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Moringa oleifera (seed husk, seed cake and water-soluble protein) as a natural adsorbent for the removal of multi-class pharmaceuticals from water

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ABSTRACT

The adsorption of *Moringa oleifera* seed cake, seed husk and water-soluble protein was studied for the removal of multi-class pharmaceuticals from water. The characteristic surface chemistry of the adsorbents was studied by Fourier-transform infrared spectroscopy analysis and scanning electron microscopy. Parameters affecting the extraction efficiency including pH, contact time and initial pharmaceutical concentration were optimized. The optimum conditions were found to be a sample pH of 5, a contact time of 80 min and a 0.5 mg/L initial concentration of the analyte. Equilibrium and kinetic models for pharmaceuticals adsorption were studied by considering the effects of concentration and contact time at the optimum conditions for each of the *Moringa* adsorbents. Freundlich's adsorption model was found to fit the experimental data. The kinetics of adsorption of all target analytes on the *Moringa* adsorbent was well defined by the pseudo-second-order model. The adsorption capacity for the seed cake ranged from 3–311, for the seed husk ranged from 7–413 and for water-soluble protein was 2–326 mg/g depending on individual pharmaceutical. The results obtained showed that the use of this plant-based sorbent can be considered as one of the most promising and low-cost for the removal of pharmaceuticals that needs surface modification to improve the adsorption for some pharmaceuticals.

Keywords: Moringa oleifera; Adsorption; Pharmaceuticals; Seed cake; Seed husk; Water-soluble protein

1. Introduction

Pharmaceuticals are widely used to prevent and treat diseases and also as growth promoters in humans and as veterinary drugs. However, they have received growing attention from environmental and health agencies all over the world and they are regarded as emerging contaminants due to their occurrence and potential deleterious effect on the aquatic ecosystem [1–4]. The presence of pharmaceuticals in the aquatic environment has been detected and reported in wastewater, groundwater and surface water [5]. The major and constant sources of pharmaceuticals to the aquatic environment are wastewater treatment plant discharges as common treatments which are generally not able to efficiently remove because of being mainly designed to eliminate conventional pollutants such as solids, nutrients and organic matters [6–8]. The issue of pharmaceutical compounds in the water system has become a major concern in terms of problems to both human health and the environment [7,9].

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Many researchers have tried to develop methods for removing pharmaceuticals from the environment. Different removal methods such as ozone-based advanced oxidation processes [10], nanofiltration [11] and biological activated carbon [12] have been reported for the treatment of water. However, most of these methods have major disadvantages especially on high operation costs [13].

One of the most preferred methods for removing pharmaceuticals in polluted water systems is adsorption-based approach [13]. In recent studies, different adsorbents such as molecularly imprinted polymers are used for the selective removal of pharmaceuticals from the environmental aqueous samples [14–16]. However, the application of this adsorbent is limited due to the high production costs associated with their preparation and selective for targeted compounds. Much research is now focused on cost effective and innovative adsorbents especially biobased ones [17]. The study reported the removal of a single antibiotic pharmaceutical in deionized and municipal water using rice (*Oryza sativa*) and coffee (*Coffea arabica*) husk wastes as natural bio-based adsorbents [18]. The use of water-soluble protein from *Moringa stenopetala* seeds for the removal of various antibiotic drugs [17] and sulphonamides [19] from wastewater has also been reported. Biosorbents are attractive because they are cheap and can be obtained often as waste products that contributing to the circular economy.

Simple to prepare, hazard-free and environment-friendly approaches are major requirements for sustainable preparation of adsorbent for removal of contaminants [13]. *Moringa oleifera* seed protein has been studied as bio-coagulant in wastewater treatment plants [20]. It has also been studied for possible for removal of anti-inflammatory drug diclofenac from water [21] and removal and adsorption of heavy metals from water [22,23]. The *Moringa* seeds extract has the coagulation properties, it has been compared to commercial coagulants like synthetic cationic polymers and alum [17,24] and this makes it selective for adsorptive removal of various contaminants.

To the best of our knowledge, no research study was done using *M. oleifera* seed cake, seed husk and water-soluble protein for the removal of different therapeutic class pharmaceuticals from water. Therefore, the objective of the present study was to investigate the efficiency of *M. oleifera* (seed cake, seed husk and water-soluble protein) for the removal of a mixture of different classes of pharmaceuticals from aqueous samples. Pharmaceuticals selected for this study are based on their frequent detection in the environment emanating from their common and frequent usage.

2. Materials and methods

2.1. Chemicals and reagent solutions

Analytical and HPLC grade chemicals were used for the experiments. Chemicals like methanol and acetonitrile were >99% in purity (Fisher Scientific Pty Ltd., London, UK). Formic acid (>96%) was supplied by Sigma Aldrich (Darmstadt, Germany). Direct-Q 3 UV Millipore system (Massachusset, UK) was used to prepare ultra-pure water. Standard pharmaceutical-grade compounds (metformin, theophylline, trimethoprim, caffeine, norfloxacin, albendazole ciprofloxacin, doxycycline hyclate, and metronidazole) all purity >99% was donated by a local company (Addis Pharmaceuticals PLC, Adigrat, Ethiopia). Working solutions, containing a mixture of each analyte, of 50 mg/L were made from the standard stock solution with methanol and water (50:50, v/v). Water-soluble protein extraction solvent, petroleum ether (37% w/v) was obtained from Associated Chemical Enterprise (Johannesburg, RSA). Precipitating salt ammonium sulfate $(NH_4)_2SO_4$ was from Analytic PLC (Johannesburg, RSA). Cellulose and dialysis tubings were sourced from Sigma-Aldrich (Johannesburg, RSA). The various therapeutic classes of the pharmaceuticals with their physicochemical properties are presented in Table 1.

