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Research Paper

Adsorption equilibrium studies of *p*-Nitrophenol *onto* macadamia nutshell waste (non-activated and activated carbon) from aqueous solutions

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Abstract— Water pollution by organic pollutants has been a source of major concern because they tend to accumulate in the body to toxic levels and yet they are not easily biodegraded. *P*-Nitrophenol (PNP), has negative effects on humans such as cancer, immune system suppression, and gastrointestinal. Various technologies have undergone changes and developed for its elimination from the wastewater such as chemical sedimentation, distillation, and solvent extraction. However, these methods have limited factors such as operational cost and their non-generable nature. Adsorption has proven to be an economically viable and easy method for elimination of these contaminants from the wastewater. This study has dealt with adsorption equilibrium studies of *p*-Nitrophenol onto Macadamia nutshell in non-activated and activated form. Macadamia nutshells were subjected to base treatment then characterized The methods of scanning electron microscopy (SEM) and Fourier-transform infrared analysis (FT-IR) were utilized in this study and further investigated on the optimization batch experiments. Initial PNP ions increased with an increase in adsorption capacity between (5 – 60) mg/L, from (0.52-0.77) mg/g and (2.38-3.14) mg/g for the unmodified macadamia nutshell (UMNS) and modified macadamia nutshell (MMNS) respectively. The highest PNP ions eradication was recorded at pH 4 and the sorbent dosage in terms of PNP percentage removal increased from 67.53%, to 87.97% and 87.97% to 94.22 % with an enhancement in the dose of 0.05 g and 0.2 g at fixed PNP concentration for both the UMNS and MMNS. This is designated to a bigger number of active adsorption sites with greater availability for adsorption process in the modified material. Adsorption equilibrium for the UMNS and MMNS was attained after 30 minutes with an optimum dose of 0.1g. The presence of the amides, hydroxyl, asymmetric and antisymmetric vibrations (C-H) and amines functional groups was detected using FTIR which captured change in the chemical functional groups modification. Topography and the shape of the adsorbents was studied by the SEM. From the equilibrium models, the sorption behaviour fitted well with and the Langmuir isotherm. The method became highly efficient for making a productive MMNS alternative to renewable carbon.

Keywords— macadamia, activated carbon, p-Nitrophenol, adsorption capacity, wastewater

1. Introduction

Water is an indispensable resource on our planet, playing a vital role in the survival of every living organism. Approximately 70% of the Earth's surface is covered by water, which exists in different states and bodies, including oceans, rivers, lakes, and glaciers. [1]. Access to clean and potable water is crucial for the well-being of humans and other life forms. According to projections, by the year 2025, a majority of the global population is expected to face susceptibility due to the issue of water scarcity. [2].

In 2019, the International Phenol study group projected the global production of phenol to approximately 16.5 million tonnes. From this, almost 50% was used in the production of Bisphenol A that is commonly found in many of everyday products including food and drink containers, dental fillings, and thermal paper receipts. Phenol formaldehyde resins are a type synthetic thermosetting polymer that is prevalent across diverse application, including adhesives, coatings and molded products.

Asia leads global phenol demand, representing more than half of the total consumption, driven by its dominant market share characteristics of the compound [3].The phenolic groups that have received the most research attention are the nitrophenols, chlorophenols, methylphenols alkyphenols and diphenylmethane derivatives. As a result of their wide-ranging use in various products, phenolic compounds are discharged into the environment through industrial wastewater generated by sectors such as textile production, wool mills, industries involved in dyeing and dye intermediates, coke ovens, pulp and paper manufacturing, and iron and steel plants. [4].

Africa, has limited statistics regarding the presence of phenolic substances in the environment and aquatic ecosystem, despite the extensive utilization of these compounds in industries being frequently used for agribusiness operations in the region. However, no constraint was imposed on these pollutants., in the water especially countries located in West Africa [3]. Therefore, phenolic compounds persist as a significant issue in. the continent of Africa along with various other developing countries. Chad, central Africa and the republic of Niger are three African nations where pollution-related deaths, adjusted for population, are most pronounced [5]. As research into the potential health effects of phenolic compounds continues, it is likely that surveillance will increase to ensure that these compounds are being used safely and effectively [6].

In Kenya, water pollution is a big problem, with an approximate of 40% of the Kenyans still dependent on unsanitary sources of water such as stagnant wells, dams, rivers, streams, ponds for survival. These sources suffer from bacterial contamination and pollution from heavy metals and organic pollutants [7,8]. This is attributed to pollutants originating from agriculture, untreated sewage, and water rich in nutrients from fish farming. [8]. Organic substances exhibit toxicity, leading to skin irritation and allergies. Furthermore, their carcinogenic nature poses significant health hazards to living organisms including the fish population and other aquatic creatures impacting the people who depend on the lake as their primary source of sustenance and as a source of drinking water [9,10].

Wastewater from industrial sections, contains the phenolic compounds that are toxic because they lie in the category of persistent pollutants from studies [11]. Therefore, it is of great need to remove them from the water and this has remained a big task for the research scientists concerning the environment and aquatic life. Human activities, including factory related, farm-based and man-made practices, have resulted in the initial part of numerous pollutants into the aquatic ecosystem. Among these pollutants, a significant portion consists of synthetic organic compounds [12].

Phenols are present in soil and sedimentary material, where they pollute both groundwater and surface water. Effluents generated by chemical companies have the potential to harbour considerable levels of phenols. Research has demonstrated that phenols are prominent compounds that occur organically and are additionally generated through human activities within the environment.

Conventional wastewater treatment methods, including chemical coagulation, electrocoagulation, membrane desalination bioremediation and adsorption, can be employed to eliminate contaminants from liquid waste streams [13]. Among these techniques of water treatment, adsorption is a favoured choice among numerous researchers and industries due to its multitude of advantages in comparison to alternative treatment methods [14–16]. It is a cheap, effective, efficient, easier to learn and can operate at a low energy supply.[16,17].

Adsorbents that have been used in the sorption of PNP, include activated carbon derived from olive cake [4], pyrolyzed pine sawdust [17], fir saw dust activated carbon [18], activated carbon from acacia glauca saw dust [19], oil palm kernel shell and kaolinite, among others[20]. These adsorbents can be regenerated, as well as be rinsed and recycled for many other additional adsorption cycles. After the aqueous solution has undergone treatment procedure, it is released into the environment for re-use [14-16].

