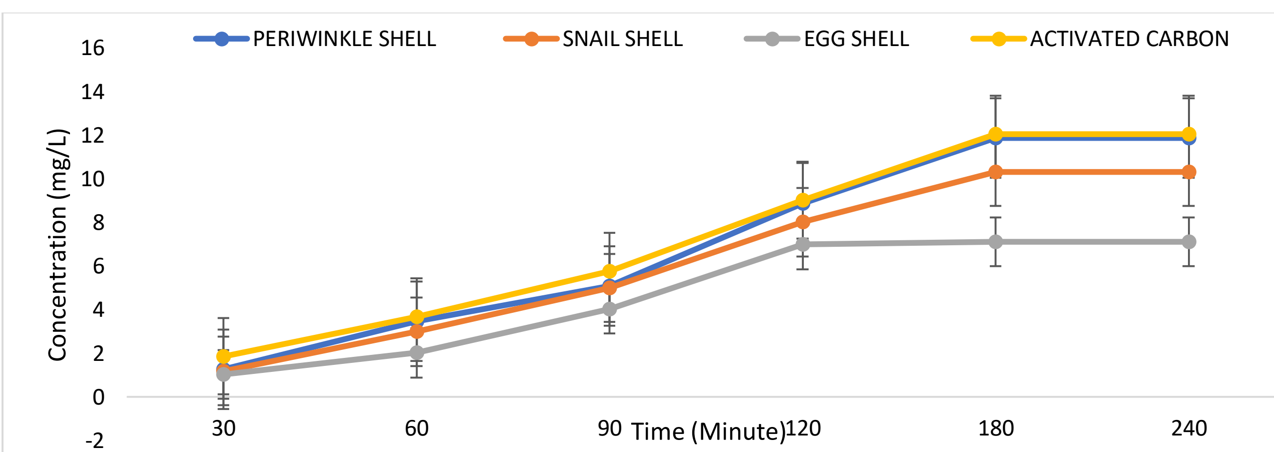

***Figure 1**: Adsorption capacities for Periwinkle, Snail and Egg shell to activated carbon on the removal of cadmium (II) ion at neutral pH, speed of 150 rpm, 20 mg/L and 25 °C*

The adsorption data was substituted into Langmuir and Freundlich adsorption models to know the best model. From Figures 2, 3, 4, 5 the correlation coefficient values (R^2) were 0.99 each for the four adsorbents. The basic assumption of the Langmuir theory is that adsorption occurs at specific homogeneous sites within an adsorbent and, once an adsorbates occupies a site, no further adsorption can occur on that site i.e valid for only monomolecular adsorption . The linear forms of the Langmuir equations are depicted in equation as shown

$$\frac{1}{q_e} = \frac{1}{Q^o} + \left[\frac{1}{bQ^o}\right] \left[\frac{1}{C}\right] \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