2.2. Instrumentation and instrument conditions

A Dionex Ultimate 3000 UHPLC-DAD (Thermo Fisher Scientific, Bremen, Germany) instrument was used. For the acquisition of the analysed compounds, a Bruker HyStar acquisition software (rev. 3.2) was used. The compound separation was achieved on a UHPLC-DAD system equipped with a Kromasil C_{18}, column (4.6 mm × 150 mm, 5 μm). Mobile phase (A) water with 0.1% formic acid and (B) methanol with 0.1% formic acid flow rate 0.8 mL/min. The analysis was carried out using Kromasil C_{18} (150 cm × 4.6 mm) 5 μm analytical columns with diode array detector. The injection volume was 20 μL, and the flow rate was maintained at 0.8 mL/min with a run time of 16 min and the analysis was performed at ambient column temperature.

2.3. Preparation of M. oleifera seed adsorbents

The *M. oleifera* seeds were obtained from a farm in Limpopo Province, South Africa. Distilled water was used to get rid of dust and soluble contaminants suspended on the seeds surfaces. They were then air-dried and divided into two groups one for seed cake and the other for husk and water-soluble protein. Preparation of seed cake was done by squeezing the seed as it is to remove the oil. The leftover formed part of the seed forms the seed cake. Further, the seed cake was washed with hexane to remove the oil remaining and then air-dried. The seed cake was prepared in powder form and allowed to pass in a 300 μm size sieve and stored in a dry container for adsorption studies. The other group of the seeds was de-shielded and the husk and the seed were separated. The seed husk was then washed with distilled water, air-dried and ground to powder using a domestic blender. The husk was removed from the seed and washed with pure water to extract water-soluble protein. This was followed by drying the seeds for 24 h in an oven at 80°C. A domestic blender was used to grind the dried seeds which were sieved to get uniform-sized particles. Extraction of water-soluble proteins from the *M. oleifera* seeds was adopted from literature with some modification [24,30]. Petroleum ether was added to the powder and stirred for 30 min to extract dissolved fats, waxes and oil. The mixture was then filtered through a Whatman paper no. 3 to separate the solution and solids. The residue was dissolved three times with the extraction solvent to make sure that the yellowish extract is no longer in the seed powder. The residue that remained in the filter paper was dissolved in deionized water. This was

stirred for 30 min to extract the water-soluble protein. The solution was then filtered to separate water-soluble protein from any water-insoluble substances. Ammonium sulfate $(NH_4)_2SO_4$ was added to the filtrate to initiate the precipitation of proteins. This process was followed by centrifugation at 4,000 rpm for 10 min, re-dissolved the supernatant with $(NH_4)_2SO_4$ until no precipitate was observed. To remove any insoluble substances, the precipitate was dissolved in pure water and filtered. The filtrate was dialyzed through a cellulose membrane to purify the protein and then freeze-dried and the powder protein was stored in a dry container at room temperature. All three adsorbents (Fig. 1) were then passed through the sieve to obtain a particle size of 300 μm. This was done to obtain a smaller particle size that offers higher sorption rates as the surface area increases.

2.4. Characterization of the adsorbents

To confirm the presence of functional groups on the prepared bioadsorbent, they were characterized by various techniques. Fourier-transform infrared spectroscopy (FTIR) equipped with attenuated total reflection (Perkin Elmer, Llantrisant, United Kingdom) was used to identify the groups present and scanning electron microscopy (SEM) JOEL model JSM 6700F (Tokyo, Japan) was used to assess the morphology.

2.5. Bach adsorption studies

Batch adsorption experiments of *M. oleifera* seed adsorbents for the removal efficiency of pharmaceutical compounds were carried out using a series of 100 mL Erlenmeyer flasks. The experiment was done using spiked ultra-pure water with pharmaceuticals (metformin, theophylline, trimethoprim, caffeine, norfloxacin, albendazole, ciprofloxacin, doxycycline hyclate, and metronidazole). Adsorbent mass of 40 mg was mixed with 30 mL aqueous solutions spiked with pharmaceutical solution in 1 mg/L concentration. This was stirred at a constant revolution of 250 rpm for 80 min on a shaker. Adsorbent mass was fixed based on the literature optimized maximum mass because *Moringa* protein yield was very small and the procedure was found very time consuming. Varying one parameter at a time was used to optimise pharmaceutical adsorption parameters. Varied parameters were sample solution pH (3–11), contact time (10–200 min) and sample concentration (0.5–10 mg/L). After adsorption, the solution was filtered using a syringe filter with 0.22 μm pore size. The filtered solution was analysed by UHPLC-DAD. Determined concentrations in the sample were used to evaluate the removal efficiency and the adsorption capacity of the adsorbents using Eqs. (1) and (2), respectively.

