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Comparative analysis of linear and nonlinear equilibrium models for the removal of metronidazole by tea waste activated carbon

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ABSTRACT

Tea waste was carbonized at 400 °C for 45 min and modified with potassium hydroxide (KOH), to enhance the active sites for the adsorption of antibiotics. The developed tea waste activated carbon (TWAC) was used as a novel eco-friendly and cost-effective adsorbent for metronidazole (MZN) removal from aqueous solution. The textural and surface properties of the adsorbent were determined using Brunauer-Emmett-Teller (BET) and FT-Raman analysis. The BET surface was found to have increased from 24.670 to 349.585 after carbonization and KOH modification. The batch experimental parameters were optimized and equilibrium time was found to be 75 min. Linear and non-linear models were carried out on the adsorption isotherm and kinetics to determine the best fit for the adsorption data. The adsorption equilibrium data were well fitted by the Freundlich isotherm and pseudo-second order models, with higher regression correlation (R^2) and smaller chi-square (χ^2), as predicted by the non-linear model. The thermodynamic results revealed the adsorption of MZN as spontaneous, physical, and consistently exothermic in character. The activation energy value of 7.610 kJ/mol further revealed that the adsorption process is dominated majorly by physical adsorption. The removal of MZN onto TWAC was best described by the non-linear adsorption isotherm and kinetics model.

Key words | activation energy, linear, metronidazole, nonlinear, tea waste

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HIGHLIGHTS

- Activated carbon developed from tea waste.
- Developed adsorbent characterization.
- Removal of metronidazole using the produced adsorbent.
- Isotherm, kinetic and thermodynamic studies.
- Comparison of both linear and nonlinear fittings.

INTRODUCTION

Pharmaceutical products, such as analgesics, hormonal drugs, antidepressants, antiepileptics, and antibiotics, are emerging contaminants that have posed a great risk to public health. This is due to excessive use and improper discharge into the environment, especially in the water cycle at low concentrations (Guo *et al.* 2017; Kang *et al.* 2018). Antibiotics, amongst other pharmaceutical products,

are usually prescribed for the prevention of bacterial infections, as well as to cure humans and livestock (Carrales-Alvarado *et al.* 2014). The presence of antibiotics in surface water may be as a result of conventionally improper treatments before their discharge. Antibiotics are discharged into water bodies through sludge and effluent from hospitals, livestock farms, agricultural and pharmaceutical

industries, as well as health care centers. The presence of these antibiotics at low concentrations in water affects the quality of human health, drinking water, and the ecosystem (Hom-Diaz *et al.* 2017; Segovia-Sandoval *et al.* 2019).

Due to its high resistance to bacteria, metronidazole (MZN) is the most widely used antibiotic in infectious disease treatment in humans. This is majorly caused by anaerobic bacteria and protozoans, including *Giardia lamblia* and *Trichomonas vaginalis*. MZN is also used as an additive in poultry and aquaculture farms, to eliminate parasites (Fang *et al.* 2011; Wang *et al.* 2016). MZN, which belongs to the antibiotic group called nitroimidazoles, is difficult to eliminate, thus accumulating easily in aqueous environments owing to its weak adsorption in soils, non-biodegradability, high water dissolubility, high mobility, and high toxicity (Tran *et al.* 2019). MZN metabolites are also potentially mutagenic, carcinogenic, and toxic. The continuous release of MZN into the aquatic environment may significantly affect the ecosystems (Hossain *et al.* 2018). The increasing level of MZN has been potentially found to be carcinogenic, mutagenic, and genetically toxic, thereby resulting in their bioaccumulation in aqueous solution (Jiang *et al.* 2018). Therefore, the removal of MZN from an aqueous solution is a necessity.

Physical, biological, and chemical methods of wide range, such as adsorption, photodegradation, advanced oxidation processes, membranes, liquid extraction, and activated sludge, have been employed in the removal of MZN from aqueous solution (Flores-Cano *et al.* 2016; Segovia-Sandoval *et al.* 2019; Sekulic *et al.* 2019). Adsorption, among others, has proven to be the most effective and is the most commonly used technique, which has significantly attracted wide attention for removal of antibiotics from aqueous solution. This is particularly due to its excellent adsorption capacity, energy efficiency, regeneration ability, ease of operation, operational free-sludge properties, economical friendliness, and availability of raw materials (Genç *et al.* 2013; Jiang *et al.* 2013). The use of activated carbons as adsorbents for adsorption, has gained wide recognition due to their chemical and textural properties (Auta & Hameed 2011).

