

Aqueous phase removal of ofloxacin using adsorbents from *Moringa oleifera* pod husks

Raymond A. Wuana^{*}, Rufus Sha'Ato and Shiana Iorhen

Department of Chemistry and Centre for Agrochemical Technology,
Federal University of Agriculture, Makurdi 970001, Nigeria

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Abstract. Chemically activated and carbonized adsorbents were prepared from *Moringa oleifera* pod husks (MOP), characterized and evaluated for their ability to remove a common antibiotic – ofloxacin (OFX) from aqueous solution. The pulverized precursor was steeped in a saturated ammonium chloride solution for a day to give the chemically activated adsorbent (AMOP). A portion of AMOP was pyrolyzed in a muffle furnace at 623 K for 30 min to furnish its carbonized analogue (CMOP). The adsorbents showed favorable physicochemical attributes. The effects of operational parameters such as initial OFX solution pH and concentration, adsorbent dosage, temperature and contact time on OFX removal were investigated. At equilibrium, optimal removal efficiencies of 90.98% and 99.84% were achieved at solution pH 5 for AMOP and CMOP, respectively. The equilibrium adsorption data fitted into both the Langmuir and Freundlich isotherms. Gibbs free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) indicated that the adsorption of OFX was feasible, spontaneous, exothermic and occurred via the physisorption mode. Adsorption kinetics obeyed the Blanchard pseudo-second-order model. The results may find applications in the adsorptive removal of micro-contaminants of pharmaceutical origin from wastewater.

Keywords: ofloxacin; *Moringa oleifera* pod husks; adsorption isotherms; adsorption kinetics; wastewater

1. Introduction

Pharmaceuticals, a diverse collection of chemical substances including human and veterinary drugs, though historically used to prevent or treat human, animal and plant diseases, are today, frequently listed among the most important emerging contaminants of concern in the environment (McBride and Wyckoff 2002, Fawell and Ong 2012, Bu *et al.* 2013). The global market for pharmaceuticals has been estimated between 100,000 – 200,000 ton/year (Zucatto *et al.* 2010). This suggests that pharmaceutical industries, especially in the developing countries, may be major sources of pharmaceutical waste in the environment (Larsson *et al.* 2007, Li *et al.* 2008). In Nigeria, for instance, one of the challenges faced by the pharmaceutical industries is the issue of pharmaceutical waste and its impact on the environment and public health owing to an improper healthcare waste management policy and plan (Ngwuluka *et al.* 2009, Fadipe *et al.* 2011). The

*Corresponding author, Ph.D., E-mail: raywuana@yahoo.com

awareness of pharmaceuticals such as analgesics, anti-depressants, contraceptives and antibiotics in wastewater aquatic ecosystems is growing with the increased investigation into emerging pollutants and with the improvement of bioanalytical techniques (Costanzo *et al.* 2005).

Antibiotics are probably the most successful pharmaceuticals so far developed to improve human health and for preventing and treating animal and plants infection as well as for promoting growth in animal farming and all these applications cause antibiotics to be released in large quantities to natural ecosystems (Cabello 2006, Martinez 2009). The fluoroquinolones (e.g., ciprofloxacin, norfloxacin, ofloxacin) belong to a class of antibiotics of great concern because they are most widely produced and used the world over and are not completely metabolized by the body. About 20-90% of fluoroquinolones ingested are excreted in their pharmacologically active forms, leading to significant loads being discharged into domestic sewage (Kümmerer 2009). Ofloxacin (OFX) is a broad spectrum fluoroquinolone that has been linked to serious side effects which include ruptured tendons and neurological damage resulting from seizures. As micro-contaminants, antibiotics in the aquatic environment may persist and be transported to reservoirs, surface and groundwater sources which supply raw water to treatment plants (Ye *et al.* 2007). In addition, these drugs cause unpleasant odors and skin disorders, and may cause microbial resistance among pathogens or the death of microorganisms which are effective in wastewater treatment (Budyanto *et al.* 2008).

Among the strategies for aqueous phase removal of contaminants of pharmaceutical origin, approaches based on activated carbon adsorption are commonly used due to their high efficiency and easy applicability (El-Sayed and El-Sayed 2014). Activated carbon is a good adsorbent owing to its superlative attributes such as large surface area, high porosity, controllable pore structure, thermal stability and low acid and base reactivity (Bhattacharya *et al.* 2006). Despite the favorable attributes, the high cost and difficulties associated with regeneration of activated carbons have hampered their industrial applications. The realization of this challenge has entailed the continued search for alternative adsorbents from cheaply available natural, renewable and biomass-based precursors in water decontamination and remediation processes (Kalderis *et al.* 2008). The potential of adsorbents from biomass such as bagasse (Ribeiro *et al.* 2011), saw dust (Bajpai *et al.* 2012), chestnut shell (Sheikh Mohammadi and Sardar 2012), cork (Crespo-Alonso *et al.* 2013), bamboo processing waste (Wu *et al.* 2013), leaves (Bajpai and Jain 2014, Hassan and Ali 2014), wood (Pouretedal and Sadegh 2014) and stalk waste (Nurchi *et al.* 2015) to remove various pharmaceuticals or their intermediates from aqueous media has been previously reported.

Consequently, the present study was aimed at preparing, characterizing and assessing the capability of adsorbents from *Moringa oleifera* pod husks (biomass) to remove a common antibiotic – ofloxacin (OFX) from aqueous phase, with emphasis on adsorption equilibria, thermodynamics and kinetics at different temperatures.

2. Materials and methods

2.1 Adsorbent precursor, chemicals and apparatus

Moringa oleifera pod husks (MOP) were collected from some stands grown in urban Makurdi (7.44°N 8.33°E), Nigeria as the adsorbent precursor. Ammonium chloride (BDH Chemicals, 99%) was used for chemical activation of the precursor. Ofloxacin, OFX (C₁₈H₂₀FN₃O₄; MW = 361.368 g/mol, see Fig. 1 for chemical structure and name) was supplied by Embassy Pharmaceutical and

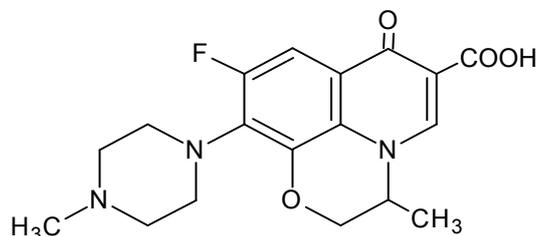


Fig. 1 Chemical structure of ofloxacin [(R)-9-fluoro-3-methyl-10-(4-methylpiperazin-1-yl)-7-oxo-3,7-dihydro-2H [1,4] oxazino[2,3,4-ij]quinoline- 6-carboxylic acid]

Chemical Limited. Major apparatuses used were glassware (borosilicate), analytical weighing balance (AE PW 184), muffle furnace (NEY M-525, USA), mechanical shaker (HY-2), thermostated water bath (DINI2877-KI), pH meter (HI96107, Hana Instruments), magnetic stirrer (Stuart SB 162 model), UV-visible spectrophotometer (Surgispec SM 7525), FT-IR spectrometer (FTIR-8400s Shimadzu, Japan).

