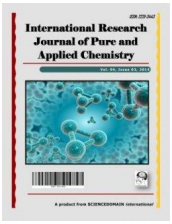

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Solid-phase Extraction of 4-Nitrophenol from Aqueous Solution by *Brachystegia eurycoma* Seed Hulls

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Authors' contributions

This work was carried out in collaboration between all the above mentioned authors. Author DJ designed the study and wrote the protocol. Authors JCI and FOO preformed the statistical analysis, managed the literature search and wrote the first draft of the manuscript with assistance from author VAA. All the authors read and approved the final manuscript.

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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 0.5 g *B. eurycoma* seed hull can effectively achieve 98% removal of 4-Nitrophenol at pH 12, temperature 25°C, 40 mins contact time, 8 mg/Linitial 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.

Keywords: B. eurycoma seed hull; Phytoremediation; 4-Nitrophenol; environmental factors.

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1. 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 darken, rubber and fungicides. This chemical has been found to induce blood disorder which might influence mortality and effect hatching, development, and reproduction in new born [1]. 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 [2]. It has also been documented to cause the inhibition of chlorophyll synthesis in plants [3]. The toxicity of nitro substituents; o-nitrophenol, m-nitrophenol, and p-nitrophenol towards growth and metabolic activities of a diazotrophic cyano bacterium Nostoclinckia, isolated from soil was observed by Megharaj et al. [4] to significantly inhibited 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 [4]. 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 [5,6] 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.

2. METHODOLOGY

2.1 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 mortal and sieved. The sieved samples were stored separately in plastic containers and labelled appropriately.

2.2 Preparation of Standard Solution of 4-Nitrophenol

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

2.3 Preparation of Standard Analytical Techniques

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

2.4 Ultraviolet Analysis Procedure

2.4.1 Working standard solution

From the stock solution of 4-Nitrophenol (1 g/L), 2, 4, 6, 8 and 10 mg/L solutions were prepared. The absorbance of each was taken at 315nm using the ultraviolent 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 200 mg/L standard analytical solution was measured into 6 sampling test tubes, in each of the test tubes 1 g 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 315 nm. 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 10 mg/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.

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

3. RESULTS

3.1 Calibration Curve of 4-Nitrophenol

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

3.2 Optimization of Contact Time (Minutes)

Fig. 2 showed that 90±0.86% of the 4-nitrophenol were adsorbed at 40 min contact time.

3.3 Optimization of Initial Concentration

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

3.4 Optimization of Biomass Dose (G)

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

3.5 Optimization of pH

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

3.6 Optimization of Temperature

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

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

3.8 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_6 H_{10} O_5) n material indicated by the very strong characteristics intensity on the diffraction pattern.

4. DISCUSSION AND SUMMARY

The adsorption efficiency (E) of 4-Nitrophenol by *B. eurycoma* seed hullwas 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 Figs. 1 to 7 and in appendix 1 to 5 respectively.