$$\text{Removal}(\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{1}$$

$$\text{Adsorption capacity}(\text{mg/kg}) = \frac{(C_0 - C_e)V}{W} \tag{2}$$

where C_0 is the initial concentration (mg/L) in the original sample, C_e is remaining concentration (mg/L) in solution after adsorption, V is the sample volume extracted in liters (L) while W represents adsorbents mass in kilogram. Experiments were carried out in triplicate. The performance of various adsorbents on the removal of pharmaceuticals was tested in real river water.

2.6. Adsorption kinetics and isotherms

Adsorption kinetics and their isotherms studies were used to know the mechanism of adsorption. This is to allow to describe how molecules or ions of adsorbate interact with adsorbent surface sites [31,32]. Two adsorption isotherm models namely, Langmuir and Freundlich whose equations are given as Eqs. (3) and (4), respectively, are used to evaluate the adsorption mechanism [31,33,34].

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{q_{\max} K_L} \tag{3}$$

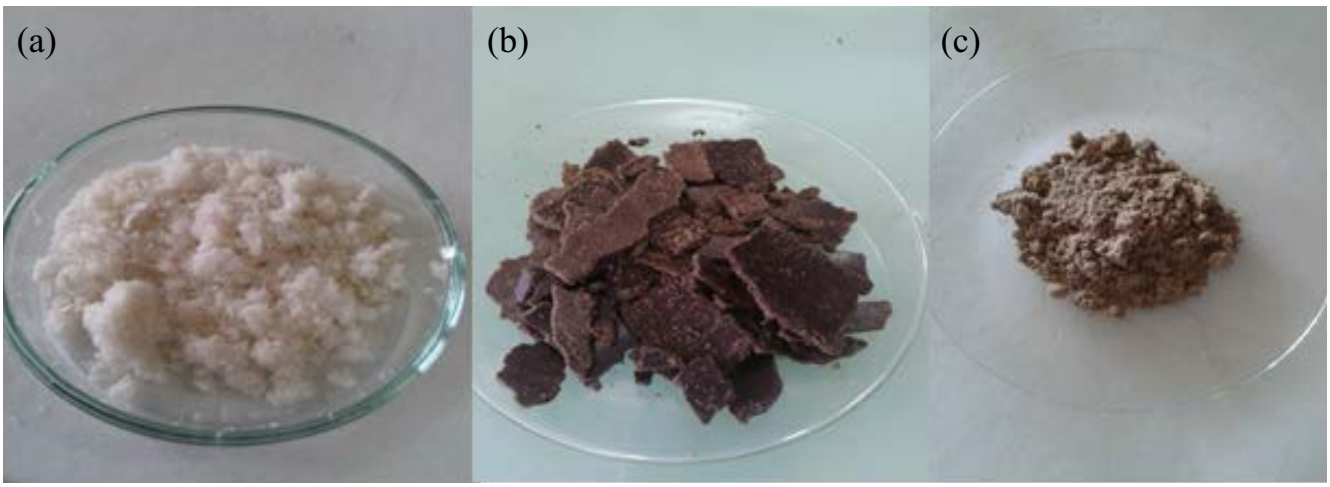


Fig. 1. *Moringa oleifera* seed adsorbents prepared for removal of pharmaceuticals.

$$\log q_e = \log k_f + \frac{1}{n}\log C_e \quad (4)$$

where k_f is constant in the Freundlich equation (L/mg), q_e is the adsorbed amounts of a molecule at equilibrium (mg/g), and K_L is the equilibrium adsorption constant for the Langmuir equation and q_{max} is the maximum adsorption capacity (mg/g) while adsorption/desorption intensity is represented as $1/n$, C_e is the concentration of the target molecules at equilibrium (mg/L), A value of $1/n \leq 1$ signifies that the adsorption is favorable [35]. R_L dimensionless equilibrium parameter that explains the favorability of the adsorption process; R_L is obtained using Eq. (5) [34].

$$R_L = \frac{1}{\left(1 + K_L C_0\right)} \quad (5)$$

where K_L is Langmuir constant (mg/g), and the initial concentration of adsorbate is given as C_0. R_L values $R_L > 1$ indicate the adsorption to be unfavorable and linear when $R_L = 1$. Favorable when $0 < R_L < 1$ means adsorption is favorable and $R_L = 0$ means adsorption is irreversible. On the other hand, to determine the adsorption kinetics of selected pharmaceuticals, pseudo-first and second-order models were used. The pseudo-first-order rate expression of the Lagergren model is generally expressed as in Eq. (6) and pseudo-second-order as in Eq. (7) [15,36]:

