A renewable, sustainable and low-cost adsorbent for ibuprofen removal

Olugbenga Solomon Bello, Oluwakemi Christiana Alao, Temitope Chris Alagbada, Oluwatobi Samuel Agboola, Omotoyosi Toheeb Omotoba and Oluwatosin Rebecca Abikoye

ABSTRACT

Adsorption efficiency of acid-modified kola nut husk (KNHA) as a non-conventional adsorbent for the sorption of Ibuprofen from aqueous media was investigated in this study. The raw and modified samples were characterized using scanning electron microscopy, Fourier transform infrared spectroscopy, electron dispersive X-ray spectroscopy pH, and Boehm titration techniques respectively. Adsorption parameters such as pH effect, adsorbate concentration, contact time, and solution temperature were studied. The amount of Ibuprofen uptake was observed to increase with a corresponding increase in adsorption operational parameters. The kinetic data was found to best fit the pseudo-second-order kinetic model. Isotherm adsorption models of Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich were utilized to analyze the adsorption data. The Langmuir isotherm model showed the best fit for experimental data with a maximum monolayer adsorption capacity of 39.22 mg/g. The values of Gibbs free energy change were negative (−164.48 to −64.045.4 kJ/mol) suggesting that the process of ibuprofen adsorption onto KNHA was spontaneous. The positive value of standard enthalpy change (+34.203 kJ/mol) suggests that the process of ibuprofen adsorption was endothermic. KNHA adsorbent was found to be efficient and viable for the uptake of ibuprofen from aqueous medium. Hence, adsorbent prepared from kola nut husk waste has proved to be effective for the adsorptive uptake of Ibuprofen from aqueous media.

Key words | adsorption isotherm, adsorption kinetics, Ibuprofen, kola nut husk, thermodynamic parameters

Olugbenga Solomon Bello (corresponding author)
Oluwakemi Christiana Alao
Temitope Chris Alagbada
Oluwatobi Samuel Agboola
Omotoyosi Toheeb Omotoba
Oluwatosin Rebecca Abikoye
Department of Pure and Applied Chemistry,
Ladoke Akintola University of Technology,
P.M.B. 4000, Ogbomoso, Oyo State,
Nigeria
E-mail: *osbello@lautech.edu.ng*

Olugbenga Solomon Bello
Department of Physical Sciences, Industrial Chemistry Programme,
Landmark University,
Omu-Aran,
Nigeria

HIGHLIGHTS

- The adsorption of IBP on KNHA was investigated.
- The average pore diameter of the adsorbent before and after activation was found to be 1.56 and 2.91 nm respectively.
- KNHA adsorbent gave a higher q_m value for IBP removal than other similar adsorbents.
- CH_3COH gave the highest percentage of IBP desorbed (95.34 %) from KNHA.
- KNHA was found to be over six times cheaper than CAC.

INTRODUCTION

Ibuprofen (IBP) belongs to the class of non-steroidal anti-inflammatory drugs (NSAIDS). This class of drugs possesses endocrine-disrupting chemicals and is generally referred to as emerging contaminants (Kanakaraju *et al.* 2018). IBP is safe in its prescribed dosage for effective relief of pains but when larger dosages are administered, it could inflict adverse effects on humans and wildlife at large. Table 1 shows some endocrine-disrupting effects of Ibuprofen. A

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Table 1 | Brief information about adsorbate

Adsorbate	Endocrine disrupting effect	Household brands	Reference
Ibuprofen	• Decrease in secretion of testosterone depending on dose and individual • Incision of sex steroid hormones in organisms • Reduction of fish production rate lowers the breeding rate per pair.	• Ibudone • Vicoprofen • Reprexian • Advil • Motrin • Proprinal	Han *et al.* (2010)

combination of IBP and diphenhydramine provides the active ingredient of household pain relief drugs with the brand names Advil PM and Motrin PM. Due to the diverse functionality of NSAIDs, they are administered to a wide range of patients suffering from diverse ailments, thereby increasing their presence in the environment owing to the fact that they are not readily biodegraded (Gupta *et al.* 2013; Qamruzzaman 2015; Ghadir *et al.* 2020). Reports have shown that the active compounds of endocrine-disrupting chemicals are usually persistent in the environment (Kümmerer 2009; Cherniwchan 2012; Bello *et al.* 2019) and are introduced through channels such as inappropriate discharge of industrial effluents into the environment and dumping of unused drugs into waste bins and dump sites. Several of these pollutants are usually of organic and inorganic origins with the organic pollutants ranging from Bisphenol A and its derivatives to metals which possess inherent toxicity (Panizza 2000; Mohan *et al.* 2014; Onwordi *et al.* 2019). IBP has been specifically reported to have concentrations ranging from 0.018 up to 2.110 μg/L in several water bodies around the world (Dziadkowiec *et al.* 2017).