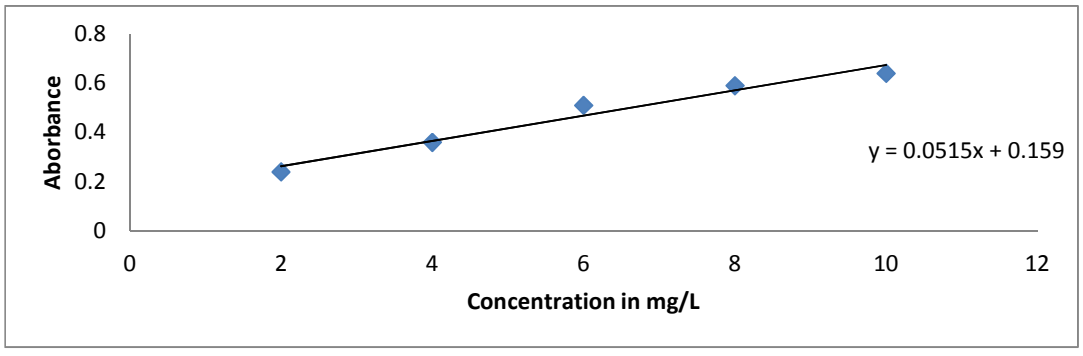

Fig. 1. Calibration curve of 4-Nitrophenol

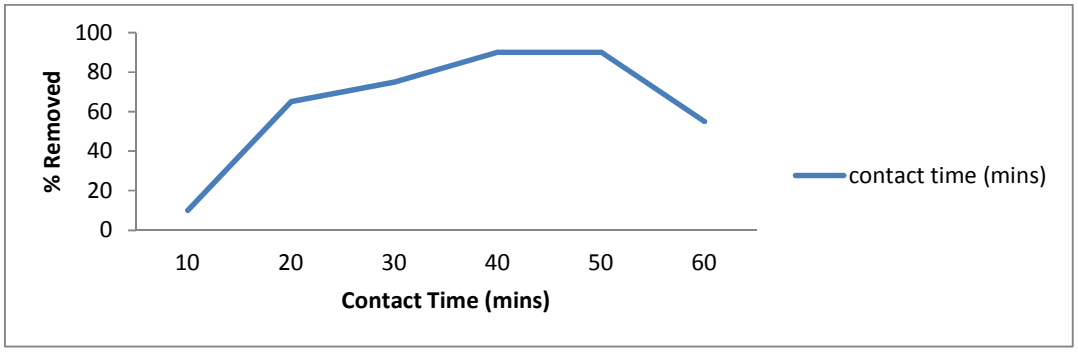

Fig. 2. Variation of percentage removal of 4NPN with Contact Time

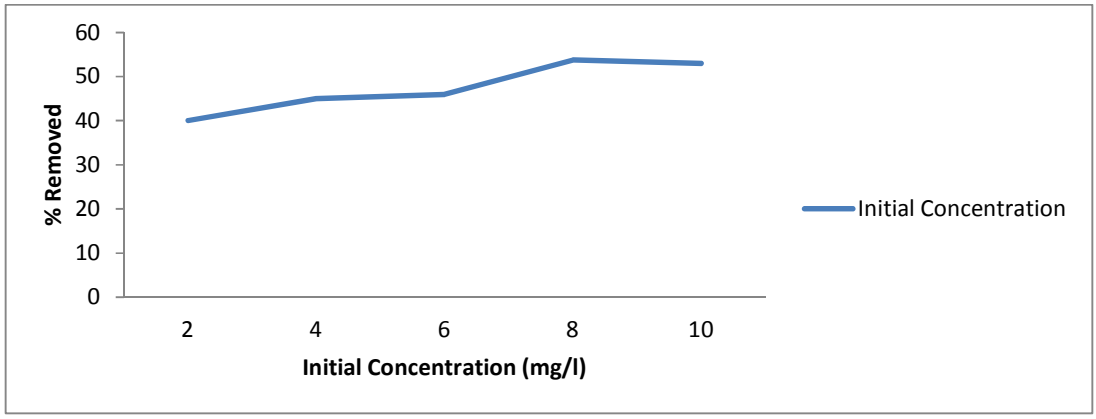

Fig. 3. Variation of percentage removal of 4NPN with Initial Concentration

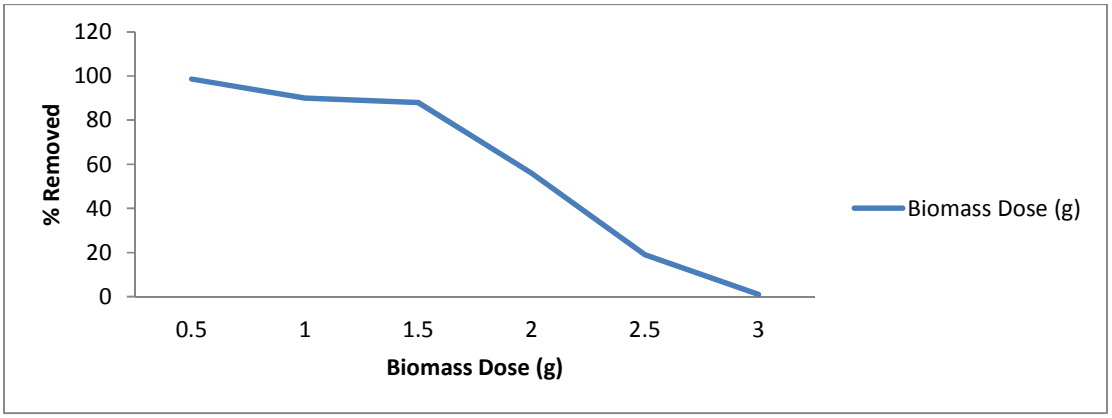

Fig. 4. Variation of percentage removal of 4NPN with Biomass Dosage

The 4-NPN concentration was varied at 2, 4, 6, 8 and 10 mg/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 8 mg/L concentration of 4-NPN and 1 g 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 [7].

From Fig. 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-Netrophenol) [8].

From Fig. 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 [9]. Removal efficiency of 54±0.65% was achieved at 8 mg/L initial concentrationof adsorbate.

From Fig. 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 0.5 g in 20 mls at 10 mg/L of 4-NPN with 98±0.84% adsorption. This result is supported by the findings of Fourest and Roux, [10]; 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. [11] suggested that an