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Development and characterization of MWCNTs from activated carbon as adsorbent for metronidazole and levofloxacin sorption from pharmaceutical wastewater: Kinetics, isotherms and thermodynamic studies

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ABSTRACT

Population growth coupled with wide spread of illness in both man and other animals have extensively increased the production and use of pharmaceutical products with various antibiotics discharged into the surrounding ecosystem. Such antibiotics when consumed by man and other living organisms cause serious health issues and therefore, there is need for urgent attention to treat such wastewater before been discharged. The application of synthesized multi-walled carbon nanotubes, MWCNTs as a novel adsorbent for the removal of metronidazole and levofloxacin in a batch adsorption process was investigated. Nickel-ferrites dope Activated carbon was produced via impregnation process and applied for the synthesis of MWCNTs in a CVD reactor. The produced nickel-ferrites doped activated carbon was characterized for thermal stability, surface area and surface morphology using TGA, BET and SEM respectively. The TGA result indicates high thermal stability of the catalyst with peak degradation temperature of 360.21 °C and slate-like nature morphology. The Brunette-Emmett-Teller result shows the surface area of pure activated carbon and Fe-Ni supported on activated carbon to be 840.38 and 650.45 m^2/g respectively. The surface morphology of the produced carbon nanotubes depicts the presence of long-strand tubes of carbon nanotubes. The results of the adsorption process revealed that the adsorption parameters were fitted to the pseudo-second order model. The kinetics model of the adsorption of metronidazole and levofloxacin on the de adsorbent is fitted to pseudo-first order kinetic while Freundlich isotherm described the sorption of metronidazole and levofloxacin with a strong bonding between the molecules of the sorbate and the surfaces of the adsorbent. The results of the study indicate the possible development of low-cost and high purity MWCNTs adsorbent for the sorption of metronidazole and levofloxacin from pharmaceutical wastewater using activated carbon derived from wood sawdust.

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Introduction

Over the decade, researchers have intensified efforts in the development of efficient and effective adsorbents towards removal of contaminants from wastewater. Several contaminants such as metronidazole and levofloxacin are contained in wastewater bodies discharged from pharmaceutical industries, discharge from fish ponds and poultry [1]. Metronidazole is introduced into the poultry and fish ponds water system during the treatment of trichomonas vaginalis and giardia lamblia, anaerobic infectious diseases found in fishes and poultry birds [2]. Metronidazole and levofloxacin are capable of being mutagenic and carcinogenic to the human DNA when accumulated above the allowable limit. According to [3–5], the accumulation of metronidazole is thus capable of causing acute toxicity in marine and freshwater habitats. Hence, there is urgent need to profer solution via effective purification technique.

Over the years, environmental engineers and scientists have contributed remarkably to the development of novel purification methods for the removal of metronidazole and levofloxacin. Nanofiltration, electrochemical degradation, osmosis, oxidation, adsorption process have been widely applied for the removal of antibiotics from pharmaceutical wastewater [6–9]. Of all these purification methods, adsorption method has been identified to be more effective and efficient with little design and monitoring cost. Due to the robustness of adsorption process for wastewater treatment, several sorbents have been developed and applied for treatment process. Such adsorbents include minerals containing clay, silica, activated carbon and nano-adsorbents [10,11]. The use of agricultural waste materials for the production of activated carbon aimed at purifying and treating wastewater has gained tremendous attention. The effectiveness of adsorption process towards efficient sorption of pollutants inherent in pharmaceuticals is dependent on several factors such as the hydrogen bonding, hydrophobic partitioning, cation bridging, metals complexing [12] and the nature of the adsorbent.

Several techniques such as carbonization, gasification and pyrolysis have been widely reported for the development of activated carbon for the treatment of wastewaters. The application of pyrolysis techniques for the development of activated carbon has gained attention of numerous researchers [13–17] as compared to carbonization and gasification processes. The appropriate feedstock's selection and the possibilities of controlling series of vital operating conditions such as reaction temperature, flow rate of inert gas, heating rate and the residence time of the introduced feedstocks into the reactor position pyrolysis as an excellent technique for activated carbon production. Pyrolysis technique has been further reported to produced activated carbon of high surface area, pore size and improved pore volume when compared to other methods of producing activated carbon whose end-product is ash-free (references).