Macadamia (Macadamia spp.) is recognized for its delicate taste and numerous health benefits, this nut is widely celebrated as the finest and most exceptional in the world. In Kenya, it is cultivated as a valuable crop and plays a significant role in generating foreign revenue, contributing approximately 10% to the global output of macadamia nuts. [21]. Macadamia genus consists of 10 species but only two species, smooth shelled and rough shelled varieties are specifically grown for their delectable edible nuts (Macadamia integrifolia- Maiden & Betche and M.tetraphyla L. A. S Johnson) respectively [21]. Macadamia was introduced in Kenya in 1946 but currently, genetic enhancement of macadamia is based on introductions from other countries and special cultivars are selected from existing cultivars. Macadamia nuts are used in the manufacture of oil because of the high vitamin E content [1].

Macadamia nut shells are normally discarded as wastes but they are quite hard and can cause damage to lawnmowers and other equipment if not properly disposed. Macadamia nut shell as a biological lignocellulose material, comprises of the lignin cellulose and hemicellulose component intimately bound to lignin which possesses a complicated chemical structure with both phenolic as well as alcoholic hydroxyl groups being accessible in the structure [23]. The main function of lignin is to impart rigidity and strength to the cell wall by acting as a structural matrix. Therefore, the method of preparation and the carbon precursor are the considerations that will determine the texture and outer layer properties of the content.

Activation is done to increase the adsorbing power of an adsorbent and is often made to alter the physical characteristics like functional groups, roughness, external area, external charge external energy and surface reactivity [24]. The types of adsorbents majorly used in adsorption comprise: porous alumina, silicon dioxide gel, activated charcoal, carbon chemical sieve, zeolite selective adsorbent and polymer adsorbents. Activated carbon is a type of carbon that undergoes processing to create finely divided carbon particles with a small volume. can be used for reactions [25]. Various agricultural residues have been employed as primary commodities for the manufacturing of activated carbon. They encompass a variety of sources, such as rice chaff [25], coir fiber [26], coir pith [27], sago waste [28] among others. The application of activated charcoal has been extensively promoted for the purpose of eliminating pollutants in wastewater, owing to its highly porous molecular structure and significant surface area. Moreover, through physical and chemical treatments, it can be further modified to enhance its adsorption capacity. [29–31].

Isotherm models such as Jovanovich, Langmuir, Freundlich, Dubini-Radushkevich (D-R) isotherm, Redlich-Peterson, Kobie-Corrigan, Vieth-Sladek, Radke-Prausnitz, Toth, Temkin, Liu, Sips, Brouers-Sotolongo among others are used to describe interaction in the behavior of the pollutants [32–34,18]. Langmuir discusses sorption occurrence at homogenous active site on the outer layer of the adsorptive material [35] while Freundlich presumes the happening on a heterogeneous surface [36]. Dubini-Radushkevich is widely employed to explain the sorption isotherms of individual substrate systems. and is similar to Langmuir but does not agree with homogenous steadfast sorption affinity Dubini-Radushkevich postulates the adsorption mechanism by filling of the pore by the sorbent and not layer by layer sorbent surface coverage [37].

The aim of this study is to assess the elimination of p-Nitrophenol from wastewater through the process of adsorption, employing activated carbon derived from macadamia agricultural residue. Sample activation is the act of adjusting the physical and chemical properties of a material’s surface to different ones from the ones initially found on the surface of that material so as to make it suitable for the purpose at hand[38]. Activation is frequently employed to modify surface characteristics, including functional groups, hydrophobicity, morphology, surface area, surface charge, surface energy, and reactivity. [24].

2. Related Work

Comparable research has been conducted to investigate the elimination of an extremely toxic phenolic compound., possessing a nitro group situated opposite to the benzyl alcohol moiety from wastewater by employing adsorption with activated carbon from acacia glauca saw dust [19].

As a highly toxic compound, PNP can negatively impact different systems and organs within the human body. It can potentially cause adverse effects on the respiratory system, cardiovascular system, nervous system, liver, and kidneys. PNP exposure has been associated with respiratory issues, such as irritation of the airways and difficulty in breathing. It may also contribute to cardiovascular problems, including heart-related disorders. Research was done to show that extended exposure to p-Nitrophenol indicated that it could result in immune system impairment, respiratory issues, fatigue, and the development of cancer [39]

To protect animal populations from the harmful effects of PNP, it is crucial to minimize their exposure to this toxic compound. Implementing proper waste management practices, adopting measures to prevent PNP contamination of natural habitats and ecosystems, and promoting environmental regulations can help mitigate the risks and safeguard the well-being of animals in our surroundings. Elsewhere, it was also studied that when rats were exposed to p-Nitrophenol, there was increased met-hemoglobin and leukemia with a high toxicity just on oral and dermal exposure [40]. Furthermore, the National environmental Agency has identified p-Nitrophenol as one of the most toxic, bio accumulative, and persistent organic compounds, capable of causing detrimental effects on both humans and animals even at extremely low concentrations The EPA's recognition of PNP's toxicity, bio-accumulative nature, and persistence underscores the importance of minimizing its release into the environment and adopting appropriate measures for its removal and remediation [41].

Similar findings regarding PNP removal have provided valuable insights into the potential use of melon-based adsorbents in water treatment applications. By utilizing natural and modified adsorbents like melon, it has been possible to develop efficient and environmentally friendly methods for the eradication of PNP from polluted water sources [42] and the removal PNP [19].

3. Experimental Method

3.1 Materials

The pre-existing solutions used in this study were prepared using purified water and the reagents employed were of high analytical purity. The PNP reagent used was of a purity of 98%, sodium hydroxide (98%), acetic acid (99.7%), and sodium acetate 98%. All the mentioned chemicals were bought from Kobian limited, Nairobi Kenya. Macadamia nuts were bought from Nyeri local market and transported to the Dedan Kimathi University Research laboratory.

Adsorbate

Stock solutions containing PNP with a concentration of 1000 µg/l were developed using water that had undergone distillation. The target concentrations were prepared by progressively diluting the concentrated solutions. Solutions of 0.1 M NaOH and 0.1 M HCl were used to modify the pH. The sodium acetate buffer was utilized to maintain the pH of the stock solution. Fresh solutions were prepared for every batch experiment throughout the working period.

Adsorbent

Macadamia nuts were bought randomly from Nyeri local market and transported to the Dedan Kimathi University Research laboratory. The kernels were then washed with tap water to remove dirt then rinsed further with highly purified water to remove impurities. The clean dried nuts, were then crushed and the inner content utilized as food while outer coverings were separated, washed and dried. They were crushed into small pieces using a hammer and air dried to eliminate moisture. Potassium hydroxide (KOH), was used for the modification of the adsorbent. Therefore, small pieces of cleaned and dried macadamia wastes of approximately 300 g were weighed on platinum containers. They were introduced into the muffle furnace and subjected to a thermal state of 600 °C for a duration of 2 hours. o produce bio char. A 100 g of the macadamia bio char was then weighed and placed in a 500 mL beaker. A 200 mL of 5 M KOH was then added i.e. a ratio of 1:2 bio char: alkali respectively [43]. The content was then soaked for 3-4 hours stirring periodically. The content was thoroughly cleaned using distilled water several times until the pH of the bio char was neutral. The content was then obtained on a filter paper. The contents were then oven dried at 105℃ for 24 hours prior to analysis [44].

