Removal of 4-Nitrophenol from Aqueous Solution by *Brachystegia Eurycoma Seed Hull* Impregnated with Titanium Oxide (TiO_2) using Solid-phase Extraction Method

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Abstract

The efficiency of Brachystegia Eurycoma Seed Hulls impregnated with Titanium dioxide (BESH/TiO_2) for the removal of 4-Nitrophenol from aqueous solution was evaluated. The study employed standard solutions of 4-Nitrophenol and different amounts of BESH/TiO_2. Parameters such as initial concentration of 4-Nitrophenol, Time, pH, temperature and adsorbent dosage were optimized, and the data generated were fitted into Langmuir and Freundlich models. The results in this study revealed that 0.5g of BESH/TiO_2 can effectively accomplish 98% removal efficiency of 4-Nitrophenol at pH 12, 50 minutes contact time, temperature of 25°C and 8 mg/L concentration of 4-Nitrophenol. However, the adsorption data did not fit into Freundlich isotherm (n = 0.77), but followed Langmuir isotherm (R_L = 0.0292), indicating that the system is Langmuir model controlled. These results have established the conditions at which BESH/TiO_2 can be used for the removal of 4-Nitrophenol from aqueous solution, and could be helpful in environmental phytoremediation applications.

Keywords: adsorption, % removal, Langmuir plot, isotherms

Introduction

Pollution is a gross contamination of an environment which is potentially harmful to humans, or to the entire ecological system. Despite the fact that living organisms require some amount of essential organic compounds such as carbohydrate, lipids, proteins, nucleic acid and enzymes. Nevertheless, other organic compounds can be detrimental to the organisms. Organic contaminants are present in the soil, water and air, and may become contaminants of food and drinking water because they are stable and persistent in the environment (Chale, 2002). 4-Nitrophenol is slightly soluble in cold water, it does not evaporate at room temperature. This is a man made with no evidence of its formation from any natural source. Therefore, humans are solely responsible for the presence of the chemical in the environment. The main source of this chemical are industrial manufacturing and processing industries (Zaidi et al., l988). It is used mainly to produce dyes, paint colouring, rubber chemicals and substances that kill muds (fungicides). The time taken for the chemical to disappear chemically in air is not known. It breaks down (degrades) in water and surface soil, but it is expected to stay longer in the deep soil of dump sites compared to surface soil and may even stay indefinitely in these soils. (Scow et al. 1986). *Brachystegia Eurycoma* is genus of tree of the sub-family caesalpinioidae. It is native to tropical climate of eastern Nigeria and has 13.26% Protein, 70.44% carbohydrate, 6.8% crude fibre and 22.4% moisture content. The seed is edible, non-toxic and biodegradable substance. Its successful application in the treatment of waste water, coal washery effluent gives its impetus to its utilization in the treatment of brewery (BRE). The aim of this research work was to determine the efficiency of *Brachystegia Eurycoma* seed hulls impregnated with TiO_2 (BESH/TiO_2) in the removal of 4-nitrophenol.

Materials and Methods

Materials/Regents

Some of the materials and reagents used in this study includes; Solid 4-niitrophenol, Powdered *Brachystegia Enrycoma* Seed Hulls (BESH), Titanium (IV) oxide (TiO_2), De-ionized water.

Preparation of 4-Nitrophenol standard solution

1g of 4 -Nitrophenol was weighed using analytical balance and dissolved in distilled water 1 litre in one litre volumetric flask. This gives the working standard solution.

Preparation of Brachystegia Eurycoma seed hulls solution

Samples of BESH were collected from processing points in Sabon Gari Local Government area of Zaria, Kaduna state, Nigeria. Samples were packaged in clean polythene bags and transported to the laboratory. They were dried at ambient conditions in the laboratory for six (6) months. When the samples were adjudged to be dry, they were grounded to powder in an agate mortal and sieved. The sieved samples were stored separately in plastic containers and labelled appropriately. 1g of powdered *Brachystegia eurycoma* seeds hulls followed by 0.25g of powdered Titanium Oxide were dissolved in 20ml of distilled water. This gives the working standard solutions of BESH/TiO_2).

