

SOLID-PHASE EXTRACTION OF 4-NITROPHENOL FROM AQUEOUS SOLUTION BY *Brachystegia eurycoma* SEED HULLS

Author details: DAVID JANE*¹, V. A. Ajibola² and F. O. Okibe²

1. National Biotechnology Development Agency, Abuja.

2. Department of Chemistry, Ahmadu Bello University, Zaria

Corresponding author: kanjane40@yahoo.com

Communication id:

IGWE JAMES CHIBUEZE

igwejames42@yahoo.com

igwejames42@yahoo.com

ABSTRACT

The adsorption of 4-Nitrophenol in aqueous solution by *B. eurycoma* seed hull was studied under the influence of environmental factors. Our result showed that 0.5g *B. eurycoma* seed hull can effectively achieve 98% removal of 4-Nitrophenol at pH 12, temperature 25°C, 40mins contact time, 8mg/L initial concentration of 4-Nitrophenol. From the data obtained in this research, the adsorption process did not fit into the Langmuir isotherm (R_L value = 0.002593) but followed the Freundlich isotherm ($n = 2.04$). This showed that *B. eurycoma* seed hulls can be used to adsorb 4-nitrophenol from aqueous solution and also used in environmental phytoremediation.

Key words: *B. eurycoma* seed hull, Phytoremediation, 4-Nitrophenol, environmental factors

INTRODUCTION

Increase in environmental contamination have led to a progressive deterioration of environmental quality, especially industrial manufacturing and processing of chemicals e.g. 4-Nitrophenol. 4-Nitrophenol as a chemical is used in the production of drug, dyes, paint colouring, leather darkening, rubber and fungicides. This chemical has been found to induce blood disorder which might influence mortality and affect hatching, development, and reproduction in new born (ATSDRUSPH, 1992). Chronic administration of any of the nitrophenols to mammals has been found to cause alterations of neurohumoral regulation and pathological changes including colitis, enteritis, hepatitis, gastritis and hyperplasia of the spleen (NRC, 1981). It has also been documented to cause the inhibition of chlorophyll synthesis in plants (USEPA, 1980). The toxicity of nitrosubstituents; o-nitrophenol, m-nitrophenol, and p-nitrophenol towards growth and metabolic activities of a diazotrophic cyanobacterium *Nostoclinckia*, isolated from soil was observed by Megharaj *et al.*, (1991) to significantly inhibit the production of cell constituents (chlorophyll a, protein and carbohydrate), 14 CO_2 uptake and activities of nitrate reductase, nitrogenase, and glutamine synthetase. Growth of the organism under photoheterotrophic conditions (0.1% acetate) did not reduce the toxicity of nitrophenols. Transmission electron microscopy revealed the secretion of mucous around the filament and induction of spore formation in the cultures subjected to nitrophenol toxicity (Megharaj *et al.*, 1991). Total removal of these toxic compounds from the environment through bioremediation is imperative, as these compounds severely threaten human and environmental health. This study therefore, proposes the use of environmental friendly waste products of plants origin (*B. eurycoma* seed hull) owing to its ability to colonize very different environments characterized by high levels of nitrogen (Okibe *et al.*, 2012; Doria *et al.*, 2012) in Nigeria to phytoremediate 4-nitrophenol from our environment and also evaluate for the best environmental factors that could exterminate this compound from the environment.

METHODOLOGY

Sampling

4-Nitrophenol was obtained from the laboratory of the Department of Chemistry, Ahmadu Bello University, Zaria and Samples of *B. eurycoma* seed hulls were collected from its processing points in Sabon-Gari Local Government area of Zaria, Kaduna State, Nigeria in November and December 2013. 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

and grounded to powdered form in a mortar and sieved. The sieved samples were stored separately in plastic containers and labelled appropriately.

Preparation of Standard Solution of 4-Nitrophenol

1g of 4-Nitrophenol was weighed using analytical balance and dissolved in 1L distilled water in 2L volumetric flask. This was used as the working standard (stock) of 4-nitrophenol.

Preparation of Standard Analytical Techniques

1g of powdered *B. eurycoma* seeds hulls was dissolved in 200ml of distilled water; this gives the working standard solutions of *B. eurycoma* seed hulls.

Ultraviolet Analysis Procedure

Working standard solution:

From the stock solution of 4-Nitrophenol (1g/L), 2, 4, 6, 8 and 10mg/L solutions were prepared. The absorbance of each was taken at 315nm using the ultraviolet 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-nitrophenol.