2.2 Preparation and characterization of *Moringa oleifera* pod husk adsorbents

The precursor (MOP) was air-dried, pulverized using mortar/pestle, and the resulting powder sieved (< 2 mm). The sieved material was activated by steeping it in a saturated ammonium chloride solution for 24 h (Okieimen *et al.* 2007). The slurry was filtered and the residue rinsed repeatedly with distilled water and air-dried to serve as the chemically activated adsorbent (AMOP). A portion of the AMOP was pyrolyzed in a muffle furnace at 623 K for 30 min. The resulting carbon was washed repeatedly with distilled water to remove ash, air-dried and stored as the carbonized adsorbent (CMOP). The adsorbents were further characterized physicochemically. Adsorbent pH was determined by dispersing 1.0-g triplicate samples of the adsorbent for 1 hour and measuring the pH of the resulting filtrate (Wuana *et al.* 2009). Bulk density was determined by the tamping procedure of Ahmedna *et al.* (2000). Attrition was determined by a procedure described by Toles *et al.* (2000). Adsorbent surface area was determined by the iodine adsorption number method during which, a 0.5-g portion of the adsorbent was dispersed in an excess of standard iodine solution followed by back-titration of the unreacted iodine with standard sodium thiosulphate solution (Okieimen *et al.* 2007). A blank titration was also performed on an aliquot of iodine solution not treated with the adsorbent. The iodine number, n_{I_2} (i.e., amount in moles of iodine adsorbed per g adsorbent) was calculated using Eq. (1); while the adsorbent surface area, A (m^2/g) was calculated with the aid of Eq. (2), a modified form of that of Shoemaker *et al.* (1989)

$$n_{I_2} (\text{mol/g}) = \frac{C_{S_2O_3^{2-}} (V_b - V_s)}{2 \times 10^3 m_a} \quad (1)$$

$$A (\text{m}^2/\text{g}) = N_o \left[\frac{C_{S_2O_3^{2-}} (V_b - V_s)}{2 \times 10^3 m_a} \right] \sigma_{I_2} \quad (2)$$

where $C_{S_2O_3^{2-}}$ is the concentration of the thiosulphate (mol/L); V_b and V_s are respectively, the titre values of the blank and adsorbent-treated iodine solutions (L); m_a is mass of the adsorbent used

(0.5 g); N_o is the Avogadro's number; and σ_{I_2} is the cross-sectional area of an iodine molecule (m^2), given as $3.2 \times 10^{-19} m^2$. Titratable surface charge was determined by the Boehm titrimetric method described by Van Winkle (2000). Fourier transform infrared (FTIR) analysis was performed according to the manufacturer's specifications.

2.3 Formation of calibration curve for uv-spectrophotometric determination of ofloxacin

A 200-mg/L stock aqueous solution of OFX was prepared. Standard working concentrations: 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 mg/L were obtained by serial dilution of appropriate volumes of the stock. Each dilution was measured in a uv-visible spectrophotometer at the wavelength where OFX absorbed the highest amount of uv radiation ($\lambda_{max} = 294 \text{ nm}$). The absorbances, were read, the linearity range of 0-50 mg/L was obtained and used for constructing the calibration curve. The calibration curve (Fig. 2) was constructed so that the absorbance results collected through experimentation could be directly converted into concentration by extrapolating through the linearity range.

2.4 Batch adsorption experiments

Batch adsorption experiments were designed to investigate the effect of operational variables such as initial solution pH, concentration, adsorbent dose, contact time and temperature on aqueous phase removal of OFX by AMOP and CMOP. Meanwhile, the chemical stability of OFX was tested at 298 K, wherein separate aliquots (50 mL) of OFX standards (10, 25 and 50 mg/L) with or without AMOP or CMOP samples (0.5 g) were equilibrated for 0, 12, 24, 48 and 72 h, followed by residual OFX assay by uv-visible spectrophotometry. The range of OFX recoveries was 97.80-101.40%, and so, it was possible to confirm that the standard OFX solutions and adsorbent-treated samples were stable for four consecutive days at 298 K. Consequently, a maximum OFX-adsorbent contact time of 4 h was chosen throughout this study to minimize possible antibiotic losses especially at the higher temperatures (308-328 K) investigated.

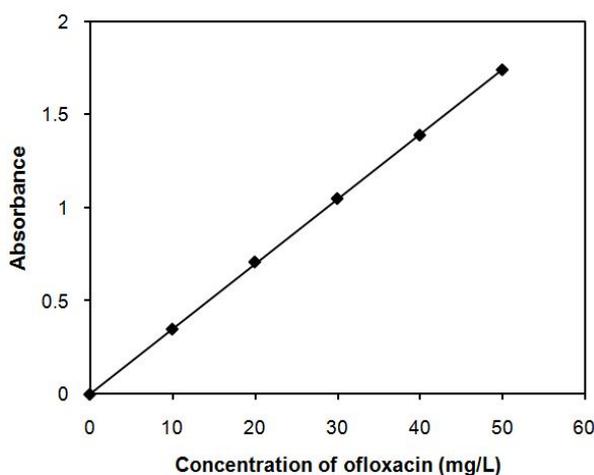


Fig. 2 Calibration curve for uv-visible spectrophotometric determination of ofloxacin in aqueous solution ($\lambda_{max} = 294 \text{ nm}$)

In order to check the effect of initial solution pH on aqueous phase removal of OFX, 0.5-g portions of AMOP or CMOP were dispersed in separate 50-mL aliquots of 50-mg/L OFX solution, which were previously adjusted to pH 2, 5, 7, 9 and 11 by drop-wise addition of 0.1 M NaOH or 0.1 M HCl, as the case may be, with the aid of a pre-calibrated pH meter. After 4 h equilibration with the aid of a mechanical shaker, the slurries were filtered and the filtrate assayed for residual OFX.

The effect of adsorbent dose on aqueous phase removal of OFX was studied by contacting different portions (0.5, 1.0, 1.5, 2.0 and 2.5 g) of AMOP or CMOP with 50-mL aliquots of 50-mg/L OFX solution on a mechanical shaker. The slurries were filtered after 4-h equilibration and the residual OFX concentration in the filtrate determined.

Adsorption isotherms for aqueous phase removal of OFX were developed at different temperatures by contacting 0.5-g portions of AMOP or CMOP with separate 50-mL portions of each of the OFX solutions prepared to furnish different initial concentrations, C_o (mg/L) in the range ($10 \leq C_o \leq 50$) at 298, 308, 318 and 328 K on a thermostatic water bath. The slurries were filtered after 4-h equilibration and the filtrate assayed for residual OFX. Adsorption thermodynamic parameters were generated from the isothermal data recorded at the different temperatures.

Finally, the effect of contact time on aqueous phase removal of OFX (i.e., adsorption kinetics) was investigated by contacting separate 50-mL aliquots of 50-mg/L OFX solution with 0.5 g of AMOP or CMOP for 0, 10, 30, 60, 120, 180, and 240 min at 298 K on a thermostatic water bath. At the elapse of each specified time interval, the slurry was filtered and the filtrate assayed for residual OFX. This procedure was repeated at 308, 318 and 328 K.

In all batch adsorption experiments, residual OFX concentrations in the filtrates were determined by measurement with a UV-visible spectrophotometer at 294 nm. The amount of OFX adsorbed (mg/g adsorbent) was calculated by the mass balance equation

$$Q \text{ (mg/g)} = \frac{(C_o - C)V}{m_a} \quad (3)$$

where C_o and C are the initial and residual OFX concentrations (mg/L), respectively; V is the aliquot of OFX solution used (50 mL = 0.05 L); and m_a is the mass of adsorbent (g) used for a particular batch treatment. The percent removal of OFX by AMOP or CMOP (removal efficiency, E) was calculated as

$$E \text{ (%) } = \frac{(C_o - C)}{C_o} \times 100 \quad (4)$$

Quality control/assurance was achieved through good laboratory practices. All glassware and plastics were properly washed with acid (1 + 1 HNO₃) and finally with distilled water and oven-dried. Procedural blank samples were subjected to similar treatments using the same amounts of reagents. In all cases, measurements were done in triplicate.