Several techniques have been employed in the removal of these endocrine disruptors which are persistent in the environment. These techniques include: membrane technology (Ciardelli *et al.* 2000; Greenlee *et al.* 2009), biodegradation, aeration (Panswed & Wongehaisuwan 1986), chlorination (Chamarro 2001), and chemical precipitation. A major setback associated with these techniques is their high cost as well as the difficulties associated with their practicability. Adsorption (Ojedokun & Bello 2016) is a promising means of sequestering unwanted contaminants from the environment with a high level of effectiveness and accuracy (Ntwampe & Bunt 2016; Othman *et al.* 2017). It is not difficult to execute and quite cost-effective. Unlike activated carbon which can be prepared from readily available agricultural wastes material, remediating the environment through the commercially available activated carbon is usually very expensive (Bello *et al.* 2020). Therefore, activated carbon prepared from agricultural wastes is usually used instead of the commercially available activated carbon since the precursors are readily available as unwanted materials. By this, unwanted waste materials littering the environment are mopped up, thereby making the environment habitable for man and animals. Different agricultural wastes that have been used include: bean husks, banana stalk, periwinkle shell (Bello *et al.* 2008), *Moringa oleifera* seed pod (Maina *et al.* 2016) mango leaf (Bello *et al.* 2014)), coconut shell (Bello *et al.* 2012), rice hull (Mukoko *et al.* 2015), tea wastes (Ahmaruzzamam & Laxmi 2010), potato peels (Arampatzidou & Deliyanni 2018), *Parthenium hysterophorus* (Mondal *et al.* 2016), and palm shell (Pamidimukkala & Soni 2018).

Kola nut is the fruit obtained from the kola tree. It belongs to the family of Malvaceae, genus of *Cola*; there are two common species: *Cola acuminata* and *Cola nitida*. It is an evergreen plant with the nut containing steroids, volatile oils, glycosides, saponins, alkaloids, and tannins (Kanoma *et al.* 2014). It is a caffeine-containing plant and a cash crop for rural farmers. The husk of the fruit is obtained after the fruit has been broken (Adebayo & Oladele 2012). Kola nut farmers have interest only in the kola fruit, thereby dumping the husk at harvest sites and sometimes burning it. In cases where the husks are dumped on refuse sites, they usually serve as breeding sites for microorganisms due to their high potassium content (Agamuthu 2009; Fabunmi 2018). These have constituted a large amount of undesirable waste and waste products, posing imminent harm to the ecological health of the ecosystem. Harnessing this waste material in remediating contaminated water bodies could be a promising means of achieving a better treatment method (Schwarzenbach *et al.* 2010). Apart from utilizing kola nut husk in soap production (Osagie & Enyi 2015), poultry feeds, biogas production (Ezekoye *et al.* 2011), and production of microbial enzymes, a high value can be placed on it by using it for adsorbent preparation (Agarry &

Ogunleye 2014). This is an effective way of preparing sustainable adsorbents from waste materials.

Adsorption can be carried out either as batch adsorption or a column adsorption analysis. Experiments that are carried out in the laboratory for the uptake of a minute quantity of adsorbate by adsorbent are referred to as batch adsorption studies. They are usually carried out to create a scheme to follow in large cases or industrial cases of production (Bello *et al.* 2017a, 2017b). Column analysis is usually conducted by administering a predetermined amount of adsorbent, thereby ensuring that the expected concentration fraction between the adsorbent and adsorbate required for adsorption is achieved (Fang *et al.* 2017).

To the best of our knowledge, no work has been reported on the use of kola nut husk activated carbon for the sorption of IBP drug from aqueous media. This study is aimed at employing kola nut husk, an agricultural waste, as a precursor material for preparing activated carbon that can efficiently trap IBP, an endocrine-disrupting compound, from aqueous environment.

MATERIALS AND METHODS

Preparation of adsorbent and activated carbon

Kola nut husks were obtained from a farm settlement in Ogbomoso, Oyo State, Nigeria. The kola nut husks were washed with distilled water and air-dried for a few days. The essence of the washing is to remove sands and other interfering dirt. The husks were obtained after the kola nut fruit was removed. The sample was pulverized with a mortar and pestle and then sieved through a 10–120 μm sieve mesh. The product obtained was kept in an airtight container for further use. Thirty grams of the dried kola nut husk was weighed using a weighing balance (Ohaus: Pioneer PA214) and transferred into a crucible. The modification was done by reacting with 1,000 mL of 0.3 M orthophosphoric acid with 50 g of 20 μm coconut husk. The reaction was carried out on an electric hotplate till a slur was formed. After the slurry formation, it was carbonized in a muffle furnace at 500 °C for 3 hours until a char was formed. The char formed was then washed to neutral pH with distilled water after which it was oven-dried to constant weight at 105 °C to remove the moisture content and other volatile adhering material. The sample formed was then stored for further use.

Preparation of adsorbate

IBP crystals obtained from the chemical store were used as the adsorbate. The physicochemical properties of the adsorbate were investigated to ensure adequate preparation of the adsorbate. One gram of IBP crystals was dissolved in 1,000 mL of ethanol to prepare the stock solution. Working concentrations were further prepared from the stock concentration.

