Comparative studies of raw and modified A*rachis hypogaea* (groundnut husk) in the treatment of industrial effluents

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Abstract

This study investigates the performance and comparison of low cost biochar made from agricultural wastes, Groundnut husk with the aim of treating palm oil and rubber processing effluent to ensure their safety before discharged into the environment. Composite sampling was employed in obtaining effluent samples which were analysed before and after treatment. The raw and modified biochars were prepared and characterized using standard methods for some selected parameters: pH, bulk density, moisture content, ash content, surface area, pore size, pore volume, and chemical functional groups. The results obtained for the palm oil mill effluent had pH of 5.20, Electrical conductivity (4371.37±11.53us/cm), Total dissolved solid (2868.67±4.73 mg/L), Total nitrogen (962.67±2.52 mg/L), Chemical oxygen demand (10955.67±9.07 mg/L) and Coliform (120 CFU/mL) while the rubber processing mill effluent had pH of 4.78±0.13, Electrical conductivity (3823.61±59.78 us/cm), Total dissolved solid (2867.44±9.61mg/L), Total nitrogen (535.00±7.55mg/L), Chemical oxygen demand (4425.67±61.70mg/L) and Coliform (100 CFU/mL). The treatment employs column adsorption studies with varying adsorbent loads. Optimum dose of adsorbent established for the effluent samples were 10g/100mL for the maximum adsorption capacity. The treatment with this dose of adsorbents (10g/100mL) shows that modified groundnut husk has the highest treatment efficiency for palm oil mill and rubber processing mill effluents in terms of reduction in the parameters monitored. A plot of the data obtained using the adsorbents conformed to the Freundlich and Langmuir isotherm models using methylene blue solution. The adsorption Isotherm of the modified groundnut husk fit better. The adsorbent under study can therefore be used as alternative in order to reduce the high cost of conventional adsorbent used in effluent management.

Keywords: Agricultural waste, Groundnut husk, Adsorbent, Palm oil mill effluent, Rubber processing effluent, Adsorption isotherm.

Résumé

Cette étude porte sur l'évaluation des performances et la comparaison d'un biocharbon à faible coût, produit à partir de déchets agricoles, notamment les coques d'arachide, dans le but de traiter les effluents issus de la transformation de l'huile de palme et du caoutchouc, afin de garantir leur innocuité avant leur rejet dans l'environnement. Un échantillonnage composite a été utilisé pour collecter les échantillons d'effluents, lesquels ont été analysés avant et après traitement. Les biocharbons brut et modifié ont été préparés et caractérisés selon des méthodes normalisées en déterminant certains paramètres sélectionnés, notamment le pH, la masse volumique apparente, la teneur en humidité, la teneur en cendres, la surface spécifique, la taille des pores, le volume des pores et les groupes fonctionnels chimiques.

Les résultats obtenus pour les effluents des huileries de palme ont montré un pH de 5,20, une conductivité électrique de 4 371,37 ± 11,53 µS/cm, une teneur en matières dissoutes totales (TDS) *de 2 868,67 ± 4,73 mg/L, une teneur en azote total de 962,67 ± 2,52 mg/L, une demande chimique en oxygène (DCO) de 10 955,67 ± 9,07 mg/L et une concentration en coliformes de 120 UFC/mL. Quant aux effluents provenant de la transformation du caoutchouc, ils présentaient un pH de 4,78 ± 0,13, une conductivité électrique de 3 823,61 ± 59,78 µS/cm, une teneur en matières dissoutes totales de 2 867,44 ± 9,61 mg/L, une teneur en azote total de 535,00 ± 7,55 mg/L, une demande chimique en oxygène de 4 425,67 ± 61,70 mg/L et une concentration en coliformes de 100 UFC/mL.*

Le traitement a été réalisé au moyen d'études d'adsorption en colonne, avec différentes masses d'adsorbant. La dose optimale d'adsorbant déterminée pour les échantillons d'effluents était de 10 g/100 mL, correspondant à la capacité maximale d'adsorption. À cette dose, le biocharbon modifié à base de coques d'arachide a présenté la meilleure efficacité de traitement des effluents des huileries de palme et des unités de transformation du caoutchouc, en termes de réduction des paramètres analysés.

L'ajustement des données obtenues avec les adsorbants aux modèles d'isothermes de Freundlich et de Langmuir, à l'aide d'une solution de bleu de méthylène, a montré une bonne conformité à ces deux modèles. Toutefois, l'isotherme d'adsorption du biocharbon modifié à base de coques d'arachide présentait un meilleur ajustement. Par conséquent, l'adsorbant étudié pourrait constituer une alternative aux adsorbants conventionnels, contribuant ainsi à réduire les coûts élevés associés à la gestion et au traitement des effluents.

Mots-clés : Déchets agricoles, coques d'arachide, adsorbant, effluents des huileries de palme, effluents de transformation du caoutchouc, isotherme d'adsorption.

الملخص

تبحث هذه الدراسة في أداء ومقارنة الفحم الحيوي منخفض التكلفة المصنَّع من المخلفات الزراعية، ولا سيما قشور الفول
السوداني، بهدف استخدامه في معالجة مياه الصرف الناتجة عن مصانع زيت النخيل ومصانع معالجة المطاط، وذلك لضمان
وقد استُخدمت طريقة أخذ العينات المركبة لجمع عينات مياه الصرف، ثم أُجريت تحاليل لها .سلامتها قبل تصريفها في البيئة
كما تم تحضير الفحم الحيوي الخام والمعدَّل وتوصيفهما باستخدام طرق قياسية لتحديد عدد من الخصائص .قبل المعالجة وبعدها
، والكثافة الظاهرية، ومحتوى الرطوبة، ومحتوى الرماد، والمساحة السطحية، (pH)المختارة، شملت الأس الهيدروجيني
.وحجم المسام، وحجم الفراغات المسامية، والمجموعات الوظيفية الكيميائية

، وموصلية كهربائية بلغت 5.20قدرها pHأظهرت النتائج أن مياه الصرف الناتجة عن مصانع زيت النخيل سجلت قيمة
لتر، ونيتروجين كلي بلغ /ملغم 4.73 ± 2868.67سم، ومواد صلبة ذائبة كلية بلغت /ميكروسيمنز 11.53 ± 4371.37
لتر، وتركيزًا من البكتيريا القولونية /ملغم 9.07 ± 10955.67لتر، وطلبًا كيميائيًا على الأكسجين بلغ /ملغم 2.52 ± 962.67
4.78قدرها pHأما مياه الصرف الناتجة عن مصانع معالجة المطاط، فقد سجلت قيمة .مل/وحدة تكوين مستعمرة 120قدره
9.61 ± 2867.44سم، ومواد صلبة ذائبة كلية بلغت /ميكروسيمنز 59.78 ± 3823.61، وموصلية كهربائية بلغت 0.13 ±
لتر، /ملغم 61.70 ± 4425.67لتر، وطلبًا كيميائيًا على الأكسجين بلغ /ملغم 7.55 ± 535.00لتر، ونيتروجينًا كليًا بلغ /ملغم
.مل/وحدة تكوين مستعمرة 100وتركيزًا من البكتيريا القولونية قدره

وقد تم تحديد الجرعة المثلى .تمت المعالجة باستخدام تجارب الامتزاز بالأعمدة، مع استخدام كميات مختلفة من المادة الممتزة
وأظهرت المعالجة .مل، وهي الجرعة التي حققت أعلى قدرة امتزاز 100/غرام 10للمادة الممتزة لعينات مياه الصرف عند
باستخدام هذه الجرعة أن الفحم الحيوي المعدَّل المصنوع من قشور الفول السوداني حقق أعلى كفاءة في معالجة مياه الصرف
.الناتجة عن مصانع زيت النخيل ومصانع معالجة المطاط، من حيث خفض القيم المسجلة للمعايير التي تمت متابعتها

كما أظهرت مطابقة البيانات التي تم الحصول عليها باستخدام المواد الممتزة توافقًا مع نموذجي متساوي الحرارة للامتزاز لكل
من فريندلِخ ولانغموير، وذلك باستخدام محلول أزرق الميثيلين. وقد أظهر نموذج متساوي الحرارة لامتزاز الفحم الحيوي
المعدَّل المصنوع من قشور الفول السوداني توافقًا أفضل مع البيانات التجريبية. وبناءً على ذلك، يمكن استخدام المادة الممتزة
محل الدراسة كبديل للمواد الممتزة التقليدية، مما يسهم في خفض التكلفة المرتفعة المرتبطة باستخدام المواد الممتزة التقليدية في
إدارة ومعالجة مياه الصرف الصناعي.