3. Results and discussion

3.1 Physicochemical attributes of *Moringa oleifera* pod husk adsorbents

The physicochemical attributes of *Moringa oleifera* pod husks adsorbents (AMOP and CMOP)

are recorded in Table 1. AMOP and CMOP had pH 6.4 and 7.1, respectively. Adsorbent pH 6-8 are acceptable for applicability for water and wastewater treatment (Okieimen *et al.* 2004). Bulk densities of 105 and 178 kg/m³ were recorded for AMOP and CMOP, respectively. This parameter gives an estimate of packing volume of an adsorbent and is important during adsorbate uptake. An adsorbent with high bulk density gives an idea of volume activity and suggests better quality performance.

AMOP and CMOP showed 9.39% and 12.55% attrition, respectively indicating that CMOP possessed a higher resistance to abrasion than AMOP. These values are high compared with 1.50-2.5% and 7.40-10.38% reported for banana empty fruit bunch and *Delonix regia* fruit pod, respectively (Sugumaran *et al.* 2012). Attrition measures the adsorbent's ability to withstand frictional forces by stirring and washing and is an important parameter in understanding loss of adsorbent during handling and regeneration.

AMOP had iodine number (mg/g) and surface area (m²/g) of 256.40 and 182.41, respectively; while corresponding values for CMOP were 310.60 and 235.79. These values are higher than those reported for *Hemidesmus indicus* (Srihari and Ashutosh 2009), base-treated and carbonized rice husks (Wuana *et al.* 2009), banana empty fruit bunch and *Delonix regia* fruit pod (Sugumaran *et al.* 2012). The iodine number gives an idea of the total surface area of an adsorbent. Adsorbents with high iodine number/surface area perform better in the removal of small sized contaminants.

The titratable surface charge (mmol H⁺ eq/g) gives a measure of the acidic and basic functional groups on the adsorbent's surface. The titratable surface acidic groups were determined by selective neutralization with a series of bases of varying strength: NaHCO₃, Na₂CO₃ and NaOH

Table 1 Selected physicochemical attributes of *Moringa oleifera* pod husk adsorbents*

Attribute	AMOP	CMOP		
pH _{water} (solid:liquid = 1:100)	6.40	7.10		
Bulk density (kg/m ³)	105.00	178.00		
Attrition (%)	9.39	12.55		
Iodine number (× 10 ⁻³ mol/g)	1.01	1.22		
Iodine number (mg/g)	256.40	310.60		
Surface area (m ² /g)	182.41	235.79		
Surface charge (mmol H ⁺ eq/g)				
NaOH	0.87	0.75		
NaHCO ₃	1.03	0.99		
Na ₂ CO ₃	0.87	0.61		
	<i>v</i> (/cm)	Functional group	<i>v</i> (/cm)	Functional group
FTIR analysis	3412.19	O – H, N – H	3436.30	O – H, N – H
	2925.15	C – H	1700.31	C = O
	1736.96	C = O	775.41	C – H
	1645.33	C = C		
	1045.45	C – O		

*AMOP: Chemically activated *Moringa oleifera* pod husks;

CMOP: Carbonized *Moringa oleifera* pod husks

whereby, NaHCO_3 neutralized carboxylic groups (strong acidic groups), those neutralized by Na_2CO_3 but not by NaHCO_3 were lactones (weak acidic groups). The weak acid groups neutralized by NaOH but not by Na_2CO_3 were postulated as phenols (very weak acidic groups (Bojić *et al.* 2013, Akl *et al.* 2014). The surface acidic groups varied as: AMOP (carboxylic > lactones \approx phenolic) and CMOP (carboxylic > phenolic > lactones). Other oxygen-based acidic functional groups which may be present on the adsorbent's surface include quinone-type carbonyls, anhydrides, ethers and cyclic peroxides (Mahmoud *et al.* 2012, Akl *et al.* 2014).

FTIR analysis helps in the identification of individual surface functional groups which could play a great role in adsorption mechanism and capacity. From FTIR spectra of the experimental adsorbents (Table 1 and Fig. 3), AMOP shows a broad peak at 3412 cm^{-1} (2500-3500 cm^{-1}) attributable to O–H stretch and N–H asymmetric stretching vibrations which could be due to inter and intramolecular hydrogen bonding. The band at 1737 cm^{-1} could be ascribed to C = O stretching vibrations indicating presence of aldehydic groups. The band at 1645 cm^{-1} could be attributed to C = C stretching of alkenes while that observed at 1,045 cm^{-1} is ascribed to C–O stretching vibration of alcohols (Sulaymon *et al.* 2013). The CMOP spectrum shows similarities to that of AMOP. Overall, the FTIR frequency shifts indicate that OFX was bound to the adsorbents via hydroxyl, amine, carboxylic, hydrogen bonding and aldehydic groups.

3.2 Effect of initial solution pH on aqueous phase removal of ofloxacin

Fig. 4 illustrates the effect of initial OFX solution pH on its aqueous phase removal by AMOP and CMOP. The adsorption capacity is influenced, to a large extent, by the initial solution pH since this affects the adsorbent's surface charge, degree of ionization and the chemical speciation of OFX (Crespo-Alonso *et al.* 2013). OFX removal efficiency decreased somewhat linearly (99.84% for AMOP and 90.98 to 74.65% for CMOP) between pH 5-7. This may be explained by the zwitterionic nature of OFX. The pK_a values of OFX are 5.20, 6.20 and 8.20 (Lin *et al.* 2004).

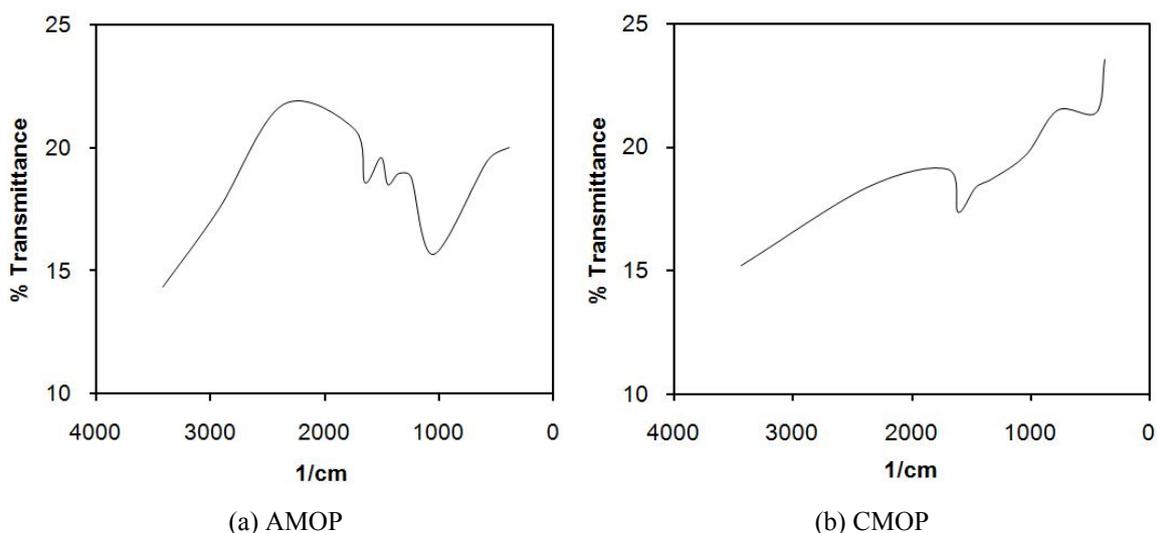


Fig. 3 Fourier transform infrared (FTIR) spectra of (a) chemically activated (AMOP); and (b) carbonized (CMOP) *Moringa oleifera* pod husks