Characterization of the adsorbent

Raw and activated kola nut husks (KNHR and KNHA, respectively) were characterized using physicochemical techniques such as Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) (Qu 2009), Boehm's titration (Boehm 1966), electron dispersive X-ray (EDX) spectroscopy, and pH of point of zero charge (pH_{PZC}). FTIR spectra were recorded from 400 to 4,000 cm^{-1}. This was used to identify the different functional groups present in the adsorbents (Bello *et al.* 2019). The SEM technique was also employed to elucidate the morphological properties of the adsorbents (Ahmad & Alrozi 2011) while the EDX spectroscopy was used to detect the elements that are present in the adsorbent (Ahmad *et al.* 2015). The point at which the surface of the adsorbent possesses no charge, that is the point when the surface is completely neutral, was identified by the pH_{PZC} method (Farahani *et al.* 2011: Mestre *et al.* 2014).

BATCH ADSORPTION STUDIES

Batch equilibrium studies

Adsorption performance of KNHA in removing IBP was carried out at three different temperatures (303, 313, and 323 K). Adsorption studies on the effects of initial IBP concentrations, solution temperature, and contact time at different temperatures for the five different working concentrations; 10, 20, 30, 40, and 50 mg/L; were carried out with varying operational parameters. The KNHA dosage was kept constant at 0.1 g/L throughout the experiment. This working concentration range and adsorbent dosage were tried after several experimental trials to ascertain the optimum range for the uptake. The adsorption process proceeded for 180 minutes with equilibrium attained in 90 minutes contact time. Five rows of 200 mL conical flasks which contained 0.1 g of KNHA and different

working concentrations of IBP solutions were carefully arranged inside a water bath schematic shaker, which was continuously agitated at a rotating speed of 120 rpm for 180 minutes. The experiment was repeated for the three working temperatures. Disposable clinical syringes were used to withdraw the samples at preset time intervals, and the concentrations of the samples were determined using a UV-Vis spectrophotometer at a maximum wavelength for IBP at 240 nm. The quantity of IBP adsorbed and the percentage removed at equilibrium was determined using Equations (1) and (2).

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

$$q_t = \frac{C_o - C_t}{W} V \quad (2)$$

where q_e is the quantity of IBP adsorbed at equilibrium, q_t is the quantity of IBP uptake at a specific time, W is the mass of KNHA in grams, V is the volume of IBP added in dm^3, C_o and C_e are the initial concentration and concentration at equilibrium of the IBP solution in mg/L.

Effects of contact time, solution temperature, and initial IBP concentration

The effects of contact time and IBP concentration were investigated. IBP solutions (100 mL) with initial concentration of 10, 20, 30, 40 and 50 mg/L were placed into 200 mL conical flasks and arranged accordingly inside the shaker; 0.1 g of KNHA was measured into each conical flask and the flasks were covered with stoppers. The shaker was operated at a speed of 120 rpm at a temperature of 303 K. The effects of solution temperature on the uptake of IBP were studied by adjusting the shaker's temperature to 313 and 323 K respectively (Alkan & Dogan 2003; Hameed *et al.* 2007; Maria *et al.* 2019).

Desorption and regeneration studies

Desorption and regeneration studies of KNHA were carried out. This was done by subjecting the adsorbent to water, acid and base treatments. The acids employed were CH_3COOH and HCl, while the bases were NaOH and CH_3COH. The most effective out of these eluents was used for the regeneration experiment.

RESULTS AND DISCUSSION

Characterization of adsorbents

FTIR analysis

FTIR analyses were carried out for both the raw and activated samples. They were carried out within the range 400–4,000 cm^{-1}. It was observed that there were appearances and disappearances of some peaks in the spectra. These peaks are indicative of the different functional groups present in the sample (Guedidi *et al.* 2014). The changes were due to the activation of the raw sample (Bekci *et al.* 2009; Bello *et al.* 2015). Table 2 gives comprehensive information about the functional groups while Figure 1(a) and 1(b) are the FTIR spectra for raw and activated kola nut husk samples.

Energy dispersive X-ray spectroscopy

EDX spectroscopy is a technique that serves as a basis for elemental comparison between the activated sample and the raw sample. It was observed that there was an increased amount of carbon in the activated sample (Figure 2(a) and 2(b)). The results obtained from EDX analysis are presented in Table 3. The amount of oxygen in the activated sample is

Table 2 | FTIR band assignments of raw and activated kola nut husks and their differences

IR peaks	Wave numbers (cm^{-1}) KNHR	KNHA	Differences	Band assignments
1	3,772.76	3,772.76	0.00	O-H stretch of alcohol
2	3,433.29	3,427.51	5.53	O-H bond of carboxyl
3	2,382.09	2,370.51	11.58	C≡N vibration of nitriles
4	1,855.52	1,855.52	0.00	C=O stretch of acid halide
5	1,789.94	1,789.94	0.00	C=O of acid halides
6	1,639.49	1,699.29	−59.72	C=C stretch of alkenes
7	1,413.82	1,384.89	28.93	C=S stretch of thioamides
8	1,278.81	1,253.73	25.10	C=S stretch of thioamides
9	1,107.14	1,093.64	13.50	C-O stretch of esters
10	678.94	696.30	−17.36	C-H deformation of disubstituted alkenes