الكلمات المفتاحية: المخلفات الزراعية؛ قشور الفول السوداني؛ مادة ممتزة؛ مياه الصرف الناتجة عن مصانع زيت النخيل؛ مياه
الصرف الناتجة عن معالجة المطاط؛ متساوي حرارة الامتزاز.

Introduction

Advances in biotechnology and bioengineering have significantly enhanced the valorization of materials previously considered waste, transforming them into valuable resources (Adeleke *et al.*, 2023). Nigeria has approximately 79 million hectares of available agricultural land, with about 44% currently under cultivation. The substantial volume of agricultural residues generated in the country presents a promising opportunity to meet domestic production demands. Most of these residues are biomass, which contains a considerable amount of energy (Nazeer *et al.*, 2024). In many developing countries, including Nigeria, agricultural wastes are neither efficiently utilized nor properly managed (Jekayinfa and Omisakin 2005). According to the United Nations Industrial Development Organization 2020 report, Nigeria generates approximately 32 million tons of waste annually, one of the largest in Africa. The composition of this waste varies depending on the nature and intensity of agricultural practices and may exist in liquid, slurry, or solid forms. These wastes are often burned or left to decompose, leading to colossal loss and contributing to environmental degradation and pollution. Such practices pose high risk to the ecosystems (Nazeer *et al.*, 2024). Materials commonly regarded as waste can be transformed into valuable resources by converting them into value-added products such as adsorbents. These bio-derived materials are potentially significant for a wide range of industrial applications, including the removal of hazardous organic compounds, odor- and taste-causing substances (Nataša Karić *et al.*, 2022), treatment of off-gases containing volatile organic compounds, decolourization, solvent recovery, treatment of industrial and municipal wastewater, remediation of surface and groundwater, food processing, pharmaceutical production, and broader environmental restoration efforts (Olafadehen *et al.*, 2012).

John *et al*. 2024 reported that an adsorbent can be considered low-cost if it is abundant in nature, requires minimal processing, and is a by-product or waste material from industrial activities. Plant wastes are inexpensive because they have little or no economic value. Studies have shown that adsorbents with high carbon content are effective in removing both organic and inorganic pollutants (Olafadehen *et al.*, 2012). Adsorption studies on untreated plant wastes include papaya wood (Saeed *et al.*, 2005), maize leaf (Babarinde *et al.*, 2006), teak leaf powder (King *et al.*, 2006), *Imperata cylindrica* (lalang) leaf powder (Hanafiah *et al.*, 2006), *Coriandrum sativum* (Karunasagar *et al.*, 2005), peanut hull pellets (Johnson *et al.*, 2002), saltbush (*Atriplex canescens*) leaves (Sawalha *et al.*, 2007b), tree fern (Ho *et al.*, 2004), rice husk ash and neem bark (Bhattacharya *et al.*, 2006), and grape stalk waste (Villaescusa *et al.*, 2004). Beyond their low cost and availability, agricultural wastes possess good adsorption capacity, selective affinity for heavy metal ions, and can be regenerated easily (Gaballah *et al.*, 1997). However, untreated plant wastes have limitations such as having high chemical oxygen demand (COD), low in there adsorptive capacity, having high biochemical oxygen demand (BOD), and elevated total organic carbon (TOC) due to the release of soluble organic compounds present in plant material. These compounds cause depletion of dissolved oxygen levels in aquatic ecosystems which threatens aquatic organisms and soil microbes (Gaballah *et al*., 1997). The Nigerian Industrial Standard (NIS, 2007), has identified polluted water sources particularly those contaminated by untreated waste as a major contributor to waterborne diseases and soil degradation in developing countries.

In Nigeria, environmental degradation has increased due to improper disposal of industrial and agricultural wastes. Industries that rely on agricultural raw materials often discharge untreated effluents into surface water bodies and soils, leading to widespread environmental pollution (Raheem and Morenikeji 2008). Wastes from palm oil and rubber processing contain both organic and inorganic contaminants, including chemicals added during processing. These effluents often have high COD and heavy metal concentrations, exceeding the permissible limits set by the National Environmental Standards and Regulations Enforcement Agency (NESREA 2011) 100 mg/L for COD; 20 mg/L for Fe; 0.5 mg/L for Cu and Zn; 5 mg/L for Mn; 0.2 mg/L for Pb; and 4 CFU/mL for total coliforms. Industrialization is expanding rapidly in Nigeria; however, little attention is given to its environmental consequences (Efe *et al*., 2024). One of the most affected environmental components is the nation's water resources. Studies conducted by Osibanjo, 2001 have shown significant alterations in the nutrient chemistry of water bodies, primarily due to the discharge of untreated wastewater. These changes in nutrient concentrations can pose serious threats to both human health and aquatic ecosystems. Heavy metals, which are frequently present in industrial effluents, are known to accumulate in streams and rivers. Many of these metals are cumulative toxins, posing long-term health risks to aquatic organisms and potentially entering the human food chain through bioaccumulation. Soil and water pollution result from physical, chemical, or biological changes in environmental quality that negatively impact living organisms or render these resources unsuitable for beneficial uses such as irrigation, recreation, industrial activities, and nature conservation (NIS, 2007; Olowoyeye, 2012). During industrial production and post-consumption activities, a portion of materials inevitably becomes waste, which is often disposed of into the environment without adequate treatment. In many instances, these wastes become waterborne or are deposited into soils, contributing significantly to environmental degradation. The environmental impact of such pollutants depends not only on their nature but also on the volume discharged (WHO, 2002a; WHO, 2002b; Awewomom *et al*., 2024). Biodegradable substances are typically broken down by natural processes and only become problematic when released in excessive quantities that exceed the environment's capacity for self-purification. In contrast, many synthetic substances produced and used by industries are either non-biodegradable or degrade extremely slowly. These recalcitrant substances can persist in the environment for long periods, leading to progressive accumulation. Many are toxic or carcinogenic and can be absorbed into the tissues of living organisms. This bioaccumulation becomes particularly concerning when these substances biomagnify through successive trophic levels in the food web, posing risks to both ecological and human health (WHO, 2002a; Ammar, 2022; Kirti *et al*., 2024).

Given these environmental challenges, this study investigated the feasibility of using both carbonized and chemically modified groundnut husk as an efficient and sustainable adsorbent for the treatment of effluents generated from palm oil and rubber processing industries. These effluents are known to contain high levels of organic matter and heavy metals, which can severely impact water and soil quality if not adequately treated.

Materials and methods

Adsorbate

The wastewater sample were collected using fabricated water sampler of 1-liter capacity from the Nigeria institute for oil palm research and the Rubber research institute Iyanomo, Benin City, both in Edo state.