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_1 t}{2.303} \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

where the rebinding time (min) is represented by t, the adsorption capacity at different time is represented by q_t (mg/g), k_1 (min^{-1}) is the first-order rate constant and k_2 is the rate constant of second-order adsorption (g/mg·min), q_e (mg/g) is the equilibrium rebinding capacity. A plot of $\log(q_e - q_t)$ vs. rebinding time t (min) results in a straight line with a correlation coefficient R^2 and k_1 were calculated from the slope of the linear plot. According to the pseudo-second-order model, t/Q_t was plotted vs. t (min) and the coefficient of determination; R^2 and k_2 were calculated from the intercept of the linear plot. The validation for the adsorption kinetic models (pseudo-first-order and pseudo-second-order) were done. The linear equations were verified using the sum of squared error (SSE) [37] given in Eq. (8):

$$\text{SSE} = \frac{\sqrt{\left(q_{e,\exp} - q_{e,\text{cal}}\right)^2}}{N} \quad (8)$$

where number of data points is represented by N for the model. The results obtained from validation values help to compare the models which can fit better with the experimental data. The best fit of the model is denoted by a lower value of SSE.

3. Results and discussion

3.1. Characterization of M. oleifera adsorbent for removal

3.1.1. Study of surface morphology

The surface morphology of the *M. oleifera* seed biosorbents was studied to characterize its surface characteristics using a SEM. Fig. 2a–c shows the SEM images of the water-soluble protein, seed husk and seed cake powders, respectively. The surface morphology of the powders confirmed that they are heterogeneous in nature. Thus, the surface morphology was expected to facilitate the adsorption of the target compounds as previously indicated by another study [19].

3.1.2. FTIR characterization before and after removal

The FTIR spectra results for the three biosorbents are shown in Fig. 3a–c. Amine and amide, functional groups, at wavenumbers 1,646; 1,531; 1,451 and 1,415 cm^{-1} associated with C=O stretch amide I, NH amide II, NH amide I band, and C–N stretch amide III, respectively were found on the water-soluble protein (Fig. 3a). These findings are consistent and agree with that reported study [17]. After the adsorption of some pharmaceuticals, there was some shift into wavenumber 3,287 cm^{-1} shifted to 3,149 cm^{-1} and 1,646 to 1,508 cm^{-1}. Wavenumbers 2,783 and 786 cm^{-1} appeared further as new peaks. The change in wavenumbers may be explained as due to the interaction between pharmaceuticals and protein powder functional groups critical in the removal process.

The FTIR spectra for *M. oleifera* seed cake (Fig. 3b) revealed a broad band centered at 3,273 cm^{-1} assigned to the O–H stretching band of the hydroxyl group and N–H stretching band of the amide group from the protein and fatty acid structure [38]. The two peaks at 2,918 and 2,850 cm^{-1} is attributed to the asymmetric and symmetric stretching which corresponds to the C–H in the CH_2 functional groups, respectively. The two peaks at 1,728 and 1,628 cm^{-1} could be attributed to the C=O carbonyl group stretching [21]. The band at 1,534 cm^{-1} is $N–H_{deformation}$ and while the peak at 1,217 cm^{-1} can be attributed to $C–O_{stretching}$ spectra [20]. The appearance of a new peak and disappearance of the peak was observed after adsorption which confirms the interaction of the compound with the adsorbent.

The obtained FTIR spectra of the *Moringa* seed husk are shown in Fig. 3c. A broadband and predominate peak around at 3,306 cm^{-1} can be assigned to O–H stretching. Due to the high content of protein in the seed husk, there is also a contribution in this region from the N–H stretching of amide groups [22,39]. The wavenumbers at 2,916 and 2,837 cm^{-1} can be attributed to symmetrical and asymmetrical C–H stretching of the CH_2 group found in fatty acids [22]. This confirms that *Moringa* husks have protein structure. In 1,800 to 1,500 cm^{-1} region, there are several overlapping bands between 1,750 and 1,630 cm^{-1}. These wavenumbers can be assigned to the C=O joined with stretching [21]. Since the seed can be heterogeneous, the carbonyl group may be linked to different neighborhoods. After adsorption, just like in the case of soluble seed protein, there is a decrease in peak intensity and in some cases shift in wavenumbers of the peaks.