The economical effectiveness and excellent sorption performance of an activated carbon are largely dependent on the type of precursor used, the activating agent, and the mode of production. Nowadays, researchers focus more on the agricultural waste materials that can be used as precursors when compared with the available commercial ones. The usefulness of activated carbons in adsorption processes cannot be overemphasized, as they offer excellent

adsorption capacity (Amin 2009). Amongst the activation method used for activated carbon preparation, chemical activation – which involves carbon material treatment with chemicals in either solid or liquid form before heat application in an inert atmosphere – offers an increasing surface area and pore development, thus making it an enhanced adsorbent. Furthermore, amongst various chemicals used for activated carbon activation, potassium hydroxide (KOH) has proven over time to be a good activating agent due to the development of its large pore size and increased surface area (Dolas *et al.* 2011; Duran *et al.* 2011). Moreover, the research work by Auta & Hameed (2011) on optimized waste tea bag activated carbon for adsorption of methylene blue and acid blue 29 using response surface methodology, reported an adsorbent surface of 854.300 m²/g, using KOH as the activating agent.

This study focused on the assessment of the adsorption potential of waste tea activated carbon, as a novel adsorbent for the adsorption of MZN. The various factors studied in the adsorption process via batch study were temperature, solution pH, adsorption time, and initial concentration. Adsorption thermodynamics, kinetics, and isotherms were used to investigate the adsorption regulatory and adsorption mechanism of this study. Linear and non-linear fittings were used to fit the adsorption data. To the best of our knowledge, no author has reported the development of waste tea activated carbon using KOH as an activating agent, as well as its use on effective removal of MZN from aqueous solution.

MATERIALS AND METHOD

Materials

Potassium hydroxide (KOH), hydrochloric acid (HCl), and metronidazole (C₆H₉N₃O₃), of analytical grade and 99.99% purity, were purchased from Sigma-Aldrich Chemicals, USA. Tea waste was handpicked from local tea shops around the Federal University of Technology, Minna, in the Bosso Local Government Area of Niger State, Nigeria. The waste tea was washed in hot distilled water for a number of times, to achieve tea waste purification (to remove soluble and colourless components) and then it was dried in an oven at 108 °C until a constant weight was attained. The granular form tea waste was then sieved with a 125 µm mesh. Stock solution (1,000 mg/L) of powdered MZN (171.180 g/mol) and purity of 97%, purchased from Sigma Aldrich, USA, was prepared by dissolving known

amount in ultrapure water/methanol solution (70%/30%, v/v) and stored at room temperature in a glass container for no longer than 15 days for further experiment. The solution was adjusted using 0.1 M of HCl and NaOH. To prepare different MZN initial concentrations of 20, 60, 100, and 150 mg/L, the stock solution was diluted in precise proportions. A standard curve for each concentration of MZN was developed by measuring the absorbance of the MZN solution at a wavelength of 340 nm using a UV/Vis spectrophotometer (Model 1700, Shimadzu, Japan).

Development of tea waste activated carbon

Tea waste was activated with KOH as the activating agent under the consideration of the following factors: temperature of activation 400 °C and activation time of 45 min. The choice of the selected operating condition was as a result of the detailed preliminary studies from literature. The impregnation ratio of the activating agent to the precursor was maintained at 1.5:1 g/g and 4 g of dried precursor (125 µm) was measured and mixed with the activating agent in a beaker. The impregnated sample was left for 24 h at room temperature, and then oven dried at 120 °C. The dry impregnated char was later transferred to the muffle furnace at 5 °C/min heating rate for carbonization under similar conditions (400 °C and 45 min) and 150 cm³/min nitrogen of 99.5% purity was flowed through the muffle furnace. After carbonization, the furnace was switched off and the prepared adsorbent was allowed to cool at room temperature. The developed activated tea waste was removed from the furnace, and then washed with 0.2 M HCl followed by washing with distilled water until a pH of 7 was attained. At the end of the experiment, the prepared tea waste activated carbon (TWAC) was dried in an oven at 105 °C for 90 min and then stored in airtight container for further use.

Adsorbent characterization studies

The precursor and prepared adsorbent textural properties were determined from the adsorption-desorption isotherms of N₂ at 77 K, using a surface area and porosimetry analyser (Micromeritics ASAP 2020). The Brunauer–Emmett–Teller (BET) method was used to determine the surface area, pore size, and pore volume distribution. Raman spectroscopy analysis was recorded at room temperature using a Micro-Raman laser spectrometer (Thermo Scientific, laser DXR 532 nm), with a scanning range between 50 and 3,500 cm⁻¹ and at a laser power of 24 MW, to determine

the functional group of the precursor and developed adsorbent.