Adsorbent Preparation

Arachis hypogaea (Groundnut husk), an agricultural waste were gathered from each waste bin from the Faculty of Life Sciences, University of Benin, Benin City Edo State Nigeria. It was taken to the Chemistry Laboratory, Department of Science Laboratory Technology. Standard procedures were followed in washing, drying and grinding of the groundnut husk. Part of the powdered groundnut husk was mixed with Zinc chloride at ratio 1:1 and carbonized at 450^{o}C for 15 minutes. After cooling, the excess zinc chloride was washed out by immersing in 1 M hydrochloric acid solution for 12 hours in a water bath at 80^{o}C. Thereafter the activated biochar was then washed repeatedly with deionized water to eliminate traces of Hydrochloric acid and Zinc chloride .This was verified by analyzing the filtered water each time using silver nitrate. The biochar was oven dried, grind and sieved to get a particular mesh size which was kept in an airtight container for further use (Okieimen *et al*., 2005).

Characterization and Adsorption Studies

The activated biochar was characterized using standard methods: moisture content was determined by drying and weighing, ash content by pyrolysis at high-temperature, pH by suspending in water and measuring with a pH meter, bulk density by mass-to-volume ratio, iodine number by iodine adsorption and titration; surface area, pore size and pore volume were determined using Brunauer-Emmett Teller (BET) method (Brunauer *et al*., 1938) through gas adsorption onto the sorbent surface, which provides insights into its surface characteristics and functional groups were determined by Fourier-transform infrared spectroscopy (FTIR) which provide an easy way on how infrared signal that passes through organic compound is absorbed at different characteristic frequencies, which are then transformed into a unique spectrum (Coates, 1996). The treatment process was carried out using a fix bed column while adsorption experiment to study the adsorption isotherm of both adsorbent. A weighed amount of adsorbents and 100 mL of palm oil effluent run through the fix bed column and the filtrate analyzed after treatment. For the adsorption isotherm study, methylene blue solution concentration 5 to 100 mg/L was used on the adsorbents. The adsorption kinetics studies were carried out under optimized conditions from 25 to 125 minutes. The mixture was filtered and the concentrations of the residual methylene blue concentrations in the filtrates were determined using the UV-VIS Spectrophotometer (PG instrument model T18) at wavelength of 540 nm. The concentration of methylene blue uptake by 1 g of the adsorbent was calculated from the following mass balance equation:

$$q_e = \frac{(C_o - C_e)V}{M} \quad (1)$$

Where q_e (mg g^{-1}) is the amount of methylene blue uptake from solution, C_e (mg L^{-1}) the methylene blue concentration in solution after adsorption, C_o (mg L^{-1}) the initial methylene blue concentration, **M** the amount of adsorbent (g) and V the volume of solution (L).

Percentage removal was calculated using the formula:

$$Removal\,(\%) = \frac{Co - Ce}{Co} \, x\, 100 \quad (2)$$

Results and discussion

Table 1: Characterization of Raw and Modified *Arachis hypogaea* (Groundnut Husk)

Parameters	Raw groundnut husk	Modified groundnut husk	P value
Ash Content	1.07±0.03	7.30±0.06	0.001
Bulk Density	0.26±0.01	0.72±0.01	0.001
Moisture	18.53±0.04	3.36±0.07	0.001
pH	7.02±0.25	6.70±0.13	0.118

95% confidence limit $p < 0.05$ indicates significant difference.

Tables 1, show that the raw groundnut husk has moisture content 18.53% and the modified groundnut husk has moisture content 3.36% respectively. The ash content was found to be 1.07% for raw groundnut husk while the modified was found to be 7.30 % respectively. The ash content is an indication of the quality of activated carbon. Bulk density was found to be 0.26, for raw groundnut husk and was found to be 0.72, for modified groundnut husk. The pH value was found to be 7.02 for the raw groundnut husk, while the modified groundnut husk was 6.70 respectively. The pH value for both the raw and modified groundnut husk fell within the acceptable pH ranges of between 6-8 which is in line with (AOAC, 2000; APHA, 2005; ASTM D4607-94, 2006; Agho and Archibong 2024).

Table 2: Functional Groups in Raw and Modified *Arachis hypogaea* (Groundnut Husk)

Frequency	Raw Groundnut Husk	Modified Groundnut Husk
2923.60	Strong absorption band (C-H stretch)	Strong and broad absorption band (C-H stretch)
2835.27		Strong and broad absorption band (C-H stretch)
1654.12	Weak absorption band (C=C stretch)	Very strong absorption band (C=C stretch)
1636.87	Medium absorption band (C=C stretch)	Strong and sharp absorption band (C=C stretch)
1459.58	Weak absorption band (Ring C-H bend)	Very strong absorption band (Ring C-H bend)
1376.85	Very strong absorption band (Ring C-H bend)	Sharp and strong absorption band (C-H bend)
1154.37	Medium absorption band (C-N stretch)	Medium to strong absorption band (C-N stretch)
721.60	Very strong absorption band (CH rocking)	Sharp and strong absorption band (CH rocking)
1462.55		Sharp and strong absorption band (C-H bend)
1304.51		Medium absorption band (C-H plane bend, CN stretch)
972.26		Medium to strong absorption band (C-H out of plane bend)

Tables 2. Shows the FTIR spectra readings of the raw and modified groundnut husk obtained at wavenumber of 4000 to 400 cm^{-1} or wavelength of 2.5 to 25µm. The characteristics from the FTIR analysis was observed that there were changes in the modified groundnut husk after chemical activation and pyrolysis process, forming a structure with larger pores which can be attributed to the breakdown of labil compounds during the process. The FTIR spectrum of the raw and modified groundnut husk shows a strong absorption signals at 2924 cm^{-1}, which characterize symmetric and asymmetric vibrations of $–CH_2-$ groups (Coates, 1996). A band near 2835 cm^{-1} shows a strong and broad signal which characterize symmetric C-H vibrations of $–C=CH_2$ group in the modified groundnut hush biochar. A band near 1654, 1637 and 1460 cm^{-1}, related to the stretching that leads to C=C of aromatic group occurs in both biochar; a band near 1377 cm^{-1}, related to the bending of C-H ring in alkane; a band near the region of 1154 cm^{-1} , related to the stretching of the tertiary amine C-N ring, and the band near 722 cm^{-1}, assigned to the rocking of CH_2 groups of lignin, cellulose or hemicelluloses are also observed (Coates, 1996). The FTIR spectrum of the modified groundnut husk shows a strong absorption band at 2924 cm^{-1} just as the raw groundnut husk. A band between 1462 and 1377 cm^{-1}, assigned to the bending of C-H ring of the alkanes and alkenes. A band near 1305 cm^{-1}, related to the bending of primary or secondary O-H, aromatic ring and primary amine CN; a band near 1154 cm^{-1}, assigned to the stretching of the tertiary amine CN. The FTIR spectrum for the raw rubber seed shell shows a strong and broad band at 2837 cm^{-1}, which characterize asymmetric stretching in $O-CH_3$ ether group. A band between 1735, 1593 and 1462 cm^{-1}, assigned to the stretching of ring and aromatic group; a band near 1377 cm^{-1}, related to the organic sulphates and aliphatic nitro compounds; a band near 1036 cm^{-1}, related to the stretching of C-O groups and or C-O-C group and the 722 cm^{-1} band is attributed to the rocking of $–CH_2$ group (Coates, 1996).

Table 3: B.E.T. Surface Area, Pore Volume, and Pore Size for Raw and Modified Groundnut Husk Biochar.

Parameter	(Raw Groundnut Husk)	(Modified Groundnut Husk)
Surface Area Data (m²/g)		
Multipoint BET	138.1	249.0
Pore Volume Data (cc/g)		
BJH Method Cumulative Absorption Pore Volume	0.0684	0.1653
Pore Size Data (nm)		
BJH Method Absorption Pore Diameter (mode Dv(d))	2.128	2.117

BET analysis shows that modified groundnut husk biochar possesses a higher surface area (249.0 m²/g) and pore volume (0.1653 cc/g) compared to the raw groundnut husk biochar (138.1 m²/g and 0.0684 cc/g, respectively), indicating superior adsorption capacity. The average pore diameters for both samples are similar (2.117 nm for raw and 2.128 nm for modified), falling within the mesoporous range, suggesting that pore structure was retained post-modification (Brunauer *et al.*, 1938).

