Science Forum (Journal of Pure and Applied Sciences)

journal homepage: https://atbu.edu.ng/science-forum/

Development of Activated Carbon and NaOH Modification for the Removal of Nickel Metal Ions from Oil Spilled Environment in the Niger Delta Region

Alexander Asanja Jock [1]*, Ago Mikyitsabu Atoshi[2] and Christiana Aloysius Edet[1]

[1]*Department of Chemical and Petroleum Engineering, University of Uyo, PMB 1017, Uyo, Nigeria*

[2]*Department of Chemical Sciences, Federal University Wukari, Taraba State, Nigeria*

ABSTRACT

The present study deals with the adsorptive removal of nickel ions from liquid phase hydrocarbons by unmodified and NaOH modified activated carbon developed from coconut shell. The activated carbon was characterized using Fourier-Transform Infra Red spectroscopy (FTIR) and scanning electron microscope (SEM). The effect of contact time and metal ion concentration on the adsorption of nickel onto unmodified and modified activated coconut shell was investigated. The initial metals ion concentration ranged from 20mg/L to 150mg/L and the maximum removal was observed at metal-ions concentration 150 mg/L. The Ni (II) ion removal efficiency was 97.76% and 96.76% for modified and unmodified activated carbon respectively. Langmuir and Freundlich isotherm models were used for equilibrium adsorption data. Langmuir isotherm proved to be a better fit. The linear and non-linear model for Pseudo first order and pseudo second order kinetic models were applied to analyze the kinetic mechanism of adsorption. Pseudo second order gains the dominance of chemisorption mechanism.

ARTICLE INFO

Article history:
Received 07 February2023
Received in revised form
08 March 2023
Accepted 08 March2023
Published 19 July 2023
Available online 19 July2023

KEYWORDS
Adsorption,
Activated carbon,
Nickel
Wastewater

1. Introduction

The exploration, production, and consumption of petroleum products are increasing worldwide, and the threat of oil pollution increases accordingly (Fingas, 2012). The movement of petroleum from the oil fields to the consumer involves many different modes of transportation including tankers, pipelines, railcars, and tank trucks (Etkin, 2011). The main sources of oil spill on the Niger Delta are vandalization of the oil pipelines by the local inhabitants, ageing of the pipelines, oil blowout from the flow stations, releases, both accidental and deliberate, from oil tankers on the high sea and the disposal of used oil into the drains by the road side mechanics. By far the most serious source of oil spill is through the vandalization of pipelines either because of civil disaffection with the political process or as a criminal activity (Omofonmwan and Odia, 2019).

***Corresponding author** Alexander Asanja Jock ✉ alsanja@gmail.com ✉ *Department of Chemical and Petroleum Engineering, Uni. of Uyo*

Oil spill is the release of liquid hydrocarbons into the environment resulting from human activities. It is considered as one of the biggest problems caused by petroleum industry in Nigeria. Frequent oil leakages from different oil facilities have polluted the air, soil, drinking water, and fishing creeks. It has destroyed many mangrove swamps and farmlands in the region. This has led to serious economic losses to local inhabitants, who depend mostly on fishing and subsistence farming for their livelihoods (Udoetok, 2015).

Spilled oil is usually recovered through the application of skimmers, sorbent, fire resistance, booms and dispersants. Several physical, chemical and biological methods such as coagulation/flocculation treatment, biodegradation processes, oxidation methods, membrane filtration, ozonation, ion exchange, irradiation, precipitation, reverse osmosis, and adsorption have been employed to removal pollutants from industrial effluents (Kumar *et al.,* 2017). Among these methods, adsorption has been found to be superior to the other techniques and it is increasingly used to remove heavy metals from the oil spilled waste water, due to its low cost, flexibility, simplicity, and ease of operation, insensitivity to toxic pollutants, high removal efficiency and environmental compatibility (Oribayo*et al.*, 2020; Pandey *et al.*, 2020a, 2020b; Siddiqui *et al.,* 2016).

Activated carbon is a microcrystalline, non-graphite form of carbon that has been process to develop internal porosity characterized by a very large specific surface area. Activated carbon is extremely porous with a very large surface area, which makes it an effective adsorbent material. This large surface area relative to the size of the actual carbon particle makes it easy to remove large amounts of impurities in a relatively small enclose space (Bansal and Goyal, 2015). Materials such as coal, bones, sawdust, palm kernel shells and coconut shells, wood, peat, lignite, nut shells and fruit stones have been used for activated carbon manufacture.

Coconut shells are excellent materials to produce activated carbon due to their high carbon content and hardness (Ratnoji and Singh, 2014). Coconut shell is composed of carbonaceous materials like lignin, cellulose and hemicellulose. Activated carbons produced from coconut shells have a tighter and more microporous structure. This is due to the inherent pore structure of the coconut shell. This micro porosity itself makes it a very efficient adsorbent (Liyanage and Pieris, 2015).