The pH point of zero charge (pHpzc) of the prepared tea waste adsorbent surface was obtained by the solid addition method described by [Auta & Hameed \(2011\)](#). 30 mL each of 0.1, 0.01, and 0.001 mol/dm³ KNO₃ were measured into 18 conical flasks of 100 mL with glass stoppers, and 0.1 g of the prepared adsorbent was added. The prepared KNO₃ solutions' pH was adjusted between 2 and 12 with either 0.1 M of NaOH or 0.1 M HCl. The samples were stirred for 12 h at 140 rpm. At the termination of time, when equilibrium was attained between the adsorbent (TWAC) and KNO₃ solution, the final pH readings were noted. The final pH values were plotted against the initial pH values of the solution (Figure not shown), and at the point where a plateau-like feature occurred on the plot, the corresponding pH reading was noted and taken as the pHpzc of the adsorbent.

Batch equilibrium studies

Equilibrium batch adsorption studies were conducted to investigate the effect of contact time, initial MZN concentration, temperature, and solution pH as follows. The equilibrium studies were performed in a set of 250 mL Erlenmeyer flasks with 100 mL of MZN at different initial concentrations (20, 60, 100 and 150 mg/L) and 0.1 g of TWAC adsorbent was added to each of the flasks. The initial pH solution of the MZN was maintained throughout the adsorption process. The flask was then placed on the water bath isothermal shaker, adjusted to the temperature of 30 °C, with a time of 2 h and shaker speed of 145 rpm. Prior to attainment of the equilibrium condition, samples were taken, filtered through Whatman No:41 filter paper and measured with the aid of a UV-Visible spectrophotometer (Shimadzu UV-160A) at a maximum wavelength of 340 nm. The batch adsorption experimental procedure was repeated with different sets of Erlenmeyer flasks containing different initials, but at temperatures of 40 and 50 °C respectively.

The percentage MZN removal, the amount of the MZN adsorbed at equilibrium q_e (mg/g) and at time t , q_t (mg/g), was calculated using the following equation:

$$(\%) \text{ MZN removal} = \frac{c_o - c_f}{c_o} \times 100 \quad (1)$$

$$q_e = \frac{(c_o - c_e)v}{w} \quad (2)$$

At equilibrium, $c_t = c_e$

$$q_t = \frac{(c_0 - c_e)}{w} v \quad (3)$$

where q_e is the amount of MZN adsorbed, (mg/g), c_0 , c_e , c_t , and c_f (mg/L) are the liquid-phase initial, equilibrium, intervals, and final MZN concentrations respectively; v (L) is the volume of the solution; and w (g) is the weight of the dry adsorbent.

RESULT AND DISCUSSION

Characterization studies

The Brunauer–Emmett–Teller analysis of the prepared adsorbent gave a BET surface area of 349.585 m²/g, pore diameter of 2.147 nm, and a pore volume of 0.1,906 cm³/g. That of the precursor (waste tea), gave a BET surface area of 24.670 m²/g, pore diameter of 1.232 nm, and pore volume of 0.0034 cm³/g, respectively. The highest BET value was acquired for the activated carbon prepared from

tea waste, when compared to that of the precursor as presented in Table 1. The highest BET value obtained for TWAC may be on account of the greater potassium hydroxide impregnation ability. The pore structure of tea waste was found to be microporous (<2 nm), while that of the tea waste adsorbent was mesoporous in nature (2–50 nm). The pH zero charge value obtained from the experimental values at different KNO₃ concentrations was 7.9±0.2.

The FT-Raman spectra of the two samples (precursor and the prepared activated carbon), revealed the presence of several peaks of functional groups. Raman spectra in Figure 1 were compared to the available studies of Bumbrah & Sharma (2015) and Bokobza et al. (2014). The spectra of the precursor showed a broad peak band around 500 cm⁻¹, indicating some amorphous sp³ bonded carbon. Absorption peaks between 600 and 650 cm⁻¹ are attributed to aliphatic C-S. The band between 854 and 876 cm⁻¹ is assigned to C-O-C. The band of 1,020 cm⁻¹ is attributed to Si-O-Si. Absorption band at 1,820 cm⁻¹ is assigned to C=O. The band at 2,100 cm⁻¹ is assigned to C≡C and the band at 2,880 cm⁻¹ is attributed to C-H. The prepared activated carbon spectra showed a peak known as the D (disordered) band at 1,350 cm⁻¹ and a relatively sharp peak at 1,488 cm⁻¹, which can be attributed to C-H vibration, also known as the pentagonal pinch mode composed of sp² bonded carbon. Similar sharp peaks at 1,451 cm⁻¹ and 1,462 cm⁻¹ were observed (Tumirah et al. 2015; Li et al. 2015). It was discovered that the process of activation reduces the very sharp peak of the precursor from 2,110 cm⁻¹ (C≡C) to a smaller peak within 2,100–2,111 cm⁻¹ as a result of the operating conditions.