3.2 Methods

Instrumentation
The identification of the functional groups present in the UMNS and MMNS was carried out using Fourier Transform Infrared Spectroscopy (FTIR) with the IRT Tracer-100 instrument manufactured by SHIMADZU in Japan. The experiments employed a Lab-line SSL2 Mechanical oscillating shaker model manufactured in Harrogate, UK. The pH solution was carefully monitored using the pH meter (*HANNA* model). The UV-Vis Spectrophotometer was utilized to analyze the amounts of p-Nitrophenol in the filtrate solution.

Scanning electron microscope
By scanning an electron beam across the sample's surface and subsequent scattering of electrons from the sample's surface, an SEM image was generated, manifesting as a distinctive signal[45].

FTIR Analysis
1 mg of the adsorbent was blended with 50 mg KBr. The combination was subsequently pulverized into a fine powder after which it was then pressed under vacuum into pellets. The pellets were then analyzed using FT/IR-4700, JASCO made in Japan FT-IR spectrophotometer.

Batch equilibrium experiments
Batch experiments were used to optimize pH, contact time, initial phenolate ion concentration and adsorbent dosage. Sorption experiments were executed using 100 mL screw top containers placed on a reciprocating shaker model, operating at 170 rpm. The effect of these parameters on the absorption process was optimized by altering the specific parameter of interest while holding the other factors steady. [46]. All the parameters were examined utilizing the UV-Vis spectrophotometer (Specord 200, Analytik Jena) for analysis.at optimal absorption wave magnitude of 400 nm [47].

Effect of pH
The influence of hydrogen ion concentrations on the uptake of PNP ions by UMNS and MMNS was examined by creating a 20 mg/L solution from a stock solution of PNP with a concentration of 1000 mg/L. Therefore, six pieces of 100ml volumetric flasks were obtained and labelled (2-6) pH. 2 ml of PNP stock solution was pipetted into each of the volumetric flasks. Acetate buffer solution prepared by Handerson Hassel-batch equation for respective pH ranges was added in each bottle. The pH of the solutions was then buffered with acetate buffer solution. 20ml was obtained from each flask and poured in empty 100 ml conical flasks. 0.1g of the absorbent material was subsequently introduced. The composite was then agitated for 1 hour at 170 rpm, then filtered. The concentration of PNP ions in the filtrate was then determined.

Effect of contact time
To investigate this, 0.1g of UMNS and MMNS adsorbents were combined with 20 mL of a PNP ions solution with a concentration of 20 mg/L in conical flasks. The pH of the solution was adjusted to 4 using a 0.1 M sodium acetate buffer. The mixtures were equilibrated for pre-determined time intervals of 1-180 minutes on a shaker at 170 rpm. The solutions were obtained via filter paper number 1 and their concentrations obtained.

Effect of adsorbent dosage
The impact on PNP sorption on the raw and activated adsorbents involved altering the amount of the adsorbent within the range of 0.025 to 200 mg to examine its influence. 20 ml of 20mg/L PNP stock solution was added on each of the sample. The solutions were buffered under the recommended parameters of pH 4 and contact duration of 30 minutes was used for both UMNS and MMNS adsorbents. The compound was equilibrated and the filtered solution examined for PNP ions.

Effect of initial PNP ions concentration
This was investigated through density variation of the PNP ions from 5-60 mg/L in batches of 20 mL solution containing 0.1g of the UMNS and MMNS adsorbents. The mixture buffered at pH 4 was stirred at 170 rpm then filtered and the concentration, obtained.

The quantity of phenolate ions absorbed per unit mass of adsorbent was calculated using equation 1.[48].

$$qe = (co - \frac{Ce}{\mathrm{m}})V \tag{1}$$

Where, qe represents the adsorption capability, while V (L) denotes the overall volume of the uniform liquid containing phenolate ions, and m (g) represents the mass of the adsorbent material.

pH$_{\mathbf{PZC}}$
The isoelectric point of the UMNS and the analysis of MMNS adsorbents was conducted using the described approach. by Singh *et al.*, (2015). In a set of beakers, a 50 mL solution of NaCl with a concentration of 0.01 M was prepared. The pH of the solution was modified within a range of 2 to 6 by introducing 0.1 M HCl and 0.1 M NaOH solutions. To prepare the solution, 0.1 g of the adsorbent was added and agitated for 48 hours until reaching the desired final pH.

Adsorption isotherms
Adsorption isotherm analyses were employed in this case to determine the efficiency of activated macadamia nutshell waste [43]. Freundlich and Langmuir isotherm simulations were used to provide physico-chemical interaction as well as establish the peak adsorption capacity of the adsorbent.[50]. Using optimum conditions obtained from the optimization analysis, the experimental data was organized and fitted to both Langmuir and Freundlich isotherm models 2 and 3 to come up with the adsorption potential.

$$\frac{Ce}{qe} = \frac{Ce}{qmax} + \frac{1}{qmax}b \qquad (2)$$

Where Ce is the equilibrium concentration of PNP ions in solution (mg/L), qe is the amount of PNP ions adsorbed per unit weight of the adsorbent (mg/g). Constants q_{max} and b are the attributes of the Langmuir equation.". q_{max} is the maximum adsorption capacity (mg/g) and b is the energy of adsorption (L/mg). Therefore, a plot of Ce/qe against Ce gives a straight line and this plot is used to obtain the Langmuir constants.
The freundlich isotherm simulation was established by applying Freundlich [51] linearized equation 3 to the experimental data.

$$In\ qe = \ln K\,F + \frac{1}{n} ln\ Ce \qquad (3)$$

Where qe is the quantity of solid ions adsorbed (mg/L) at equilibrium, Ce denotes the final concentration at equilibrium (mg/L), K_F (adsorption capacity) and n (adsorption intensity) are freundlich constants. A plot of ln q_e against ln Ce gave a straight line that used to determine K_F and n from the intercept and slope respectively.