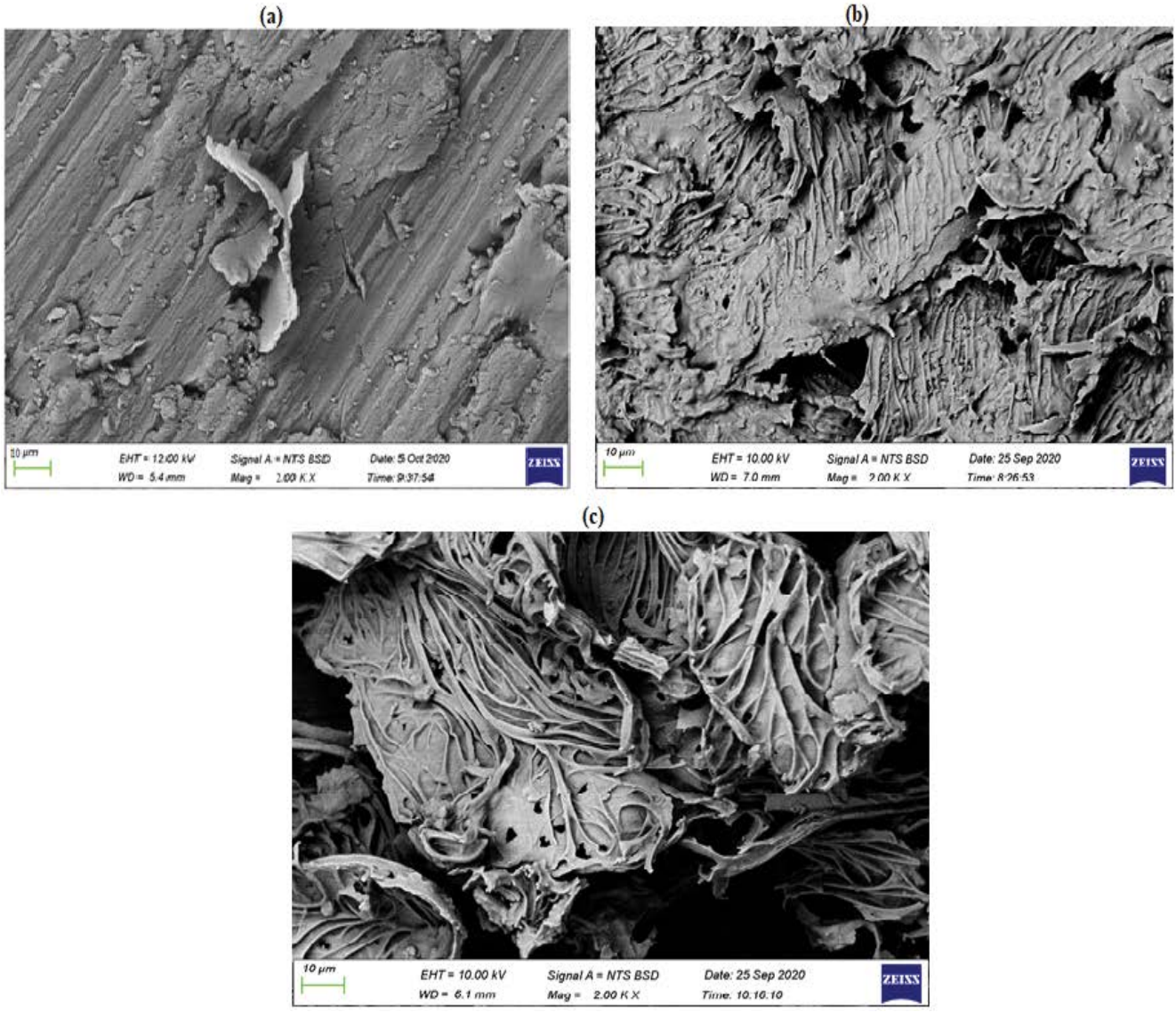


Fig. 2. Scanning electron microscopy images of water-soluble protein powder (a), seed cake (b), and husk (c) of *Moringa oleifera* seed.

3.2. Optimisation of the Moringa biosorbents for the removal of pharmaceuticals from water

The three types of *Moringa* biosorbents were optimised for the removal of selected pharmaceuticals (metformin, theophylline, trimethoprim, caffeine, norfloxacin, albendazole, ciprofloxacin, doxycycline hyclate, and metronidazole) from water. Different parameters that affect the removal efficiency were studied. These parameters are contact time, initial concentration and pH effect. Optimised parameters were varied one parameter at a time while keeping the others constant.

3.2.1. Effect of pH

Results for varying the effect of sample pH in the removal of multi-class pharmaceuticals from an aqueous solution is shown in Fig. 4. The number of pharmaceuticals removed at different sample pH besides being pH dependent was also affected by the type of *Moringa* biosorbent. Overall, a sample pH of 5 showed the highest removal efficiencies for most pharmaceuticals. The optimum sample pH of 5 was more pronounced on *Moringa* seed cake as an adsorbent. In other *Moringa* biosorbent, the trend on the effect on sample pH was not very pronounced. Sample pH 5 and 9 seem to have given close to optimum removal efficiencies for the other two with more pharmaceuticals slightly still removed at pH 5. This could be attributed to varying functional groups present in these biosorbents [19]. The study reported by Araujo et al. [21] on the removal of pharmaceuticals using *Moringa* as an adsorbent, sample solution pH of 5 was an optimum pH giving relatively high adsorption on the adsorbent. The other reported study also shows that the maximum removal was attained at pH 5 and pH 6 of the sample solution [19]. The sample pH effects studies are important as they affect both the chemistry of the analytes