Table 1 | BET analysis

Adsorbent	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Micropore volume (cm ³ /g)	Pore size (nm)
Tea waste	24.670	0.00340	0.00190	1.232
TWAC	349.585	0.191	0.0987	2.147

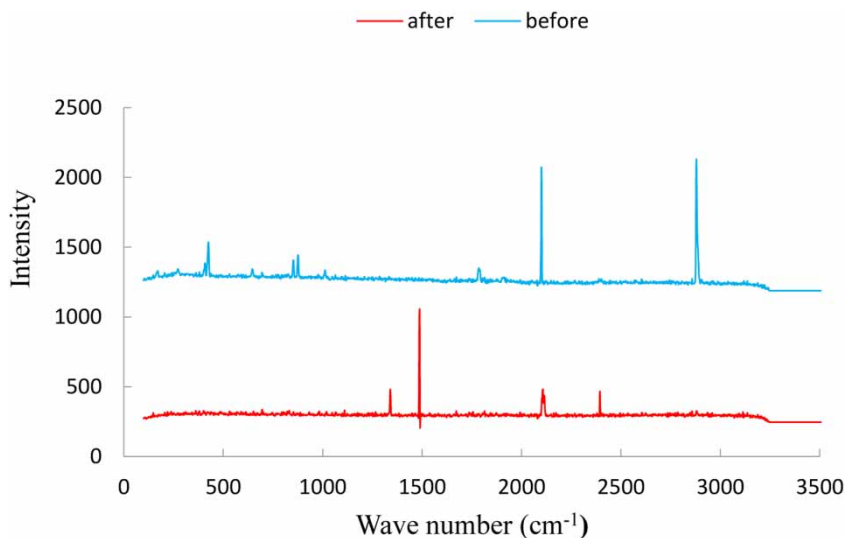


Figure 1 | FT-Raman spectra of the precursor and prepared tea waste activated carbon.

Effect of solution pH

The effect of solution pH was tested between pH ranges of 2–10 for a constant dosage of 0.1 g and 100 mg/L MZN concentration, at 30 °C for 75 min as depicted in Figure 2. The solution pH is vital in the adsorption process as it significantly affects interaction between MZN and the adsorbent surface charge in the solution. MZN percentage removal increases as the solution pH increases; thus, the highest MZN uptake was achieved at a higher pH of 10. The MZN pKa value of 2.58 showed that their molecule is almost at a protonated state at $\text{pH} \leq 2$ (Carreras-Alvarado *et al.* 2014). Furthermore, the value of the pH_{pzc} obtained for the adsorbent is an indication that the adsorbent surface becomes positive at $\text{pH} < \text{pH}_{\text{pzc}}$ and negative at $\text{pH} > \text{pH}_{\text{pzc}}$. Therefore, at lower pH, an increasing number of hydrogen ions in the solution made the surface of the adsorbent more positively charged, thereby leading to an electrostatic repulsion between the adsorbent and the adsorbate (Ahmad & Alrozi 2010). However, at high pH, the percentage removal of MZN increases significantly due to the increase of electrostatic attraction between the solid and liquid phase, because of the decrease in positive charges in the solution (Ramavandi & Akbarzadeh 2014). This result is similar to the work of Segovia-Sandoval *et al.* (2019), who concluded that the higher uptake of MZN at higher pH may be due to hydrophobic and $\pi - \pi$ dispersive interaction between the prepared activated carbon and MZN.

Effect of initial MZN concentration and equilibrium time

The effect of concentration and adsorption time was investigated on the percentage removal of MZN onto TWAC as presented in Figures 3 and 4. It was observed from the rate curve that the percentage removal of MZN increases with increasing initial concentration and time, which was further followed by a slow approach and equilibrium was finally attained as shown in Figure 5. The obtained results showed that adsorption capacity of 18.1 mg/g was achieved in 15 min at a concentration of 20 mg/L, while it took 45 min to attain equilibrium with concentrations of 60 and 100 mg/L. The adsorption capacity at 60 and 100 mg/L was 49.5 and 85 mg/L, respectively. At the higher concentration of 150 mg/L, the equilibrium position was achieved in 75 min and the adsorption capacity was found to be 126.2 mg/g. The result trend can be accredited to more vacant sites in the initial stage of the adsorption process, which tend to be occupied as the adsorption process continues, thereby resulting into a decrease in the removal of MZN (Ahmad & Alrozi 2010). Consequently, at a lower concentration of MZN, the equilibrium position was achieved faster than at a higher concentration, owing to the fact that the availability of more vacant sites was lesser in number than the adsorbate. Furthermore, it was observed that the adsorption time increased beyond the equilibrium time (75 min), which resulted in a negligible variation of MZN percentage removal (Sandra *et al.* 2013; Sepehr *et al.* 2016).