When crude oil is spill, the consequence is the release of petroleum hydrocarbon into the environment. The characteristics of the oil affect the way the oil spreads as well as the hazard it might pose to the affected environment. Among the physicochemical processes that have proved useful for this, adsorption onto activated carbon is especially important because it is difficult to decompose organic substances and heavy metals can be selectively removed by activated carbon.

Heavy metals find their way into the effluent from industries such as mining, metal processing, tanneries, pharmaceuticals, pesticides, organic chemicals, rubber and plastics, lumber and wood products, fuels and petroleum, and photographic materials (Okafor *et al.,* 2016).

This study is aimed at treating wastewater contaminated by oil spillage using activated carbon developed from coconut shell. The removal efficiency of the heavy metal ion by the activated carbon in the oil spilled wastewater will be determined. Isotherm and kinetic studies on adsorption mechanism of nickel metal ion on the coconut shell activated carbon adsorbent will also be conducted. The choice of coconut shell over other waste raw materials is due to its availability and low cost.

2.0 Materials and methods

2.1 Samples collection and modification

The coconut shell sample was collected at Akpan Andem market, Akwa-Ibom, Uyo. South-South, Nigeria. The coconut shell was washed with water to remove dust and fungus. The sample was sun dried for 48 h and further dried in an oven at 110°C for 4 h. 1kg of dried sample was pulverized and sieved through 75µm. 200g of sieved sample was pre-carbonized in a muffle furnace at 300^{o}C for 12 h. The sample was then withdrawn from the furnace and cooled in a desiccator.

10g of pre-carbonized sample was measured into 250 ml beaker containing 2M of NaOH solution in 1:5 ratio. The sample was carbonized in a muffle furnace at 600^{o}C for 12 h and cooled in desiccators. It was then washed several times with de-ionized water until a pH range between 7 and 8 was obtained. The

washed activated carbon sample was dried in an electric oven at 105°C to a constant weight. The modified and unmodified samples were characterized and used for adsorption experiments.

2.2. Sample characterization

Developed activated carbon adsorbent was characterized for chemical composition, surface morphology and functional groups. The chemical compositions of the activated carbon samples were determined by energy dispersive X-ray fluorescence of the model PW4030 X-ray photometer that uses a rhodium anode tube. The sample film was placed firmly in a waxed and gold-plated sample holder. The energy dispersive patterns were obtained with the help of a computer attached to the instrument and each compound recorded in percentage. The micro- structure and functional groups of the samples were determined using scanning electron microscopic (SEM) and Fourierinfra-red transform equipment respectively.

2.3 Preparation of stock solution

The solutions of heavy metals ions were prepared from analytical grade of nickel (II) Sulfate Heptahydrate,$NiSO_4.7H_2O$. Stock solutions of 1000 mg/L concentrations for Ni (II) metal ions were prepared by dissolving $NiSO_4.7H_2O$ in 1 L of distilled water. Thereafter, the stock solutions were further diluted to obtain working solutions to desired initial concentration (20, 40, 60, 90,120 and 150mg/L).

2.4 Batch adsorption

The adsorption process was carried out by varying metal ion concentrations and contact time for isotherm and kinetic studies, respectively. For the effect of contact time, 50 mL of each Ni (II) ion solution was added in a 100 mL volumetric flask containing 0.5g of the activated carbon. Beakers containing the solution were kept in an orbital shaker at various contact times (10–60 mins.) and constant speed of 200 rpm at 25°C. After each time, the mixture was filtered and the metal concentration remaining in the supernatant was analyzed by an atomic absorption spectrometer (AAS). For the effect of initial concentration, standard metal solutions ranging from 20 to 150 mg/L were prepared by diluting the stock solutions. 0.5 g of activated carbon sample was mixed with 50 mL of the metal solution in 150 mL Erlenmeyer flasks. The mixture was shaken at 200 rpm stirring rate and at 25°C for 30 minutes. The suspension was filtered and the residual concentrations of heavy metal were analyzed using an atomic absorption spectrometer (AAS) (Shimadzu, AA-6880 Series, Japan).

The adsorption capacity and percentage removal of nickel (II) ion by the activated carbon for each sample was calculated using Eq. 1.