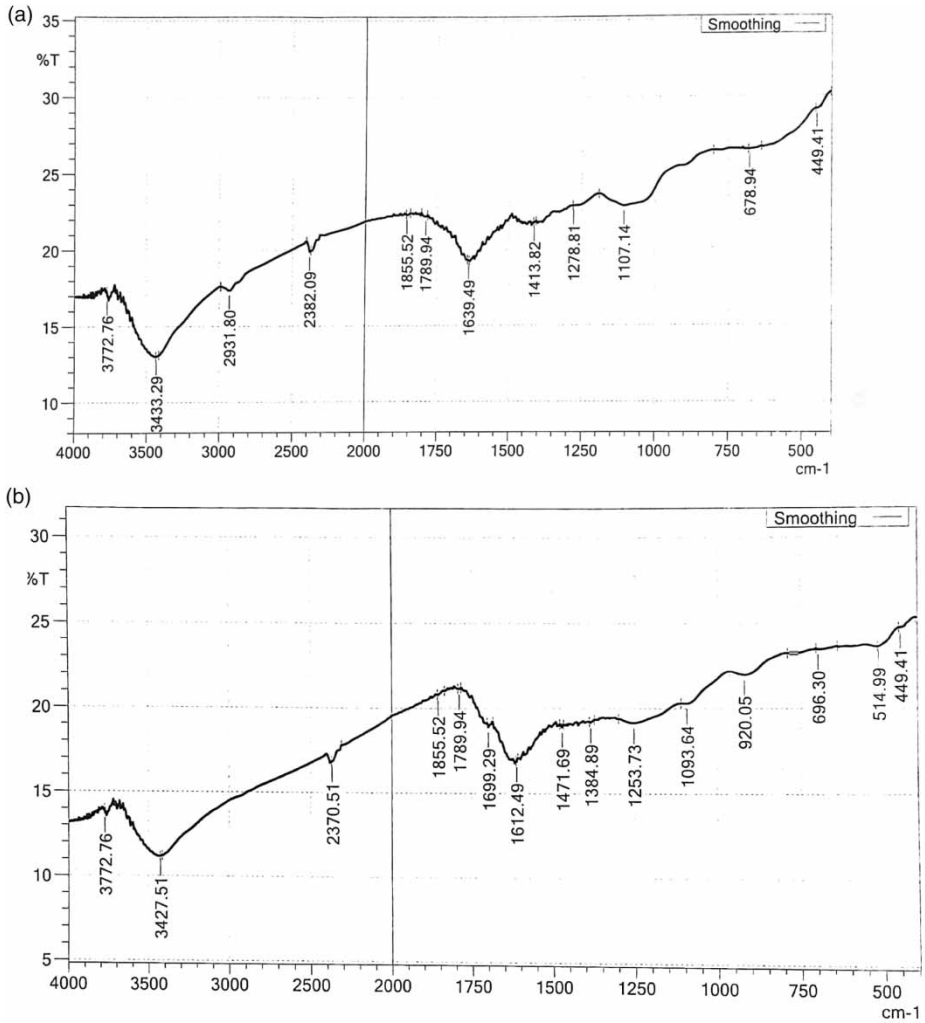

Figure 1 | (a) FTIR spectrum of raw kola nut husk, (b) FTIR spectrum of activated kola nut husk.

lower than that of the raw sample and some elements present in the raw sample were observed to be absent in the activated sample. These differences observed in the activated and raw samples are largely as a result of the activation process. The increased carbon content is an indication that kola nut husk is a good precursor for preparing activated carbon resulting in a good uptake of IBP due to its ability to catenate with other elements. Okpe *et al.* (2018) also documented a similar observation.

Scanning electron microscopy

Scanning electron micrographs were utilized to detect pore enlargement of the sample after activation. It was observed that the activated sample possesses well developed prominent pores, unlike the raw sample. Figure 3(a) and 3(b) represent micrographs obtained from raw and activated kola nut husk respectively. The larger pores in the activated samples suggest that IBP trapping from aqueous solution will be more efficient using the activated sample (Rao *et al.* 2006; Bello *et al.* 2015). The figure also reveals that there is an increase in the surface area of the adsorbent. Thus, the larger the surface area, the greater the amount of adsorbate removed (Santhi *et al.* 2010; Fouzia & Abu 2018).

pH of point of zero charge

pH_{PZC} is a resultant parameter that depends on the overall effect exerted by the diverse functional groups present in the KNHA (Bello *et al.* 2017a, 2017b). In a plot of ΔpH