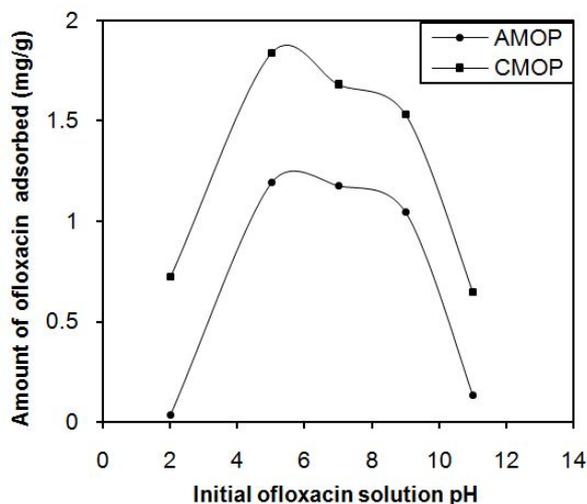


Fig. 4 Effect of initial solution pH on aqueous phase removal of ofloxacin by chemically activated (AMOP) and carbonized (CMOP) *Moringa oleifera* pod husks

At low pH (acidic medium), OFX is positively charged; while the adsorbents, on the other hand, possess a net negative charge and the interactions favor adsorption (Lin *et al.* 2004, Crespo-Alonso *et al.* 2013). At pH 5, high ionic interactions occur between the cationic OFX and AMOP or CMOP surface leading to high OFX removal. At pH 7, where the dominant OFX species in solution is the zwitterion, a cationic state can still be considered as a major contributor to sorption, hence an appreciable amount of OFX was removed from solution. At pH 9, the anionic state of OFX is the dominant species furnishing adsorbent-adsorbate repulsions and consequently, a further decrease in removal efficiency (Goud *et al.* 2005, Tang *et al.* 2007, Maheshwari *et al.* 2013). The very low and outlying removal efficiencies at pH 2 (39.20% for AMOP and 54.71% for CMOP) and pH 11 (48.76% for AMOP and 67.53% for CMOP) are possibly due to the alteration of the physicochemical properties of the adsorbents at these extreme pH values (Crespo-Alonso *et al.* 2013). Overall, the optimum pH for OFX removal was recorded at pH 5, somewhat in agreement with the findings of Punyapalukul and Sitthisorn (2010). Bajpai *et al.* (2012) also reported that pH 5.8 was optimum during the sorptive removal of ciprofloxacin by sawdust.

3.3 Effect of adsorbent dosage on aqueous phase removal of ofloxacin

The effect of AMOP and CMOP dosage on aqueous phase removal of OFX is shown in Fig. 5. OFX uptake decreased with increase in adsorbent dosage for both AMOP (3.48 to 2.60 mg/g) and CMOP (3.81 to 3.50 mg/g). This trend may be explained on the basis of the mass balance relationship in Eq. (3). At increasingly higher sorbent dosages (0.5-2.5 g), fixed initial OFX concentration (50 mg/L) and fixed aliquot volume (50 mL), the available OFX molecules are unable to cover all the exchangeable sites on the adsorbents, leading to decreased OFX uptake at higher dosages (Moyo *et al.* 2012, Fasoto *et al.* 2014). OFX removal efficiency expressed as a function of only the initial and final OFX concentration in Eq. (4), on the other hand, increased with increase in adsorbent dosage (52.04-69.49% for AMOP and 70.39-76.10% for CMOP).

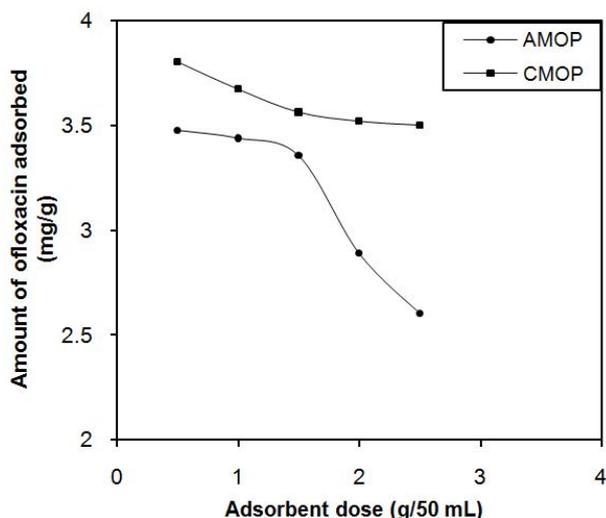


Fig. 5 Effect of adsorbent dosage on aqueous phase removal of ofloxacin by chemically activated (AMOP) and carbonized (CMOP) *Moringa oleifera* pod husks

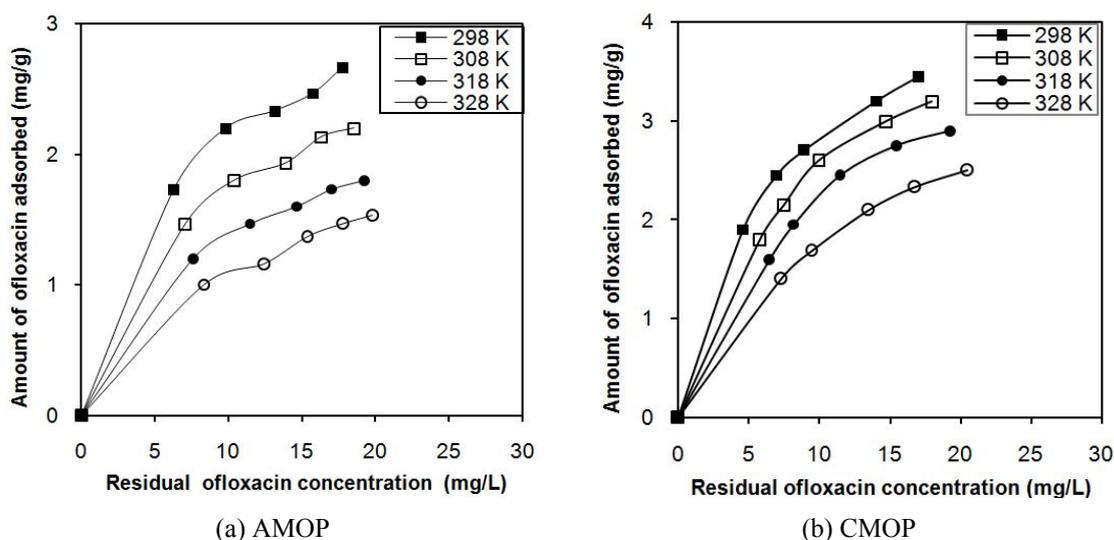


Fig. 6 Isotherm profiles for aqueous phase removal of ofloxacin by: (a) chemically activated (AMOP); and (b) carbonized (CMOP) *Moringa oleifera* pod husks at different temperatures

3.4 Equilibrium adsorption capacities and isotherm profiles

Equilibrium data from adsorption experiments are usually presented in the form of an isotherm, which graphically displays the ratio of adsorbed to non-sorbed solute per unit mass of the adsorbent at constant temperature. The isotherm profiles are important in providing information regarding the nature and mechanism of sorption for a particular adsorbate-adsorbent system. The isotherm profiles for the aqueous phase adsorption of OFX on AMOP and CMOP at the different

temperatures are illustrated in Fig. 6. Consistent with Giles *et al.* (1974) classification, the isotherms for AMOP and CMOP were somewhat L-shaped indicating that the intermolecular forces of OFX are comparatively weaker than the sorptive forces, which also implies that the activation energy of adsorption is independent of surface coverage.