$$q_e = (C_0 - C_e) \times \frac{V}{m} \qquad (1)$$

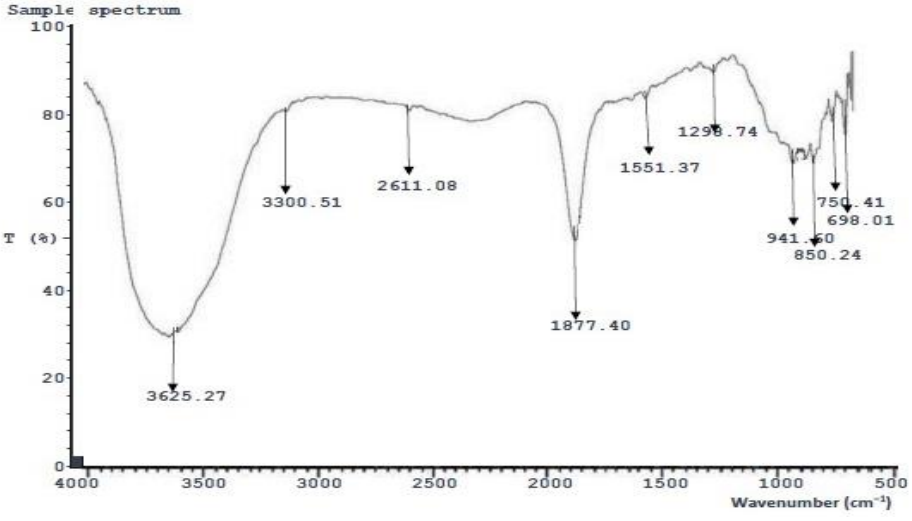
Where C_o is the initial concentration (mg/L), C_e is the concentration at final equilibrium (mg/L) of metal ion solution, V volume of the metal-ion solution in (L), m is the amount of adsorbent in (g).

3.0 Results and discussion

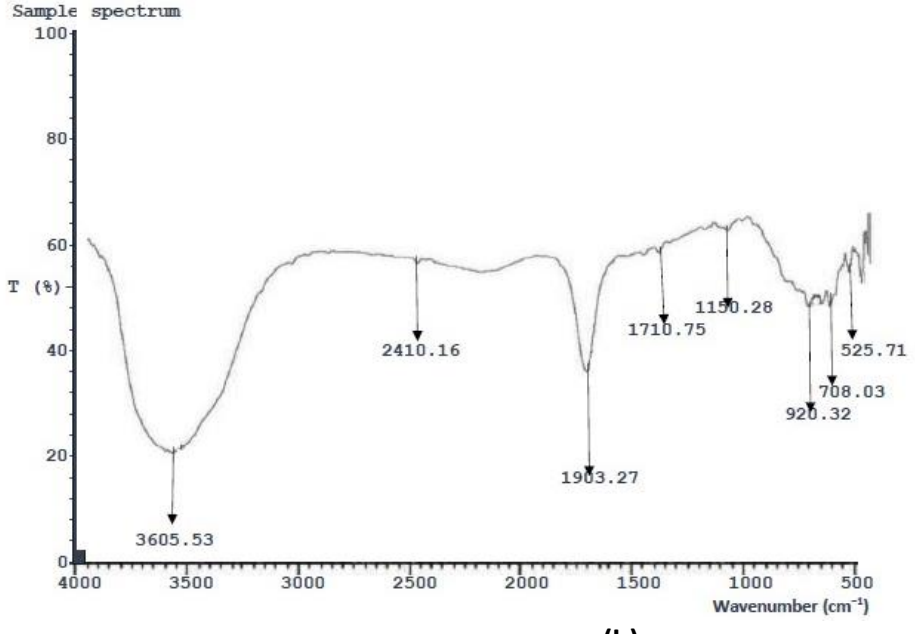
3.1 Fourier transform infrared

The spectra of both samples revealed the existence of different functional groups with either a disappearance, reduction or broadening of the peaks after the process of modification with NaOH.

The FTIR spectrum of the sample is shown in Figure 1. The spectra of modified (Fig, 1a) and unmodified (Fig. 1b) activated carbon are in the wave number range of 4000 – 500 cm



(a)



(b)