20mls of the 200mg/L standard analytical solution was measured into 6 sampling test tubes, in each of the test tubes 1g of *B. eurycoma* seed hulls (Biomass) was added, samples were mounted on the shaker and shaken vigorously for 10, 20, 30, 40, 50 and 60mins respectively. These were filtered and their absorbances were taken at 315nm. This allowed for determination of optimal time as results were tabulated and time of highest absorbance of 4-Nitrophenol by *B. eurycoma* seed hull was observed. Both equilibrium concentration and percentage of 4-Nitrophenol (NPN) absorbed by biomass were also determined. The experiment was repeated but this time optimal time, biomass dose, pH, and temperature were kept constant while the concentration of 4-NPN was varied (2, 4, 6, 8, and 10mg/L were used). At equilibrium, after vigorous shaking, samples were filtered and absorbance recorded in a tabular form, to obtain optimal 4-NPN concentration.

Biomass dose, pH, and temperature were varied respectively, absorbance of 4-NPN was at each point taken and the results recorded. Equilibrium concentrations and percentage of 4-NPN extracted by biomass were also determined using equation 1, where C_i and C_f represent initial and final concentration of 4NPN respectively. Graphs were plotted accordingly to express the results.

$$4 - NPN(\%) \text{ Extraction} = \frac{C_i - C_f}{C_i} \times 100 \text{ ----- 1}$$

RESULTS

CALIBRATION CURVE OF 4-NITROPHENOL

The result below showed the calibration curve of 4-Nitrophenol at 315nm using the ultraviolet spectrophotometer.

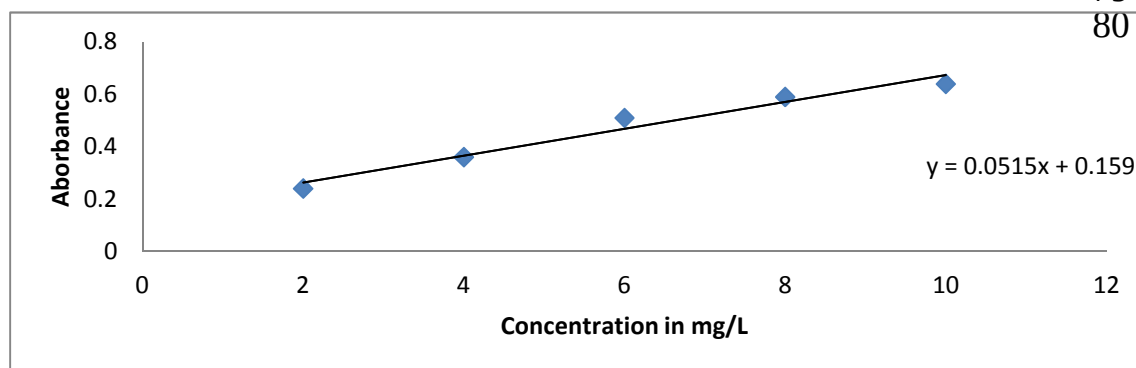


Figure 1: Calibration Curve of 4-Nitrophenol

Optimization of Contact Time (Minutes)

Figure 2 showed that $90 \pm 0.86\%$ of the 4-nitrophenol were adsorbed at 40min contact time.

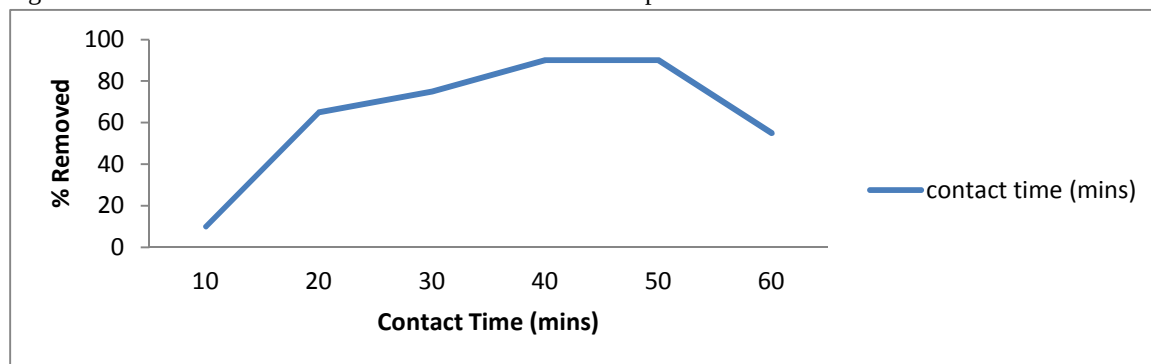


Figure 2: Variation of percentage removal of 4NPN with Contact Time.