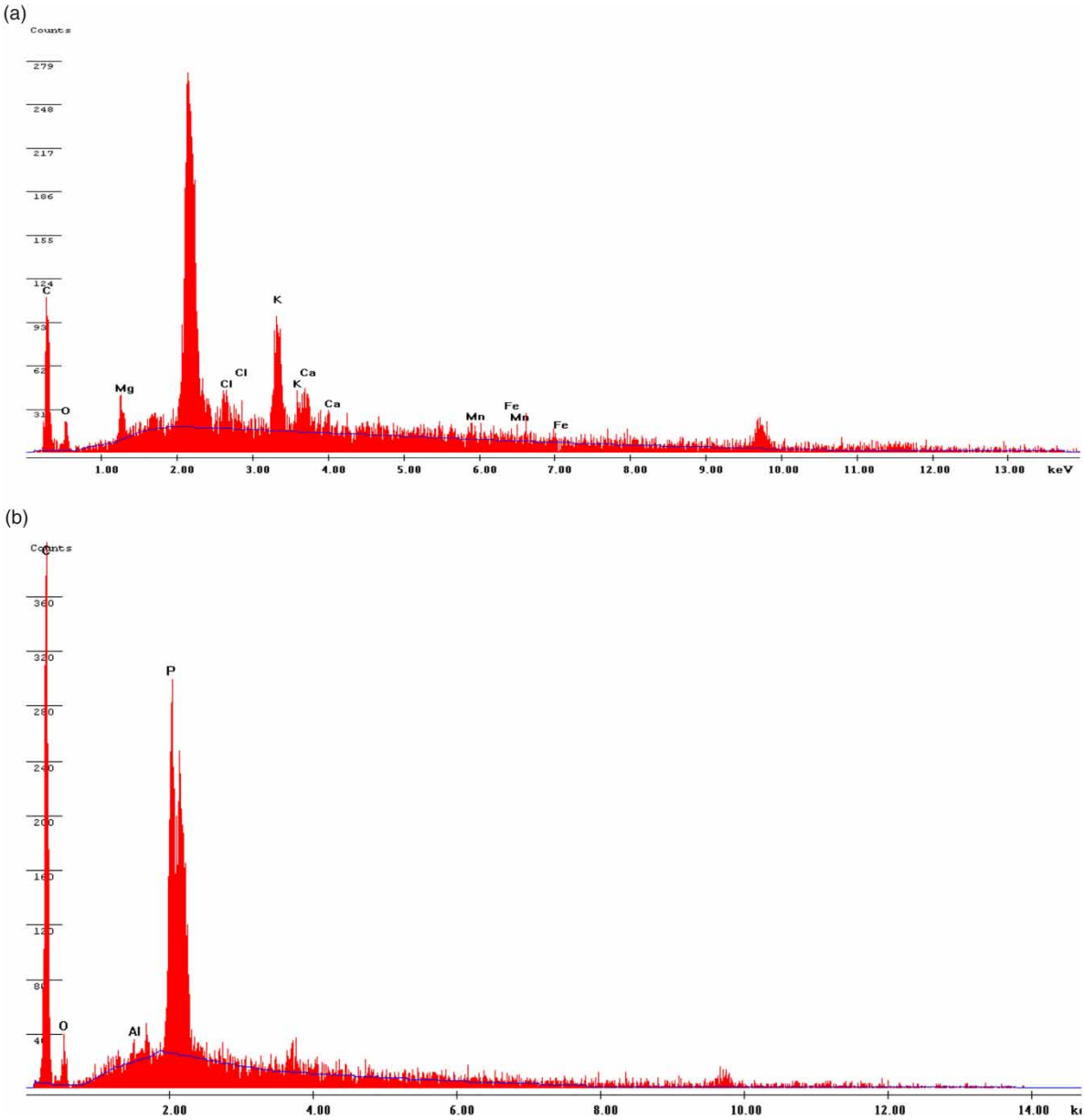

Figure 2 | (a) EDX spectrum of raw kola nut husk, (b) EDX spectrum of activated kola nut husk.

(change in pH) against pH_0 (initial pH), the pH_{PZC} is the point where the resultant curve passes through the pH_0 region (Figure 4). In the case of KNHA, the value of pH_{PZC} is 5.32 (Figure 4). This implies that the adsorption of cation is more effective at pH above the pH_{PZC} while anion adsorption is more effective at pH below the region (Al-Degs *et al.* 2000). Depending on the medium used for the adsorption process, KNHA will adsorb IBP molecules from aqueous solutions at varying proportions.

Brunauer–Emmett–Teller

The Brunauer–Emmett–Teller (BET) surface area, micropore volume and average pore diameter are reported in Table 4. The average pore diameter of the adsorbent before and after activation was found to be 1.56 and 2.91 nm respectively. This shows that KNHR was microporous while KNHA was mesoporous. The mesopore volume and mesopore contribution of KNHA to the

Table 3 | EDX characteristics of kola nut husk adsorbents

S/N	Elements	KNHR (At %)	KNHA (At %)
1	C	67.76	88.54
2	O	10.28	4.51
3	Mg	2.78	–
4	Mn	2.28	–
5	Ca	3.81	–
6	K	9.10	–
7	Cl	2.16	–
8	Fe	1.84	–
9	Al	–	0.21
10	P	–	6.75
	Total	100	100