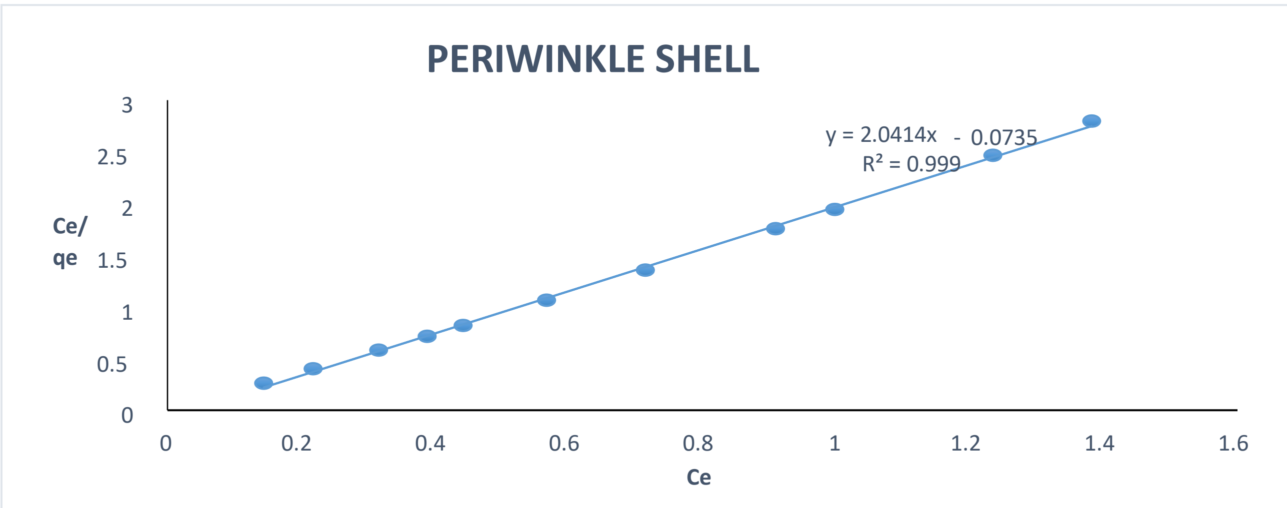

Figure 2: Langmuir Adsorption Isotherm at neutral pH, speed of 150 rpm, 20 mg/L, and 25 °C for Periwinkle Shell powder.

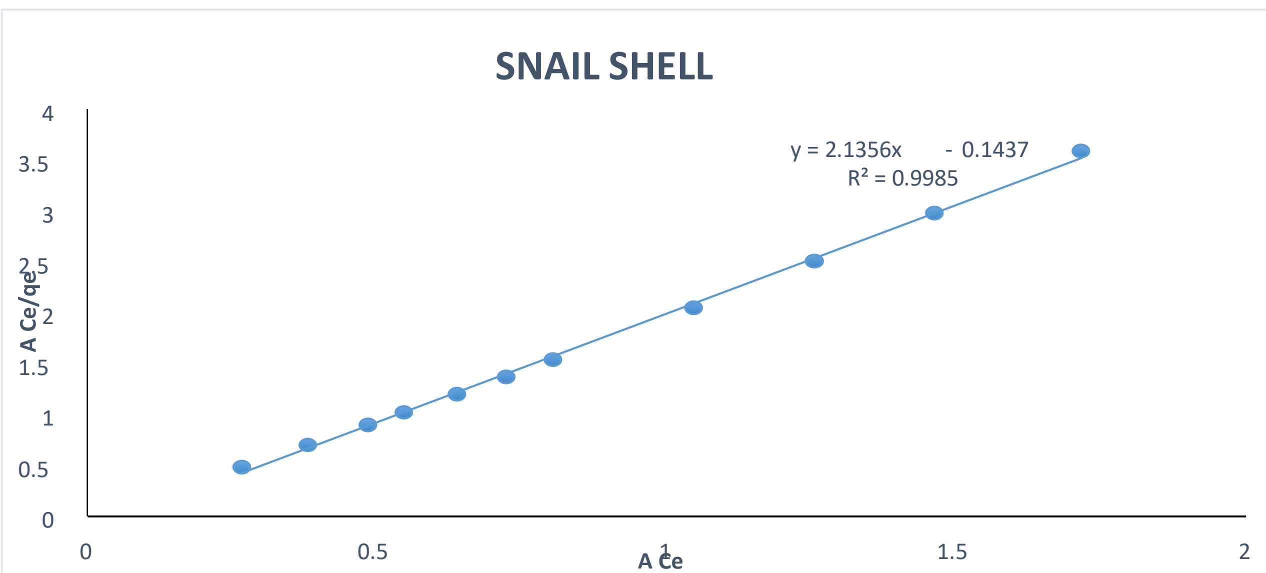

Figure 3: Langmuir Adsorption Isotherm at neutral pH, speed of 150 rpm, 20 mg/L, and 25°C for Snail Shell powder.