Ultraviolet Analysis Procedure

Working standard solution

From the stock solution of 4-Nitrophenol (lg/L), 2, 4, 6, 8, l0 mg/L solutions were prepared. The absorbance of each was taken at 315nm using the ultra-violent spectrophotometer (uv spectrophotometer). The measurements were taken and tabulated. A standard curve was obtained by plotting absorbance versus concentration of prepared standard solutions of 4-m'trophenol. 20ml of the 2mg/L was measured into 6 sampling bottles, in each of the bottles 1g of *B. Eurycoma* seed hulls (Biomass) weighed was added, bottles were mounted on the shaker and shaken vigorously for 10,20.30. 40. 50 and 60 mins respectively. These were filtered and absorbance was taken at 315nm. This allowed for determination of optimal time as results were tabulated and time of highest absorbance of 4-Nitrophenol by the *B. Eurycoma* was picked. Both equilibrium concentration and percentage of 4-Nitrophenol extracted by biomass were determined. The experiment was repeated for optimal time, biomass dose, pH, and temperature were kept constant while the concentration of 4NPN was varied (2, 4, 6, 8, 10mg/L were used). At equilibrium, after vigorous shaking, samples were filtered and absorbance recorded tabular, to obtain optimal 4NPN concentration. Biomass dose, pH, and temperature were varied respectively, absorbance of 4NPN was at each point taken and recorded. Equilibrium concentrations and percentage of 4NPN extracted by Biomass were determined. Graphs were plotted accordingly.