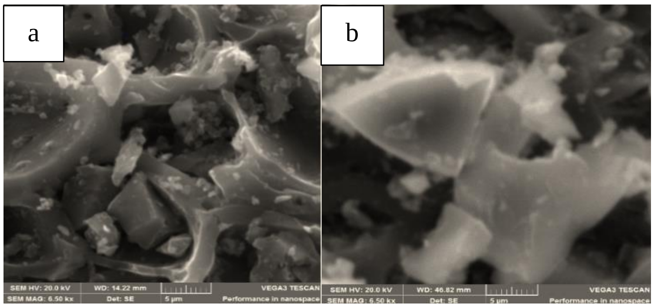
This was done in 100 mL Erlenmeyer flasks comprising 20 mL PNP ions solutions of varying concentrations between 5-60 mg/L at 25±0.5° C and optimum conditions of: 0.1 g adsorbent dosage; 30 minutes, contact time; and solution pH of 4.0 for both the UMNS and MMNS adsorbents. After the equilibrium time, the concentration of the PNP ions was determined [52].

All these was achieved in 100 mL Erlenmeyer flasks containing 20 mL PNP ions solutions of varying concentrations between 5-60 mg/L at 25±0.5℃ and optimum conditions of: 0.1 g adsorbent dosage; 30 minutes, contact time; and solution pH of 4.0 for both the UMNS and MMNS adsorbents. After the equilibrium time, the concentration of the PNP ions was determined [52].

4. Results and discussion

Results obtained from the characterization process of unmodified and modified adsorbents using SEM and FT-IR were expressed as actual concentrations (qe (mg/g). and discussed. Optimization findings and equilibrium models, were also explained.

Scanning Electron Microscope (SEM) Analysis



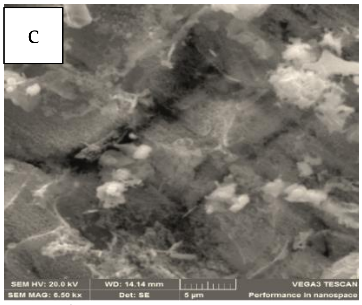


Figure1: SEM images for (a) UMNS (b) MMNS (c) MMNS loaded with PNP ions

From the figure 1, UMNS image (a) revealed a relatively even exterior and a stratified composition devoid of significant cavities. MMNS image (b) demonstrated intensive fragmentation on the surface and depolarization of the parent polymer that led to increased number of pores. The fragments in the MMNS structure implies that lignin and cellulose had been broken down. This can be elucidated by the fact that activation in alkaline matrix is favourable for the adsorption of the PNP ions. This is because oxidation of cross linked carbon enhanced the texture of the material that led to the development of the porosity [18]. Therefore, activation of the material with KOH increases the surface area that enhances adsorption characteristics [23]. Comparable findings were made by [21,34]. Figure 1 (c) shows that after adsorption of PNP ions, the ions covered outermost part of the adsorbent with pores. The loaded PNP ions macadamia nutshell structure was more rigid with restrained surface which was attributed to PNP ions occupying the pores.

FTIR Analysis

FTIR spectra of unmodified and modified macadamia nutshell adsorbent in different capacity is presented by figures 2 - 5.

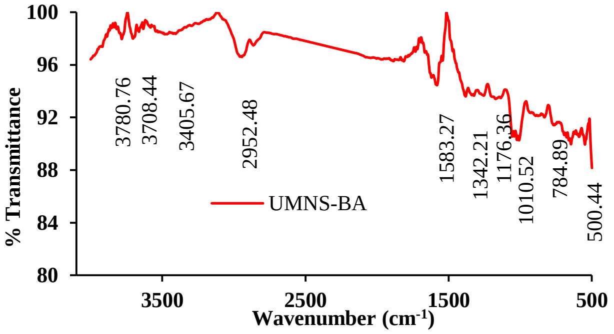


Figure 2: Fourier transform infrared spectrum for UMNS adsorbent before adsorption

The spectral features observed at 3780.76 cm-1 and 3708.44 cm-1 in figure 2 represent the stretching vibrations of the O-H, N-H, and C-H molecular groups, indicative in the single bond region of between (2500-4000) cm^{-1} [55]. The source of these peaks can be an aromatic primary amines and secondary alcohols or amides. The spectral peak observed at 3405.67 cm -1 represents the stretching vibratory motions of the hydroxyl (-OH) chemical functionalities. From studies, the frequency range between (3500-3200) cm^{-1} of the FT-IR spectrum show peaks corresponding to -OH bonds [35,36]. The absorption region at 2952.48 cm^{-1} is designated to $-CH_3$ and $-CH_2$

symmetric and asymmetric vibration stretch whose source is aliphatic groups in carboxylic acid [57]. The indication at 1583.27 cm^{-1} is attributed to N-H bend available in macadamia material biomass while the peaks at 1342.21 cm^{-1}, 1176.36 cm^{-1} and 1010.52 cm^{-1} are designated to -CH_2 bend, C-O-C group and C-O stretching vibrations from UMNS [55]. The intensive peaks between 800 cm^{-1} and 450 cm^{-1} are consistent to C-O and off-plane N-O derivatives [55].

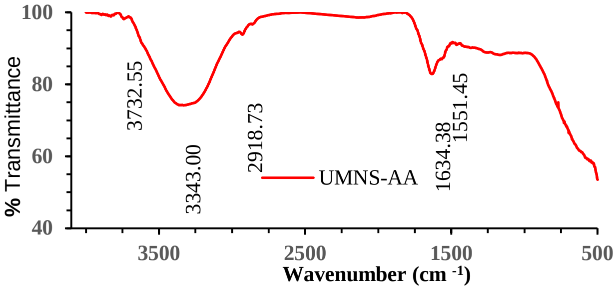


Figure 3: Fourier transform infrared spectrum for UMNS adsorbent after adsorption

The small peak at 3732.55 cm^{-1} as seen in figure 3 is designated d to N-H stretching vibrations from the amide groups in the nutshell [55]. A broad peak between (3555-3200) cm^{-1} is designated to -OH stretching vibrations from hydroxyl functional groups of PNP and alcohols [53]. Narrow small peak at 2918.73 cm^{-1} is designated to the vibrational stretching of C-H bonds." and anti-symmetric vibratory motions from the MMNS. The peak at 1634.38cm^{-1} assigned to C=C stretching aromatic vibrations in the regions of the MMNS This peak only appeared after adsorption whose source is PNP. The peaks at 1551.45 cm^{-1} is designated to an N-H bend from ammonium salts in the UMNS material [18].