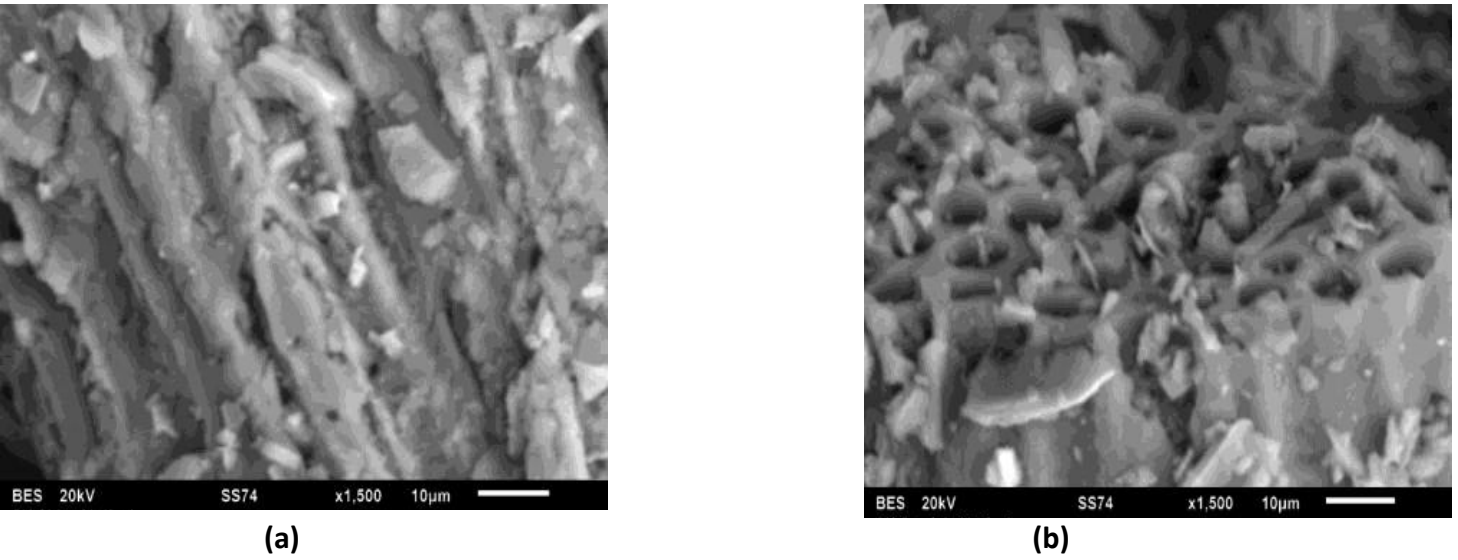
Figure1: FTIR spectrum for (a) modified and (b) unmodified coconut husk activated carbon

The band width observed at 3625.27-3605.53 cm^{-1} was assigned to O–H stretching of hydroxyl groups such as hydrogen bonding. N–H stretching for amine was observed at 3300.51cm^{-1}. Some major detectable peaks at band widths 2611.09-2410.16, 1903.27-1877.40, 1710.75-1551.37, 1298.77-1150.28 and 941.60-920.32 cm^{-1} were assigned to aldehyde group (C-H stretching), aromatic (C-H bending), ester (C-O stretching) and alkenes (C=C bending) respectively. The appearance of hydroxyl functional group in the modified sample may be due to the interaction of the activated carbon with NaOH used for the

modification. Generally, the FTIR revealed the presence of alcohol, amine, aromatics, aldehydes and alkene in the sample.

3.2 Scanning Electron Micrograph

The SEM images of unmodified and modified activated carbon are shown in Fig. 2a and 2b.



(a) (b)

Figure 2: Micrograph of activated carbon from coconut husk activated carbon (a) unmodified and (b) modified

Figure 2(b) shows that the pores on the activated carbon were enlarged after treatment using 2M NaOH. The development of these pores in the modified sample may be due to the effects of modification agent at high temperature which broke down the lignocellulosic materials followed by volatilization of volatile compounds (Bello *et al.* 2019). This demonstrated that modification of the sample with NaOH leads to the development of pores on the precursor surfaces, thereby leading to activated carbon with large porous surface areas and structures. The development of pores coupled with an enhanced surface area is requisite properties of an effective adsorbent. The presence of these pores in the both samples indicates potential sites for adsorption (Jock, *et al*. 2021).

3.3 Effect of initial concentration

The removal efficiency of Ni (II) ions is calculated using Eq. 1;

$$\%R = \frac{C_i - C_f}{C_i} \qquad (1)$$

% R is the amount of metal ions removed, C_i and C_f are the initial and final concentrations (mg/L) of the metal ions respectively. The percentage of Ni (II) ions removed increases gradually for both modified and unmodified adsorbent as initial metal ion concentration increases until equilibrium is attained as shown in Figure 3. This is because at higher initial metal ion concentration, the active site of the adsorbent would be surrounded with more metal ions which get locked-up in the free pores of the adsorbent and the trapping pores becomes limited for adsorption to occur (Jock *et al*. 2020).