In this present study, activated carbon was applied as a catalyst support for the synthesis of carbon nanotubes in CVD equipment. The synthesized MWCNTs was used as a novel adsorbent for the sorption of metronidazole and levofloxacin from pharmaceutical wastewater. The kinetics, isotherm and the thermodynamic study were investigated to study the adsorption behaviour of the sorbate onto the surfaces and the pores of the sorbent.

Material and methodology

Materials

Acetylene and argon gases used were soured from BOC Nigeria and were of analytical grade with percentage purity of 99.99%. $Fe(NO_3)_3{\cdot}9H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$ were of analytical grade with 99.99% purity supplied by Sigma Aldrich.

Development of activated carbon

Activated carbon was prepared via pyrolysis method. Sawdust was obtained from local saw-mill in Minna, Niger State, Nigeria. The sawdust was cleaned of dirt to remove external materials then sieved through a 500 micrometre sieve size. The sieved sample was washed several times using distilled water then dried for 6 h at 120 °C in air furnace. The dried sample was then pyrolysed in a horizontal furnace for a period of 1.5 h at 500 °C under the flow of argon gas. The obtained activated carbon was washed several times with distilled water, dried and kept for further use.

Synthesis of nickel-ferrite catalysts

Equal concentration of 0.25 M of $Fe(NO_3)_3{\cdot}9H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$ were measured then dissolved into conical flask containing 50 mL distilled water. To the obtained salts solution, 8 g of the prepared activated carbon was impregnated, stirred at known stirring speed and at 100 °C to remove moisture and form a semi-dried cake. The mixtures were left to impregnate overnight and the slurries were dried using a static oven at a temperature of 120 °C for 6 h. The resulted dried sample was calcined at 400 °C for 1 h under the flow of argon gas, cooled, grinded and sieved through 150 µm sieves. The nickel-ferrite containing catalyst was stored for analysis and for further application in the production of carbon nanotubes.

Carbon nanotubes production

A known weight of 1.0 g of the developed catalyst (Pure AC, Fe-Ni/AC) were weighed and channelled into horizontal reactor's tube via the quartz tube. The system was purged at 20 mL/min from room temperature to the reaction temperature

Table 1
BET surface area of the developed catalysts.

Catalyst	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
Pure AC	840.38	0.1990	1.7431
Fe-Ni/AC	650.43	0.2542	2.0507

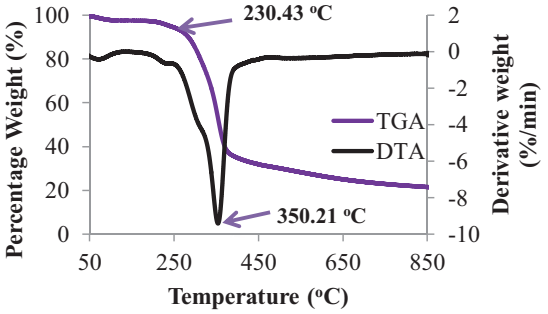

Fig. 1. TGA thermograph of the developed activated carbon.

of 700 °C to purge air and any other gaseous impurity from the quartz tube reactor. The reactant, acetylene was passed through the catalytic reactor at 100 mL/min for 30 min while the flow of the inert gas was increased to 200 mL/min to serve as a carrier gas. The acetylene flow was truncated and the reactor was purged at 20 mL/min until it was cooled to room temperature. The CNTs produced with each of the catalysts (Pure AC, Fe-Ni/AC) were removed, packaged in an airtight container and analysed to determine their surface properties.

Collection of wastewater sample

The obtained pharmaceutical wastewater was kept in freezer to prevent organisms' growth and other possible chemical changes to occur. The initial concentration of metronidazole and levofloxacin were tested using UV-Spectroscopy technique.

Adsorption studies

Using batch adsorption process, the produced nano-materials having appreciable surface properties were applied as an adsorbent for the treatment process. The effects of adsorbent dosage, temperature and contact time were studied on the percentage sorption of the antibiotics; metronidazole and levofloxacin on the developed sorbent. The obtained results were then applied for the kinetic, thermodynamics and isotherm study.

Results and discussion

Over the years, the search for high quality CNTs with 100% purity are on the increase. Such CNTs having remarkable purity are pertinent to the evolving area of carbon nanotubes' applications. Creating such active materials requires creative and expert approach of researchers on the basic factors affecting the process of CNTs synthesis. Some of the reported factors enabling the actualization of such high purity CNTs are the nature of catalyst support, method of catalyst preparation and composition of catalyst (active metals to supported materials) used during the CNTs synthesis.