Table 4: Characterization of Palm Oil Mill Effluent.

Parameters	Unit	Palm oil mill effluent	NESREA Effluent Limit for discharge

		Mean±SD	Water	Land
pH		5.20±0.03	6.5-8.9	6.5-8.9
Conductivity	µs/cm	4371.37±11.53		
TDS	NTU	2868.67±4.73	500	500
Total Nitrogen	mg/L	962.67±2.52	10	10
Available Phosphorus	mg/L	572.33±3.51	10	-
Chemical Oxygen Demand (COD)	mg/L	10955.67±9.07	100	100
Potassium,	mg/L	729.00±4.58		
Magnesium	mg/L	221.00±3.61	100	-
Calcium	mg/L	122.67±2.52	100	-
Sodium	mg/L	133.67±2.08		
Iron	mg/L	252.50±2.07	20	-
Zinc	mg/L	63.10±0.49	0.5	-
Copper	mg/L	59.34±0.98	0.5	-
Manganese	mg/L	16.52±1.23	5.0	-
Lead	mg/L	3.20±0.39	0.2	-
Coliform	CFU / mL	120±0.00	4 CFU/mL	5CFU/mL

The physicochemical analysis of palm oil mill effluent (POME) reveals significant environmental concerns when compared with NESREA discharge limits. The effluent's acidic pH (5.20 ± 0.03) falls below the acceptable range (6.5–8.9), potentially harming aquatic and soil biota. Its high electrical conductivity (4371.37 ± 11.53 µS/cm) indicates elevated salinity, although not directly regulated. Total dissolved solids (TDS: 2868.67 ± 4.73 mg/L), total nitrogen (962.67 ± 2.52 mg/L), and available phosphorus (572.33 ± 3.51 mg/L) all greatly exceed NESREA limits (500 mg/L for TDS; 10 mg/L for nitrogen and phosphorus), increasing the risk of eutrophication and oxygen depletion. The chemical oxygen demand (COD) is exceptionally high (10,955.67 ± 9.07 mg/L), over 100 times the permissible limit (100 mg/L), indicating a substantial organic load. Nutrient elements such as potassium (729.00 ± 4.58 mg/L), calcium (122.67 ± 2.52 mg/L), and magnesium (221.00 ± 3.61 mg/L) are present in concentrations that may disrupt soil balance. Heavy metals including iron (252.50 ± 2.07 mg/L), zinc (63.10 ± 0.49 mg/L), copper (59.34 ± 0.98 mg/L), manganese (16.52 ± 1.23 mg/L), and lead (120 mg/L) severely exceed NESREA limits, posing toxicity risks to both ecosystems and human health. Coliform count (5 CFU/mL) also surpasses the safe threshold, suggesting possible pathogenic contamination (NESREA 2011; APHA, 2005; EPA, 2015; Kanu and Achi 2011).

Table 5: Characterization of rubber processing effluent

Parameters		Rubber processing effluent	NEASREA Effluent limit for discharge	
	Unit	Mean ±SD	Water	Land
pH		4.78±0.13	6.5-8.9	6.5-8.9
Conductivity	µs/cm	3823.61±59.78		

TDS	NTU	2867.44±9.61	500	500
Total Nitrogen	mg/L	535.00±7.55	10	10
Available Phosphorus	mg/L	258.67±4.16	10	-
Chemical Oxygen Demand (COD)	mg/L	4425.67±61.70	100	100
Potassium,	mg/L	364.00±17.09		
Magnesium	mg/L	180.00±6.00	100	-
Calcium	mg/L	88.33±4.04	100	-
Sodium	mg/L	61.33±3.06		
Iron	mg/L	152.85±1.83	20	-
Zinc	mg/L	48.11±0.13	0.5	-
Copper	mg/L	53.13±0.36	0.5	-
Manganese	mg/L	12.76±0.08	5.0	-
Lead	mg/L	4.83±0.05	0.2	-
Coliform	CFU	100±0.00	4CFU/mL	5CFU/mL

The characterization of rubber processing effluent reveals significant deviations from NESREA's permissible discharge standards, indicating severe environmental concerns. The effluent exhibits strong acidity with a pH of 4.78 ± 0.13, which falls well below the acceptable range of 6.5–8.9, potentially harming aquatic organisms and soil health. The total dissolved solids (TDS) level of 2867.44 ± 9.61 mg/L exceeds the NESREA limit of 500 mg/L, indicating high salinity that may affect water quality and soil structure. Similarly, total nitrogen (535.00 ± 7.55 mg/L) and available phosphorus (258.67 ± 4.16 mg/L) are alarmingly higher than the 10 mg/L limit, suggesting a high nutrient load capable of triggering eutrophication and oxygen depletion in water bodies. The chemical oxygen demand (COD) was measured at 4425.67 ± 61.70 mg/L, over 40 times the regulatory threshold of 100 mg/L, reflecting a substantial organic burden that can severely deplete dissolved oxygen in receiving waters. Elevated levels of potassium (364.00 ± 17.09 mg/L), magnesium (180.00 ± 6.00 mg/L), and calcium (88.33 ± 4.04 mg/L) also suggest potential risks to soil fertility and nutrient imbalance, with magnesium exceeding the land discharge limit of 100 mg/L. Heavy metal concentrations are critically high. Iron (152.85 ± 1.83 mg/L), zinc (48.11 ± 0.13 mg/L), copper (53.13 ± 0.36 mg/L), and manganese (12.76 ± 0.08 mg/L) all greatly exceed NESREA standards (20 mg/L for iron, 0.5 mg/L for zinc and copper, and 5.0 mg/L for manganese), posing serious risks of toxicity to aquatic life and potential bioaccumulation. The coliform count (5 CFU/mL) slightly surpasses the permissible limit of 4 CFU/mL, indicating microbial contamination and potential public health concerns (NESREA 2011; APHA, 2005; EPA, 2015; Kanu and Achi 2011).

Table 6: Optimum Dose Determination for the Treatment of Palm Oil Mill Effluent using Raw *Arachis hypogaea* (Groundnut Husk).

Parameters		Initial Conc.	2 g	4 g	6 g	8 g	10 g	12g	14g
pH	Mean	5.17±0.02	5.69±0.03	5.61±0.02	5.85±0.02	5.43±0.01	5.42±0.03	5.72±0.02	5.88±0.01
EC	Mean	4371.37±11.53	2197.07±29.02	1443.77±20.79	885.90±9.78	656.97±15.99	491.67±6.04	504.13±9.34	504.67±6.00
TDS	Mean	2834.00±61.65	1529.00±12.77	1126.67±49.00	667.67±11.85	479.33±3.51	289.33±2.52	302.67±9.81	314.00±6.08
TNK	Mean	960.33±5.69	626.67±5.51	481.67±4.73	298.67±12.58	210.33±2.52	128.33±3.51	137.00±3.61	147.00±4.58
Iron	Mean	252.26±1.92	165.21±3.14	137.73±3.69	115.62±4.20	99.56±3.92	78.21±4.86	88.45±1.34	90.57±1.12
Zinc	Mean	62.34±0.57	49.02±0.32	43.33±1.01	38.65±1.44	33.61±1.68	24.10±2.77	28.09±0.88	29.29±0.16
Copper	Mean	57.83±1.10	39.54±1.37	34.75±0.90	25.73±1.06	20.93±1.71	15.17±1.49	17.63±0.23	17.74±0.09
Manganese	Mean	15.24±0.48	8.36±0.97	7.02±0.13	5.94±0.45	4.11±0.57	2.74±0.84	3.85±0.09	3.94±0.05
Lead	Mean	3.42±0.21	2.88±0.20	2.12±0.28	1.45±0.42	1.18±0.12	0.80±0.18	1.06±0.05	1.21±0.03
COD	Mean	10898.67±59.34	1271.67±67.32	813.33±49.01	678.00±16.70	395.67±17.95	293.67±6.51	313.67±3.06	320.00±2.00

Treatment of palm oil mill effluent with increasing doses of raw *Arachis hypogaea* (groundnut husk) showed progressive improvement in pollutant removal. pH increased slightly, indicating mild neutralization. Significant reductions were observed in electrical conductivity and TDS, which dropped from 4371.37 µS/cm and 2834.00 mg/L to 491.67 µS/cm and 289.33 mg/L respectively at 12 g, with minimal change beyond this dose. Total nitrogen reduced from 960.33 mg/L to 128.33 mg/L, while COD dropped drastically from 10,898.67 mg/L to 293.67 mg/L at 12 g, indicating effective organic load removal. Heavy metals (Fe, Zn, Cu, Mn, Pb) also showed maximum reduction at 12 g. Beyond this dosage, further reduction was negligible. 12 g of raw groundnut husk is the optimum dose for efficient removal of organic and inorganic pollutants from POME (NESREA 2011; APHA, 2005; EPA, 2015; Kanu and Achi 2011; Jatto *et al*., 2013).