increase in biomass concentration can lead to interference between molecule binding sites. Fourest [12] 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 Fig. 5 (optimization of pH), maximum absorption was observed at pH 12. This is in line with the work of Frii and Meyers-Keith [7]. 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 [11]. Optimum removal efficiency was 97±0.51% at the pH 12.

From Fig. 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. [13] 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 [10]. Also higher temperatures induce has been observed to induce higher mobility of the adsorbents, causing desorption [14].

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 RL was obtained as -0.0147. These values

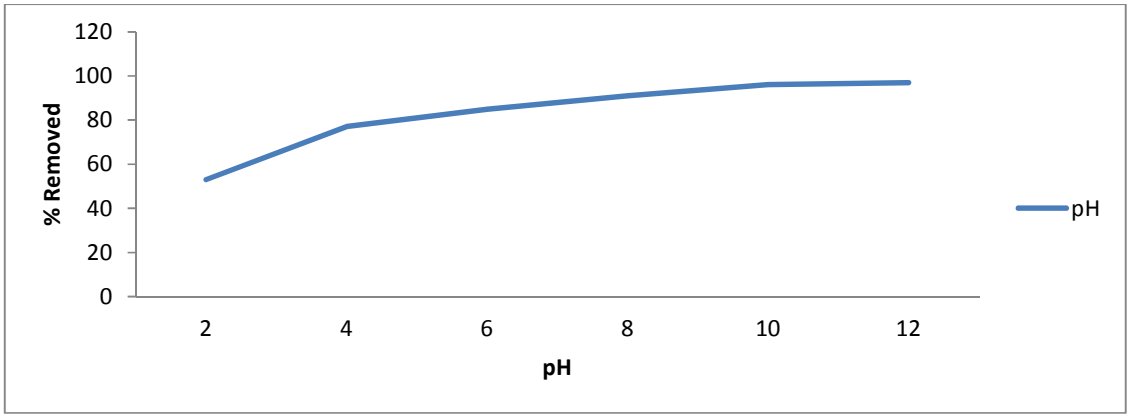

Fig. 5. Variation of percentage removal of 4NPN with pH

indicate that the adsorption of 4-Nitrophenol by *B. eurycoma* seed hull does not conform to the Langmuir isotherm theory. The Freundlich isotherm (Fig. 7) 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 (Fig. 7).

The diffractogram (Fig. 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.