At the operating initial concentrations [$10 \leq C_o$ (mg/L) ≤ 50], the ranges of equilibrium adsorption capacities, Q_e (mg/g) for AMOP at the various temperatures were: 298 K ($1.733 \leq Q_e \leq 2.878$); 308 K ($1.467 \leq Q_e \leq 2.200$); 318 K ($1.200 \leq Q_e \leq 1.800$) and 328 K ($1.000 \leq Q_e \leq 1.533$). Corresponding ranges for CMOP were: 298 K ($1.900 \leq Q_e \leq 3.450$); 308 K ($1.800 \leq Q_e \leq 3.200$); 318 K ($1.600 \leq Q_e \leq 2.899$) and 328 K ($1.405 \leq Q_e \leq 2.505$). Adsorption capacities increased with increase in OFX initial concentration and this may be attributed to increase in collisions between adsorbate and adsorbent. Conversely, adsorption capacities decreased with increase in temperature, indicating the exothermic nature of the sorption process. Removal efficiencies, E (%) across the temperatures investigated ranged as: AMOP ($16.66 \leq E \leq 64.44$) and CMOP ($25 \leq E \leq 70.15$). Comparatively, CMOP can be considered as more potent than AMOP possibly due to the higher porosity and surface area of the former.

3.5 Adsorption isotherm models

Equilibrium data for the aqueous phase removal of OFX by AMOP and CMOP were fitted into the linearized forms of the Langmuir and Freundlich models given by Eqs. (5) and (6), respectively

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_o} + \frac{1}{K_L Q_o} \quad (5)$$

$$\ln Q_e = \frac{1}{n_F} \ln C_e + \ln K_F \quad (6)$$

where Q_e is the equilibrium amount of OFX adsorbed per unit mass of the adsorbent (mg/g), and C_e is the equilibrium (residual) concentration (mg/L). Q_o is the maximum amount of OFX adsorbed per unit mass of adsorbent (mg/g) corresponding to complete coverage of the adsorptive sites, K_L (L/mg) is the Langmuir affinity constant related to the energy of adsorption. K_F is Freundlich constant ($\text{mg}^{1-1/n_F} \text{L}^{1/n_F} / \text{g}$), related to the adsorption capacity and n_F is a dimensionless empirical parameter related to the adsorption intensity which varies with the heterogeneity of the material (El-Maghraby and Taha 2014). A linear plot of C_e/Q_e versus C_e gives the inverse of the slope as Q_o and K_L is derived from the intercept; while a linear plot of $\ln Q_e$ versus $\ln C_e$ gives the inverse of the slope as n_F and intercept as K_F . The Langmuir and Freundlich isotherm plots are presented in Figs. 7 and 8. The parameters thereof are recorded in Table 2.

3.5.1 Langmuir isotherm parameters

The Langmuir model assumes that adsorption occurs at homogeneous sites and forms a monolayer. The characteristics of the Langmuir isotherm are determined by a dimensionless constant called the separation factor, R_L expressed as

$$R_L = \frac{1}{(1 + K_L C_o)} \quad (7)$$

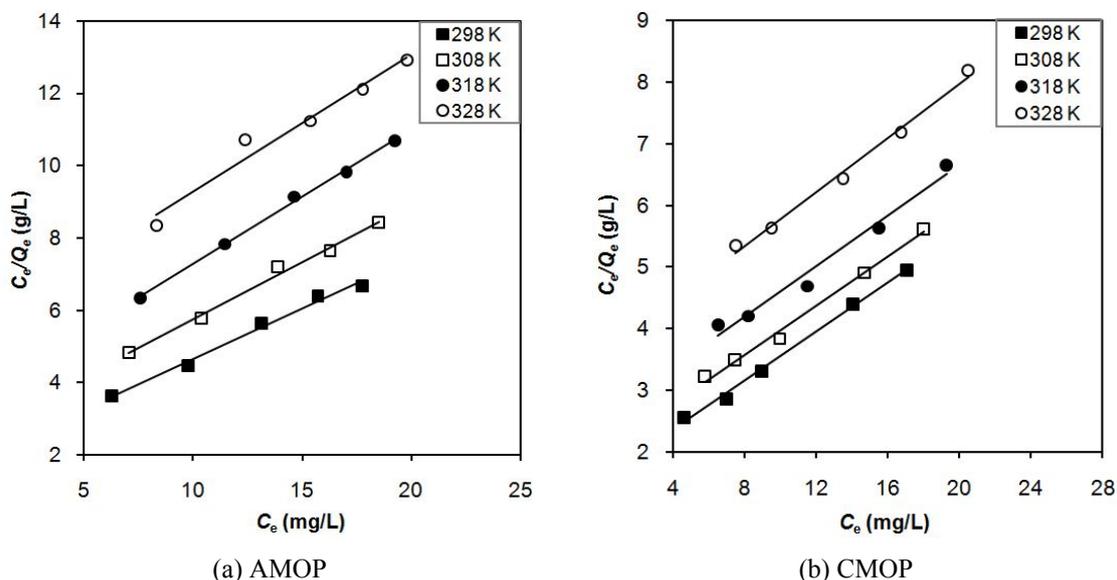


Fig. 7 Linearized Langmuir isotherms for aqueous phase removal of ofloxacin by: (a) chemically activated (AMOP); and (b) carbonized (CMOP) *Moringa oleifera* pod husks at different temperatures

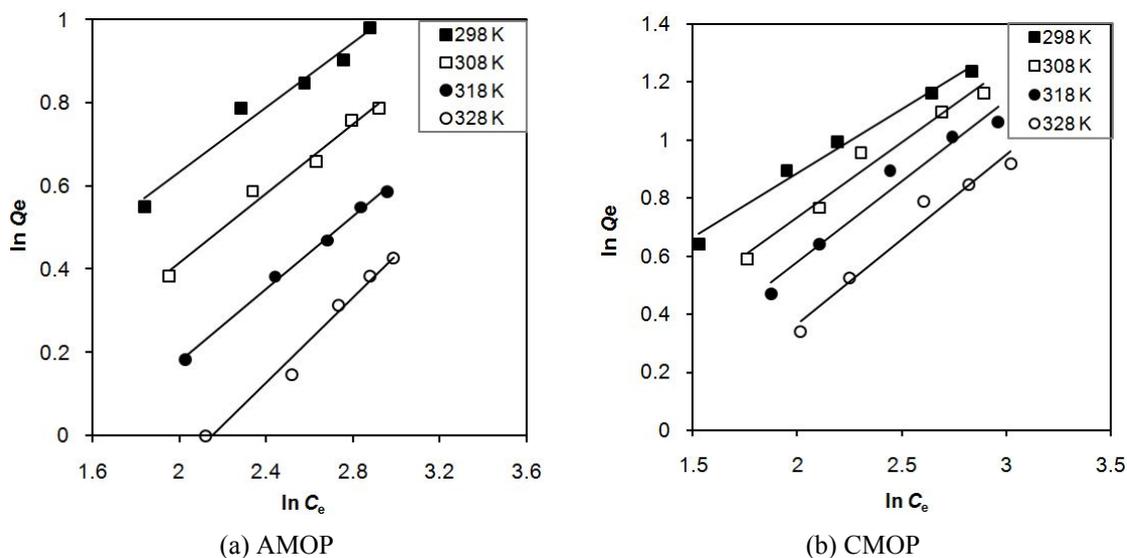


Fig. 8 Linearized Freundlich isotherms for aqueous phase removal of ofloxacin by: (a) chemically activated (AMOP); and (b) carbonized (CMOP) *Moringa oleifera* pod husks at different temperatures

where K_L (L/mg) and C_o (mg/L) retain their meaning as defined in Eq. (5). R_L indicates the nature of adsorption process such that $R_L > 1$, $R_L = 1$, $0 < R_L < 1$, and $R_L = 0$ represent unfavorable, linear, favorable and irreversible adsorption, respectively. Table 2 shows that at the temperatures (298 – 328 K) considered in this study, ranges of Langmuir parameters: Q_o (mg/g), K_L ($\times 10^4$ L/mol), R_L and R^2 for OFX-AMOP systems were ($2.639 \leq Q_o \leq 3.597$), ($2.493 \leq K_L \leq 5.384$), ($0.120 \leq R_L \leq$