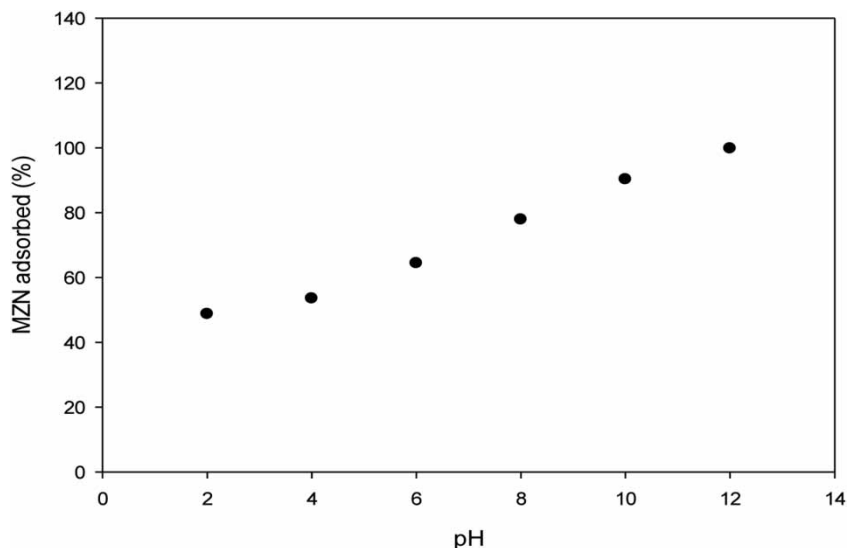


Figure 2 | Effect of pH on the adsorption of MZN on TWAC at 30 °C (rpm = 145; V = 100 mL; W = 0.1 g; C₀ = 100 mg/L and time = 75 min).

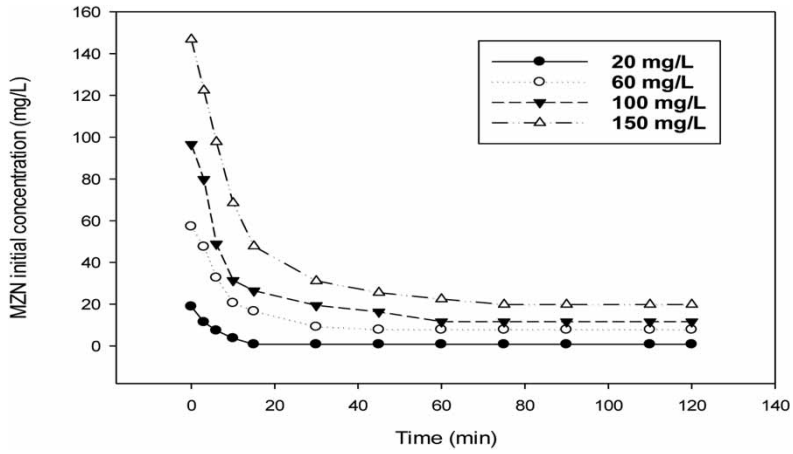


Figure 3 | Effect of concentration on the adsorption of MZN on TWAC at 30 °C; rpm = 145, V = 100 mL, W = 0.1 g, pH = 7).

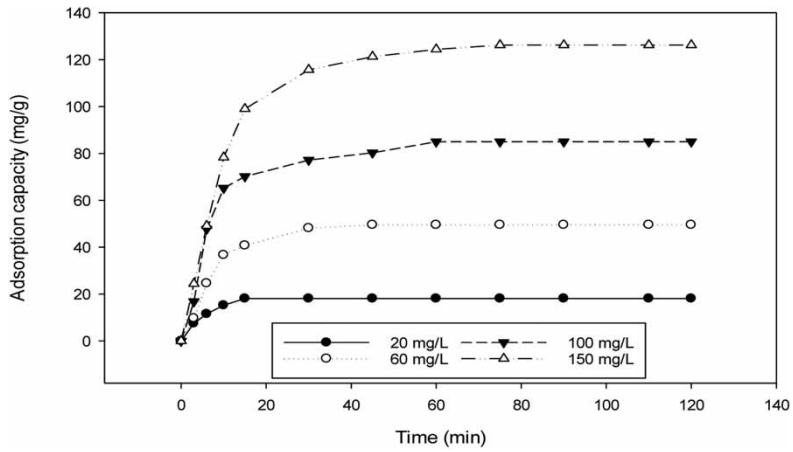


Figure 4 | Effect of adsorption time on MZN removal by TWAC at (30 °C, rpm = 145, V = 100 mL, W = 0.1 g, pH = 7).