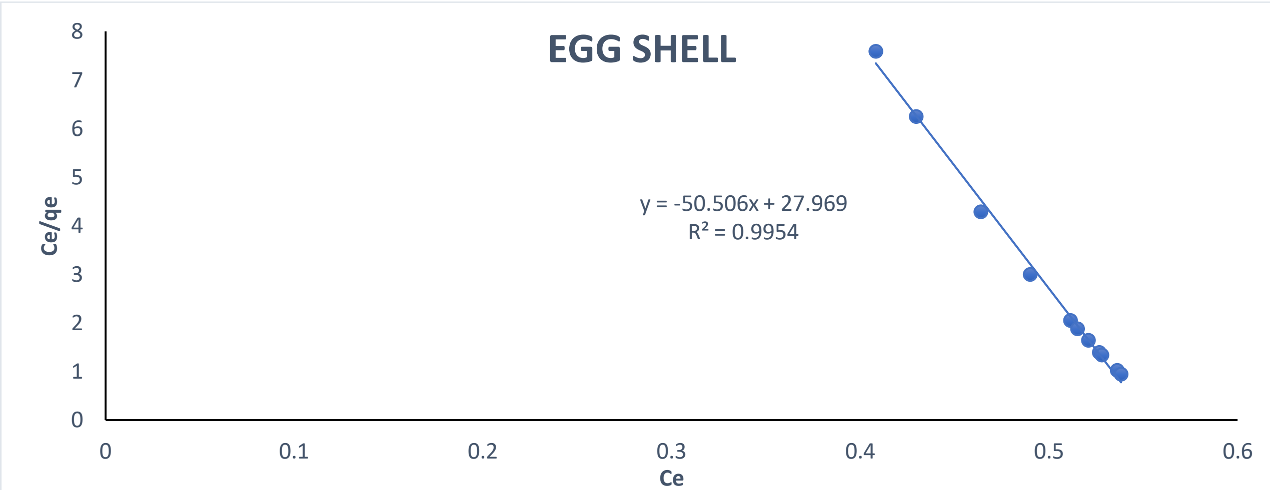

Figure 4: Langmuir Adsorption Isotherm at neutral pH, speed of 150 rpm, 20 mg/L, and 25 °C for Egg Shell powder.

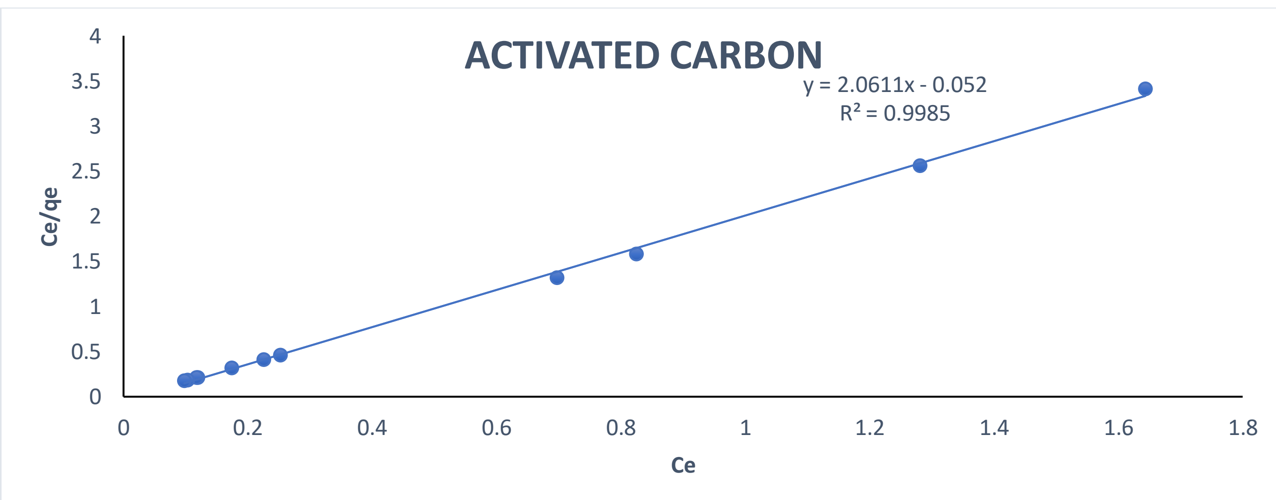

Figure 5: Langmuir Adsorption Isotherm at neutral pH, speed of 150 rpm, 20 mg/L, and 25 °C for Activated carbon.