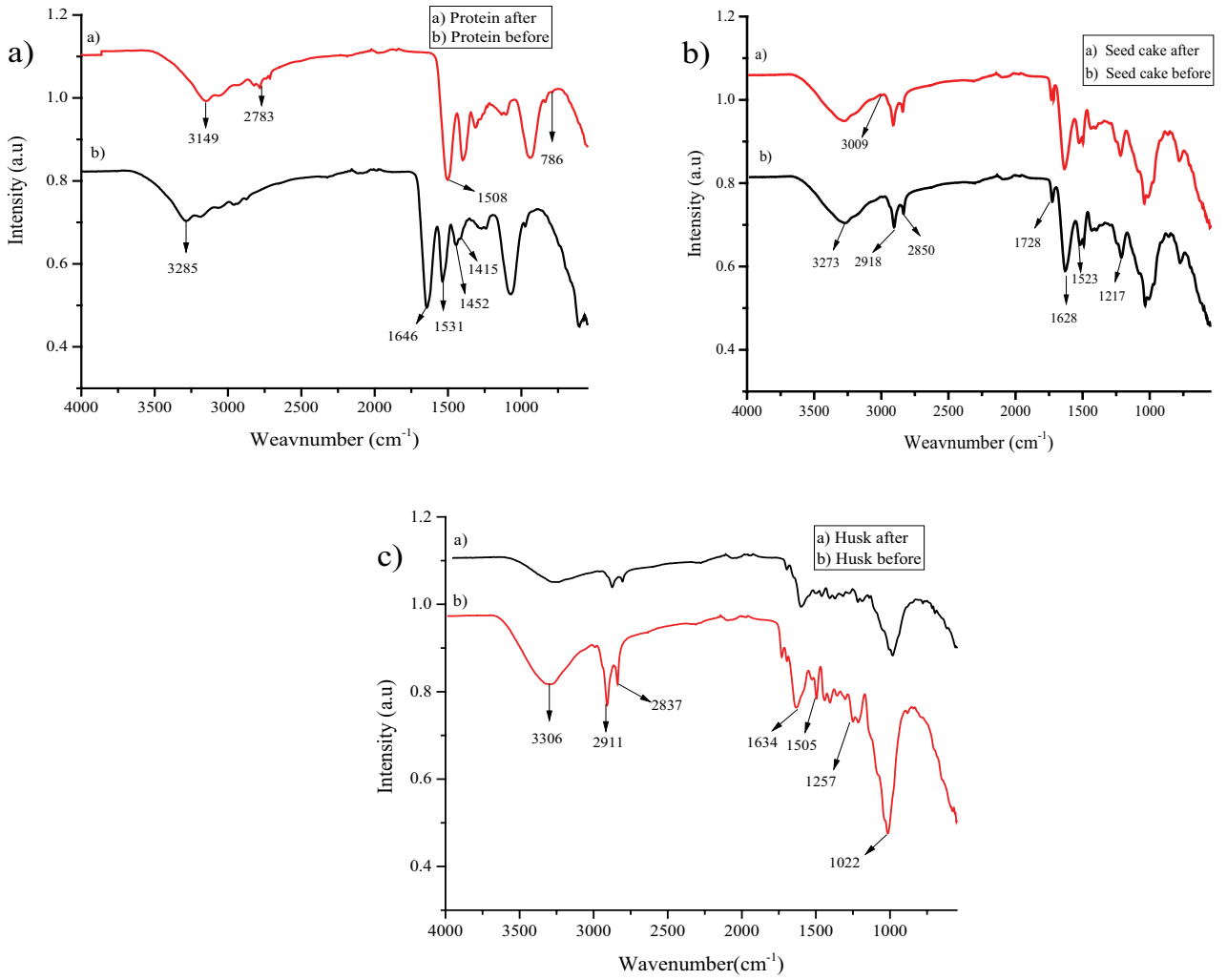


Fig. 3. (i) Fourier-transform infrared spectroscopy spectra of *Moringa oleifera* seed water-soluble protein powder (a) after and (b) before adsorption. (ii) FTIR spectra of *Moringa oleifera* seed cake powder (a) after adsorption and (b) before adsorption. (iii) FTIR spectra of *Moringa oleifera* seed husk powder (a) after and (b) before adsorption.

and that of the biosorbents. One important parameter that affects the adsorption is the isoelectric point (IEP) [40]. This is the pH as which the molecule or surface of the material has no net charge and thus neutral. A study by Belbali et al. [41] on the coagulation of turbid wastewater with an active component extracted from *M. oleifera* seeds reported an isoelectric point the protein at pH 6.5–7.5. This may explain the slightly high adsorption observed at pHs 5 and 9 which are both below the and above the reported isoelectric point, respectively. Most target pharmaceuticals at pH 5 would be positively charged as per their pK_{as} (Table 1) which could have enhanced the adsorption with *Moringa* seed biosorbents. It should however be noted that extraction conditions have also been noted to influence IEP of *Moringa* based biosorbents [42]. Solution pH of 5 was selected as an optimum for all the biosorbents as a compromise.

3.2.2. Effect of contact time

The results for varying the effect of contact time from 10 to 200 min are shown in Fig. 5. The results that analyte adsorption was very fast. Most extraction was reached within first 30 min. This can be attributed to the presence of several biobased adsorbent active sites. Further increase on contact time up to 80 min increased removal efficiency further. However, thereafter remained constant up to 200 min studied time. 80 min extraction time reached equilibrium almost all analytes. However, *M. oleifera* water-soluble protein adsorbent shows that time variation in the range considered in this study does not affect the removal of pharmaceuticals. Nonetheless, 80 min extraction time was used as an optimum time throughout the study.