Optimization of Initial Concentration

The result below showed that removal efficiency of $54 \pm 0.65\%$ was achieved at 8mg/L initial concentration of the adsorbate.

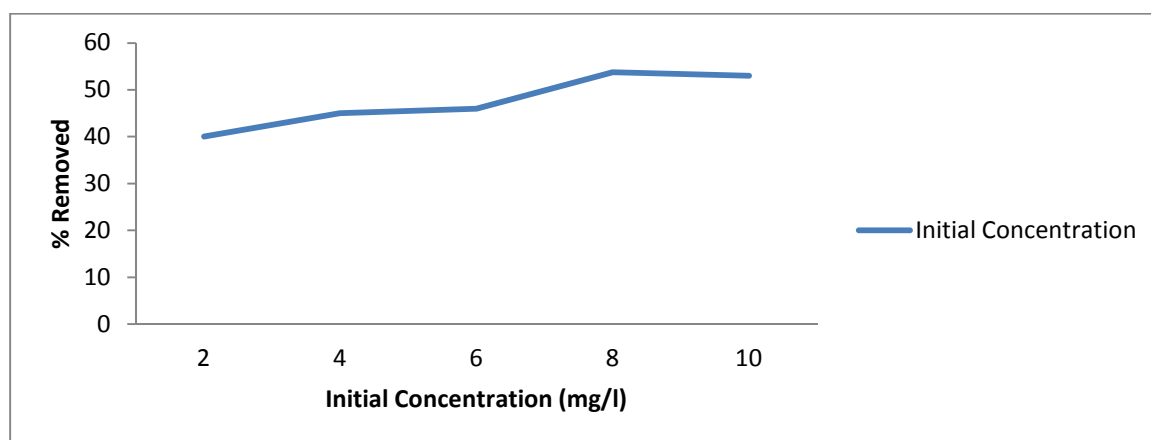


Figure 3: Variation of percentage removal of 4NPN with Initial Concentration.

Optimization of Biomass Dose (G)

The result below showed that biomass dose also affected the adsorption efficiency. Ninety eight percent ($98 \pm 0.84\%$) adsorption was noted at the least dose of 0.5g in 20mls at 10mg/L of 4-NPN.

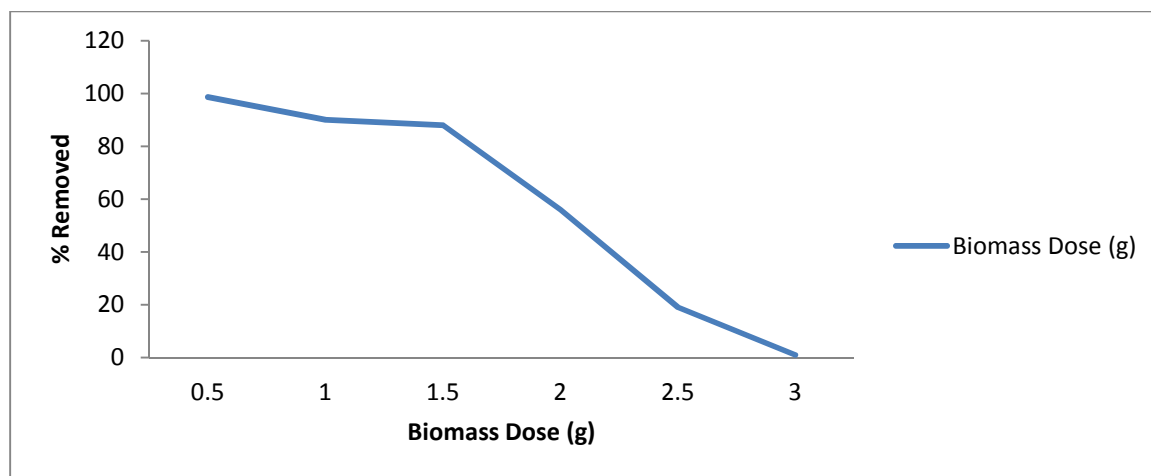


Figure 4: Variation of percentage removal of 4NPN with Biomass Dosage

Optimization of pH

The result below showed that the optimum removal efficiency ($97 \pm 0.51\%$) of 4NPN was achieved at the pH 12