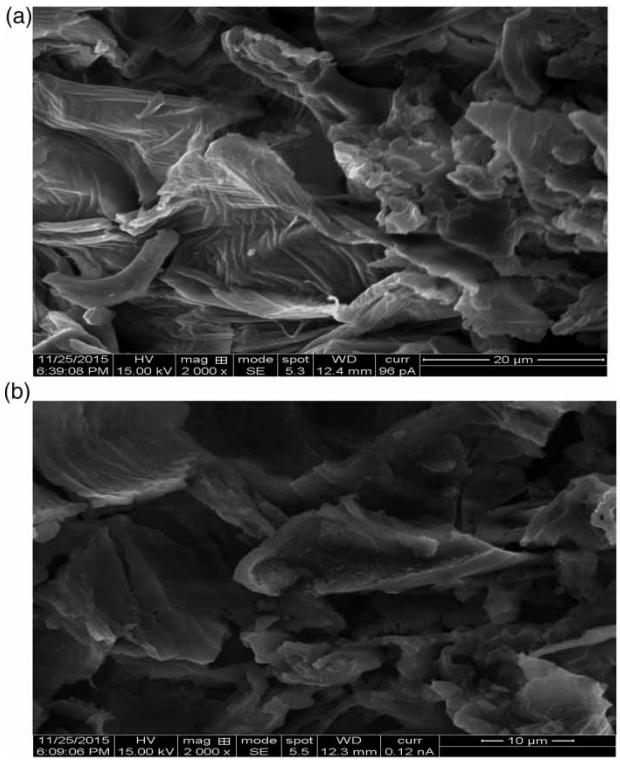

Figure 3 | (a) SEM of raw kola nut husk (magnification: × 2,000), (b) SEM of activated kola nut husk (magnification ×2,000).

porous texture was higher (>70%) than that of KNHR (<25%) (Table 4). This accounts for the high adsorption efficiency of KNHA. Mesopores act as transporting arteries, and contribute to the adsorption of IBP on the adsorbent. A similar result was obtained in our previous studies of the adsorption of IBP on bean husks and orange peels (Bello *et al.* 2019, 2020).

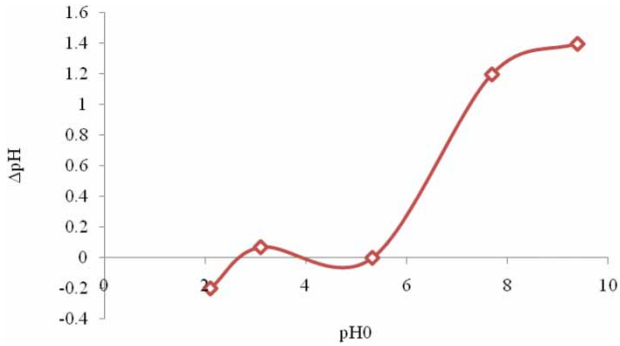

Figure 4 | A plot of pH of point of zero charge of KNHA.

Table 4 | Surface pore characteristics of kola nut husk

S_{BET} (m^2/g)	V_{mic} (m^3/g)	V_{mes} (m^3/g)	V_{tot} (m^3/g)	V_{mes}/V_{tot} (%)	D_p (nm)
Before activation					
311	0.228	0.687	0.915	24.91	1.56
After activation					
712	0.146	0.435	0.581	74.87	2.91

Note: D_p, average pore diameter; S_{BET}, BET surface area; V_{mes}, mesopore volume; V_{mic}, micropore volume; V_{tot}, total volume (mic + mes).

ADSORPTION KINETIC STUDIES

Kinetics of IBP uptake by KNHA was studied using four different kinetic models. These are the pseudo-first-order (Lagergren & Svenska 1898), pseudo-second-order (Ho & Mckay 1999), Elovich (Aharoni & Ungarish 1976), and intra-particle diffusion model (Weber & Morris 1963).

Adsorption kinetic data analysis helps in the determination of the rate-determining step of the adsorption process. The pseudo-first-order kinetic model did not provide the best correlation for the adsorption data. From Table 5, it can be seen that the experimental and calculated values of q_e do not agree for the pseudo-first-order kinetic model. The regression coefficient value (R^2) for the pseudo-first-order is also lower compared to that of the pseudo-second-order. Similarly, the sum of squared errors (SSE) values obtained for the pseudo-first-order model is high. On the other hand, the pseudo-second-order model exhibited close agreement between the experimental and calculated values of q_e. It also has low SSE values. This suggests that the kinetic data is best correlated with the pseudo-second-order kinetic model. This is indicative that two interacting surfaces were engaged during the adsorption process. Values of the regression co-efficient tending towards unity were also