The surface areas of the prepared catalyst were analysed using BET technique under N_2 flow. The result of the surface area, pore sizes and pore volume of the developed nano-materials were presented in Table 1.

From Table 1, the BET surface area of the pure AC and Fe-Ni/AC were 840.38, 650.43, 540.32 and 324.65 m^2/g respectively. The surface area of the pure activated carbon was found to be excellent compared to formulated catalyst. This could be as a result of absent of doping agent on the surfaces of the material. There was an observable decrease in the surface area of the pure Fe-Ni/AC catalyst as compared to the starting AC. The impregnation of Fe and Ni containing compounds resulted into the formation of nickel ferrites which possesses the ability of being deposited on the surfaces and the pores of the AC hence, decreases the surface area and the pore volumes of the catalyst material.

The thermal stability of the produced activated carbon was determined using PerkinElmer TGA equipment and the result of the analysis is as depicted in Fig. 1.

The TGA as depicted in Fig. 1 indicates the thermal behaviour of the developed activated carbon obtained via pyrolysis technique. The thermograph shows that the onset temperature at which the activated carbon begins to degrade was at 230.43 °C with peak temperature of 350.21 °C. This marked temperature shows that the pure activated obtained could be used for carbon nanotubes synthesis though with remarkable weight loss at elevated temperature. This observable peak degradation temperature is lower to the TGA properties depicted by kaolin according to the report of [18].

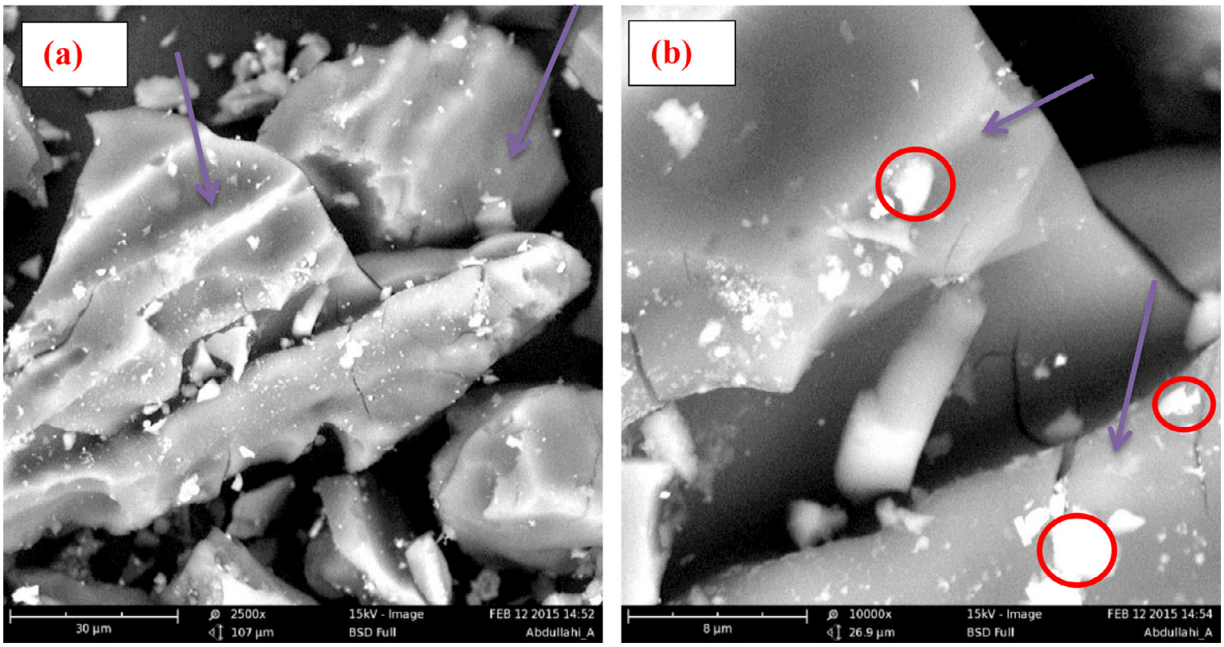

Fig. 2. SEM micrographs of the developed activated carbon at different magnifications.