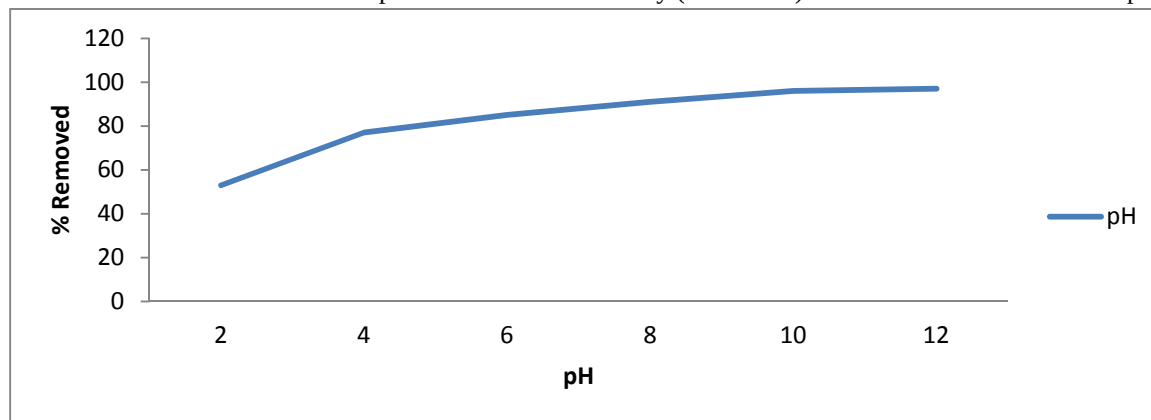


Figure 5: Variation of percentage removal of 4NPN with pH

Optimization of Temperature

The result below showed that *B. eurycoma* seed hull adsorption $91 \pm 0.36\%$ of 4-NPN at 25°C and an increase in temperature, adsorption efficiency decreased.

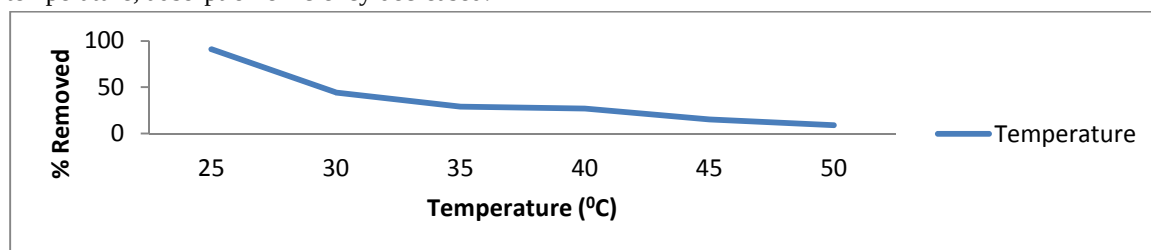


Figure 6: Variation of percentage removal of 4NPN with Temperature

Adsorption Isotherm Data for Langmuir Model at different *B. eurycoma* Seed Hulls (Besh) Loading (0.5-3) G for 4-Nitrophenol Adsorption

The slope S , $S = \frac{dy}{dx} = \frac{1.4-1.3}{2-0.1} = \frac{1.2}{1.9} = 0.63$