Results

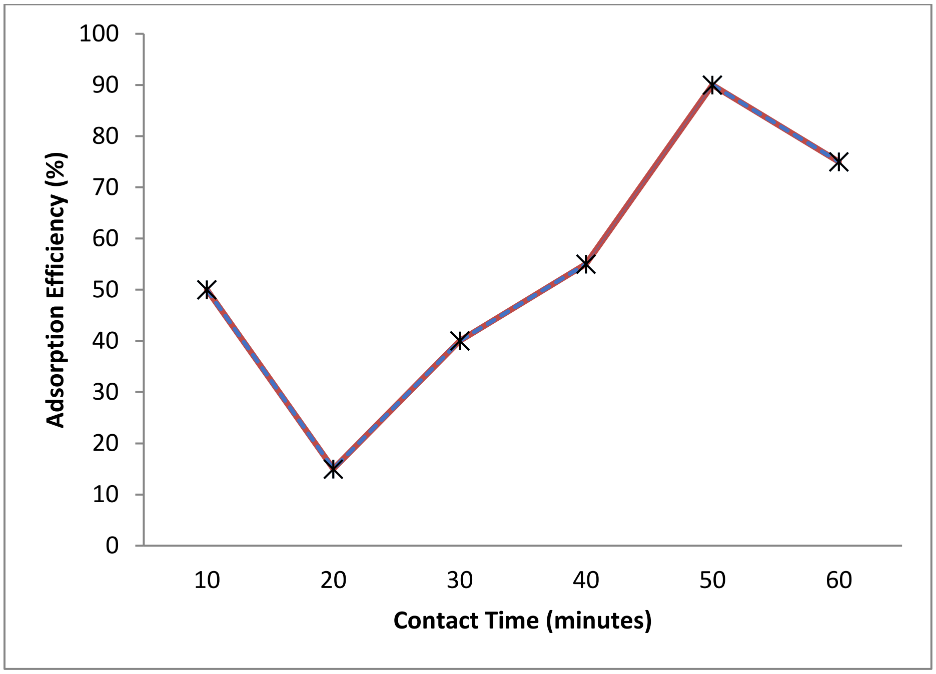

Figure 1: Variation of adsorption efficiency (%) of 4NPN with contact time

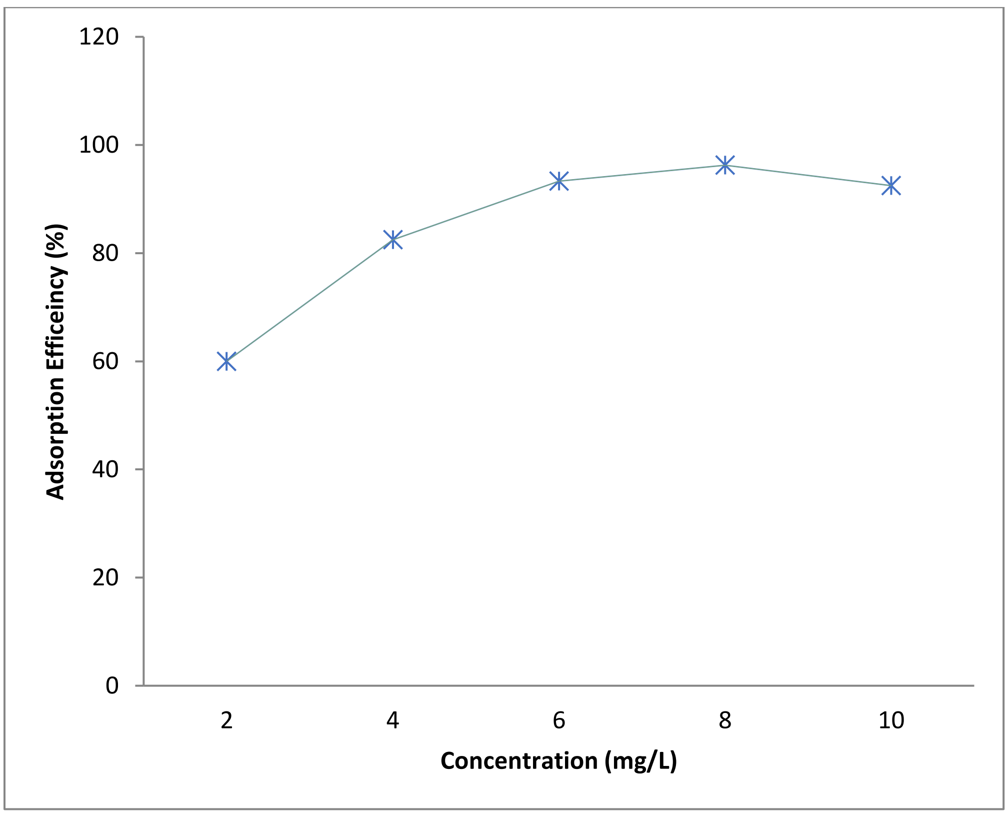

*Figure 2***:** Variation of adsorption efficiency (%) of 4-Nitrophenol with concentration