The structural properties showing the surface morphology of the produced activated carbon was determined via the Scanning Electron Microscopy technique and the result of the analysis is shown in Fig. 2.

The surface morphology of the activated carbon obtained via pyrolysis in argon environment depicts a slate-like surfaces (indicated with an arrow) and whitish particles on the surface as indicated with a circles as depicted in Fig. 2a and b. The formation of the whitish particles on the surfaces of the produced slate-like activated carbon could be as a result of incomplete combustion process taking place in the furnace during the pyrolysis process.

The developed catalysts were employed in the CVD reactor for the synthesis of carbon nanotubes using acetylene gas a carbon source. The properties of the produced CNTs was characterized using the SEM, TEM, XRD and BET for the surface morphology, internal structure, crystallinity and surface area.

The surface morphology of the developed CNTs is shown in Fig. 3. The SEM micrographs depict the surface make-up of the CNTs nano-materials.

The HR-SEM results shown in Fig. 3(a,b) revealed that the CNTs produced are not completely formed during the nucleation process. There are densely populated growths of condensed and short strand of CNTs formation as observed in Fig. 3(a,b). The formation of high dense and populated short-growth of CNTs might be resulted from the absence of inhibitor such as the transition metal(s) (Fe-Ni) which has the ability to enhance the decomposition of the acetylene gas. In the same phase, as depicted in Fig. 3(c-d), the CNTs produced have an improved structural composition with identified and long strand of CNTs formation which was produced at the same operating condition. It can be deduced from Fig. 1(c,d) that the incorporation of transition metals; Fe-Ni into the activated carbon catalyst matrix aid in the enhancement of carbon conversion in the nucleation process of carbon nanotubes formation in a CVD reactor. The presence of branched growth of carbon nanotubes with irregular tubes architectures were also observed as shown in Fig. 3d. The results depicted in Fig. 3c,d indicate that activated carbon is a perfect and good support material for the synthesis of improved and tailored CNTs for materials engineering applications when doped with Fe-Ni.

The crystallinity of the developed CNTs was determined via X-Ray Diffractometer (XRD) technique. The result of the analysis is presented in Fig. 4.

The result as depicted in Fig. 4 shows the effect of doping activated carbon with transition (catalytic enhanced metals) on the phase of the CNTs produced in a CVD technique. The phase angle at the 2 theta equals 25.67 and 43.28° show the formation of graphitized carbon. The formations of these peaks are observable in both the carbon nanotubes produced from Fe-Ni/Activated Carbon and pure activated carbon though at varied intensity and FWHM as shown in Table 2. The wideness in the diffraction angles at 25.67 and 43.28° indicate the presence of inherent amorphous nature of the support material; sugarcane bagasse. The peak at around 51.00 and 75.34° is associated with the formation of nickel ferrites crystals ($NiFe_2O_4$). This observation of peak formation was observed by Abdulkareem, et al. (2017) during the process of synthesizing MWCNTs via the use of Fe-Ni-Co supported on $CaCO_3$. Comparatively, the formations of two distinct peaks were formed when pure activated carbon was used as a catalyst material for the synthesis of CNTs. The peaks were also observed at the same diffraction angle when the activated carbon was doped with nickel ferrites nanoparticle for CNTs synthesis.