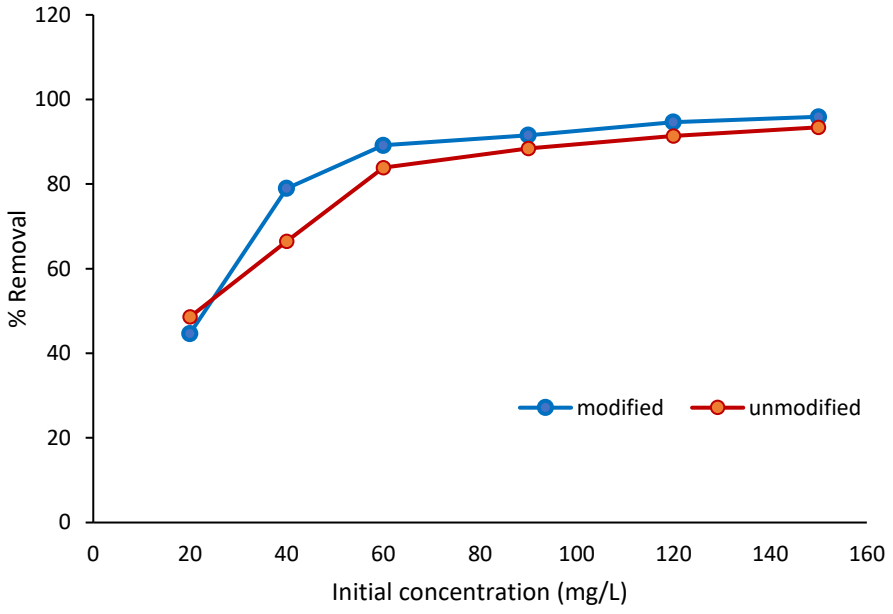


Figure 3: **Effect of initial concentration on Ni (II) adsorption onto modified and unmodified activated carbon**

3.4 Adsorption isotherms

The isotherm models employed on the experimental data were Langmuir and Freundlich. The adsorption parameters evaluated are summarized in Table 1. The Langmuir isotherm provides information on uptake capabilities and it shows the equilibrium adsorption behaviour. The sorption isotherm is based on a homogeneous surface with identical active sites and restricted to a monolayer (Akpomie and Dawodu, 2015). The linear and non linear form of Langmuir isotherm model is given by Eq. 2 and 3 respectively.

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (2)$$

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (3)$$

q_m is the Langmuir constant for maximum adsorption capacity, and b is the Langmuir constant. The parameter q_e(mg/g) is the quantity of metal ions adsorbed on the activated carbon. The constants q_m and b presented in Table 1, were evaluated from the slope and the intercept of the linear plot of C_e/q_e against $C_e$as shown in Figures 4 and 5.

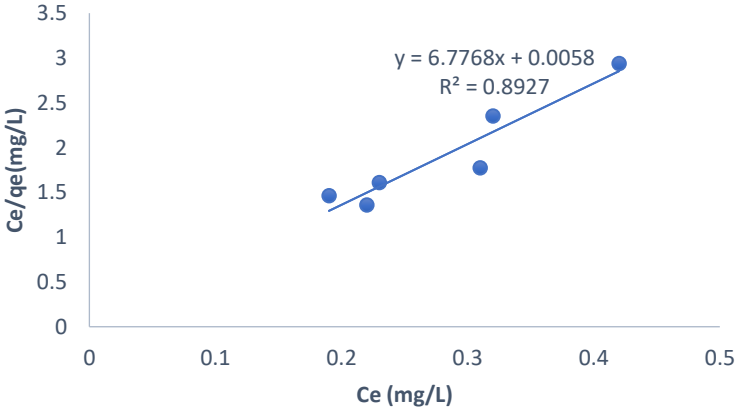


Figure 4: Langmuir isotherms for adsorption of nickel (II) ion onto unmodified activated carbon.

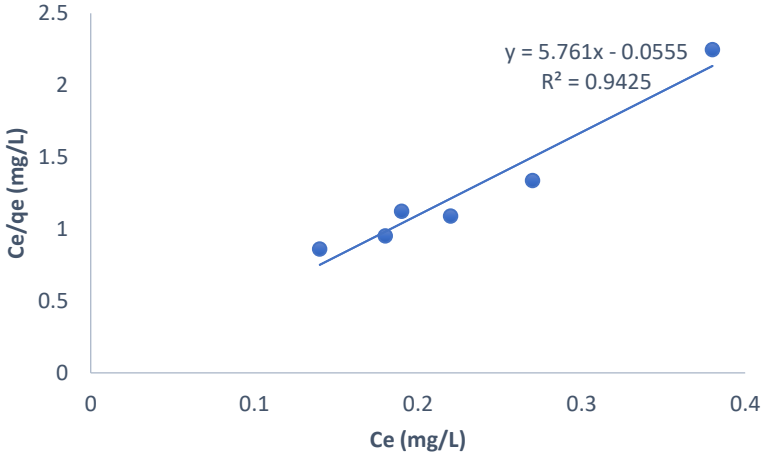


Figure 5: Langmuir isotherms for adsorption of nickel (II) ion onto unmodified activated carbon.

Table 1: Langmuir isotherm constants for Ni (II) adsorption onto activated carbon for Linear and non-linear models.

Sample	Linear			Non-linear		
	q_m(mg/g)	b (l/mg)	R^2 (%)	q_m (mg/g)	b (l/mg)	R^2 (%)
Modified	0.176	-104.96	89.27	0.199	49.895	97.97
Unmodified	0.184	-6.374	90.25	0.160	44.159	96.4

The Freundlich isotherms is an empirical expression based on multilayer adsorption on a heterogeneous surface. The linear form of this model is given by Eq. 4and non-linear by Eq. 5.

$$\text{Log}\, q_e = \text{Log}\, k_f + \frac{1}{\text{n}}\text{Log}C_e \qquad (4)$$

$$q_e = K_f\, C_e^{1/\text{n}} \qquad (5)$$

Where, q_e is the equilibrium constant of adsorbate in solid phase (mg/g) and C_e is the equilibrium concentration of the adsorbate in liquid phase (mg/L), K_f is the Freundlich constant related to the sorption capacity (mg/g) $(\text{mg/L})^{1/\text{n}}$ and n is a dimensionless constant related to the adsorption intensity of the adsorbent.