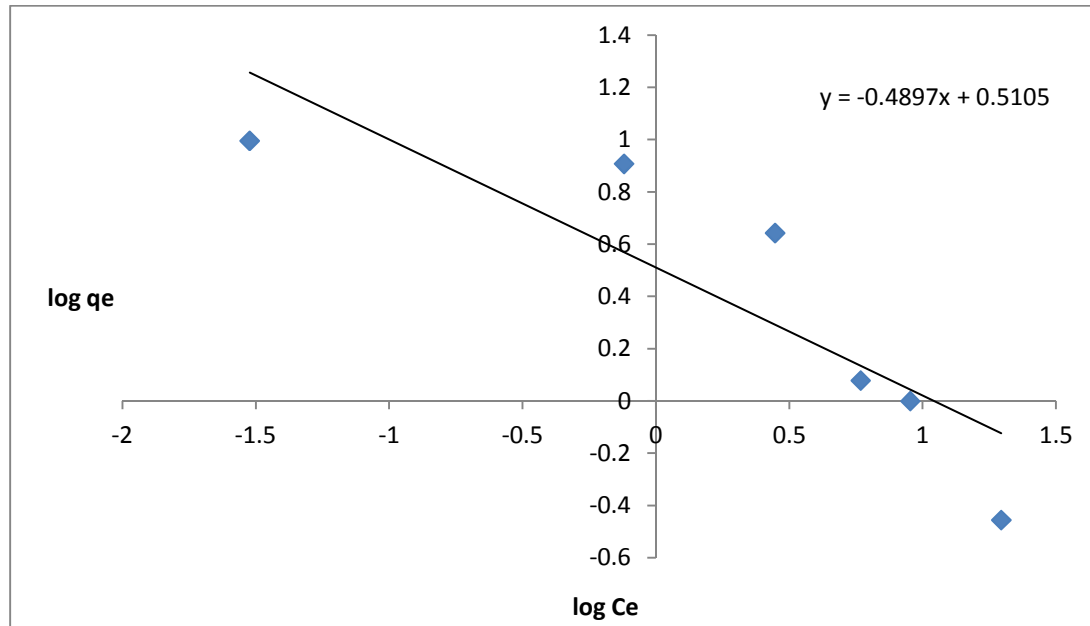


Figure 7: Freundlich Plots for Adsorption of 4-Nitrophenol on *B. eurycoma* Seed Hulls

X-ray diffraction pattern of *B. eurycoma*

The diffractogram result below showed the X-ray diffraction pattern for *B. eurycoma*. It was found that the adsorbent consist of cellulosic ($C_6H_{10}O_5$) n material indicated by the very strong characteristics intensity on the diffraction pattern.

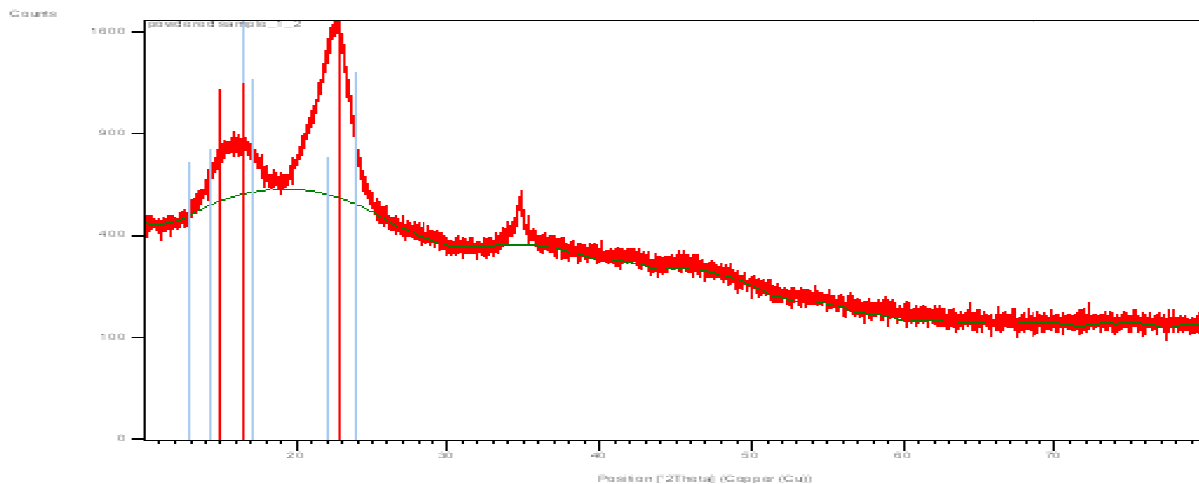


Figure 8: X-ray diffraction pattern of *B. eurycoma*.

DISCUSSION AND SUMMARY

The adsorption efficiency (E) of 4-Nitrophenol by *B. eurycoma* seed hull was studied in this work by varying the concentrations of 4-Nitrophenol, time, pH, temperature and biomass dose of *B. eurycoma* seed hull. The obtained results are represented graphically in Figures 1 to 6 and in appendix 1 to 5 respectively.

The 4-NPN concentration was varied at 2, 4, 6, 8 and 10mg/L at a constant biomass concentration of 1g and pH 5.5. Also, pH was further varied at 2, 4, 6, 8, 10 and 12 at 8mg/L concentration of 4-NPN and 1g biomass concentration. Generally, the adsorption efficiency increased with increase in concentration of 4-NPN, though at different magnitudes. The adsorption efficiency (E) was not less than 40% within pH range of 2 - 12. Since, adsorption is determined by equilibrium, it is largely influenced by pH, biomass concentration and the interaction between different metallic ions (Frii and Meyers-Keith, 1986).