The plot of 1/qe against 1/C would give a straight line with slope 1/ bQo and intercept of 1/ Qo. Qe is the amount of adsorbate removed per unit weight of adsorbent. Q_o is a constant relating to single layer adsorption capacity b is the constant which measure the surface energy of the adsorption process C is the concentration of adsorbate in solution at equilibrium.

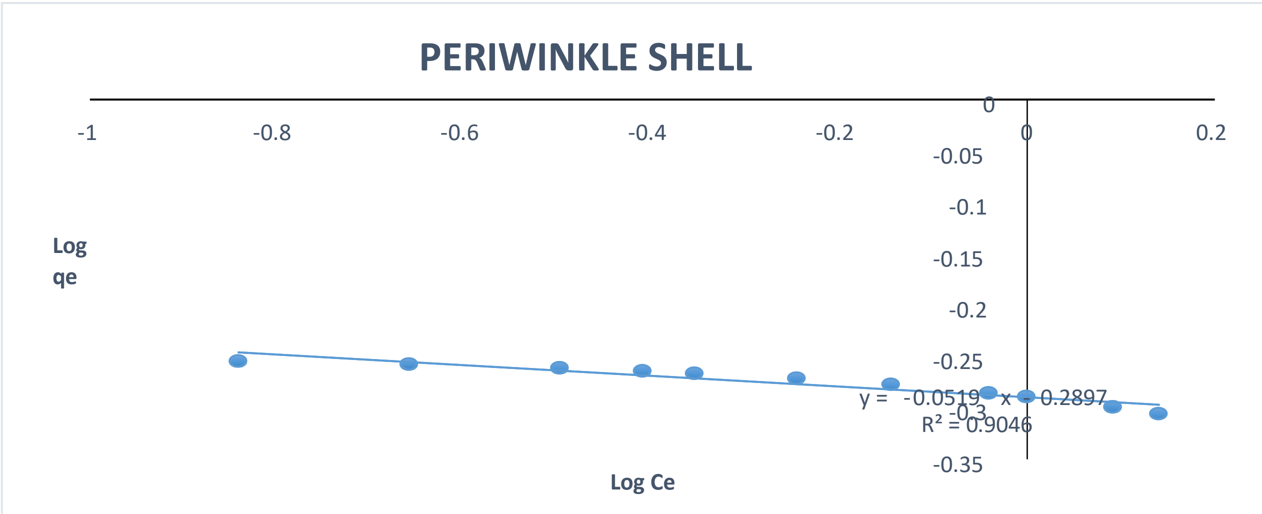

Figure 6: Freundlich Adsorption Isotherm at neutral pH, speed of 150 rpm, 20 mg/L, and 25 °C for Periwinkle shell powder.