Table 2 Isotherm parameters for aqueous phase removal of ofloxacin by chemically activated (AMOP) and carbonized (CMOP) *Moringa oleifera* pod husks at different temperatures

Adsorbent	Isotherm parameters	298 K	308 K	318 K	328 K
AMOP	Langmuir				
	Q_o (mg/g)	3.597	3.165	2.681	2.639
	K_L (L/mg)	0.149	0.123	0.105	0.069
	$K_L (\times 10^4 \text{ L/mol})$	5.384	4.445	3.794	2.493
	R_L	0.120	0.140	0.160	0.160
	R^2	0.989	0.992	0.997	0.968
	Freundlich				
	$K_F (\text{mg}^{1-1/n} \text{L}^{1/n} / \text{g})$	0.867	0.662	0.497	0.332
	n_F	2.577	2.410	2.288	1.953
	R^2	0.970	0.982	0.966	0.982
CMOP	Langmuir				
	Q_o (mg/g)	5.051	5.025	4.902	4.567
	K_L (L/mg)	0.127	0.100	0.080	0.061
	$K_L (\times 10^4 \text{ L/mol})$	4.589	3.614	2.891	2.204
	R_L	0.140	0.170	0.200	0.25
	R^2	0.995	0.993	0.976	0.991
	Freundlich				
	$K_F (\text{mg}^{1-1/n} \text{L}^{1/n} / \text{g})$	2.262	1.934	1.795	1.718
	n_F	1.000	0.739	0.586	0.559
	R^2	0.985	0.971	0.963	0.965

0.160) and $(0.968 \leq R^2 \leq 0.997)$, respectively. Corresponding ranges for the OFX-CMOP sorption systems were: $(4.567 \leq Q_o \leq 5.051)$, $(2.204 \leq K_L \leq 4.589)$, $(0.140 \leq R_L \leq 0.250)$ and $(0.976 \leq R^2 \leq 0.995)$. Overall, Q_o , K_L and R_L decreased with increase in temperature, implying that the sorptive removal of OFX was less favorable at higher temperatures. Actual values of the Langmuir parameters were correspondingly higher for OFX-CMOP than the OFX-AMOP sorption system, qualifying CMOP as the more potent of the experimental adsorbents. The values of R_L are within the range $(0 \leq R_L \leq 1)$ of favorable OFX adsorption for both adsorbents (Maheshwari *et al.* 2013).

3.5.2 Freundlich isotherm

The Freundlich isotherm postulates heterogeneous energetic distribution of active sites, accompanied by interaction between adsorbed molecules. Table 2 shows that at 298-328 K considered in this study, the ranges of Freundlich parameters: $K_F (\text{mg}^{1-1/n} \text{L}^{1/n} / \text{g})$, n_F and R^2 for OFX-AMOP systems were $(0.332 \leq K_F \leq 0.867)$, $(1.953 \leq n_F \leq 2.577)$ and $(0.966 \leq R^2 \leq 0.982)$. Corresponding ranges for OFX-CMOP sorption systems were: $(1.718 \leq K_F \leq 2.262)$, $(0.559 \leq n_F \leq 1.000)$ and $(0.963 \leq R^2 \leq 0.985)$. K_F and n_F for both adsorbents decreased with increase in temperature, indicating that the uptake of OFX was less favorable at higher temperatures. The values of n_F recorded in this study fall within the range $0 \leq n_F \leq 10$ and signify favorable OFX

adsorption (Maheshwari *et al.* 2013). In magnitude, the Freundlich parameters were correspondingly higher for OFX-CMOP than the OFX-AMOP sorption system portraying CMOP as the more potent of the experimental adsorbents.

3.6 Thermodynamics of aqueous phase removal of ofloxacin

Thermodynamic parameters such as Gibbs free energy change (ΔG°), enthalpy change (ΔH°), entropy (ΔS°) were derived from the Langmuir isotherm parameters. The Gibbs free energy change was calculated using

$$\Delta G^\circ = -RT \ln K_L \tag{8}$$

where R is the universal gas constant (8.314 J/mol.K), T is the temperature (K). Meanwhile, the values of K_L , the Langmuir affinity constant, were first converted from L/mg basis to L/mol basis with the aid of Eq. (9) before substitution in Eq. (8)

$$K_L (\text{L/mol}) = K_L (\text{L/mg}) \times 10^3 (\text{mg/g}) \times MW (\text{g/mol}) \tag{9}$$

where MW is the molecular weight of OFX (361.368 g/mol).

The enthalpy (ΔH°) and entropy (ΔS°) parameters were respectively estimated from the slope and intercept of the Van't Hoff equation

$$\ln K_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{10}$$

where R and T retain their meaning as defined in Eq. (8). Actual values of ΔH° and ΔS° were respectively obtained from the slope and intercept of the $\ln K_L$ (L/mol) versus $(10^3 \text{ K})/T$ plot (Fig. 9). Some thermodynamic parameters for aqueous phase removal of OFX by AMOP and CMOP are summarized in Table 3. Negative values of ΔH° (kJ/mol), -19.90 for OFX-AMOP and -19.65

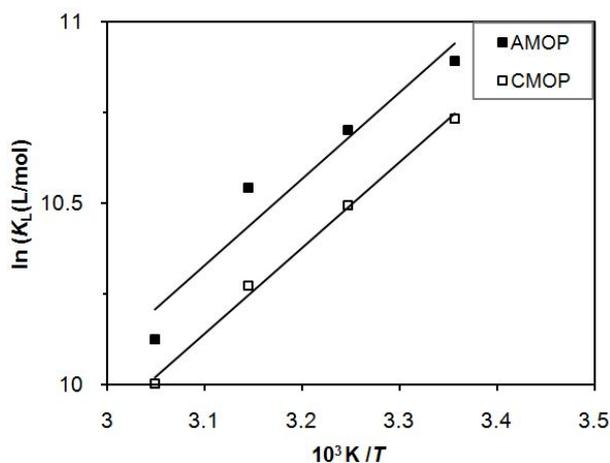
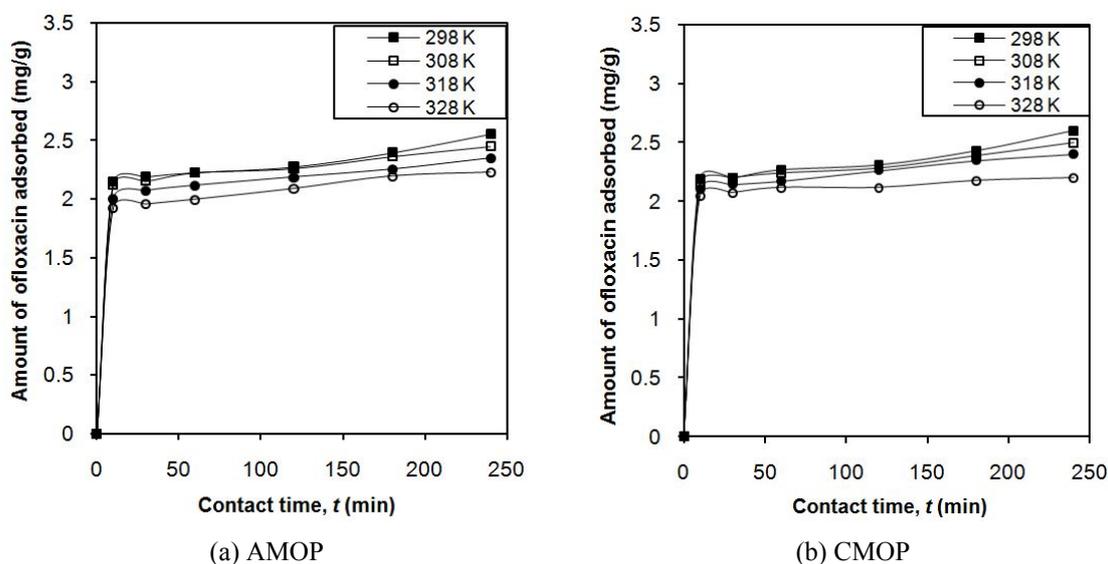