Figures 6 and 7 are plots of log $q_e$versus log $C_e$with the slope 1/n and the intercepts logK_f. The Freundlich model parameters K_f and n are summarized in Table 2. The K_f values are 0.197 $(\text{mg/g})/(\text{mg/L})^{1/\text{n}}$ for the modified and 0.160 $(\text{mg/g})/(\text{mg/L})^{1/\text{n}}$ for unmodified activated carbon.

The significance of the n value is as follows: n < 1 (chemical process); n = 1 (linear) and n > 1 (physical process). The positive values for 'n' in the modified and unmodified activated carbon in non-linear model represent physical process while the negative values of 'n' in the linear model show chemical process. The experimental data fitted well into Langmuir isotherms with correlation coefficient (R^2) of 97.97% for modified and 96.40% unmodified in the non-linear model. It demonstrated that adsorption for all nickel metal ions is by monolayer adsorption on the homogeneous surface. This also shows the homogeneous distribution of active sites on the surface of adsorbent having the same affinity for adsorption with no interaction between the adsorbed molecules. Similarly, the value of 1/n which is less than one indicates that the adsorption process follows a normal Langmuir isotherm (Lee and Zaini, 2020). However, the negative values obtained for the constants in the linear model indicates that the linear method just verify the hypothesis of linear regression instead of verifying the theory of adsorption model. These negative results show the real complexities and problems in estimating the isotherm and kinetic parameters by linearization technique. (Jock *et al.,* 2021).

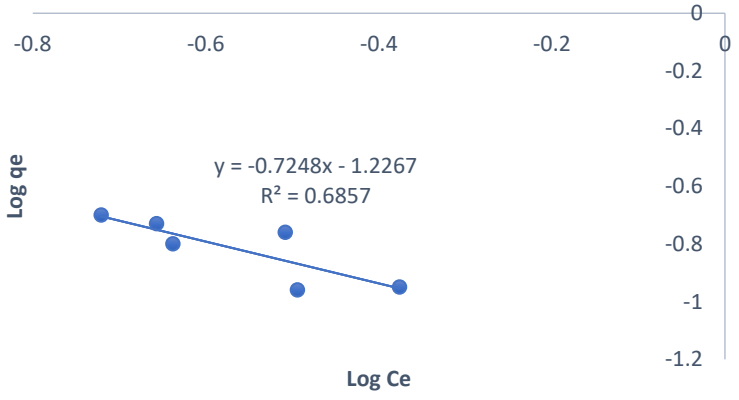


Figure 6: Freundlich isotherms for adsorption of nickel (II) ion onto unmodified activated carbon.

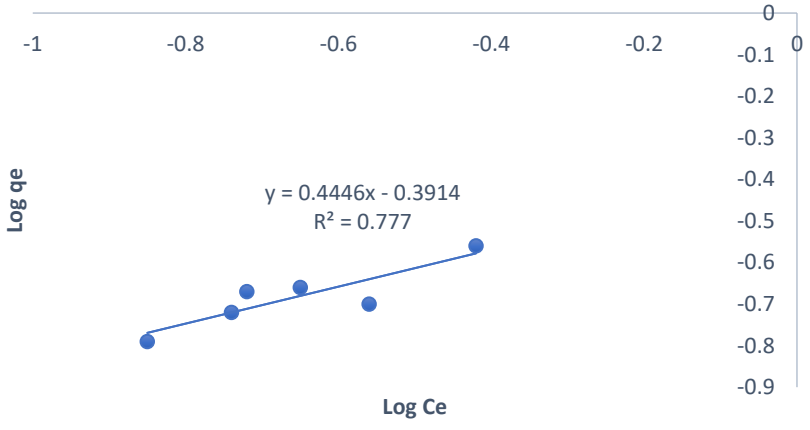


Figure 7: Freundlich isotherm for adsorption of nickel (II) ion onto modified activated carbon.