3.2.3. Effect of the initial pharmaceutical concentration

The results for varying the initial concentration from 0.5–10 mg/L are shown in Fig. 6. The results show that an increase in the sample concentration resulted in a rapid drop in the removal efficiency. The sudden decrease observed is due to the reduction of active sites on the *Moringa* adsorbent. However, it was observed that the number of pharmaceuticals adsorbed per unit mass of adsorbent (adsorption

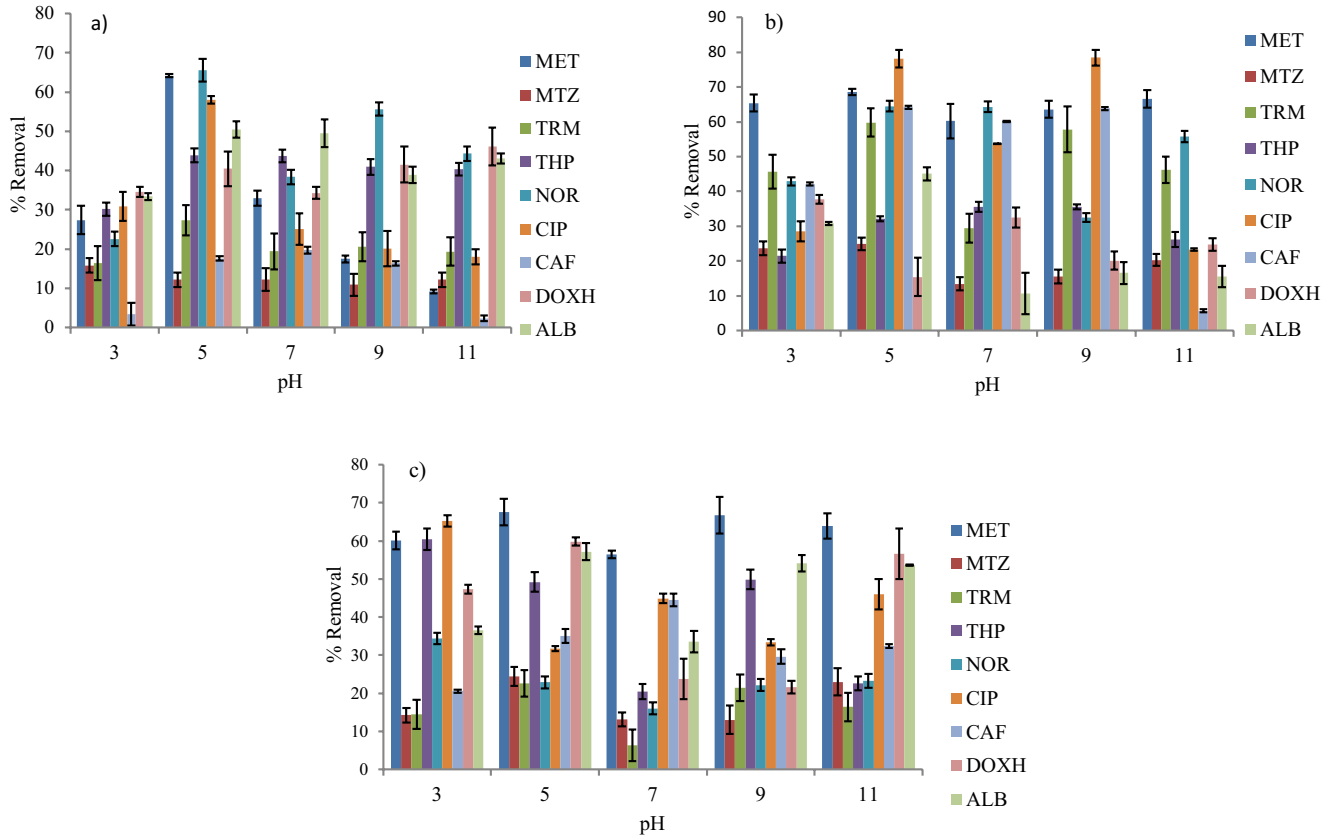


Fig. 4. Effect of pH on the removal of pharmaceuticals by (a) seed cake, (b) husk and (c) water-soluble protein. The other parameters were kept constant (adsorbent dosage of 40 mg, analyte concentration of 0.5 mg/L each, the sample volume of 30 mL, contact time of 60 min and room temperature).

capacity) in (mg/g) increased with increased sample concentration. This trend was found similar to the reported studies done using *Moringa stenopetala* seeds water-soluble protein as a biosorbent for the removal of antibiotics and sulphonamides [17,19]. The adsorption capacity for the *Moringa* biosorbents, seed cake ranged from 3–311, for the seed husk from 7–413 mg/g and water-soluble protein was 2–326 mg/g. The result implies seed husk has the highest adsorption capacity compared to other biosorbents.