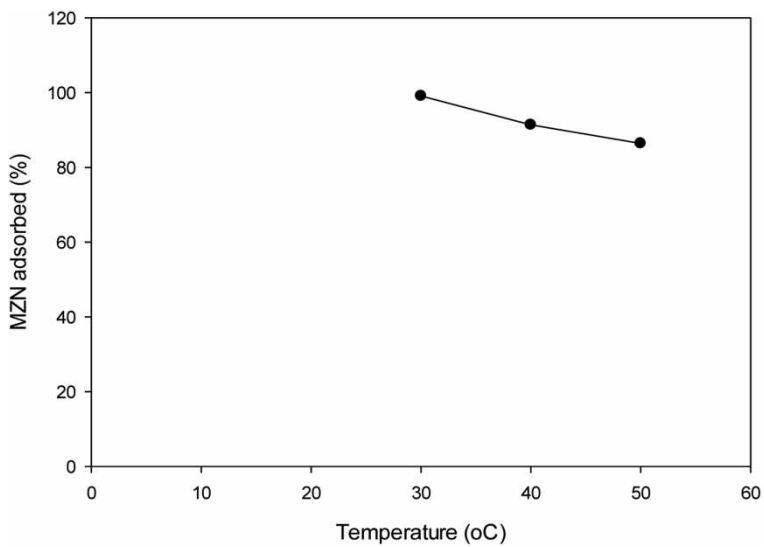


Figure 5 | Effect of temperature on the adsorption of MZN on TWAC at (rpm = 145, V = 100 mL, W = 0.1 g, pH = 7, time = 75 min; C₀ = 100 mg/L).

Effect of temperature

The percentage adsorption of MZN on temperature was investigated at various temperatures of 30, 40, and 50 °C, with a 100 mg/L initial MZN concentration at 75 min equilibrium time. The graph plotted in Figure 5 revealed that MZN percentage removal was higher at decreasing temperature. This could be attributed to the fact that water solubility increases as the temperature increases, thereby leading to the attractive force between the adsorbate and the adsorbent. The removal of MZN onto the prepared activated carbon is an exothermic process (Jodeh et al. 2016).

Adsorption isotherm

Adsorption equilibrium establishment occurs when an adsorbent (solid phase) comes into close contact with the adsorbate (liquid phase) for a certain period of time. In this study, Langmuir, Freundlich, and Temkin isotherms were used to test the adsorption equilibrium data (Kumar & Sivanesan 2007). The linear and non-linear form of these model equations are given as (Foo & Hameed 2010):

$$q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \quad (4)$$

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}} \quad (5)$$

$$q_e = K_F C_e^{1/n} \quad (6)$$

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \quad (7)$$

$$q_e = B \ln (A_T C_e) \quad (8)$$

$$q_e = B \ln A_T + B \ln C_e \quad (9)$$

$$B = \frac{RT}{b_T} \quad (10)$$

where C_e is the equilibrium concentration of adsorbed MZN (mg/L); q_e is the amount of MZN adsorbed (mg/g); (q_{max}) is the maximum adsorption capacities (mg/g); K_F and n are Freundlich equilibrium coefficients. The n value gives information on adsorption process favourability, while K_F is the adsorbate adsorption capacity. A_T is the maximum binding energy, b_T is the heat of adsorption (J/mol), R is the gas constant (8.314 J/Kmol), and T is temperature in Kelvin (K).

To evaluate the goodness of fit of an isotherm and kinetic model, the chi-square error was employed, as the R^2 might not be a sufficient criterion to determine the best fit model. The incorporation of the Chi-square together with the R^2 , was used in determining the isotherm fitness to the adsorption process. The Chi-square (χ^2) equation is calculated as:

$$\chi^2 = \sum_{i=1}^N \frac{(q_{e,exp} - q_{e,cal})^2}{q_{i,cal}} \quad (11)$$

The equilibrium adsorption isotherm results obtained for both linear and non-linear plots, together with their R^2 and χ^2 values, are calculated and presented in Table 2. It was observed from the result that the Langmuir model fitted well to the linear fitting with R^2 values of 0.917, which is higher than the values obtained for the Freundlich (0.901) and Temkin (0.830) models. The Langmuir model was further affirmed by the smaller value of χ^2 (0.253) obtained when compared to the other models. Furthermore, the result of the non-linear fitting showed a good fit to the Freundlich model, with R^2 (0.999) and smaller value of χ^2 (0.0223). The comparison of both fittings in terms of their R^2 and χ^2 values strongly indicates that the adsorption of MZN onto TWAC best followed the Freundlich isotherm.