Table 2: Freundlich isotherm constants for Ni(II) adsorption onto activated carbon for linear and non-linear models

Samples	Linear			Non-Linear		
	K_f(mg/g).(L/mg)$^{1/n}$	n(l/mg)	R^2 (%)	K_f(mg/g).(L/mg)$^{1/n}$	n(l/mg)	R^2 (%)
Modified	0.406	-2.249	77.7	0.1979	18.041	95.78
Unmodified	0.1844	-1.379	68.58	0.1600	16.932	93.96

3.5 Adsorption kinetics

Pseudo first order and Pseudo second order kinetic models were applied to evaluate the adsorption mechanism of the experimental data. The pseudo first and second order kinetic linear models are given by Eq. 6 and Eq. 7 respectively.

$$Log\ (q_e - q_t) = \text{Log}\ q_e - (\frac{k_1}{2.303})t \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_{e2}} + \frac{t}{q_e} \quad (7)$$

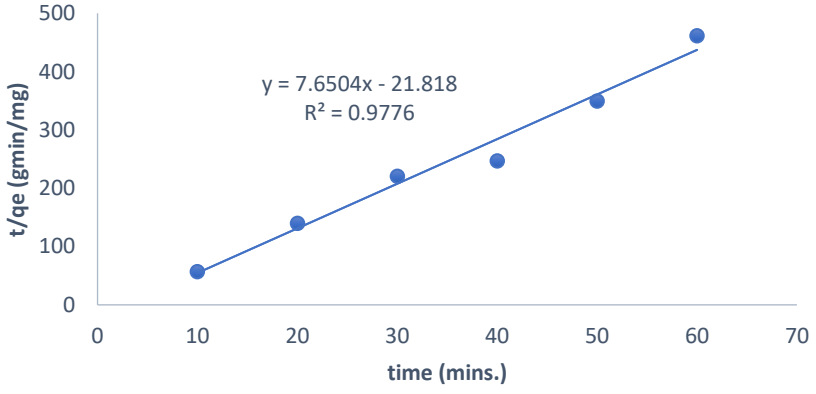
The non-linear pseudo first order is by given by Eq. 8 and second order kinetic non-linear model by Eq. 9.

$$q_t = q_e\,(1- e^{-k_1 t}) \quad (8)$$

$$q_t = \frac{(K_2 q_e 2t)}{(1+ k_2 q_e t)} \quad (9)$$

Where K_1 (min^{-1}) and K_2 (g/mg min) are the pseudo first order and pseudo second order rate constants, Q_e(mg/g) and Q_t(mg/g) are metal ion adsorbed at equilibrium and at time t (mins) respectively. Plots of log $(Q_e - Q_t)$ against (t) gave a very poor fitted curves and it is not presented in this work. Thus indicating that the adsorption process was not described by pseudo-first order kinetic.

The plots oft/Q_t verses time (t) for pseudo second order kinetics are presented in Figures 8 and 9 for modified and unmodified respectively. The constants generated for linear and non-linear models are summarized in Table 3. Based on the high values of R^2 for modified (0.98) and unmodified (0.97) activated carbon, suggests that the Ni (II) ion adsorption process is controlled by physisorption mechanism.



i.

Figure 8: Pseudo-second order model for adsorption of Ni (II) metal on modified activated carbon.

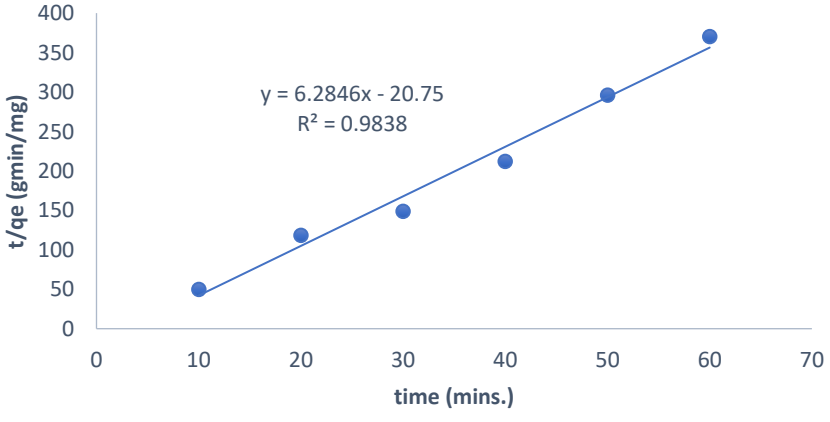


Figure 9: Pseudo-second order model for adsorption of Ni (II) metal on unmodified activated carbon.

Table 3: Pseudo second order kinetics constant for the adsorption process for linear and non-linear model

Samples	Linear			Non-linear		
	K_2(g/mg/min)	Q_e(mg/g)	R^2 (%)	K_2(L/min)	Q_e(mg/mg)	R^2 (%)
Modified	16.101	18.041	97.76	56913.64	0.182	97.75
Unmodified	-2.639	16.932	98.38	56910.53	0.148	96.76

CONCLUSION

The adsorption of Ni (II) ions onto activated carbon adsorbent was conducted. The adsorbent was characterized and used for the treatment of oil spilled contaminated water in a batch mode. Adsorption isotherms and kinetics were studied. The maximum efficiency of Ni (II) ions removal was 95.92% and 93.42% for modified and unmodified activated carbon respectively. The Langmuir equilibrium isotherms showed better fit compared to Freundlich isotherm model indicating a homogeneous and monolayer nature of the activated carbon adsorbent. The pseudo-second order kinetic model fitted better on the experimental data. The results showed the potential of activated carbon in the treatment of wastewater laden with Ni (II) ion.