Fig. 9 Van't Hoff $\ln K_L$ (L/mol) versus $(10^3 \text{ K})/T$ plots for aqueous phase removal of ofloxacin by chemically activated (AMOP) and carbonized (CMOP) *Moringa oleifera* pod husks at different temperatures

Table 3 Thermodynamic parameters of aqueous phase removal of ofloxacin by chemically activated (AMOP) and carbonized (CMOP) *Moringa oleifera* pod husks at different temperatures

Adsorbent	T (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/Kmol)
AMOP	298	-26.99	-19.90	24.169
	308	-27.41		
	318	-27.88		
	328	-27.61		
CMOP	298	-26.59	-19.65	23.39
	308	-26.87		
	318	-27.16		
	328	-27.27		

Fig. 10 Rate curves for aqueous phase removal of ofloxacin by: (a) chemically activated (AMOP); and (b) carbonized (CMOP) *Moringa oleifera* pod husks at different temperatures

for the OFX-CMOP scenario can be attributed to the exothermic nature of the adsorption process. The enthalpy value is used to differentiate between physisorption and chemisorption. In the literature, values of ΔH° in the range $[-83 \leq \Delta H^{\circ} \text{ (kJ/mol)} \leq -830]$ represent chemisorption; while those in the range $[-8 \leq \Delta H^{\circ} \text{ (kJ/mol)} \leq -25]$ signify physisorption (Dula *et al.* 2014). ΔH° values obtained in this study indicate that the adsorption of OFX on AMOP and CMOP is via physisorption. Positive values of ΔS° (kJ/mol), i.e., 24.17 for OFX-AMOP and 23.39 for OFX-CMOP imply an increase in the degree of disorder, hence the spontaneous nature of OFX adsorption on AMOP and CMOP. The negative values of ΔG° (kJ/mol) for adsorption of OFX both adsorbents ranging from $[-27.88 \leq \Delta G^{\circ} \text{ (kJ/mol)} \leq -26.59]$ indicate the spontaneous nature of the adsorption process. From literature, ΔG° values ranges from $[-20.00 \leq \Delta G^{\circ} \text{ (kJ/mol)} \leq 0.00]$ represent physisorption; while those in the range $[-400.00 \leq \Delta G^{\circ} \text{ (kJ/mol)} \leq -80.00]$ indicate

chemisorption (Dula *et al.* 2014). The ΔG° values recorded in this study values support the physisorption mechanism.

3.7 Adsorption kinetics

In addition to the adsorption capacity, derived from equilibrium considerations; the adsorption time (defined as the time taken to remove one-half of the initial concentration of the adsorbate) is another important parameter used for defining an adsorbent and selecting appropriate operating conditions for the design of a wastewater treatment scheme (Marshall *et al.* 1999). Rate curves for aqueous phase removal of OFX by AMOP and CMOP are illustrated in Fig. 10.

For both adsorbents, OFX uptake increased very rapidly within the first 10 min but slowed down beyond this point, gradually rendering plateaux at higher contact times for all the temperatures studied, signifying that the process would not offer additional kinetic advantage when contact times longer than 4 h were employed. The uptake of OFX, somewhat diminished as temperatures were raised from 298-328 K, implying that OFX adsorption was less favorable at higher temperatures.

The experimental data for the aqueous phase removal of OFX by AMOP and CMOP as a function of contact time were fitted into the Lagergren pseudo-first-order (LFOR); Blanchard pseudo-second-order (BSOR) and the Weber-Morris intraparticle diffusion (WMID) kinetic models represented by Eqs. (11), (12) and (13), respectively

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (11)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad (12)$$

$$Q_t = k_{id} \sqrt{t} + C \quad (13)$$

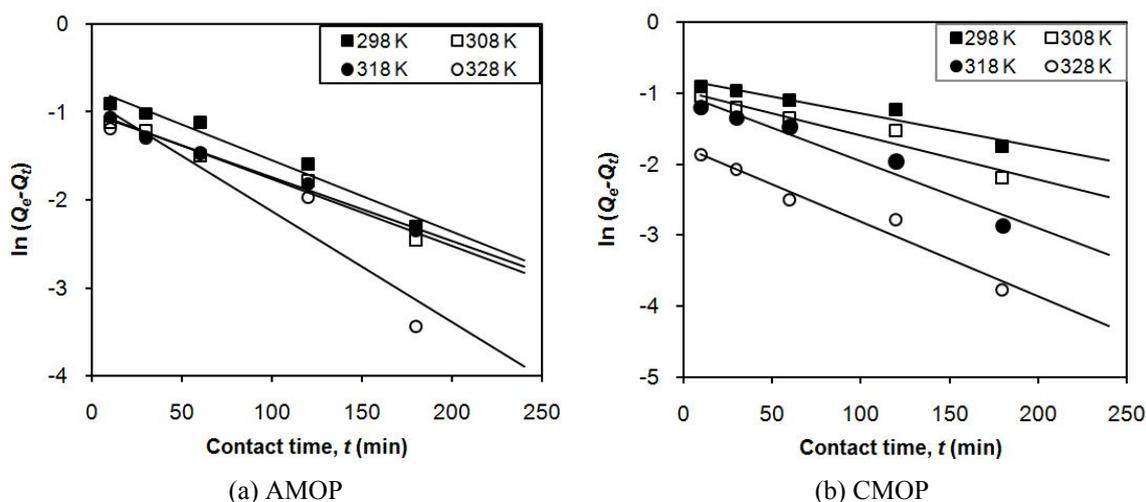


Fig. 11 Lagergren pseudo-first order plots for aqueous phase removal of ofloxacin by (a) chemically activated (AMOP) and (b) carbonized (CMOP) *Moringa oleifera* pod husks at different temperatures