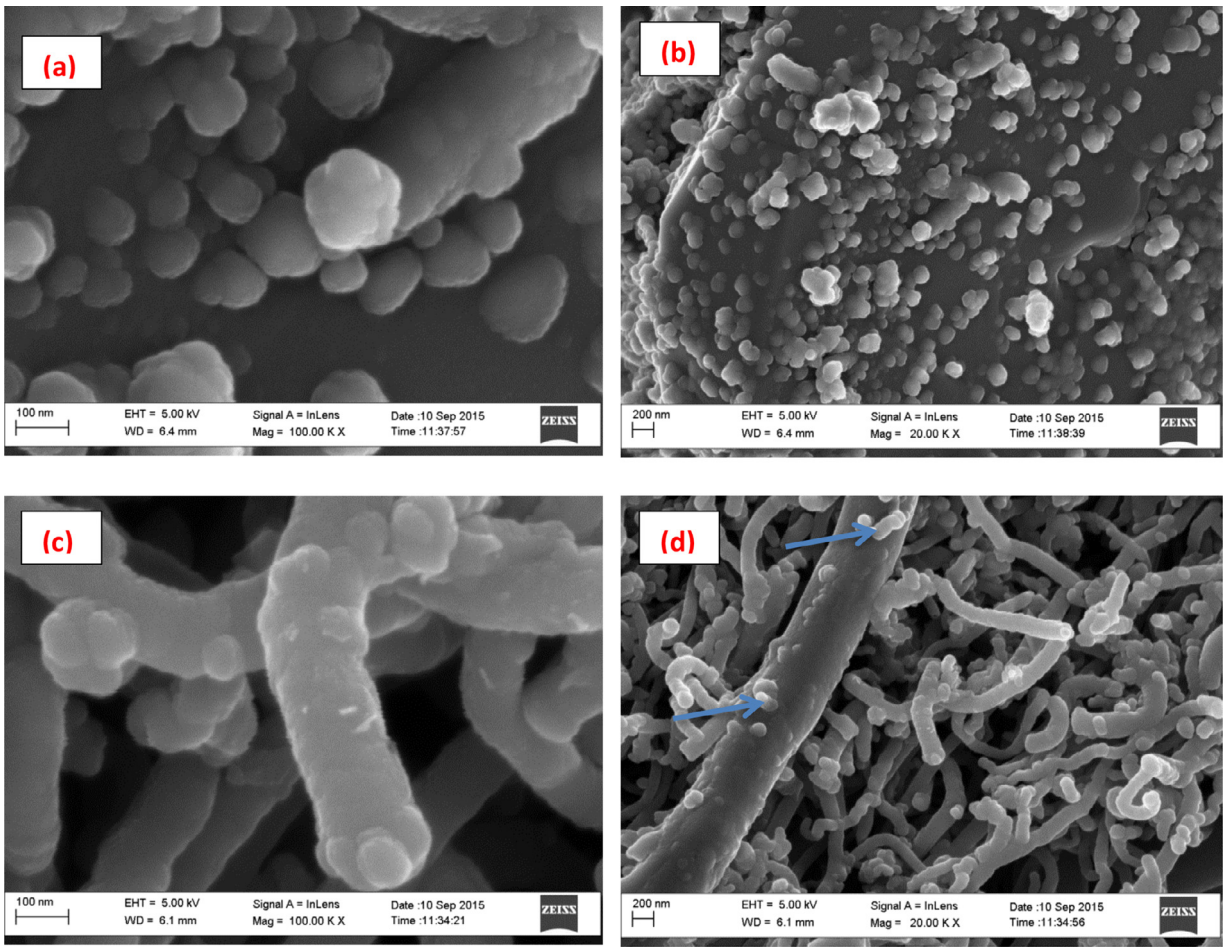

Fig. 3. HR-SEM Micrographs of CNTs from (a-b) pure activated carbon and (c-d) Fe-Ni supported on activated carbon.

Table 2
Crystallite size determined from XRD data.

S/N	Diffraction Angle	FWHM (Radian)		Crystallite Size (nm)	
		CNTs from Pure AC	CNTs from Fe-Ni/AC	CNTs from Pure AC	CNTs from Fe-Ni/AC
1	25.67	0.08988446	0.06047566	1.65	2.46
2	43.28	0.05270894	0.04555309	2.96	3.42
3	51.00		0.01797689		8.92
4	75.34		0.01343904		13.63

Furthermore, two pronounced peaks were formed on the CNTs produced from Fe-Ni/Activated carbon. These peaks formation might be attributed to the production of aligned and long tube carbon nanotubes without any accompanied metallic impurities.

The crystallite size of the produced CNTs were estimated from the XRD data using the Scherer equation as depicted in Eq. (1) (Chen et al., 2006).

$$D = \frac{K\lambda}{\beta COS\theta} \tag{1}$$

Where D represents the particle size diameter, β = full width at half maximum (FWHM), λ is the wave length of X-ray (0.1541 nm), θ is the diffraction angle and K is the Scherrer constant (0.94).