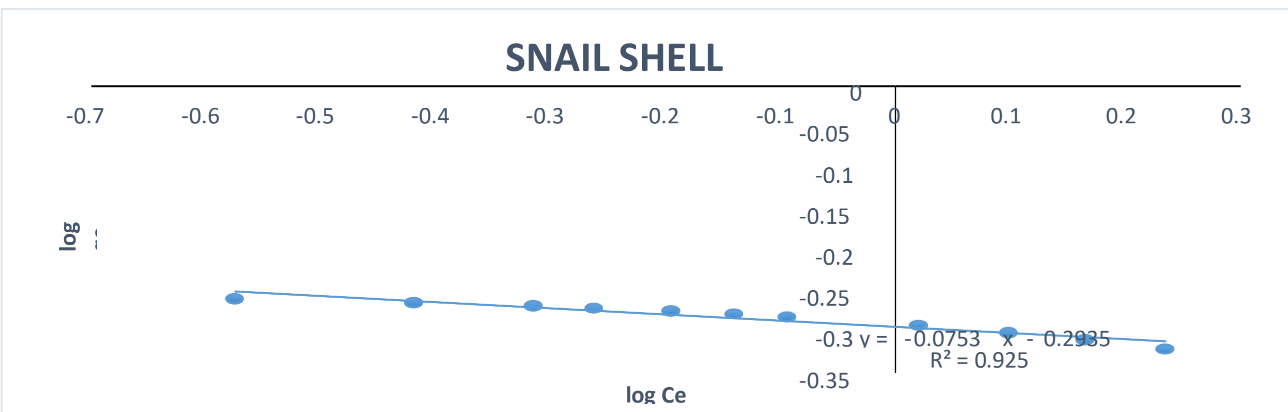

Figure 7: Freundlich Adsorption Isotherm at neutral pH, speed of 150 rpm, 20 mg/L, and 25 °C for snail shell powder

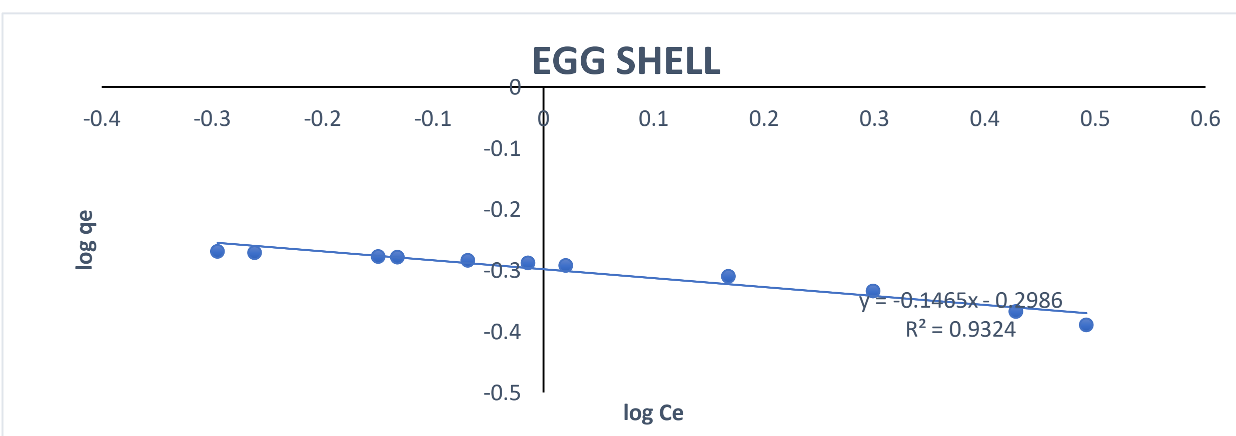

Figure 8. Freundlich adsorption isotherm for Cadmium (II) ions removal at a speed of 150 rpm, neutral pH, initial concentration of 20mg/L and temperature of 25°C with egg shell.