Competing interests

The authors declare that there are no competing interests.

REFERENCES

Akpomie, G. K., and Dawodu, A. F., (2015). Potential of a low-cost bentonite for heavy metal abstraction from binary component system. *Beni-Suef University Journal of Basic and Applied Sciences:* 1–13.

Bansal, R. P. and Goyal, M. (2015). Activated Carbon Adsorption, CRC Press, Taylor & Francis Group, 6000 Broken Sound Parkway NW, Suite 300 Boca Raton, FL, USA.

Bello, S.O., Adegoke, A.K., Fagbenro, O.S. and Lameed, S.O. (2019). Functionalized coconut husks for rhodamine-B dye sequestration, *Applied Water Science,* 9:189, 1-15.

Etkin, D. S. (2011). Spill occurrences: A world overview, in Oil Spill Science and Technology. Gulf Publishing Company: New York. 7–48.

Fingas, M. F. (2012). The Basics of Oil Spill Cleanup. Taylor and Francis, New York.

Jock, A. A., Innocent, O. O., Uwem, E. I., Lawrence, P. G., and Ojo, A. (2021). Chromium and nickel metal ions removal from contaminated water using Nigerian bentonite clay. *Water Practice & Technology*, 16(3):825-836.

Jock, A. A., Anietie, N. O., Uchechukwu H. O., Festus, T., and Edmond, O. A., (2020). Adsorption of Nickel Ions from Petroleum Wastewater onto Calcined Kaolin Clay: Isotherm, Kinetic and Thermodynamic Studies. *Hungarian Journal of Industry and Chemistry*, 48(2):45–49.

Kumar, P. S., Sivaprakash, S. and Jayakumar, N. (2017). Removal of methylene blue dye from aqueous solutions using Lagerstroemia indica seed (LIS) activated carbon. *International Journal Material Science*, 2(12):107–116

Lee, Z. L., and Zaini, M. A. A. (2020). One-step $ZnCl_2$/$FeCl_3$ Composites Preparation of Magnetic Activated Carbon for Effective Adsorption of Rhodamine B Dye. *Toxin Reviews*, 97(12):1–19.

Liyanage, C. D. and Pieris, M. (2015). A physico-chemical analysis of coconut shell powder. *Procedia Chemistry*, 5 (16): 222-228.

Okafor, P. C., Okon, P. U. Daniel, E. F. and Ebenso, E. E. (2016). Adsorption capacity of coconut (*Cocos nucifera L.*) Shell for lead, copper, cadmium and arsenic from aqueous solutions. *International Journal of Electrochemical Science*, 7 (123): 54–69.

Omofonmwan, S. I. and Odia, L. O. (2019). Oil exploitation and conflict in the Niger-Delta Region of Nigeria. *Journal Human Ecolology*, 26 (1):25-30.

Oribayo, O., Olaleye, O. O., Akinyanju, A. S., Omoloja, K. O. and Williams, S. O. (2020). Coconut Shell-Based Activated Carbon as Adsorbent for the Removal of Dye from

Aqueous Solution: Equilibrium, Kinetics, and Thermodynamic Studies. *Nigerian Journal of Technology*, 39 (4):1076–1084.

Pandey, S., Do, Y. J., Kim, J. and Kang, M. (2020a). Fast and highly efficient removal of dye from aqueous solution using natural locust bean gum based hydrogels as adsorbent. *International Journal of Biological Macromolecules*, 4 (143): 60–75.

Pandey, S., Fosso-Kankeu, E., Spiro, J. M., Waander, F., Kumar, N., Ray, S. S., Kim, J. and Kang, M. (2020b). Equilibrium, kinetic, and thermodynamic studies of lead ion adsorption from mine wastewater onto MoS_2-clinoptilolite composites. *Materials Today Chemistry*, 2 (18): 1–11.

Ratnoji, S. and Singh, N. (2014). A study of coconut shell-activated carbon for filtration and its comparison with sand filtration. *International Journal of Renewable Energy and Environmental Engineering*, 2 (5): 201-204.

Siddiqui, F., Soliman, Y. M., House, W. and Ibragimov, A. (2016). Pre-Darcy Flow Revisited Under Experimental Investigation. *Journal of Analytical Science and Technology*, 7 (2):1–9.

Udoetok, I. A. (2015). Composition and distribution of petroleum hydrocarbons of Idu-Ekpeye oil spillage site in Niger-Delta, Nigeria, M.Sc. Thesis, University of Port Harcourt, Nigeria.