From Table 2, the average crystallite size of CNTs produced from both the pure activated carbon and the nickel ferrite doped activated carbon were depicted. The Average crystallite size for CNTs from pure AC and CNTs from Fe-Ni/AC were found to be 2.31 and 7.11 nm respectively. The increment in the particle size is attributed to the formation of nickel ferrites which accompanied the produced carbon nanotubes in the CVD reactor. Therefore, to maintain a low particle size of CNTs

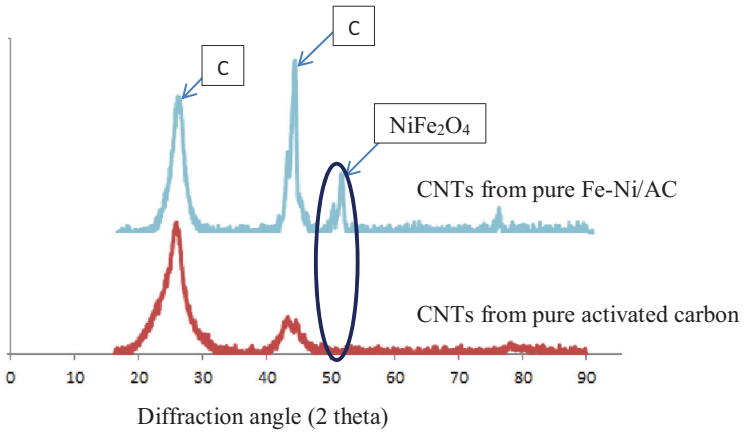

Fig. 4. XRD spectral of CNTs developed from both pure activated carbon and Fe-Ni/AC.

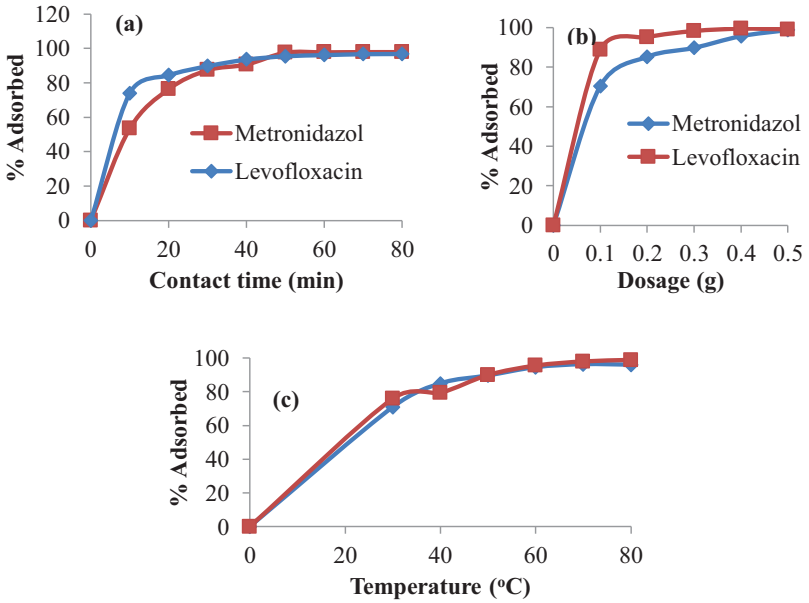

Fig. 5. Effects of (a) contact time (b) adsorbent dosage and (c) temperature on the percentage removal of metronidazole and levofloxacin from pharmaceutical wastewater.

material, it's required to operate the CVD equipment with only the activated carbon without the incorporation of doping agent as an active part of catalyst. Also, the synthesis of low nanosized CNTs is also promoted with the absence of doping agent on the catalyst material. The surface area of the CNTs produced from pure activated carbon was determined to be 501.31 m^2/g; an appreciable property for possible application in adsorption process.

The carbon nanotubes produced via pure activated carbon was employed in the treatment of pharmaceutical wastewater in removing metronidazole and levofloxacin. Batch adsorption method was employed and the kinetic, thermodynamic and isotherm studies were studied. The effects of contact time, adsorbent dosage and temperature on the percentage sorption of levofloxacin and metronidazole from pharmaceutical wastewater is as shown in Fig. 5.

The kinetic model fitting the experimental data were analysed using the Elovic, pseudo-first order and pseudo-second order kinetic model. The expressions are depicted in Eqs. (2)–(6).

$$qt = \frac{1}{\beta e}\ln(\alpha\beta e) - \frac{1}{\beta e} lnt \tag{2}$$

Eq. (2) represents the Elovic kinetic model where q_t represents the initial rate of the adsorption in mg/min as dq_t/q_t approaches βe when the $q_{t=0.}$ βe is related to the degree of surface coverage and the activation energy for the chemisorption

Table 3
Kinetics parameters obtained from the kinetics model adopted.