Table 5 | Kinetic parameters for the adsorption of IBP on KNHA at 303 K

Kinetic models	10 mg/L	20 mg/L	30 mg/L	40 mg/L	50 mg/L
Pseudo-first-orderkinetic model					
$q_{e(\exp)}$ (mg/g)	4.802	9.984	14.748	19.707	24.161
$q_{e(\mathrm{cal})}$ (mg/g)	1.257	2.326	2.358	2.659	5.202
k_1 (min)	0.011	0.022	0.016	0.018	0.035
R^2	0.891	0.890	0.995	0.952	0.927
SSE %	0.958	2.139	5.555	7.758	10.243
Pseudo-second-order kinetic model					
$q_{e(\mathrm{cal})}$ (mg/g)	4.804	10.000	14.706	20.000	24.390
k_2 (min)	0.133	0.323	0.132	0.167	0.219
R^2	0.999	1.000	0.999	1.000	1.000
SSE %	0.008	0.007	0.012	0.131	0.102
Elovich model					
R^2	0.893	0.973	0.989	0.947	0.887
α (mg/(g min))	2E5	6.0E13	3.8E32	1.2E26	3.9E74
β (g/mg)	3.831	3.759	5.587	3.344	7.407
Intraparticle diffusion model					
R^2	0.899	0.840	0.842	0.839	0.929
C_1	0.008	0.008	0.006	0.010	0.006
k_{diff} (mg/g)	4.178	9.493	14.160	19.060	23.740

Table 6 | Isotherm data analysis of adsorption of IBP on KNHA

Isotherm model	303 K	313 K	323 K
Langmuir			
Q_m (mg/g)	15.870	28.220	39. 680
K_{L} (L/mg)	0.708	0.462	0.311
R_{L}	0.028	0.030	0.060
R^2	0.987	0.981	0.994
Freundlich			
K_{F}	9.818	7.413	3.532
n_f	1.029	1.016	1.032
R^2	0.863	0.956	0.961
Temkin			
K_T	4.888	1.053	2.187
b_T	0.432	1.732	0.199
R^2	0.966	0.904	0.857
B	11.330	11.750	10.962
DBR			
Q_o (mg/g)	3.987	4.259	4.217
B ($\mathrm{mol^2/kJ^2}$)	1.0×10^{-7}	3.0×10^{-6}	6.0×10^{-8}
E (kJ/mol)	1.500	2.900	2.200
R^2	0.869	0.890	0.964

AC: activated carbon.

observed for the pseudo-second-order kinetic model. Hanbali *et al.* (2020) also reported a similar trend of experimental data fitting the pseudo-second-order kinetic model most for the adsorption of IBP onto functionalized carbon nanotubes. In the case of the Elovich model, the desorption constant (β) increased with increasing IBP concentration. This implies that the activation energy of the reaction increased with an increase in concentration. The Elovich constant (α) decreased with an increase in IBP concentration (Table 5).

ADSORPTION ISOTHERM STUDIES

Four different equilibrium isotherms; Langmuir, (Langmuir 1918) Freundlich (Freundlich 1906), Temkin (Temkin & Pyzhev 1940), and Dubinin–Radushkevich (DBR) (Dubinin & Radushkevich 1947); were used to correlate the adsorption data to discover the model which gave the best fit. In the case of the Langmuir isotherm, the value of the maximum monolayer capacity uptake of the adsorbent (Q_m), was found to increase with an increase in adsorption temperatures with 39.68 mg/g as the highest value (Table 6). An increase in temperature also increases the mobility of the adsorbate molecule. Mobility increase caused by increased temperature resulted in higher adsorbate removal. The Langmuir constant (K_{L}) and the dimensionless constant (R_{L}) were found to increase with increasing temperature. The R_{L} values for the three temperature ranges were less than 1 suggesting that the adsorption of IBP onto KNHA was favorable (Table 6). In the case of the Freundlich model, the Freundlich adsorption constant (K_{F}) reduced with increasing adsorption temperatures. K_{F} value at 303 K (9.818) was observed to be 2.78 times greater than that of 323 K (3.532) (Table 6). High values of K_{F} indicate that there is very good interaction between KNHA and IBP. The Freundlich coefficient (n_f) values for the three temperatures were observed to be less than 10. The highest value of n_f is 1.032 with a corresponding value of $1/n_f$ =0.968. This suggests that the adsorption is favorable. The values of R_{L} and $1/n_f$ values being less than 1 are indicative of an excellent physical adsorption process. The Langmuir isotherm has R^2 values that are higher than those of the Freundlich model, with the highest value being 0.994. This is indicative that the Langmuir model best explains the adsorption isotherm. Mestre *et al.* (2007), Delgado *et al.* (2015), Puszkarewicz *et al.* (2017), and Mellah & Harik

(2020) reported the same observations for the adsorption isotherm of IBP. In the case of the Temkin model, the value of the constant B can be used to predict the enthalpy of the adsorption experiment. Positive values (11.330, 11.750, and 10.96) were obtained for the three temperatures, which reveals an endothermic process (Table 6). The adsorption equilibrium constant (b_T) was also calculated using the Temkin model. Dubinin–Radushkevich's model is appropriate as a tool for detecting the mean free energy of the adsorption process in terms of porosity (E). E values obtained are less than 8 kJ/mol (1.5, 2.9, and 2.2 kJ/mol respectively); this suggests that the adsorption process is physical in nature, i.e. physisorption (Table 6). This implies that the uptake of IBP from aqueous solution by KNHA is governed by a physical phenomenon. R^2 value of the isotherm models was used to judge the model with the best fit. The Langmuir model has the highest R^2 value. Hence, the adsorption experiment can be best illustrated with the Langmuir model. Judging from the value of R^2, the isotherms considered are rated in this order: The Langmuir > Freundlich > Temkin > DBR. Comparisons of the maximum monolayer adsorption capacities of IBP with other adsorbents are reported in Table 7.