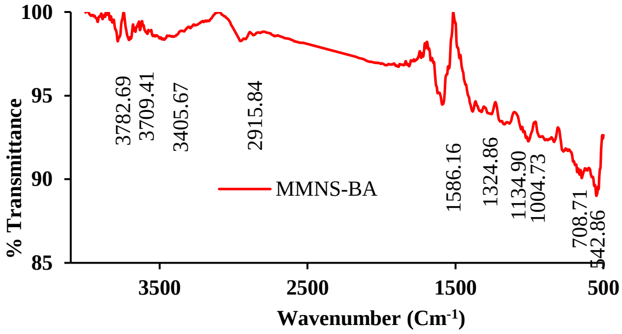


Figure 4: Fourier Transform infrared spectrum for MMNS adsorbent before adsorption

From the spectrum in figure.4, small peaks at 3782.69 cm^{-1} and 3709.41 cm^{-1} lying in the single bond region with either O-H, N-H or C-H are attributed to amide functional groups that gives narrow peaks between (3600-3645) cm^{-1} [58] . A peak at 3405.67 cm-1 is designated to an O-H stretch from either secondary or tertiary alcohol and phenols. The peak at 2915.84 cm^{-1} is designated to C-H symmetric and anti-symmetric vibration, which reduced after modification because of deprotonation that had occurred to a large extent [53]. This means that there is availability of negative charge that will aid in the process of adsorption. A comprehensive peak at 1586.16 cm^{-1} is allotted to N-H vibrations from the amides found in the aromatic moiety of the nutshell substrate [53]. The minor peak at 1324.86 cm^{-1} is designated to -CH_2 in the MMNS material. They became weaker and reduced in size because of loss of cellulose and hemicellulose after modification [53]. A broad peak at 1004.73cm^{-1} is designated to C-O-C stretch vibrations that falls within the range of between (1050-1155) cm^{-1} of the spectrum and is from alcohols or alkyl substituted ethers [59]. There are sharp small peaks between (800-450) cm^{-1} identical to N-O an out of plane bending derivatives and C-O vibrations MMNS [58]. According to Yan *et al.*, (2108), the availability of the reactive sites implicated in the sorption led to chemical transitions in surface chemical anchors during modification. Therefore, revelation of diverse electron-rich moieties such as amino groups, amine groups and NH2 groups resulted in donation of an electron to the acceptor aromatic ring framework of PNP, thereby revealing this phenomenon. Additionally, NO_2 being an electron accepting group increased interactions between the PNP and the sorbent material resulted in intensified eradication f PNP [60].

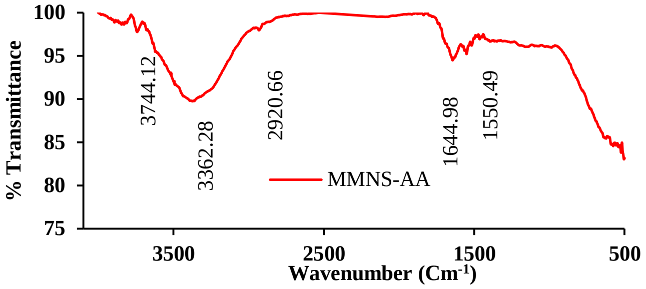


Figure 5: Fourier Transform infrared spectrum for MMNS adsorbent after adsorption

In figure 5, the infrared spectra of the MMNS after sorption, shows very small peaks at 3744.12 cm^{-1} designated to N-H stretching vibrations from amides. The broadening of the peak at 3362.28 cm^{-1} is designated to overlap of the -OH stretching oscillation of the carboxylic acid and *p*-Nitrophenol following adsorption had taken place [18]. From studies, OH group vibrations are often highly responsive to the surroundings since they exhibit significant spectral changes in hydrogen-bonded species [61]. There are functional groups that had been involved in hydrogen bonding causing broadening of the peaks. The peak at 2920.66 cm^{-1} is designated to C-H symmetric and asymmetric vibrations. The peak at 1644.98 cm^{-1} is allotted to C=C vibrational mode aromatic oscillations in the aromatic regions of the MMNS and the peak at 1550.49 cm^{-1} is designated to N-H bend from PNP [61]. There is a decrease in the N-H peak, because it has been used in the adsorptive phenomenon.

Optimization Experiments

The effect on pH

The influence of pH remains a significant factor for the PNP ions removal because of the influence it has on both the solution chemistry and the adsorbent's surface properties. The electrical surface potential of the MMNS relies on the pH of the solution. The findings were presented in figure 6

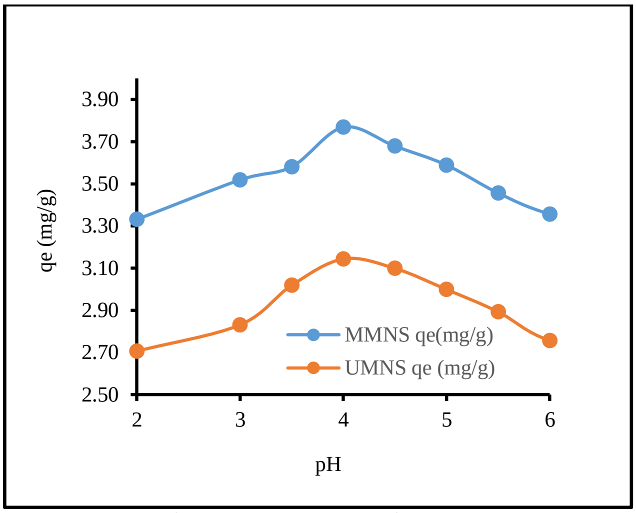


Figure 6: Impact of pH on the bio sorption of PNP ions onto UMNS and MMNS adsorbents *(V, 20 ml; C_0, 20 mg/L; dosage, 0.10 g; pH 3; T, 298 K; agitation rate, 170 rpm; contact time, 30 minutes).*

Results from figure 6 clearly showed that the adsorption capacities of PNP ions for both UMNS and MMNS amplified as the pH level rose to an upper limit of pH 4 (3.143 mg/g) and (3.768 mg/g) respectively. PNP is an acid with low acidity and exhibits a pKa value of 7.15. When starting pH solution was in acidic range, majority of the adsorbate were in molecular form [19]. The surfaces of the MMNS were protonated producing more H^+ ions which predominated as solution hydrogen ion concentration was less than the isoelectric point (pH_{PZC} = 4.1) according to figure 10. The adsorbent surface experienced repulsive electrostatic forces, leading to a reduction in the amount of adsorption that took place. At the optimum pH, the adsorbent surface exhibited a nearly neutral net charge, which eliminated any repulsive forces on the adsorbent limiting repulsion and therefore adsorption capacity was maximum (3.769 mg/g and 3.144 mg/g) for the MMNS and UMNS separately. As the pH increased to higher than 4, towards alkaline, the concentration of H^+ decreased meaning repulsion was also decreased leading to deprotonation. The removal ability increased from 3.144 mg/g to 3.769 mg/g in unmodified and chemically altered forms respectively. This is designated to the N-H groups on the surfaces of the adsorbent which possessed a negative charge when the pH was greater than the pH_{PZC} developing a high affinity for PNP ions. This is line with figure 2.6 by surveys executed by Dhorable *et al*., (2016) and Popovici *et al*., (2021). In this state, electrostatic repulsion predominated between the adsorbate and the adsorbent causing a considerable decrease in the removal capacity of PNP ions. This was designated to increase in disintegration of PNP ions and the concentration of H^+ because of an increase in diffusion barrier of the negatively charged PNP ions [62]. The findings are in agreement with the documented observations in prior investigations [19,63].