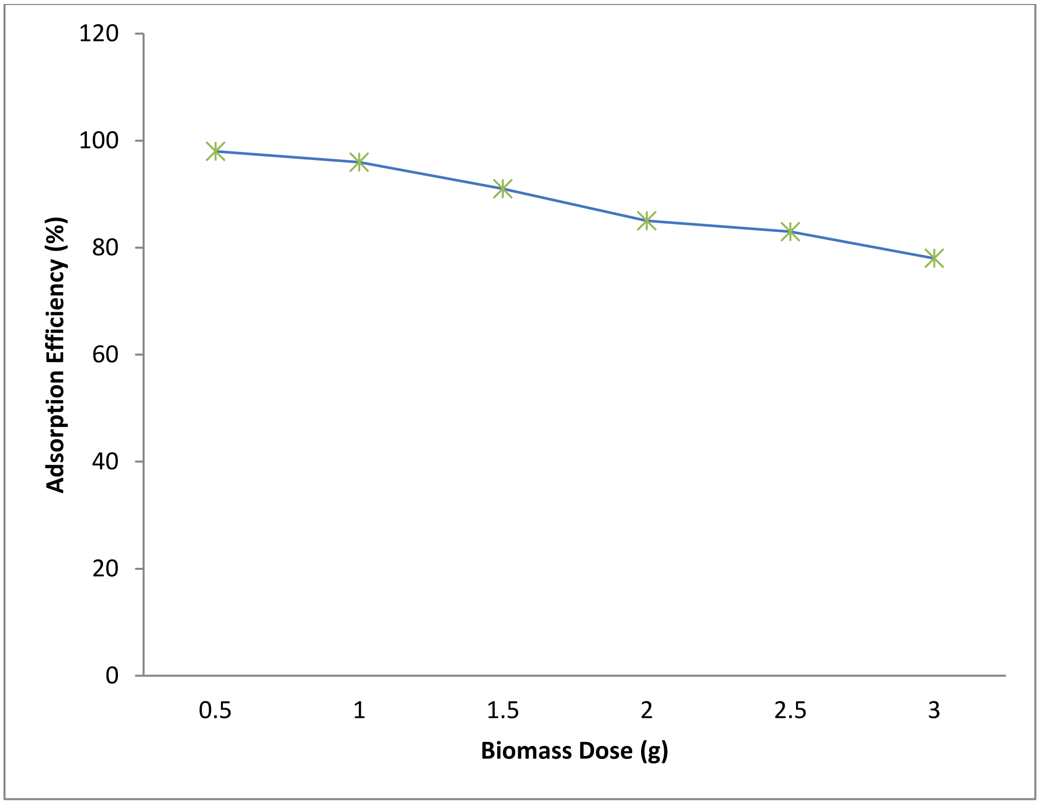

Figure 3: Variation of adsorption efficiency (%) of 4-NPN with biomass dose

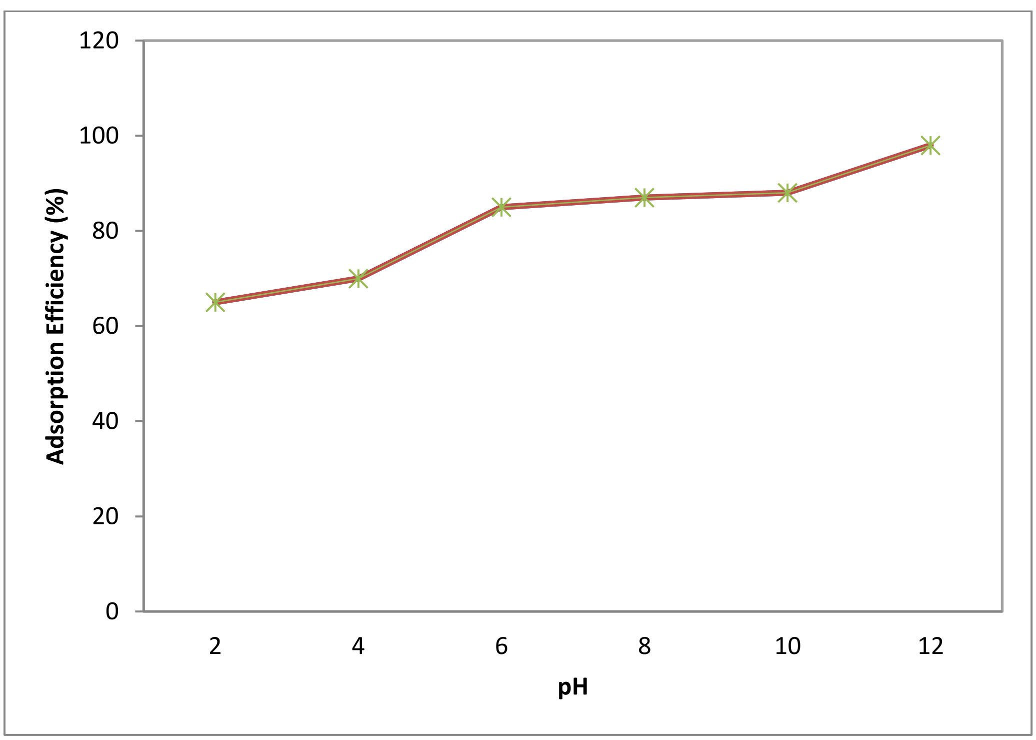

Figure 4: Variation of adsorption efficiency (%) of 4-NPN with pH

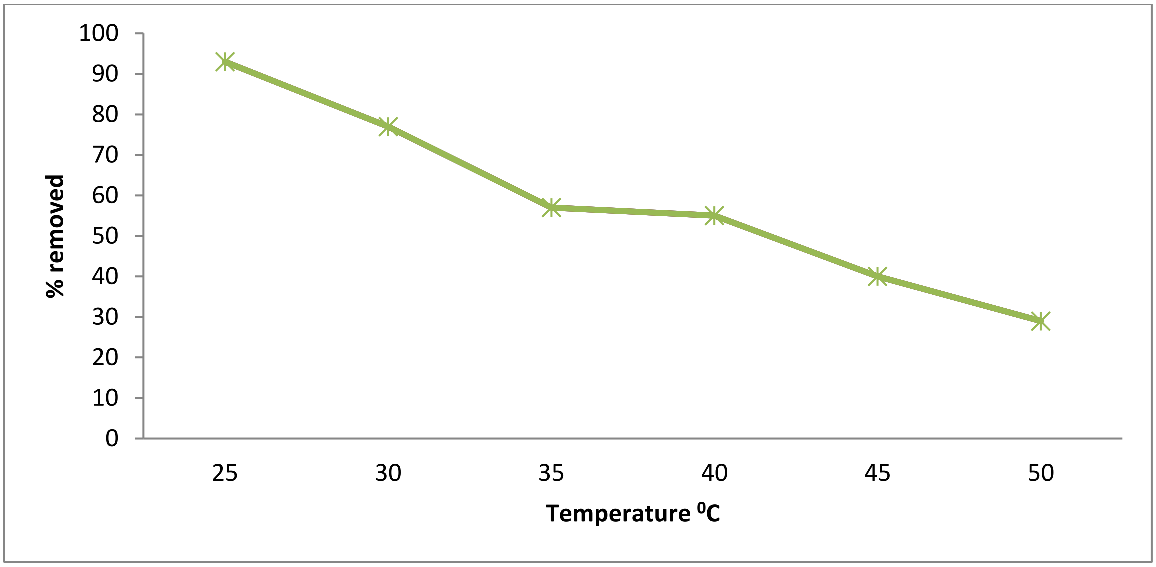

Figure 5: Variation of adsorption efficiency (%) with temperature

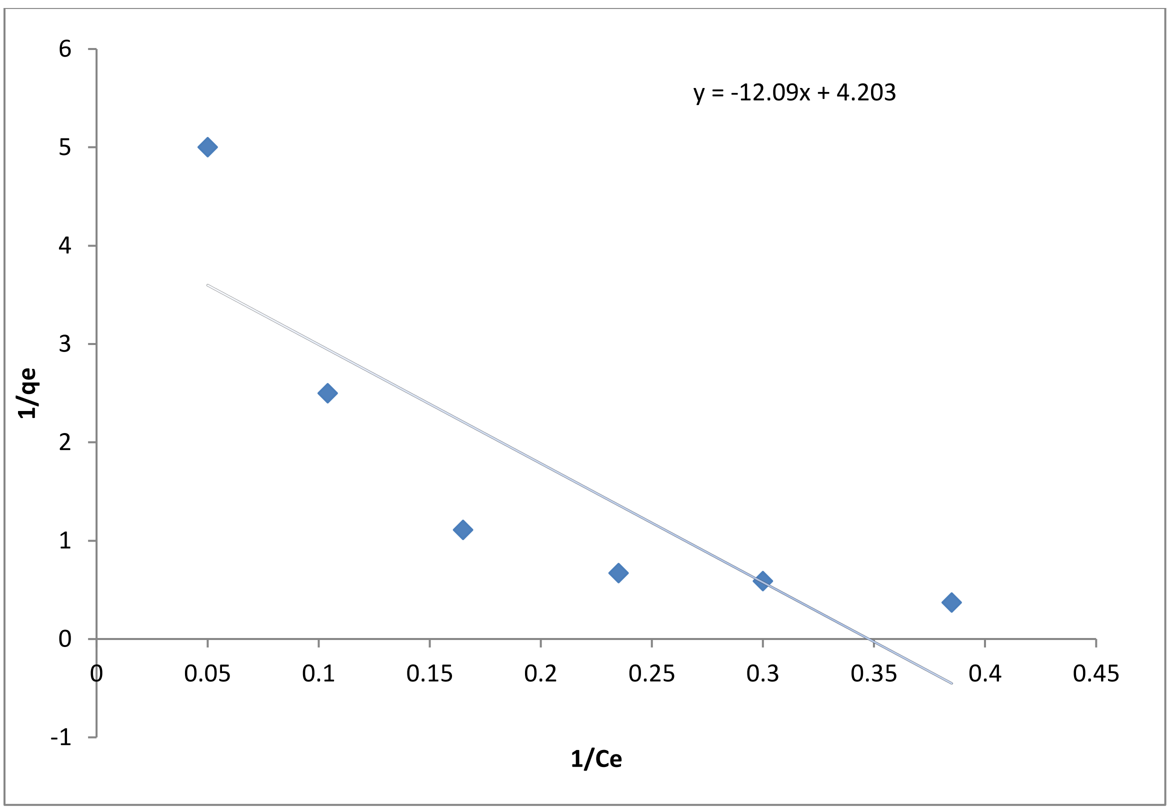

Figure 6: Langmuir plots for the adsorption of 4Nitrophenol by BESH/TiO_2

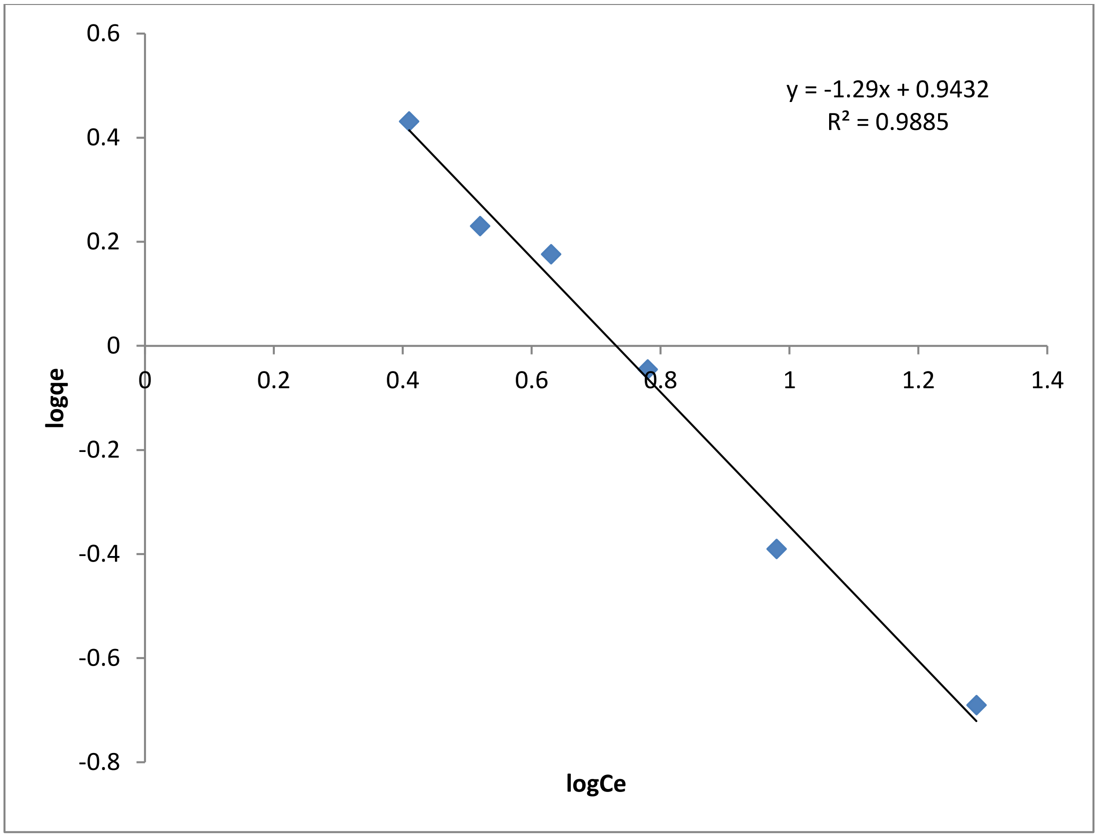

Figure 7: Freundlich plots for the adsorption of 4Nitrophenol by BESH/TiO_2

Discussion of Results

The removal efficiency of 4-Nitrophenol by *B. Eurycoma* seed hull impregnated with TiO_2 (BESH/TiO_2) was carried out by changing the initial concentrations of 4-Nitrophenol, contact time, pH, temperature and biomass dose. Figure 1 showed variation of adsorption efficiency of the 4-nitrophenol with contact time after every 10mins for 1hour. The result showed removal of 4-nitrophenol up to 90±0.2% at 50 min contact time. It could be observed that the adsorption rate decreased at 20mins before it increased steadily up to 50mins. The slow