Table 7: Optimum Dose Determination for the Treatment of Palm Oil Mill Effluent using Modified *Arachis hypogaea* (Groundnut Husk).

		Initial Conc.	2 g	4 g	6 g	8 g	10 g
pH	Mean	5.17±0.02	5.90±0.03	6.56±0.05	6.48±0.04	6.81±0.03	6.99±0.19
EC	Mean	4371.37±11.53	1228.18±52..52	873.92±5.61	446.15±3.61	288.55±1.07	184.02±3.23
TDS	Mean	2834.00±61.65	879.00±3.61	492.33±5.51	272.33±15.57	138.92±4.13	96.06±1.16
TNK	Mean	960.33±5.69	327.33±3.51	260.67±6.51	142.33±4.51	89.37±2.11	7.49±0.88
Iron	Mean	252.26±1.92	125.05±2.08	114.30±4.31	81.58±1.11	62.89±1.08	5.25±0.89
Zinc	Mean	62.34±0.57	32.91±2.15	30.72±0.67	22.96±1.09	16.35±0.95	2.08±0.44

Copper	Mean	57.83±1.10	31.48±1.14	24.32±1.38	17.38±0.86	13.64±1.03	0.41±0.05
Manganese	Mean	15.24±0.48	7.81±0.27	4.92±0.36	3.26±0.54	2.41±0.43	0.22±0.02
Lead	Mean	3.42±0.21	1.17±0.05	0.97±0.04	0.79±0.05	0.35±0.04	0.09±0.01
COD	Mean	10898.67±59.34	667.67±13.05	324.67±7.51	278.00±12.49	136.00±10.58	81.67±5.51

The treatment of palm oil mill effluent using modified groundnut husk showed excellent performance across all parameters. The pH increased from 5.17 to 6.99 at 10 g, moving closer to the neutral range, which is safer for the environment. Electrical conductivity and total dissolved solids dropped sharply from 4371.37 µS/cm and 2834.00 mg/L to 184.02 µS/cm and 96.06 mg/L respectively, indicating effective removal of dissolved salts. Total nitrogen decreased significantly from 960.33 mg/L to just 7.49 mg/L at 10 g, showing strong nutrient removal. Heavy metals such as iron, zinc, copper, manganese, and lead were also greatly reduced iron fell from 252.26 mg/L to 5.25 mg/L, while lead dropped from 3.42 mg/L to 0.09 mg/L making the treated effluent much less toxic. The chemical oxygen demand (COD), a key indicator of organic pollution, decreased from 10,898.67 mg/L to 81.67 mg/L, showing very effective removal of organic matter (Okieimen *et al*., 2005).

Table 8: Optimum Dose Determination for the Treatment of Rubber Processing Effluent using Raw *Arachis hypogaea* (Groundnut Husk).

		Initial Conc.	**2 g**	**4 g**	**6 g**	**8 g**	**10 g**	**12g**	**14g**
pH	Mean	4.78±0.13	5.62±0.01	5.69±0.06	5.46±0.02	5.33±0.02	5.86±0.03	5.90±0.03	5.61±0.04
EC	Mean	3823.00±59.92	1319.67±2.52	1241.00±3.61	1076.33±9.50	877.67±3.79	652.00±2.00	761.33±3.21	770.00±2.00
TDS	Mean	2866.67±9.71	710.33±20.60	572.67±5.03	461.33±6.66	434.33±4.04	364.67±2.52	455.33±2.52	461.00±1.00
TNK	Mean	535.00±7.55	373.67±2.08	322.67±2.08	174.33±2.08	114.00±2.00	57.00±1.00	65.33±1.53	67.33±0.58
Iron	Mean	152.85±1.83	107.15±2.23	83.96±1.18	68.80±1.58	54.24±1.96	29.05±1.66	31.53±1.23	32.61±0.89
Zinc	Mean	48.11±0.13	41.17±0.60	29.17±1.34	22.69±0.84	17.13±1.36	11.69±0.82	13.06±0.72	12.98±0.45
Copper	Mean	53.14±0.36	41.20±0.59	31.18±0.96	23.38±0.94	18.03±1.17	10.70±0.80	12.79±0.17	12.62±1.04
Manganese	Mean	12.76±0.08	8.97±0.28	6.49±0.31	4.15±0.47	2.01±0.22	0.98±0.10	1.08±0.06	1.07±0.09
Lead	Mean	4.83±0.05	4.00±0.14	3.44±0.30	2.81±0.35	2.57±0.42	1.65±0.56	2.28±0.21	2.41±0.41
COD	Mean	4425.67±61.70	543.33±8.08	329.67±5.69	211.33±4.04	151.33±17.56	93.33±3.06	101.33±4.73	109.67±3.51

Table 8 indicates that increasing the dosage of raw *Arachis hypogaea* (groundnut husk) from 2 g to 12 g significantly enhanced the treatment efficiency of rubber processing effluent. The pH increased slightly toward neutrality, while electrical conductivity (EC) and total dissolved solids (TDS) decreased markedly, indicating a reduction in ionic and dissolved loads. Total Kjeldahl nitrogen (TKN) declined from 535.00 to 57.00 mg/L, and heavy metals such as Fe, Zn, Cu, Mn, and Pb were substantially removed, with the lowest concentrations observed at 12 g. Chemical oxygen demand (COD) also dropped sharply from 4425.67 to 93.33 mg/L, reflecting a high level of organic load reduction. The optimal treatment performance was achieved at 12 g, beyond which further increases in dosage did not result in significant improvement (Okuo *et al*., 2008).

Table 9: Optimum Dose Determination for the Treatment of Rubber Processing Effluent using Modified *Arachis hypogaea* (Groundnut Husk).