Table 2 | Adsorption isotherm fitting parameters on MZN removal onto TWAC

Isotherms	Parameters	Values		R^2	χ^2	R^2	χ^2
		Linear	Non-linear				
Langmuir	q_{max}	166.667	187.567	0.944	0.253	0.917	0.0342
	K_L	0.857	0.902				
Freundlich	K_F	65.517	71.556	0.901	0.340	0.999	0.0223
	$1/n$	0.324	0.201				
Temkin	A_T	6.666	3.520	0.830	3.567	0.885	1.143
	b_T	60.702	72.567				

The applicability of this model to best fit the adsorption process was proved by the higher R^2 and smaller χ^2 values. The smaller χ^2 value of the Freundlich model was good because it showed the closeness of the experimental data to the calculated data. A value of $1/n$ between 0 and 1 indicates the surface heterogeneity and favourability of the adsorption process. The adsorbent surface becomes more heterogeneous as the values get closer to 0 (Obayomi & Auta 2019). The $1/n$ value of 0.201 showed that the TWAC adsorbent surface is heterogeneous and the adsorption of MZN onto the adsorbent is favourable. This finding is similar to the results obtained on photocatalytic degradation of metronidazole in aqueous solution by copper oxide nanoparticles (El-Sayed *et al.* 2014), and the adsorption of metronidazole in aqueous solution by Fe-modified saprolite (Ding & Bian 2015). The prepared TWAC adsorbent was compared to other adsorbents and their adsorption capacity is presented in Table 3.

Adsorption kinetic

The non-linear and linear form of pseudo-first-order equation is given as (Lagergren & Svenska 1898):

$$q_t = q_e(1 - e^{-k_1 t}) \quad (12)$$

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (13)$$

Table 3 | Adsorption capacity of MZN onto various adsorbents

Adsorbent	q_{\max} (mg/g) values	References
Tea waste AC	187.567	This study
Canola residue	21.42	Manjunat <i>et al.</i> (2017)
CuO nanoparticle	25.90	El-Sayed <i>et al.</i> (2014)
SiC nanoparticle	114.817	Fakhri <i>et al.</i> (2017)
Coffee residue-based AC	126	Flores-Cano <i>et al.</i> (2016)
Siris seed pods AC	196.31	Ahmed & Theydan (2013)
Fe-modified sepiolite	5.62	Ding & Bian (2015)

Table 4 | Adsorption kinetic linear fitting parameters on MZN removal onto TWAC at 303 K

C_0 (mg/L)	$q_{e, \text{exp}}$ (mg/L)	Pseudo-first order				Pseudo-second order			
		$q_{e, \text{cal}}$ (mg/g)	k_1 (min^{-1})	R^2	χ^2	$q_{e, \text{cal}}$ (mg/g)	K_2 ($\times 10^{-3}$) (g/mg.min)	R^2	χ^2
20	18.240	10.400	0.0763	0.867	5.910	16.480	42.561	0.997	0.188
60	58.020	46.660	0.0747	0.893	2.774	55.520	3.987	0.997	0.113
100	97.150	85.470	0.0729	0.881	1.596	92.0900	2.411	0.998	0.278
150	146.250	124.740	0.0845	0.878	3.709	142.860	2.187	0.996	0.0804

The non-linear and linear form of the pseudo-second order equation is given as (Ho & McKay 1999):

$$q_t = \frac{K_2 q_e^2 t}{1 + k_2 q_e t} \quad (14)$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{K_2 q_e^2} \quad (15)$$

where k_1 (min^{-1}) and k_2 (g/mg.min) are the rate constant of first and second order adsorption.

The kinetic models, linear and non-linear fittings parameters are calculated and tabulated in Tables 4 and 5. The results of the two kinetic models investigated for both linear and non-linear fittings showed that the pseudo-second order gave the best fit to the adsorption process. The goodness of fit of the pseudo-second order is more applicable and better predicted by the non-linear fittings, with closeness of their R^2 values as unity, and smaller values of χ^2 predicting the closeness of the experimental data to be calculated. The conformity of the pseudo-second order to fit the adsorption process non-linearly was further affirmed by the closeness of the experimental adsorption capacity ($q_{e, \text{exp}}$) to the calculated adsorption capacity ($q_{e, \text{cal}}$). The suitability of the non-linear form to best fit the pseudo-second order to the adsorption process has been reported (Zaharaddeen *et al.* 2015; Moussout *et al.* 2018). Smaller rate constant values (k_2) of the pseudo-second order are an indication that adsorption takes place faster at lower concentration (Obayomi *et al.* 2020). The ability of the pseudo-second order to best fit the adsorption showed the possibility of chemical interaction between the adsorbent and adsorbate (Saleh *et al.* 2019; Obayomi *et al.* 2020). The adsorption of MZN by TWAC is more suitable to the non-linear form of the pseudo-second order kinetic model than the linear form. Similar results on the pseudo-second order describing best the adsorption process were reported by Ahmed & Theydan (2013) who studied a micro-wave-assisted way of preparing microporous activated