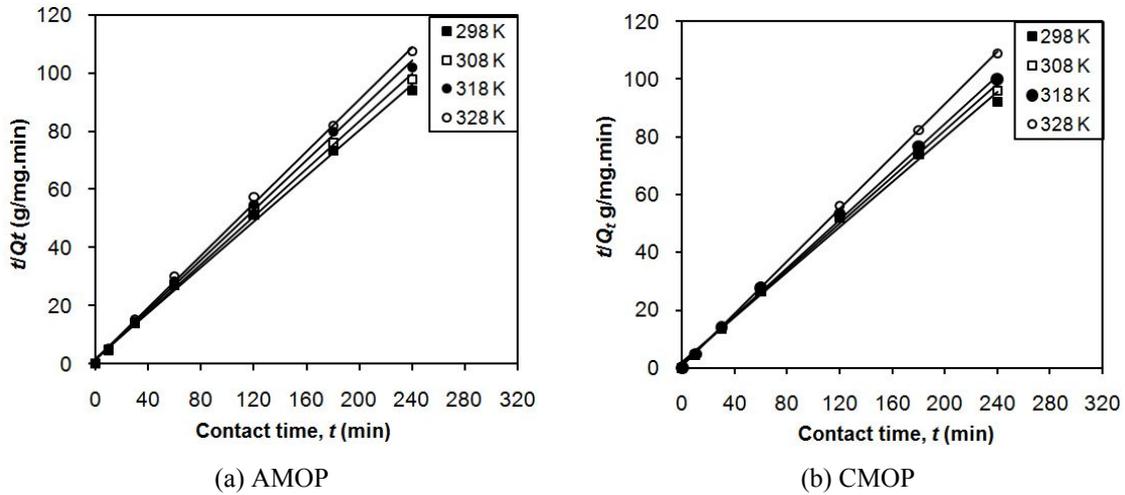


Fig. 12 Blanchard pseudo-second order plots for aqueous phase removal of ofloxacin by: (a) chemically activated (AMOP); and (b) carbonized (CMOP) *Moringa oleifera* pod husks at different temperatures

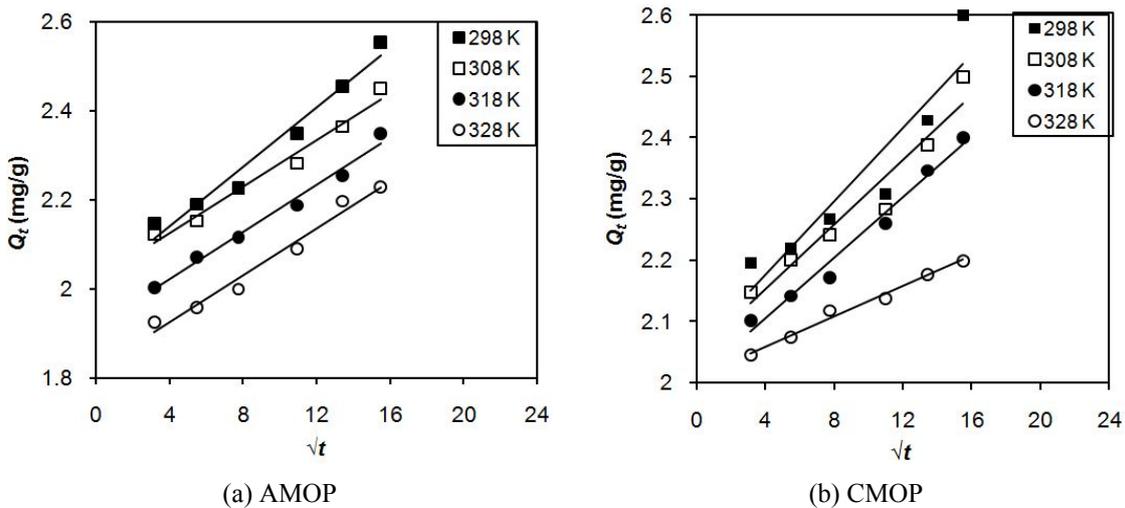


Fig. 13 Weber-Morris particle diffusion plots for aqueous phase removal of ofloxacin by: (a) chemically activated (AMOP); and (b) carbonized (CMOP) *Moringa oleifera* pod husks at different temperatures

where Q_e and Q_t are respectively, the amounts of OFX adsorbed at equilibrium and at a specified time (mg/g); k_1 (/min), k_2 (g/mg.min) and k_{id} (mg/g.min^{1/2}) are the LFOR rate constant, BSOR rate constant and WMID rate constant, respectively. In the BSOR model, the quantity $k_2 Q_e^2$ equals the initial adsorption rate, h . Figs. 11-13 represent the plots rendered by the corresponding models; while Table 4 records the parameters thereof.

Considering the OFX-AMOP sorption system, the ranges of kinetic parameters recorded across the temperatures were: [$0.7 \leq k_1 (\times 10^{-2} \text{ /min}) \leq 1.2$], [$8.9 \leq k_2 (\times 10^{-2} \text{ g/mg.min}) \leq 12.4$], and [2.6

Table 4 Kinetic parameters for aqueous phase removal of ofloxacin by chemically activated (AMOP) and carbonized (CMOP) *Moringa oleifera* pod husks at different temperatures

Adsorbent	Kinetic parameter	298 K	308 K	318 K	328 K
AMOP	Lagergren				
	k_1 (/min)	0.008	0.007	0.007	0.012
	R^2	0.965	0.975	0.991	0.905
	Blanchard				
	k_2 (g/mg.min)	0.0897	0.121	0.122	0.124
	R^2	0.997	0.998	0.998	0.998
	Weber-Morris	0.033	0.026	0.026	0.026
	R^2	0.968	0.977	0.983	0.975
CMOP	Lagergren				
	k_1 (/min)	0.004	0.006	0.009	0.010
	R^2	0.927	0.939	0.955	0.962
	Blanchard				
	k_2 (g/mg.min)	0.083	0.107	0.131	0.317
	R^2	0.995	0.997	0.999	0.999
	Weber-Morris	0.030	0.026	0.024	0.012
	k_{id} (mg/g.min ^{1/2})	0.867	0.937	0.979	0.986

$\leq k_{id}$ ($\times 10^{-2}$ mg/g.min^{1/2}) ≤ 3.3]. Corresponding ranges for OFX-CMOP were: $[0.4 \leq k_1$ ($\times 10^{-2}$ /min) $\leq 1.0]$, $[8.3 \leq k_2$ ($\times 10^{-2}$ g/mg.min) $\leq 31.7]$, and $[1.2 \leq k_{id}$ ($\times 10^{-2}$ mg/g.min^{1/2}) $\leq 3.0]$. The kinetic parameters were of the order: $k_1(10^{-3}) < k_{id}(10^{-2}) < k_2(10^{-1})$. Actual values of k_1 and k_2 increased with increase in temperature, whereas k_{id} showed a converse trend for both adsorbents.

Linear plots from the WMID model did not pass through the origin suggesting that intra-particle diffusion was not the sole rate determining step in the sorption process (Hamad *et al.* 2011, Maheshwari *et al.* 2013). Based on the coefficient of determination, R^2 , the BSOR model recorded the highest values relative to LFOR and WMID indicating that the adsorption kinetics was well interpreted by the BSOR model.

4. Conclusions

The study has demonstrated that ammonium chloride-treated (AMOP) and carbonized (CMOP) *Moringa oleifera* pod husk possess favorable physicochemical attributes. Preliminary stability check showed that aqueous OFX solutions were stable for days. Aqueous phase removal of OFX revealed that at equilibrium, the highest removal efficiencies of 99.84% and 90.98% were recorded at solution pH 5 for CMOP and AMOP, respectively. At fixed initial OFX concentration and fixed aliquot volume, OFX uptake decreased with adsorbent dose. The equilibrium adsorption data was well modelled by the Langmuir and Freundlich isotherms. Gibbs free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) indicated that the adsorption of OFX was feasible,

spontaneous, exothermic and physisorptive in nature. Kinetic considerations revealed that for both adsorbents, OFX uptake was most rapid within the first 10 minutes rendering plateaux beyond this point. The adsorption of OFX on AMOP and CMOP was well represented by the Blanchard pseudo-second-order kinetic model. These adsorbents may become useful whenever sorptive removal is the option in decontamination of pharmaceutical effluents/wastewater.

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