		Initial Conc.	**2 g**	**4 g**	**6 g**	**8 g**	**10 g**	**12g**	**14g**
pH	Mean	4.78±0.13	5.62±0.15	5.41±0.14	5.55±0.19	5.73±0.11	6.49±0.14	5.55±0.25	5.64±0.25
EC	Mean	3823.00±59.92	852.00±4.00	673.33±1.53	543.67±5.86	374.67±3.06	209.67±5.51	228.33±5.51	231.67±6.03
TDS	Mean	2866.67±9.71	585.00±3.61	382.33±5.69	313.00±3.61	178.33±6.81	112.33±2.52	149.00±2.65	159.33±2.08
TNK	Mean	535.00±7.55	214.33±2.52	168.00±5.57	111.33±7.02	72.33±2.52	6.41±0.03	41.00±1.73	55.67±2.89
Iron	Mean	152.85±1.83	81.46±0.94	52.41±0.57	45.17±1.59	24.40±1.20	3.68±0.03	15.94±2.50	18.46±1.24
Zinc	Mean	48.11±0.13	28.26±0.53	20.89±0.14	14.74±0.53	9.48±0.85	1.46±0.06	6.00±0.38	6.23±0.61
Copper	Mean	53.14±0.36	36.20±5.00	22.08±0.59	12.04±0.80	8.31±0.26	0.31±0.03	3.57±0.38	4.69±0.15
Manganese	Mean	12.76±0.08	5.21±0.45	3.40±0.19	1.23±0.26	0.79±0.06	0.18±0.01	0.36±0.02	0.45±0.03
Lead	Mean	4.83±0.05	2.21±0.07	1.02±0.05	0.61±0.04	0.27±0.02	0.09±0.01	0.15±0.03	0.21±0.01
COD	Mean	4425.67±61.70	329.00±1.73	231.00±6.56	158.33±7.64	102.33±1.53	51.33±1.15	60.33±2.52	64.67±3.06

Table 9 shows that increasing the dosage of modified *Arachis hypogaea* (groundnut husk) from 2 g to 12 g significantly enhanced the treatment of rubber processing effluent. The pH rose from 4.78 to 6.49, approaching neutrality. EC and TDS decreased markedly, from 3823.00 to 209.67 µS/cm and 2866.67 to 112.33 mg/L, respectively, indicating effective reduction of ionic and dissolved substances. TKN dropped sharply from 535.00 to 6.41 mg/L, while heavy metals such as Fe, Zn, Cu, Mn, and Pb were drastically reduced, with minimum concentrations at 12 g. COD also declined significantly from 4425.67 to 51.33 mg/L, reflecting substantial organic load removal. Optimal performance occurred at 12 g, beyond which further increase in dosage yielded minimal additional improvement (Okieimen *et al*., 2005; Agho and Archibong 2024).

Table 10: Adsorption Capacity for each Adsorbent at Optimum analyte Removal in Palm Oil Mill Effluent.

Parameters	Initial Conc	RG	MG
pH	5.17±0.02	5..42±0.03	6.99±0.19

EC	4371.37±11.53	491.67±6.04	184.02±3.23
% REMOVAL		88.77	95.79
TDS	2868.67±4.73	289.33±2.52	96.06±1.16
% REMOVAL		89.91	96.65
TNK	962.67±2.52	128.33±3.51	7.49±0.88
% REMOVAL		86.67	99.22
Iron	252.50±2.07	78.21±4.86	5.25±0.89
% REMOVAL		69.03	97.92
Zinc	63.10±0.49	24.10±2.77	2.08±0.44
% REMOVAL		61.81	96.70
Copper	59.34±0.98	15.17±1.49	0.41±0.05
% REMOVAL		74.44	99.31
Manganese	16.52±1.23	2.74±0.84	0.22±0.02
% REMOVAL		83.41	98.67
Lead	3.20±0.39	0.80±0.18	0.09±0.01
% REMOVAL		75.00	97.19
COD	10955.67±9.07	293.67±6.51	81.67±5.51
% REMOVAL		97.32	99.25
Coliform	120 CFU/ml	10 CFU/ml	2 CFU/ml
% REMOVAL		91.67	98.33

RG: Raw Groundnut Husk
MG: Modified Groundnut Husk

Table 10. compares the adsorption performance of raw (RG) and modified (MG) *Arachis hypogaea* (groundnut husk) at optimal conditions for treating palm oil mill effluent. The modified adsorbent outperformed the raw form across all parameters. pH increased from 5.17 to 6.99 with MG, indicating better pH stabilization. EC and TDS removals were higher with MG at 95.79% and 96.65%, respectively, compared to 88.77% and 89.91% for RG. MG also showed superior removal of TNK (99.22%), iron (97.92%), zinc (96.70%), copper (99.31%), manganese (98.67%), and lead (97.19%), significantly exceeding RG's performance. COD reduction reached 99.25% with MG, compared to 97.32% for RG. Coliform count dropped from 120 CFU/mL to 2 CFU/mL with MG, yielding 98.33% removal, against 91.67% for RG. Overall, the modified groundnut husk demonstrated significantly enhanced adsorption capacity and pollutant removal efficiency (Okieimen *et al*., 2005; Agho and Archibong 2024).

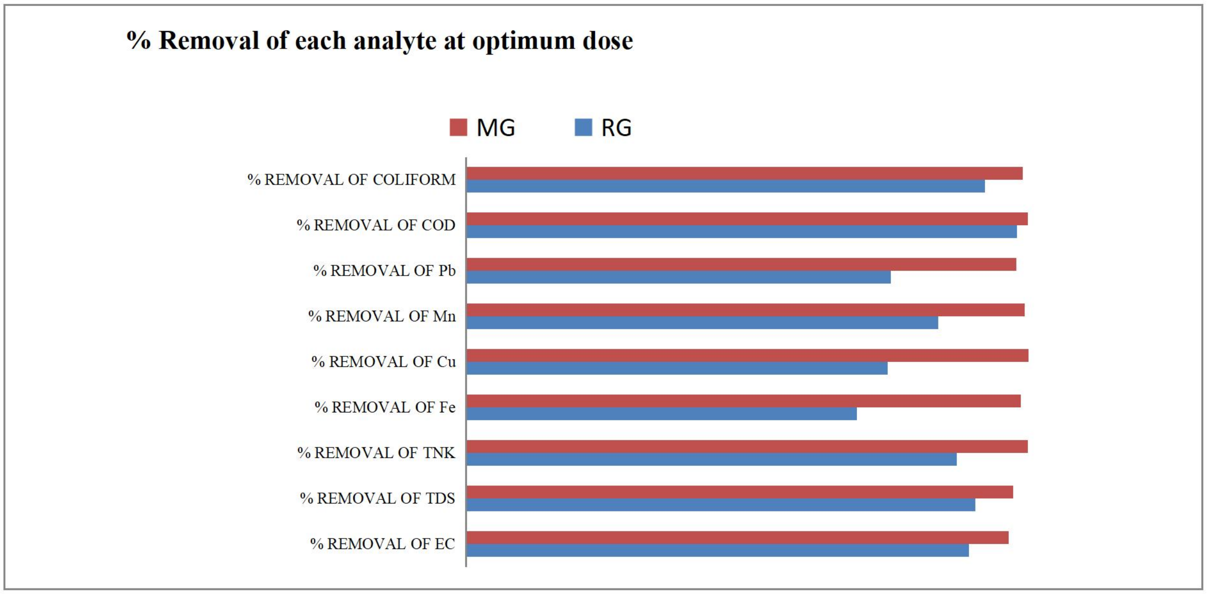


Figure. 1. Graphical Representation of Adsorption Capacity for Raw and Modified Adsorbent at Optimum dose. The percentage Removal of each analyte in palm oil mill effluent statistically indicates that the modified groundnut husk Adsorbs better.

RG: Raw Groundnut Husk

MG: Modified Groundnut Husk

Table 11: Adsorption Capacity for each Adsorbent at Optimum analyte Removal in Rubber Processing Effluent.