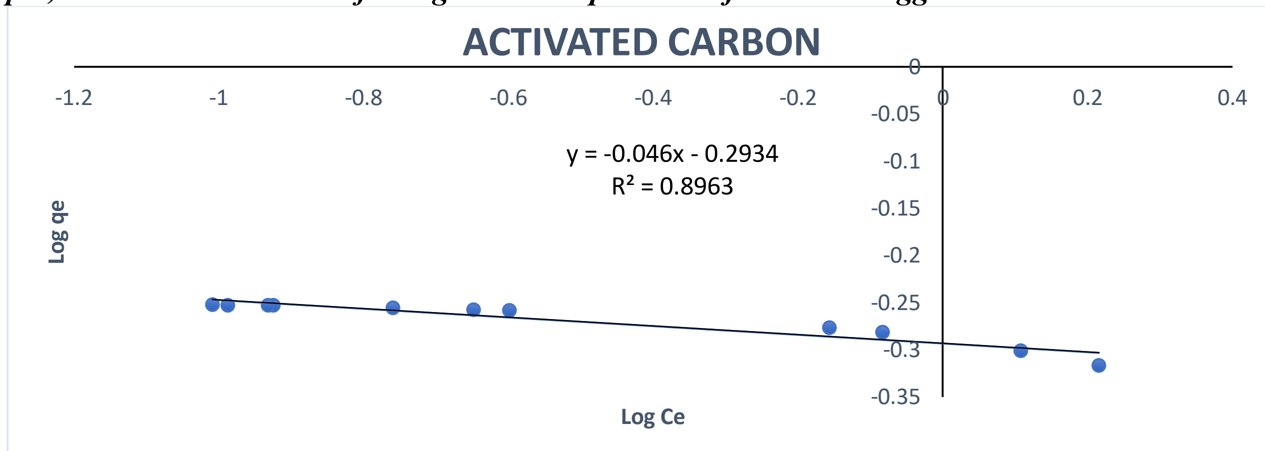

Figure 9: Freundlich adsorption isotherm for Cadmium (II) ions removal at a speed of 150 rpm, neutral pH, initial concentration of 20mg/L and temperature of 25°C with activated carbon.

According to Freundlich isotherm model, the adsorption in Figures 6, 7, 8, 9 had the correlation coefficient (R^2) values of 0.93, 0.94, 0.93 and 0.89. respectively The Freundlich equation is basically empirical, its ability to describe adsorption process on surface adsorption sites that are energetically heterogeneous.Freundlich adsorption isotherm is expressed as:

$\text{Log } q_e = \log k_f + 1/n \log C$ ……(3)

where: n is a constant related to efficiency of sorption and sorption energy.

K_f is a constant measuring adsorption capacity

q_e is the amount of adsorbate removed per unit weight of carbon

C is the equilibrium concentration of the adsorbate in solution[16].

The plot of log qe versus log C will give a straight line with 1/n and log K_f as slope and intercept respectively [17].

The cadmium ion adsorption fit well with both Freundlich and Langmuir adsorption model for the adsorbents. The cadmium ion metals were homogenously and heterogeneously distributed over the surface of the adsorbents each. This agrees with the work of [18] on the adsorption Capacities of Coconut and Palm-Kernel Shell Adsorbents for the Sorption Cadmium (II) ions from Aqueous Solution. The kinetics of their reaction is best represented by a pseudo-second-order rate model as shown in Figures 10, 11, 12 and 13. These signifies that the rate of reaction is directly proportional to the concentration of the Cadmium (II) ions adsorbate and the adsorbents each. This agrees with the work of [14] on the effects of pH on sorption of manganese, cadmium and lead from aqueous solution by maize cobs.

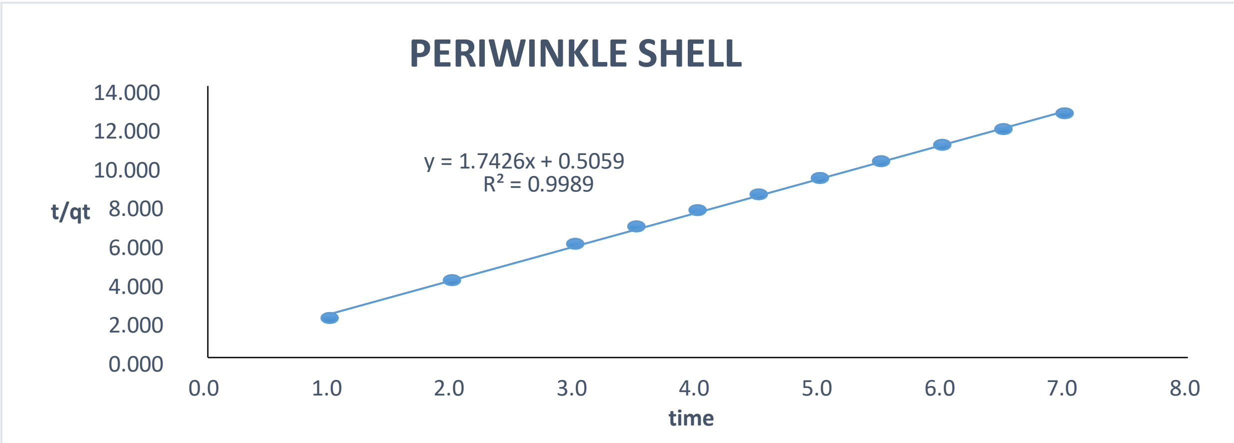

Figure 10: pseudo-second order (Ho) kinetic model plot of Cadmium (II) ions adsorption at a speed of 150 rpm, neutral pH, initial concentration of 20mg/L and temperature of 25°C Periwinkle Shell.