The effect on contact time

The effect of the interaction period on the removal of PNP ions by UMNS and MMNS was examined by altering the agitation time in 10-minute intervals. The experimental data was obtained and Figure 7 showcases the observed outcomes.

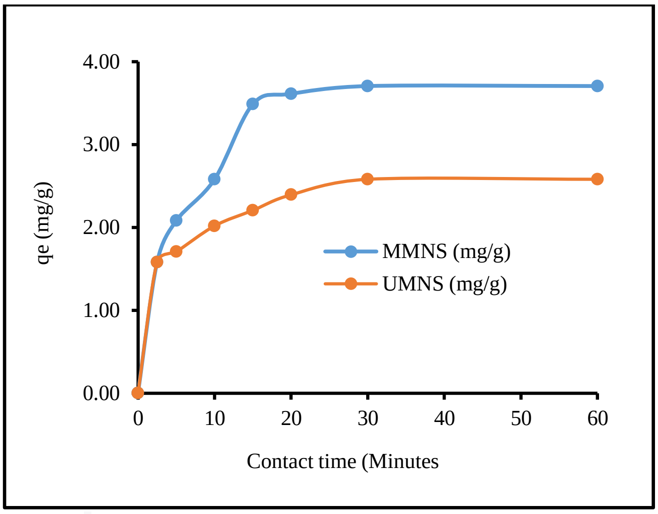


Figure 7: The correlation between the duration of contact and the adsorption efficiency of PNP ions on UMNS and MMNS adsorbents: *(V, 20 ml; C_0, 20 mg/L; dosage, 0.10 g; pH 3; T, 298 K; agitation rate, 170 rpm; contact time, 30 minutes).*

The results in figure 7 showed a rapid increase in contact time with a peak adsorption capability of 2.581 mg/g and 3.706 mg/g for both UMNS and MMNS respectively. This occurred within optimum time (30 minutes), beyond which the uptake decreased and then stabilized. A stable equilibrium condition is obtained because of complete occupancy of binding sites [64]. Rapid uptake of the PNP ions was attributed to the more binding sites which were available initially. Both adsorbents attained equilibrium within a shorter duration of time with increased removal capacity from 2.581 mg/g to 3.706 mg/g for the unmodified and modified adsorbents respectively. Yadav *et al*., (2019) and Ndiritu *et al*., (2021), made similar conclusion.

Effect on initial concentration

The effect of the initial concentration of PNP on its removal was investigated by gradually changing the concentration within the range of 5 to 60 mg/L, while maintaining the other parameters at their optimized levels for both UMNS and MMNS. The results were illustrated in the figure 8.

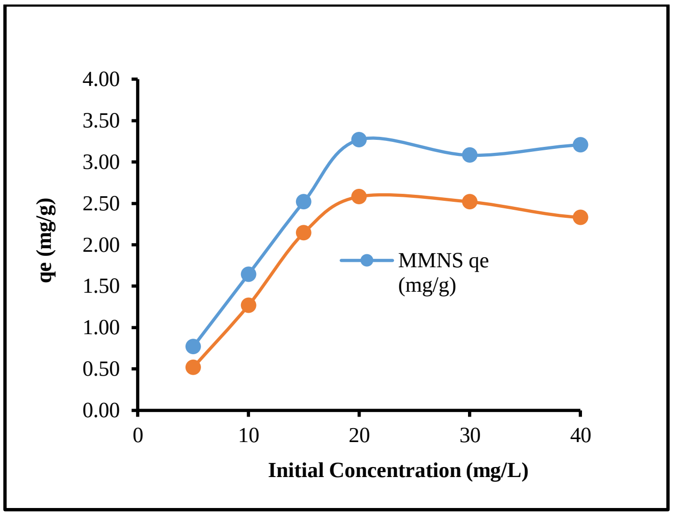


Figure 8: The correlation between the initial concentration and the adsorption capacity of PNP ions on adsorbents (V, 20 ml; C_0, 20 mg/L; dosage, 0.10 g; pH 3; T, 298 K; agitation rate, 170 rpm; contact time, 30 minutes).

The adsorption capacity intensified as the starting concentration of the PNP ions rose from 0.5187 mg/g to 2.331 mg/g as well as 0.7687 mg/g to 3.144 mg/g for the UMNS and MMNS respectively. The reason for this is, at starting concentration, there was accessibility of functional sites for the adsorption of the PNP ions. Nevertheless, with the elevation of concentration, the utilization of active sites persisted as PNP ions reached their peak adsorption of 20 mg/ L depleting the availability of these sites. Once a plateau was reached, it indicated that there were no further active sites available to adsorb the remaining PNP ions. [65]. The modification of the adsorbent improved the adsorption process as a result of an augmentation in the porosity of the a 66-68dsorbent surface and micro rough texture. Similar findings were documented in previous results by [54], [66-68].

The impact of dosage concentration

The influence of the adsorbent dosage on the absorption of PNP ions was examined by adding varying amounts of the adsorbent, ranging from 0.025 g to 0.2 g, to a fixed 20 mL solution containing PNP ions with a concentration of 20 mg/L. Results were obtained and illustrated in figure 9.