Parameters	Initial Conc	RG	MG
pH	4.78±0.13	5.86±0.03	6.49±0.14
EC	3823±59.92	652.00±2.00	209.67±5.51
% REMOVAL		82.95	94.52
TDS	2866.67±9.71	364.67±2.52	112.33±2.52
% REMOVAL		87.28	96.08
TNK	535.00±7.55	57.00±1.00	6.41±0.03
% REMOVAL		89.35	98.80
Iron	152.85±1.83	29.05±1.66	6.41±0.03
% REMOVAL		80.99	97.59
Zinc	48.11±0.13	11.69±0.82	3.68±0.03
% REMOVAL		75.70	96.96

Copper	53.14±0.36	10.70±0.80	1.46±0.06
% REMOVAL		79.86	99.42
Manganese	12.76±0.08	0.98±0.10	0.31±0.03
% REMOVAL		92.32	98.59
Lead	4.83±0.05	1.65±0.56	0.09±0.01
% REMOVAL		65.84	98.14
COD	4425.67±61.70	93.33±3.06	51.33±1.15
% REMOVAL		97.89	98.86
Coliform	100	15 CFU/ml	3 CFU/ml
% REMOVAL		85.00	97.00

RG: Raw Groundnut Husk
MG: Modified Groundnut Husk

Table 11 presents the adsorption performance of raw (RG) and modified (MG) *Arachis hypogaea* (groundnut husk) at optimum conditions for the treatment of rubber processing effluent. The modified adsorbent demonstrated superior removal efficiency across all parameters. pH increased from 4.78 to 6.49 with MG, indicating improved neutralization. EC and TDS removal reached 94.52% and 96.08% with MG, compared to 82.95% and 87.28% for RG. MG achieved higher reductions in TNK (98.80%), iron (97.59%), zinc (96.96%), copper (99.42%), manganese (98.59%), and lead (98.14%), significantly outperforming RG. COD removal improved from 97.89% with RG to 98.86% with MG. Coliform count decreased from 100 to 3 CFU/mL with MG, reflecting 97.00% removal, as opposed to 85.00% with RG. Overall, the modified groundnut husk exhibited markedly enhanced adsorption capacity and treatment efficiency compared to the raw form (Okieimen *et al*., 2005; Agho and Archibong 2024).

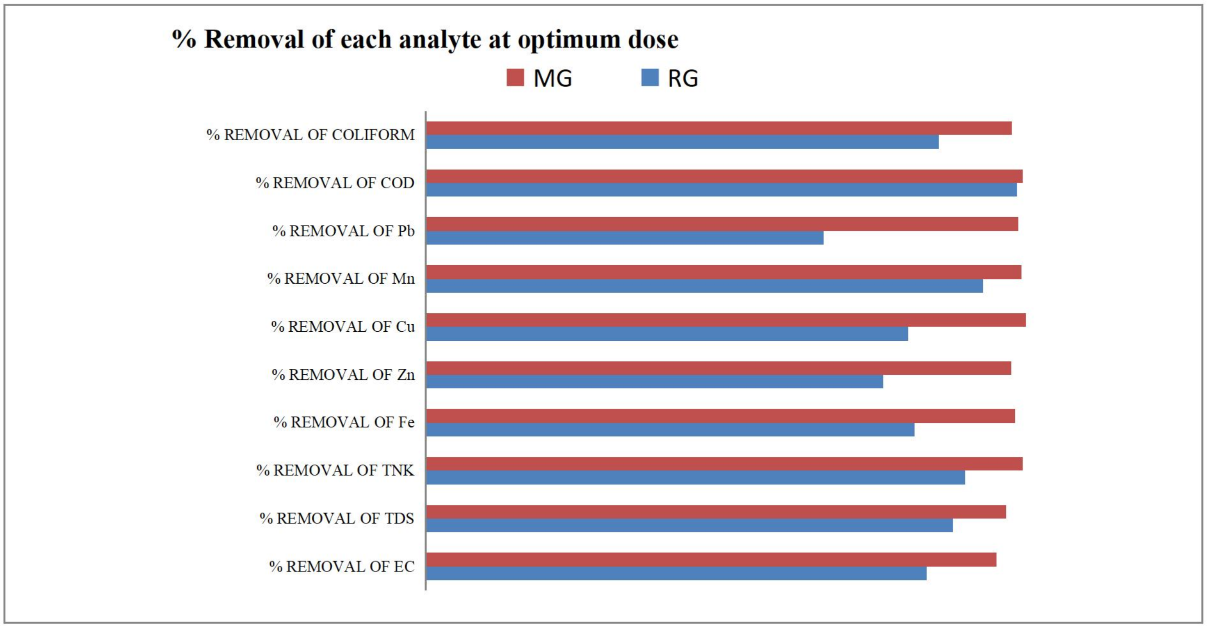


Figure. 2. Graphical Representation of Adsorption Capacity for each Adsorbent at Optimum dose. The percentage Removal of each analyte in rubber processing effluent statistically indicates that the modified groundnut husk is better than the other adsorbents.

RG: Raw Groundnut Husk

MG: Modified Groundnut Husk

Adsorption Isotherm Studies

For a better representation of the equilibrium adsorption behaviour, it is best to have a satisfactory description of the equation state between the phases composing the adsorption system (adsorbent and adsorbate). Adsorption mechanism of the interactions of cations on the adsorbents surface is better explained using the adsorption isotherms. Freundlich and Langmuir isotherm models were tested with the experimentally obtained equilibrium data from the methylene blue results (Freundlich, 1906).

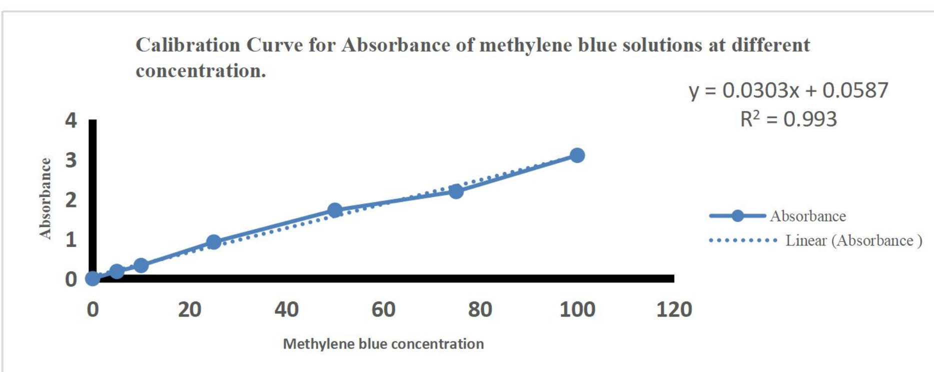


Figure 3: Calibration curve for Absorbance of Methylene Blue Solutions at different concentration.

Table 12: Results for Methylene Blue Adsorbed by the Raw and Modified Adsorbents.

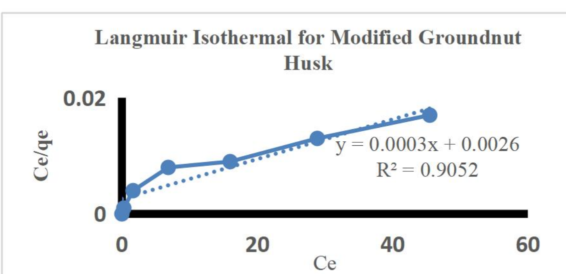
S/N	Initial conc. Methylene blue	Concentration RG	Concentration MG
1	0	0	0

2	5	1.40	0.28
3	10	4.00	1.65
4	25	11.93	6.85
5	50	25.60	16.00
6	75	43.13	28.88
7	100	62.40	45.50

RG: Raw Groundnut Hush
MG: Modified Groundnut Hush

Table 13: Results of the Effect of raw and modified adsorbents on the removal of methylene blue from its concentrates.

	Raw groundnut husk				Modified groundnut husk			
Initial conc.	**Ce**	**Amount removed**	**% removal**	**ge(mg/kg)**	**Ce**	**Amount removed**	**% removal**	**ge(mg/kg)**
0	0	0	0	0	0	0	0	0
5	1.40	3.60	72	180	0.28	4.72	94.40	236
10	4.00	6.00	60	300	1.65	8.35	83.50	417.5
25	11.93	13.07	52.28	653.5	6.85	18.15	72.60	907.5
50	25.60	24.40	48.80	1220	16.00	34.00	68.00	1700
75	43.13	31.87	42.49	1593.5	28.88	46.12	61.49	2306
100	62.40	37.60	37.60	1880	45.50	54.50	54.50	2710



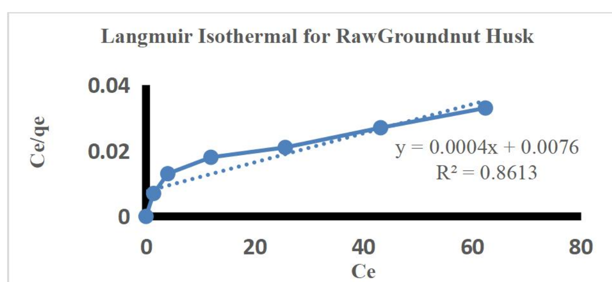


Figure 4a: Langmuir Isotherm for Raw Groundnut Husk **Figure. 4b:** Langmuir Isotherm for Modified Groundnut Husk.