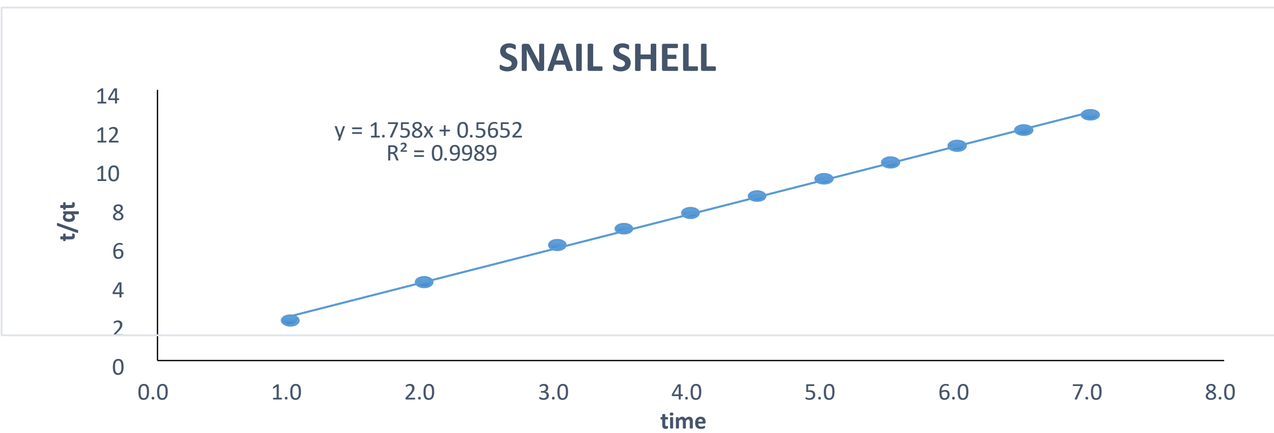

Figure 11: pseudo-second order (Ho) kinetic model plot of Cadmium (II) ions adsorption at a speed of 150 rpm, neutral pH, initial concentration of 20mg/L and temperature of 25°C Snail Shell.