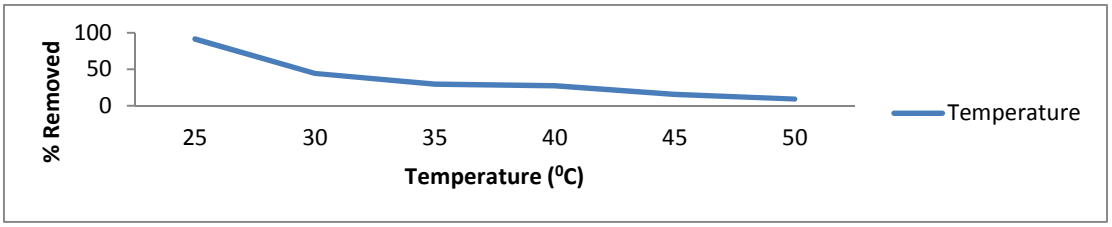

Fig. 6. Variation of percentage removal of 4NPN with temperature

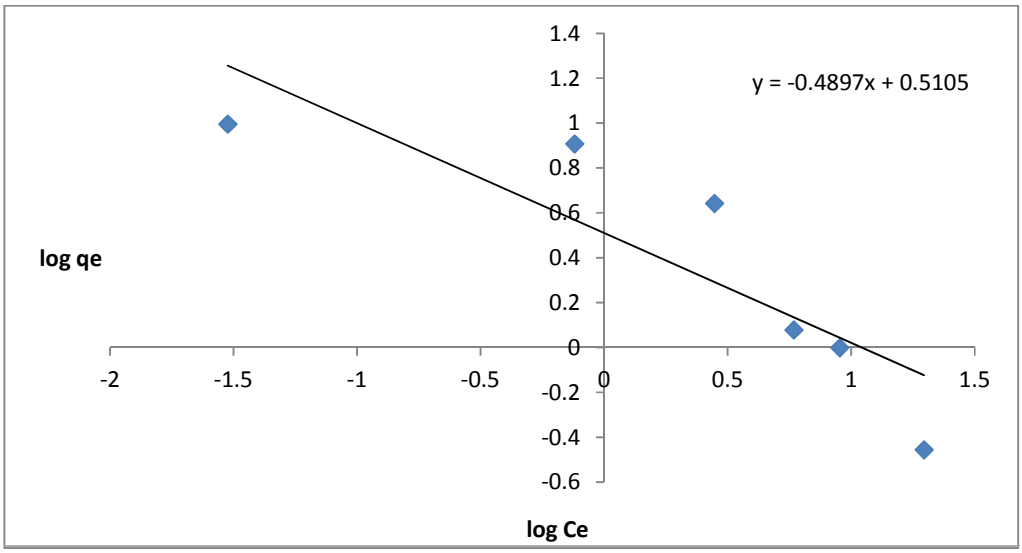

Fig. 7. Freundlich plots for adsorption of 4-Nitrophenol on *B. eurycoma* seed hulls

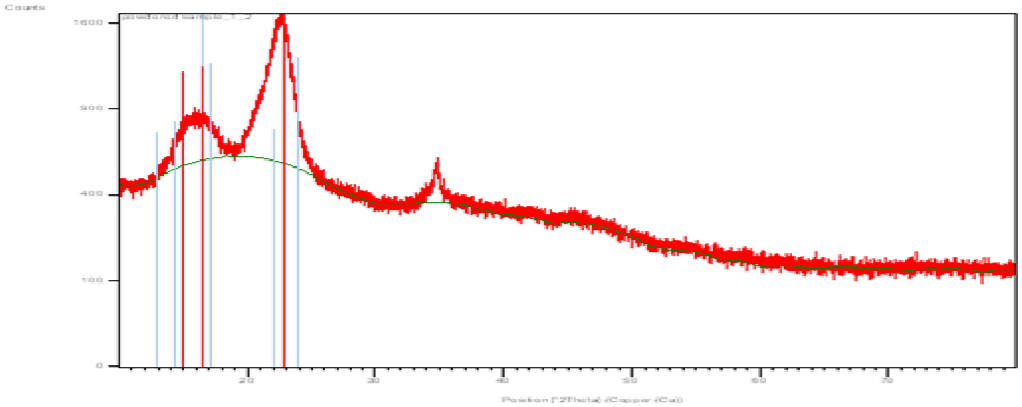

Fig. 8. X-ray diffraction pattern of *B. eurycoma*

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.

5. 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 0.5 g in 20 mls of 8 mg/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.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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