Pollutants	Kinetics	Parameters	Quantity
Metronidazole	Pseudo-first order kinetic	q_e,exp (mg/g)	4.8032
		q_e,cal (mg/g)	6.2201
		k(min^{-1})	0.0776
		R^2	0.5309
	Pseudo-second order kinetic	q_e,exp (mg/g)	4.8032
		q_e,cal (mg/g)	5.4525
		k(min^{-1})	0.0202
		R^2	0.9971
	Elovic Model	β	0.9488
		α	1.6338
		R^2	0.9294
Levofloxacin	Pseudo-first order kinetic	q_e,exp (mg/g)	9.8235
		q_e,cal (mg/g)	1.1874
		k(min^{-1})	0.0162
		R^2	0.1304
	Pseudo-second order kinetic	q_e,exp (mg/g)	9.8235
		q_e,cal (mg/g)	10.4822
		k(min^{-1})	0.0219
		R^2	0.9998
	Elovic Model	β	0.8699
		α	103.71
		R^2	0.9556

process (g/mg).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

Eq. (3) represents the second order kinetic model where the initial sorption rate at $q_t = 0$ is represented as h (mg.g^{-1}min^{-1}). Hence,

$$\frac{t}{q_e} = \frac{1}{H} + \frac{t}{q_t} \tag{4}$$

The plot of $\frac{t}{q_e}$ against time, t gives a linear relation that gives the q_e (adsorption capacity), k_2 (adsorption constant) and H (initial rates of adsorption in mg.g^{-1}min^{-1}) obtained on the graph.

$$\log(q_e - q_t) = \log q_e - \frac{K}{2.303} t \tag{5}$$

Eq. (5) depicts the first order kinetic model where k represents the first order adsorption rate of the process (L.min^{-1}) obtained from the plot of log (q_e/q_t) against t while the adsorption capacity (q_e) was obtained using Eq. (6).

$$q_e = \frac{(c_o - c_e)v}{M} \tag{6}$$

Where v shows the volume of the effluent (mL), Co and Ce depict the initial and equilibrium concentration and M represents the mass of the sorbent. The results of the kinetic model are shown in Table 3.

From Table 3, the Pseudo-First order, Pseudo-second order and Elovic Model were adopted for the kinetic models of Metronidazole and Levofloxacin sorption. The graph of quantity adsorpbed at time, t against the $t^{1/2}$ indicates the occurrence of two or more sorption steps during the adsorption process.; the swift transfer of adsorbate on to the surfaces of the adsorbent via chemical/physical means, the intraparticle diffusion and the adsorbent surfaces saturation. From Table 3, the obtained R^2 value for the pseudo-first order kinetic models depicts a very low values. The observed low value of the correlation coefficient indicate a noticeable discripancies in the obtained experimental values and the theoretical values. This indicates that the pseudo-first order kinetic model gives a poor fitting. The R^2 values for the pseudo-second order kinetic models were more appreciable than the Elovic and the pseudo-first order models. The correlation coefficients for both metronidazole and levofloxacin were obtained to be closer to unity. Therefore, the pseudo-second order model defines the adsorption of the adsorbates as a slow process through transport to the sorbent surfaces and diffusion to the adsorbent pores while the initial swift adsorption is described by the psedo-first order model.

The Langmuir and the Freundlich Isotherm models were employed for the adsorption of Levofloxacin and Metronidazole onto the surfaces and the pores of the developed MWCNTs obtained from Fe-Ni supported on activated carbon catalyst. The result of the Isotherm data is as presented in Table 4.

From Table 4, the values of the KL, the adsorption coefficients for both the Langmuir and Freundlich were determined for both the Metronidazole and Levoflaxacin. The value of the adsorption coefficients were estimated via the linear model and the sorption coefficient, L /mg was observed to be highest for the removal of Metronidazole in Langmuir model. The obtained

Table 4
Isotherm parameters for the sorption of Metronidazole and Levofloxacin from Pharmaceutical wastewater.

Pollutants	Isotherm	Parameters	Quantity
Metronidazole	Langmuir	K_L(L/mg)	62.2161
		a_L (L/mg)	13.0208
		Q_o (mg/g)	0.20928
		R_L	0.01613
		R^2	0.6897
	Freundlich	K_f	0.7047
		I/n	0.3852
		n	2.5961
		R^2	0.8598
Levofloxacin	Langmuir	K_L(L/mg)	42.1757
		a_L (L/mg)	25.8393
		Q_o (mg/g)	0.61267
		R_L	0.0114
		R^2	0.6768
	Freundlich	K_f	1.2277
		I/n	0.4681
		n	2.1363
		R^2	0.9123

Table 5
Thermodynamic parameters of metronidazole and levofloxacin sorption.