Table 5 | Adsorption kinetic non-linear fitting parameters on MZN removal onto TWAC at 303 K

C ₀ (mg/L)	q _{e, exp} (mg/l)	Pseudo-first order				Pseudo-second order			
		q _{e, cal} (mg/g)	k ₁ (min ⁻¹)	R ²	χ ²	q _{e, cal} (mg/g)	K ₂ (×10 ⁻³) (g/mg.min)	R ²	χ ²
20	18.240	6.600	0.0824	0.800	20.529	18.480	38.251	0.999	0.00312
60	58.020	62.990	0.0930	0.900	0.392	59.520	3.281	0.999	0.0378
100	97.150	66.870	0.842	0.842	13.711	97.0900	2.429	0.998	0.0000371
150	146.250	113.500	0.0831	0.884	9.450	145.860	1.924	0.999	0.00103

carbon from siris seed pods, for adsorption of metronidazole antibiotics. Similarly, Orellana *et al.* (2013) also reported nitroimidazoles adsorption on activated carbon cloth from aqueous solution.

Thermodynamics of adsorption

The effect of temperature was investigated on MZN adsorption by prepared activation to determine the feasibility and the nature of the adsorption process. The data obtained were evaluated in terms of thermodynamics and the equations are given as:

$$\Delta G = \Delta H - T\Delta S \quad (16)$$

$$\Delta G = -RT \ln K_c \quad (17)$$

$$K_c = \frac{Q_e}{C_e} \quad (18)$$

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (19)$$

The slope and intercept from $\ln K_c$ against $1/T$ plot were used to evaluate the entropy (ΔS) and enthalpy (ΔH) values. K_c is the distribution coefficient.

The thermodynamic parameters calculated on removal of MZN by TWAC are tabulated in Table 6. Negative values of free Gibb's energy (ΔG), enthalpy (ΔH), and

entropy (ΔS) revealed that the adsorption of MZN on TWAC is spontaneous, exothermic in nature, physical (involves weak Van der Waals forces) and involves random decrease at the adsorbate-adsorbent interface. Similarly, negative of ΔG , ΔH , and ΔS values have been reported by (Çalışkan & Göktürk 2010) on adsorption characteristics of sulfamethoxazole and metronidazole on activated carbon.

The adsorption activation energy (E_a) was calculated from the Arrhenius equation to further affirm the adsorption type on the adsorption process, as assumed by the thermodynamic.

$$\ln k_2 = -\frac{E_a}{R} \left(\frac{1}{T} \right) + \ln A \quad (20)$$

where E_a is the activation energy (kJ/mol), A is the Arrhenius constant, and k_2 is the pseudo-second order rate constant of the non-linear fittings, at 100 mg/L. The E_a value between 5 and 40 kJ/mol connotes physisorption, while a value between 40 and 800 kJ/mol implies chemisorption (Saleh 2015).

The Arrhenius plot of $\ln k_2$ against $1/T$ (figure not shown) slope gave the E_a value of 7.61 kJ/mol. The value of E_a affirmed further that the removal of MZN on TWAC requires less energy and is majorly dominated by physical adsorption.

Table 6 | Thermodynamic parameters of MZN adsorption on WTAC

Conc. (mg/L)	Gibbs free energy ΔG (kJ/mol)			Enthalpy ΔH (kJ/mol)	Entropy ΔS (J/Kmol)
	3	40	50		
20	-16.926	-13.838	-11.345	-103.692	-286.749
60	-10.123	-9.663	-8.378	-37.346	-89.376
100	-7.775	-6.98	-6.218	-32.050	-80.139
150	-7.532	-6.709	-5.819	-34.212	-88.045

CONCLUSIONS

This study reported the effective removal of MZN onto tea waste activated carbon (TWAC) as a potential adsorbent from aqueous solution. Batch adsorption efficiency tests were performed, where the effect of experimental parameters such as solution pH, initial concentration, contact time, and temperature were optimized. The adsorbent pH was reported to be between 7.7 and 8.1. Rapid uptake rate of MZN was reported within the first 15 min, followed by attainment of equilibrium at 75 min. The comparison of the linear and non-linear fittings of the isotherms and kinetics model studied showed that the results were better fitted to non-linear Freundlich and pseudo-second order models, respectively. The removal of MZN onto TWAC was spontaneous and physical in character. The experimental results obtained are a good demonstration that TWAC can be effectively used as an adsorbent for the removal of MZN from wastewater. Therefore, the non-linear models are more viable and powerful in describing the adsorption isotherm and kinetic data on the removal of MZN onto TWAC.

DATA AVAILABILITY STATEMENT

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

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