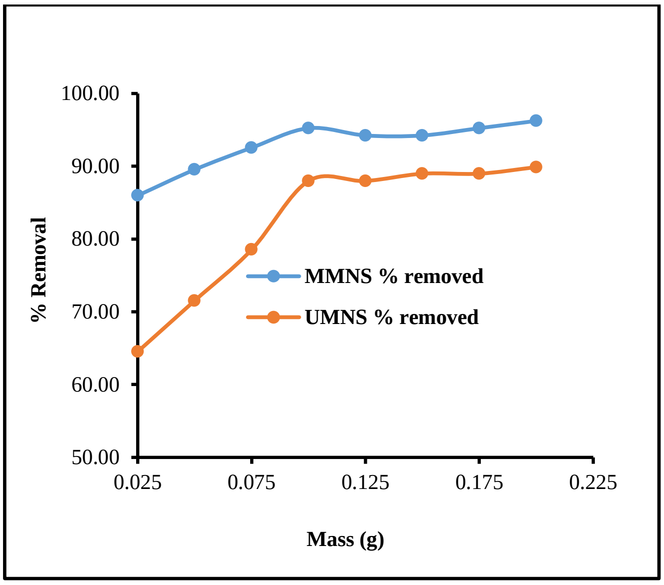


Figure 9: Impact of sorbent dosage on the adsorption of PNP onto UMNS and MMNS adsorbent *(*V, 20 ml; $C_{0,}$ 20 mg/L; dosage, 0.10 g; pH 3; T, 298 K; agitation rate, 170 rpm; contact time, 30 minutes*).*

The findings depicted in figure 9 exhibited a rise in the percentage of removal. of PNP ions, up to an optimum of 0.1 g (94.22 % for MMNS and 87.97 % for UMNS) beyond which slight increase in the removal of PNP ions was observed. Higher percentage removal at higher adsorbent dosage is attributed to increases in surface area resulting from adsorbent biomass and also there is an overlap of the binding sites decreasing the rate of adsorption and saturation effect of adsorption active sites because of the interaction of the particles. Percentage removal increased from and to 87.97 % and 94.52 % after chemical modification [69]. At maximum point, the adsorbent adsorbed as many PNP ions as it could and any additional dosage of the adsorbent would not result in further adsorption [65]. Findings are in line earlier reported findings by Tang *et al.*, (2007) and Ndiritu *et al.*, (2021).

Point zero charge

The ΔpH versus pH plot obtained from the solid addition method was used to analyze the point of zero charge of the adsorbent [70]. The pH_{Pzc} was found to be 4.10 for both the UMNS and MMNS adsorbents as shown in figure 10.

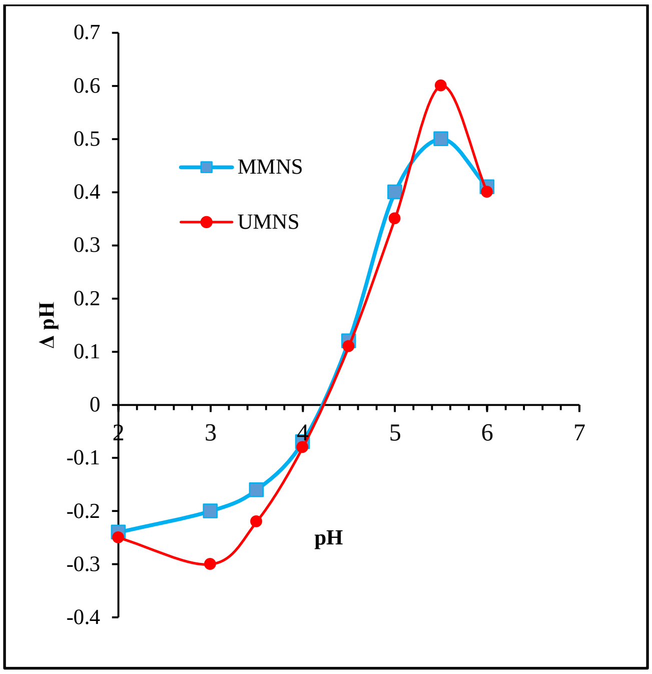


Figure 1: Determination of point zero charge for UMNS and MMNS

During the investigation on the process of adsorption, it was noted that the solution exhibited a rise in pH when the adsorbent was added. The result of the isoelectric point obtained, indicated that surface charge of the adsorbents exhibited a positive net charge below the point of zero charge pH_{Pzc} and a negative electrostatic charge above the $pH_{Pzc.}$ Consequently, the adsorption of cations on a surface with a negative charge and anions on a surface with a positive charge was facilitated [71]. At lower pH, values (pH. <pH_{PZC}), the outer layer of the adsorbent displayed an increased concentration of protonated -OH groups, resulting in a higher abundance of H^+ ions. This phenomenon influenced the adsorbent and its basic groups, (NH_2, N=N) of the PNP molecules becoming positively charged. The positively charged PNP molecules permeated the arrangement and configuration of the empty spaces within the adsorbent material's structure by substituting H^+ on absorbing medium leading to an elevation in the adsorption of PNP molecules [72]. Comparable results were acquired by Prasant *et al.*, (2016) and Yadav *et al*., (2019).

5. Equilibrium studies

Efficiency of the adsorbents on PNP was confirmed using the Langmuir and freundlich isotherms. Fig. 11 shows the Langmuir plot of PNP removal by UMNS and MMNS and Figure 12, a representation of Freundlich plot.

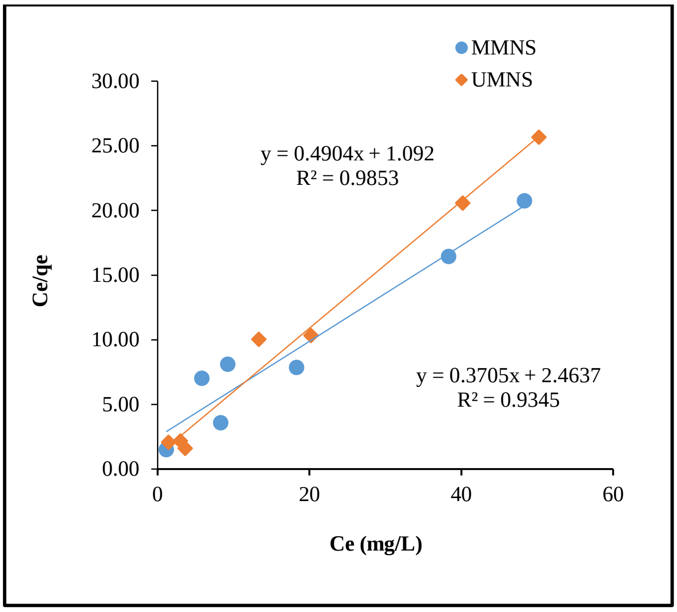


Figure 10: Langmuir isotherms for adsorption of PNP ions on MMNS & UMNS

The activation of the material with KOH increased the surface area that enhanced efficiency in the adsorption characteristics because of the best pore structure observed in the SEM, which was reflected in the best fit for the Langmuir isotherm.