From Figure 2 (optimization of contact time), the rate of adsorption of 4-NPN increased steadily with time, highest adsorption was obtained at 40mins and that was retained for the next 10mins, thereafter, a decline was observed. The initial rapid rate of adsorption may be due to the availability of surface of the adsorbent (BESH) for the 4-Nitrophenol present in solution. Optimum removal efficiency at 40min contact time was 90 ± 0.86 % achieved. The later slow adsorption rate part of the curve may be due to the electrostatic hindrance caused by already adsorbed adsorbate (4-Nitrophenol) (Ghosh and Goswami, 2005).

From Figure 3 (optimization of initial concentration), initial concentration uptake capacity increases with increase in initial concentration be due to the availability of more 4-Nitrophenol in solution for adsorption. Higher initial adsorption (4-Nitrophenol) provide higher driving force to overcome various mass transfer resistances of 4-Nitrophenol from aqueous to the solid phase, resulting in higher collision between 4-Nitrophenol and the active site of the BESH (Sharma *et al.*, 2010). Removal efficiency of 54 ± 0.65 % was achieved at 8mg/L initial concentration of adsorbate.

From Figure 4 (optimization of biomass dose), it can be observed that biomass dose also affected the adsorption efficiency; this was best noted at the least dose of 0.5g in 20mls at 10mg/L of 4-NPN with 98 ± 0.84 % adsorption. This result is supported by the findings of Fourest and Roux, (1992); that biomass in solution seem to influence the specific uptake of 4-NPN i.e. for lower value of biomass concentration, there is an increase in the specific uptake of 4-NPN. While Gadd *et al.*, (1987) suggested that an increase in biomass concentration can lead to interference between molecule binding sites. Fourest (1992) invalidated this hypothesis by attributing the responsibility of the specific uptake decrease to metal concentration shortage in solution. Hence, the biomass dose factor should be taken into consideration in any application of *B. eurycoma* seed hull biomass as adsorbent.

From Figure 5 (optimization of pH), maximum absorption was observed at pH 12. This is in line with the work of Frii and Meyers-Keith (1986). pH has been documented to affect the solution chemistry of 4-NPN, the activity of the functional group in the biomass and competition of metallic ions (Gadd *et al.*, 1987). Optimum removal efficiency was 97 ± 0.51 % at the pH 12.

From Figure 6 (optimization of temperature), the adsorption of 4-NPN by *B. eurycoma* seed hull was 91 ± 0.36 % obtained at 25°C. With increase in temperature, adsorption efficiency decreased. Aksu *et al* (1992) had observed that temperature seems not to affect the adsorption in the range of 20 - 35°C. However, it is worthy to note that increase in temperature increases thermal energy. The decrease in the percentage of adsorption with rise in temperature may be due to desorption caused by an increase in the available thermal energy (Fourest and Roux, 1992). Also higher temperatures induce has been observed to induce higher mobility of the adsorbents, causing desorption (Pandey *et al.*, 2010).

To determine isotherm equilibrium; two isotherms, namely, Langmuir and Freundlich were tested. The Langmuir isotherm gave a slope of 0.6041 and a b value of -6.8936 while R_L was obtained as -0.0147. These values indicate that the adsorption of 4-Nitrophenol by *B. eurycoma* seed hull does not conform to the Langmuir isotherm theory. The Freundlich isotherm yielded a slope of 0.4897 and an n value of 2.04. This indicates that the adsorption of 4-Nitrophenol by *B. eurycoma* seed hull conformed to the Freundlich isotherm which suggest that adsorption of 4 nitrophenol by *B. eurycoma* is heterogeneous, not mono layer.

The diffractogram (Figure 8) shows the X-ray diffraction pattern for *B. eurycoma*. It was found that the adsorbent consist of cellulosic ($C_6 H_{10} O_5$) n material indicated by the very strong characteristics intensity on the diffraction

pattern. The diffraction peak broadening observed indicate the smaller crystallite size in the adsorbent materials and more stacking faults, micro-strain, and other defects in the crystal structure

CONCLUSION AND RECOMMENDATIONS

Adsorption of 4-Nitrophenol using *B. eurycoma* seed hull was carried out in this study. The maximum adsorption efficiency was observed at 25°C (room temperature), pH 12, with biomass dose of 0.5g in 20mls of 8mg/L concentration of 4-Nitrophenol. To ensure effective adsorption of 4-Nitrophenol in a polluted environment using *B. eurycoma* seed hulls, biomass dose and pH should be strictly considered.

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