Adsorption thermodynamic studies

Temperature was employed as a tool to investigate the adsorption thermodynamic. Thermodynamic parameters of standard enthalpy change (ΔH^0), standard entropy change (ΔS^0), and standard Gibbs free energy change (ΔG^0) were evaluated. They reveal the nature of the reaction, the kind of interaction that exists between the two interacting surfaces and the feasibility of the reaction respectively. Negative values of ΔG^0 confirm that the reaction is spontaneous. The positive value of the enthalpy change (ΔH^0) reveals that the reaction is endothermic. Thermodynamic parameters obtained in this study as shown in Table 8 indicated that the adsorption of IBP onto KNHA is endothermic, feasible, and thermodynamically favored.

Table 7 | Comparison of the value of the maximum monolayer adsorption capacity of IBP with other adsorbents

Adsorbent	Adsorbent capacity (Q_m) mg/g	References
Honey comb	4.49	Dubey *et al.* (2010)
AC from *Artemisia vulgaris*	16.73	Dubey *et al.* (2010)
AC from olive waste cake	9.09	Baccar *et al.* (2012)
Modified chitosan	32.19	Bany-Aiesh *et al.* (2015)
AC from peanut hull	28.0	Torez-Pérez *et al.* (2012)
AC from kola nut	39.68	This study

AC: activated carbon.

Desorption and regeneration studies

In view of the cost implication of the adsorbent, regeneration and possible reuse of KNHA was investigated. This was done by subjecting the adsorbent to water, acid and base treatments. The acids employed were CH_3COOH and HCl, while the bases were NaOH and CH_3COH. CH_3COH gave the highest percentage desorbed (95.34%); 0.1 M CH_3COH was used to desorb IBP molecules from KNHA over several cycles (Figure 5). It was observed that the percentage desorption of IBP remained fairly constant without significant change for four cycles (Figure 5). To be concise, 3% decrease in the percentage of IBP adsorbed was observed between the first and fourth cycles (Figure 5). Obviously, the results obtained proved that KNHA desorbed with CH_3COH after each adsorption step is very effective for IBP removal from aqueous solution.

COST ANALYSIS

Using adsorption techniques on large scale requires analysis of the cost implications in the preparation of the adsorbent.

Table 8 | Thermodynamic parameters for the removal of IBP onto KNHA

Temp (K)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (kJ/(mol K))	E_a (kJ/mol)
303	−164.48	34.203	0.103	13.316
313	−133.117			
323	−64.045			

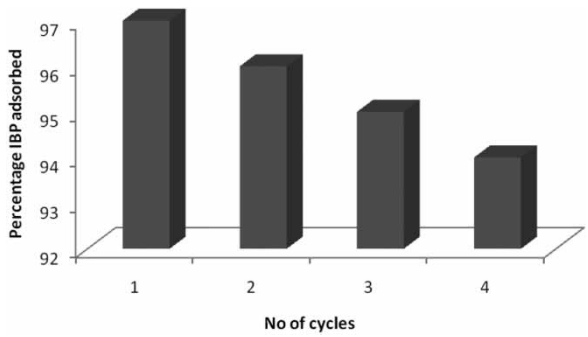

Figure 5 | The reusability of KNHA for the removal of IBP for four cycles (each cycle lasted for 60 min).

Table 9 | Cost breakdown of KNHA and CAC

	Price (USD)	
Cost breakdown	**KNHA (1 kg)**	**CAC (1 kg)**
Purchase of activated carbon		255
De-ionized water	10.38	–
Electricity supply	2.57	–
H_3PO_4	16.67	–
Transportation	9.30	4.5
Filter paper	3.60	–
Gross cost	42.52	259.5
Cost difference (CAC – KNHA)	216.98	

The net cost of preparing the activated carbon is usually determined by several factors such as cost of the precursor, cost of activating agent, and cost of running necessary appliances. In the case of KNHA, it was prepared from a readily available agricultural waste. Table 9 shows a breakdown of the cost incurred in preparing 1 kg of KNHA in comparison with the commercially available activated carbon (CAC). From the cost evaluation, KNHA was found to be over six times cheaper than CAC.

CONCLUSION

In this study, the efficiency of kola nut husk activated carbon was studied. KNHA was found to have an adsorption capacity greater than some of the previously reported studies (Table 7). The adsorption study was governed by a physical process, i.e physisorption. The isotherm model that gave the best correlation was Langmuir, and the kinetics of the adsorption process fitted most the pseudo-second-order kinetic model judging from R^2 values and low SSE values recorded. The KNHA is six times cheaper compared to CAC. Thermodynamic analysis revealed that the adsorption reaction was spontaneous and that the reaction was exothermic in nature. The study also revealed that KNHA is a promising low-cost adsorbent that can be used in removing IBP from wastewater.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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