Sorbate	Temp (°C)	$(\Delta H)^o$ (kJ/mol)	$(\Delta S)^o$ (kJ/mol)	$(\Delta G)^o$ (kJ/mol)
Metronidazole	303	59.8675	−206.5450	122.4500
	313			124.5160
	323			126.5810
	333			128.6470
	343			130.7120
	353			132.7780
Levofloxacin	303	37.9135	−136.4490	79.2577
	313			80.6222
	323			81.9866
	333			83.3511
	343			84.7156
	353			86.0801

parameters derived from the both the Isotherm models were presented in Table 4. The degree of adsorption favourability is expressed with the "n"; the adsorption characteristics. Generally, the n value < 1 indicates the poor adsorption characteristics, $1<n<2$ also implies that the adsorption process is moderately difficult while the adsorption characteristics ranging from 2–10 is said to be good. From the depicted results from Table 4, adsorption characteristics of Metronidazole and Levofloxacin were found to be 2.5961 and 2.1363 respectively. The obtained values for the two adsorbates indicate that the adsorption of Metronidazole and Levofloxacin on to the surfaces and the pore surfaces of the developed sorbent were fairly good. This behaviour indicates that the sorption process takes place in a unified mechanism due to physicochemical characteristics properties of the sorbent under study.

The thermodynamic parameters such as the enthalpy change ($\Delta H°$), Gibbs free energy ($\Delta G°$) and entropy change ($\Delta S°$) are very important parameters needed to understand the thermodynamic behaviour of the adsorption process for the sorption of metronidazole and levofloxacin onto the surfaces and the pores of the developed MWCNTs adsorbent. Eqs. (7) and (10) represents the mathematical representation of the thermodynamic parameters.

$$\ln \mathrm{Kc} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{7}$$

$$\Delta G^o = \Delta H^o \Delta S^o \tag{8}$$

Where R is the gas constant, K_c is the equilibrium constant and T is absolute temperature, K. The data were fitted to generate the Gibb's free Energy, Enthalpy and entropy of the sorption process for developed MWCNTs sorbent.

The results depicted on Table 5 indicates that the thermodynamic properties were temperature dependent. The positive values of the obtained $\Delta G°$ for the working temperatures indicate that the sorption of metronidazole and levofloxacin were not spontaneous in nature while the negative values of the entropy implies that the sorption process is entropy driven. The high value of the enthalpy confirms the presence of strong bonding existing between the molecules of the sorbate and the surfaces of the adsorbent. The change in enthalpy is an important parameter that predicts the nature of sorption taking place during the adsorption process. The values of ΔH for metronidazole was found to be greater than

40 kJ/mol; this indicate the sorption od metronidazole on to the surfaces of the developed MWCNTs from aqueous solution is chemisorption and that of levofloxacin sorption is physisorption. This finding is in accordance with the findings of [19].

Conclusion

From the results of the analysis obtained, the developed activated carbon has the potential properties that enable it application as catalyst support for the synthesis of carbon nanotubes in a catalytic vapour deposition equipment. Also, pure activated carbon produced via physical activation process depicts an excellent catalytic properties in the decomposition of acetylene gas to form a nucleated carbon material, CNTs. The pure activated carbon possesses an appreciable surface area compared to the nickel-ferrite doped activated carbon. Furthermore, the XRD spectral of the synthesised MWCNTs produced from pure activated carbon shows a formation of graphitic carbon at 2 theta angles of 25.67 and 43.28° for both the CNTs produced from pure activated carbon and that of Fe-Ni/activated carbon except for the formation of ferrite peaks. The developed MWCNTs obtained using pure activated carbon depicts effective and efficient sorption of metronidazole and levofloxacin from pharmaceutical wastewater with favourable adsorption behaviour. The adsorption process leading to the removal of metronidazole and levofloxacin were multilayers in nature. This study demonstrated for the first time, the potential characteristic properties of activated carbon as an excellent support material for the synthesis of good quality CNTs and its possible application for metronidazole and levofloxacin sorption.

Declaration of Competing Interest

None.

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