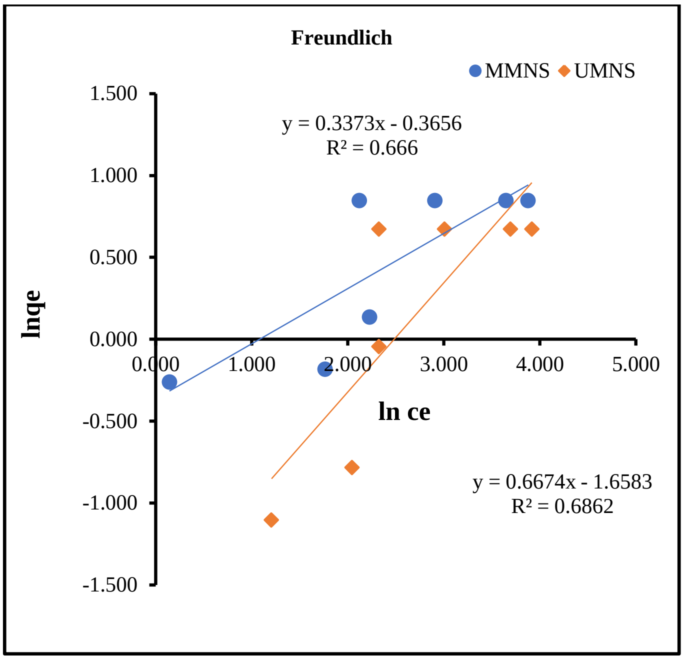


Figure 11: Freundlich Isotherms for adsorption of PNP ions on MMNS & UMNS

From figure 12, the R^2 for both the UMNS and MMNS adsorbents were < 0.9 meaning that the adsorption studies did not fit well with the Freundlich isotherm. It also suggests that the adsorption process may not be adequately be described by the Freundlich model.

The recorded parameters from both models are presented in Table 1

Table 1: Equilibrium models and their calculated parameters:

Equilibrium models	Adsorbent	Parameters	Values
Langmuir isotherm	UMNS	b (L/mg)	0.4491
		Q_{m}. cal. (mg/g)	2.0390
		$Q_{m.}$ exp. (mg/g)	1.9560
		R_2	0.9853
	MMNS	b(L/mg)	0.1504
		$Q_{m.}$ cal. (mg/g)	2.6990
		$Q_{m.}$ exp (mg/g)	2.3333
		R_2	0.9345
Freundlich isotherm	UMNS	1/n	0.6674
		R_2	0.6862
		$K_{F\ (mg/g)}$	0.4309
	MMNS	1/n	0.3337
		R_2	0.6666
		$K_{F\ (mg/g)}$	0.0220

When the Langmuir constant (b) = 0, favourable when 0< b <1, linear when b =1 and unfavourable when b >1. An elevated b value signifies an enhanced affinity of the adsorbent towards PNP ions [73].

Results in Table 1 for UMNS and MMNS adsorbents gave R^2 >0.9000 for Langmuir adsorption model which demonstrated that the adsorption of PNP ion is monolayer and chemisorption in nature [68], as shown in figure 11. The MMNS adsorbent had higher adsorption capacity than UMNS, an effect of chemical modification. The value of b < 1 showed an increased affinity of PNP ions for both the UMNS and MMNS adsorbents [62,18]. The adsorption capacity *(q_{max})* of PNP ion was in conformity with experimental data by Dhorabe *et al*., (2016). From the results obtained in FT-IR, the basic moieties containing nitrogen and graphitic structure could function as Lewis bases because they have available π electrons that participated in weak Interactions between the aromatic rings of the PNP molecules involving π-electrons [18, 60, 65].The activation of the material with KOH increased the outer layer area that enhanced efficiency in the adsorption characteristics because of the best pore structure observed in the SEM, which was reflected in the best fit fort the Langmuir isotherm [23].

6. Conclusion

The FT-IR results confirmation showed that the UMNS adsorbent contained amine (-NH_2) and nitro (NO_2) functional groups, while the MMNS adsorbent contained hydroxyl (-OH) and (-COOH) groups in addition which are favorable for adsorption. This supports the objective of activating carbon derived from macadamia nutshell using KOH. Therefore, the modification significantly improved the adsorption properties of the material. The parameters of pH, contact time, sorbent dosage on PNP ions concentration highly affected the adsorption capacity of the PNP ions. The uptake of PNP ions was enhanced through chemical modification, resulting in improved adsorption capacity of 2.333 mg/g for MMNS compared to 1.956 mg/g for the UMNS and gave a comprehensive explanation of Langmuir isotherm model. Characterization of the adsorbent by the SEM increased morphology and surface morphology adsorbent. This improved adsorption of PNP due to more adsorption sites which were exposed through modification that caused interaction between the adsorbent and the target molecules. In general, in conclusion the macadamia nutshell wastes have the potential to effectively remove PNP ions from any industrial wastewater when modified with KOH

Data Availability
Data will be available and accessible through the designated channels. The author will ensure this by either depositing it in a reputable data repository or by providing access upon request. This will facilitate transparency, reproducibility, and the potential for further analysis or validation by other researchers in the field hence promote collaboration and contribution to the advancement of scientific knowledge.

Conflicts of interest
The authors declare no competing interests associated with this research and agree to submit the work to the Journal "International Journal of Scientific Research in Chemical Sciences'' The work has not been published to another journal.

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Author's contribution
The author's investigation into the adsorption properties of activated carbon derived from macadamia nutshell brings not only scientific advancements but also potential benefits to society. By successfully enhancing the adsorption capacity through chemical modification with KOH, the author's work paves the way for more efficient and cost-effective removal of PNP ions from industrial wastewater. This holds significant promise for addressing environmental pollution and ensuring cleaner water resources. Furthermore, the utilization of macadamia nutshell waste as an adsorbent showcases the potential for sustainable waste management practices, reducing waste accumulation and promoting a circular economy. Overall, the author's contribution contributes to both scientific understanding and practical applications, ultimately benefiting society by tackling water pollution and promoting sustainable solutions.

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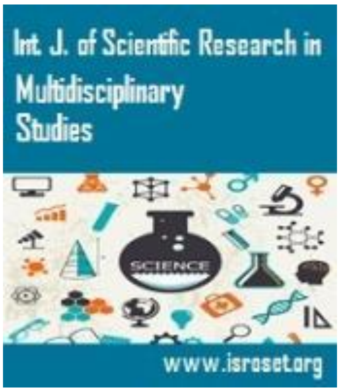
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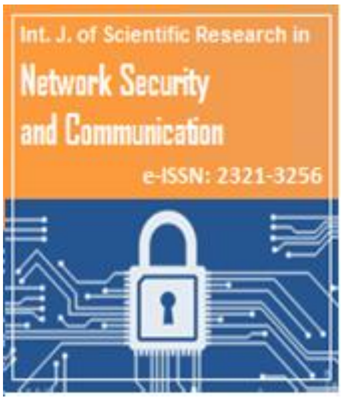
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