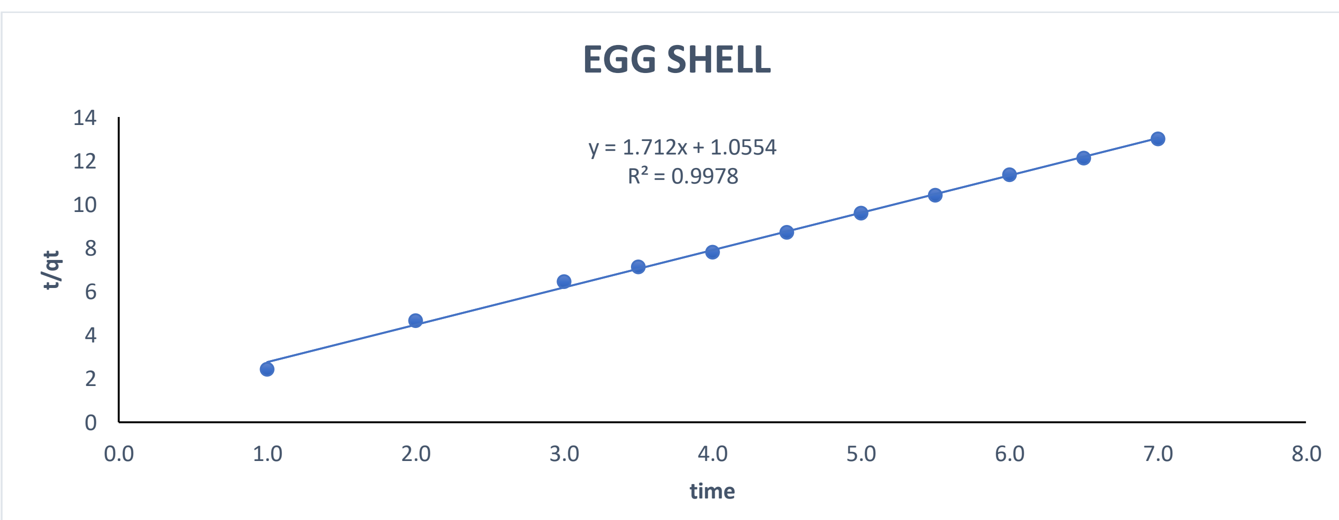

Figure 12: pseudo-second order (Ho) kinetic model plot of Cadmium (II) ions adsorption at a speed of 150

rpm, neutral pH, initial concentration of 20mg/L and temperature of 25°C with egg shell

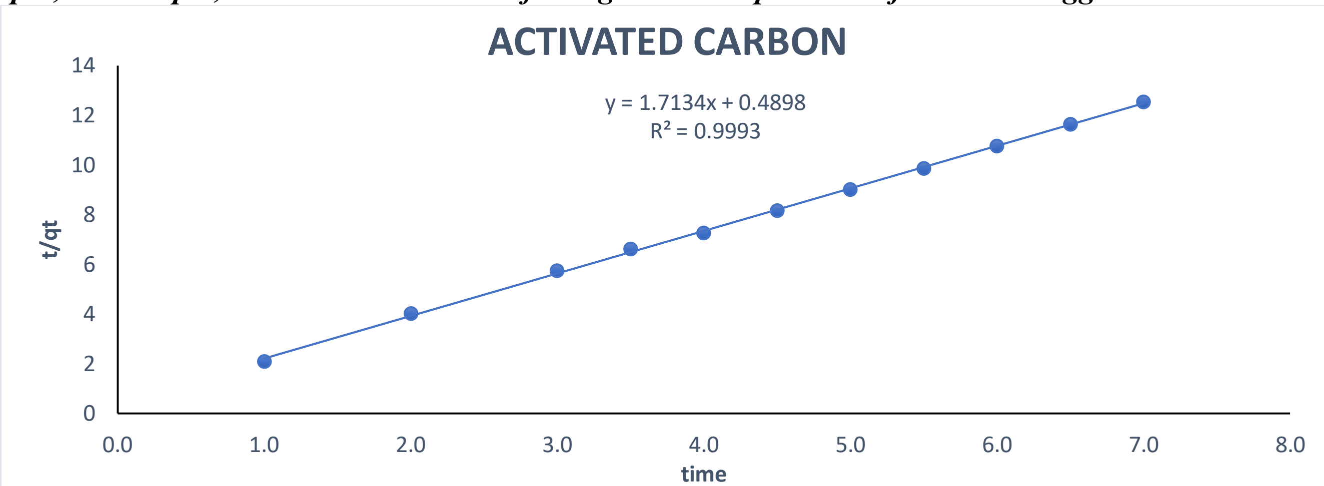

Figure 13: pseudo-second order (Ho) kinetic model plot of Cadmium (II) ions adsorption at a speed of 150 rpm, neutral pH, initial concentration of 20mg/L and temperature of 25°C with activated carbon

4. CONCLUSION

The varied operational parameters that were noticed throughout the investigation process show that the removal of cadmium ((11) ion was reliant on contact time with different adsorption capabilities. The major mechanism of physisorption was indicated by the equilibration time of 180 minutes at which equilibrium for cadmium ions adsorbed. The kinetics of their reaction is best represented by a pseudo-second-order rate model. The heterogeneous and homogeneous adsorptions of the cadmium (II) ions on the adsorbent surface follow the Langmuir and Freundlich isotherm models. The results demonstrate that periwinkle has a larger potential for cadmium ((11) ion adsorption than snail and egg shell adsorbents. The study revealed that using periwinkle, snail or egg shell adsorbents were more practical and cost effective than the use of activated carbon.and also efficient for removing cadmium ((11) ions from textile effluent.

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