The adsorption data were further analysed using Langmuir equation (Langmuir, 1916). This isotherm is applicable when the extent of adsorbate coverage is limited to one molecular layer. This isotherm equation gives the fractional coverage q in the form of;

$$q = \frac{q_{max} K_a C}{1 + K_a C}$$

Where q_{max} is maximum adsorbent uptake.

K_a is the Langmuir constant related to energy of adsorption, which quantitatively reflects the affinity between the adsorbent and the adsorbate.
The Lagmuir parameters were obtained by fitting the experimental data to linearized equation derived from the following equation;

$$\frac{C_e}{q_e} = \frac{1}{q} = \frac{1}{q_m} + \frac{1}{Kaq_m C}$$

A plot of $\frac{1}{q}$ versus $\frac{1}{c}$ resulted in a straight line graph of slope $\frac{1}{Kaq_m}$ and an intercept of $\frac{1}{q_m}$ as shown above for the four adsorbent used.

Table 14: R_L Values for the Different Adsorbents at Different Concentrations of the Analyte (Methylene Blue).

Analyte	**Initial conc**	**R_L Values for Different Adsorbents**	
		RG	**MG**
Methylene Blue	5	0.010	0.023
	10	0.005	0.011
	25	0.002	0.005
	50	0.001	0.002
	75	0.0007	0.002
	100	0.0005	0.001

RG: Raw Groundnut Husk
MG: Modified Groundnut Husk

The essential characteristics of Langmuir isotherm can be described by the dimensionless constant separation factor for equilibrium parameter R_L, which is indicative of the isotherm shape that predicts whether an adsorption system is favourable or unfavourable. According to Sunil *et al.*,2014 R_L is defined as;

$$R_L = \frac{1}{1 + K_a C_o}$$

Where K_a is the Langmuir constant.
Values of R_L are shown in the Table for varied concentration methylene blue solution respectively. For all the adsorbent used in these experiment, the R_L values falls between zero and one, ($0 < R_L < 1$), which is an indication of the favourable adsorption of the methylene blue on the adsorbents (Langmuir, 1916).

the dimensionless parameters ($R_L = 1/(1 + bCo)$ which is a measure of adsorption favourability, was found to be in the range of $0.023 < R_L$ 0.0005 ($0 < R_L < 1$) and this confirm that the analyte removal using the raw and modified groundnut husk and rubber seed shell was a favourable adsorption process.

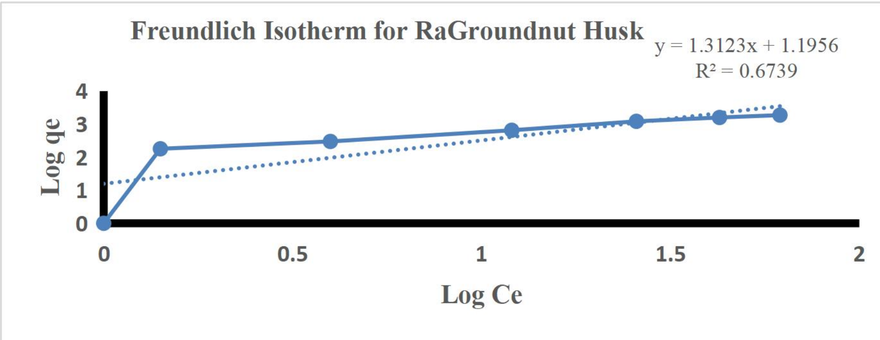


Figure 5: Freundlich isotherm for raw Groundnut husk

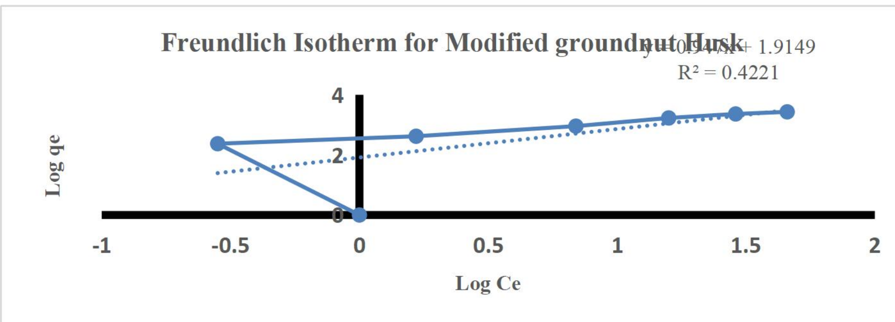


Figure 6: Freundlich Isotherm for Modified Groundnut Husk.

From Figures 9- 12 the Freundlich isotherm considers for non-ideal sorption onto heterogeneous surfaces (Freundlich, 1906). This is based on the idea that the adsorption depends on the energy of the adsorption sites. Freundlich isotherm is written as :

$$Log\ q_e = \log K_f + \frac{1}{n}\log C_e$$

where K_f is the Freundlich constant and $\frac{1}{n}$ is the heterogeneity factor.

The correlation coefficient (R^2) of the adsorption isotherm data showed that adsorption of methylene blue on the adsorbents were fitted also to Freundlich isotherm model. Sunil *et al*., 2014 states clearly that n (Freundlich coefficient) value which is between 1 and 10 confirmed the heterogeneity of an adsorbent and it indicates that the bond between the methylene blue ion and the adsorbents is strong. From the n (freundlich coefficient) values, our experimental data shows that the modified groundnut husk favourably fit into the adsorption model (Freundlich, 1906).

Table 15: Estimate of Isotherm Parameters for Methylene Blue Adsorption.

Adsorbent	**Methylene blue**	**Langmuir**			**Freundlich**		
		R^2	**Ka**	**q_m**	**R^2**	**K**	**n**
RG	Methylene blue	0.861	19.000	131.580	0.674	15.690	0.762
MG	Methylene blue	0.905	8.670	384.620	0.422	82.210	1.056

RG: Raw Groundnut Husk
MG: Modified Groundnut Husk

The Langmuir and Freundlich isotherm were used to describe the biosorption of different concentrations of methyl orange by heterogeneous periphyton surfaces by Yonghong, *et al*., 2017. The values of qm (maximum adsorption uptake) evaluate the approximate amount of methyl orange adsorption onto the biofilm. The amount of uptake by the modified groundnut husk exceeds all other adsorbent from the experimental data which further indicate its uptake ability.

Conclusion

It can be concluded that both the raw and modified groundnut husk can be considered a low cost alternative for treatment of industrial effluents for toxic metal and chemical oxygen demand removal before discharge into the environment. The effective treatment of industrial wastewater for the removal or reduction in the parameters determined is among the most important issues for many industrialized countries. Results obtained from the characterization of the materials showed that it had high potential to be employed as an effective adsorbent in removing toxics and would be useful for the design of wastewater treatment plants in most of our industries at a cheaper rate. This is just a small area of application of agricultural biomass in the production of adsorbent for cleanup of industrial effluent before its discharge, which saw many diverse requirements in preparation and characterization like many of its contemporary types from research that can serve as alternative biochar

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Acknowledgements

The author's greatly acknowledge the contributions of the members of Chemistry/ Chemical petroleum Laboratory, Department of Applied Chemical Science, Faculty of Science Laboratory Technology, University of Benin, Benin City and also the constructive comments and suggestions of the anonymous reviewers and editor that helped improved the quality of the paper.

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