rate of adsorption may be attributed to the electrostatic hindrance caused by the adsorbate adsorbed. Figure 2 revealed percentage of removal efficiency with varied concentration of 4-nitrophenol at 2, 4, 6, 8 and 10 mg/L at a constant biomass dosage of 1g. However, the uptake capacity of initial concentration increased as the concentration increases which could be due to the presences of large amount of 4-Nitrophenol in the solution. As such, higher adsorption rate of 4-Nitrophenol give higher driving force to overwhelm mass transfer resistances of 4Nitrophenol from aqueous to the solid phase, which caused higher collision rate between the 4-Nitrophenol and the active site of the BESH. The result indicated highest removal efficiency of 96.25% at 8 mg/L initial concentration of the adsorbate. Fig. 3 (optimization of biomass dose), depicted adsorption efficiency of 98% at a least biomass dose of 0.5 g, which is in agreement with the findings of Jane et al., (2015). In Fig. 4 (optimization of pH), the peak absorption was observed at pH 12 with optimum removal efficiency of 98%, which is also in line with the reports of Jane et al., (2015), Frii and Meyers-Keith [7]. The pH is a factor reported to affect the solution chemistry of 4-NPN and the activity of the biomass.

The result in Fig. 6 (optimization of temperature) revealed that the adsorption of 4-NPN by BESH/TiO_2 was 98% obtained at 25°C. However, adsorption efficiency decreased with increase in temperature. It is important to note that increase in temperature increases thermal energy, and decrease in the percentage of removal efficiency with increase in temperature could result to desorption due to increase in the thermal energy [10]. In addition, higher temperatures result to higher mobility of the adsorbents.

The data generated were fitted in two equilibrium isotherms namely, Freundlich and Langmuir were isotherms. The Freundlich isotherm (Fig. 7) showed a slope of 1.29 and with n -value of 0.77, which indicates that the adsorption of 4-Nitrophenol by BESH/TiO_2 does not conform to the Freundlich isotherm theory. The Langmuir isotherm gave a slope of -12.09 and R_L constant was calculated as 0.0292. This indicates that the adsorption of 4-Nitrophenol by BESH/TiO_2 conformed to the Langmuir isotherm which suggest that adsorption is homogeneous, and a continuous monolayer.

Conclusion

The present study showed that the removal of 4 - Nitrophenol from aqueous solution of the conditions of the experiment, the effectiveness and efficiency of *Brachystegia Eurycorna* seed Hulls in the presence of Titanium (iv) oxide (TiO_2) for the treatment of the solution of 4-nitrophenol was successfully conducted. The system operates best at 8mg/L, 0.5g BESH doze and pH 12, with maximum adsorption efficiency of 98%. The major advantage of BESH being that it is environment friendly, cheap, abundant, with a simple preparation protocol. Finally, the greatest sources of this contaminant (4-Nitophenol) are generally man made. These include industrial waste, agricultural practice and waste disposal (dumps and incinerators). By various mechanisms this toxic organic substance accumulates in both human and edible animal tissues, which comprised of direct contamination of the diet, biological modification, translocation of plants in the ecosystem and environmental effects.

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