3.3. Adsorption isotherms and kinetics

3.3.1. Adsorption isotherms

Langmuir and Freundlich's adsorption isotherm models were used to study the type of analyte interactions with the biosorbents (Table 2). The Langmuir parameters, q_{max} and K_L, were calculated from the intercepts and slopes, respectively, of the linear plot of C_e/q_e vs. C_e. Similarly, Freundlich parameters were calculated from the slope and intercept, respectively, of the linear plot of $\log q_e$ vs. $\log C_e$ [43]. The results show favorable adsorption of analytes because the Langmuir dimensionless equilibrium constant (R_L) is less than one and greater than zero. The Freundlich isotherm is indeed favorable for the adsorption because the value of n (heterogeneity factor) is greater than one. Looking at R^2 values from the adsorption models, suggest that both models were generally good for the compounds, but the Freundlich model provided the best correlation. Multilayer adsorption was further confirmed by fitting of Freundlich isotherm.

3.3.2. Adsorption kinetics

Table 3 shows the values from pseudo-first and pseudo-second-order kinetic models with rate constants (k_1, k_2, and q_e). These were determined from the intercept and slope of the curves as a function of time (Table 3). The pseudo-first-order kinetics model R^2 value of the plotted curve was in the range of 0.0260–0.9518. For the pseudo-second-order kinetics model it was in the range of 0.9083–0.9991. The lowest possible value, sum of error squared (SSE) was used to compare the best fit of these models (Table 3). The pseudo-second-order kinetics model gives the lowest SSE values. The results also support adsorption process of multiclass pharmaceuticals on *Moringa* adsorbent. Therefore, chemisorption could be the rate-limiting step in the adsorption of multi-class pharmaceuticals with *M. oleifera* seed biosorbents [34].

3.4. Application of the adsorbent on real river water samples

The optimized method for the *Moringa* adsorbents was applied for the removal of multiclass pharmaceutical compounds from the standard mixture solution spiked

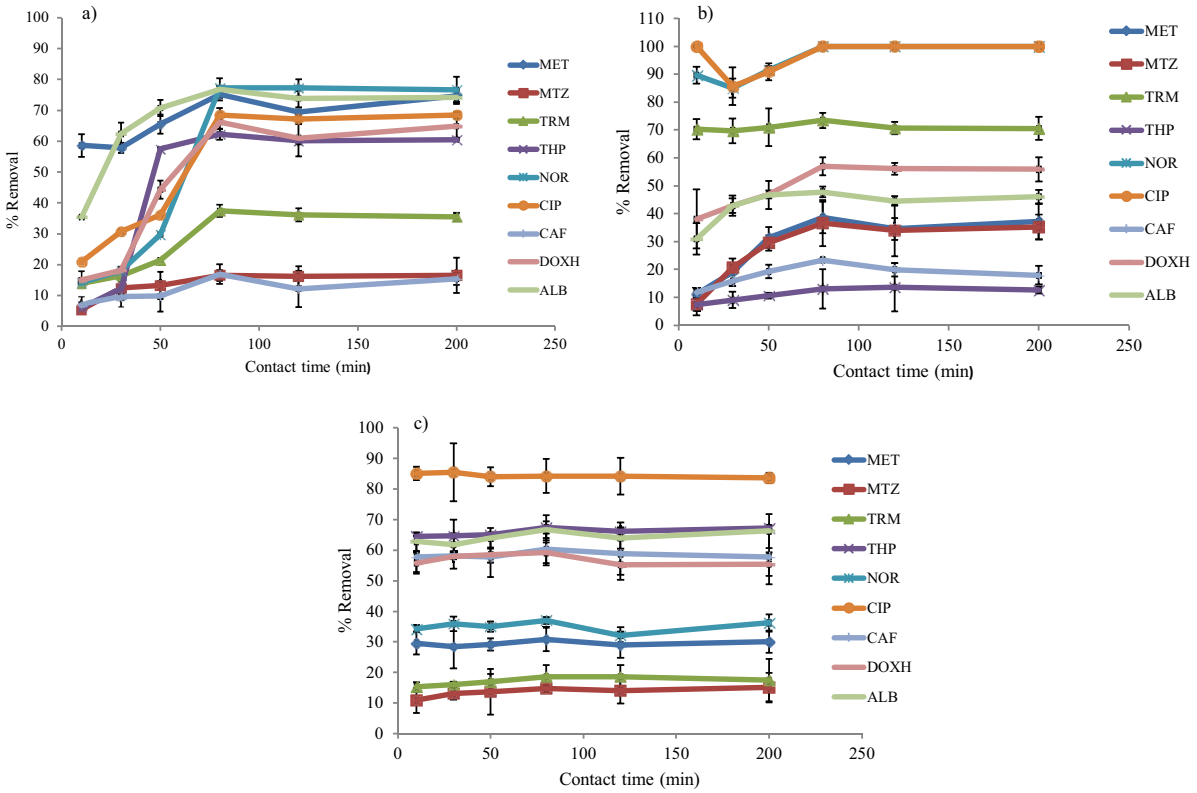


Fig. 5. Effect of contact time on the removal of pharmaceuticals, (a) seed cake, (b) husk and (c) water-soluble protein. Other parameters were held constant (adsorbent dosage of 40 mg, a sample volume of 30 mL, agitation speed of 250 rpm, initial concentration 0.5 mg/L, sample pH at 5 and room temperature).

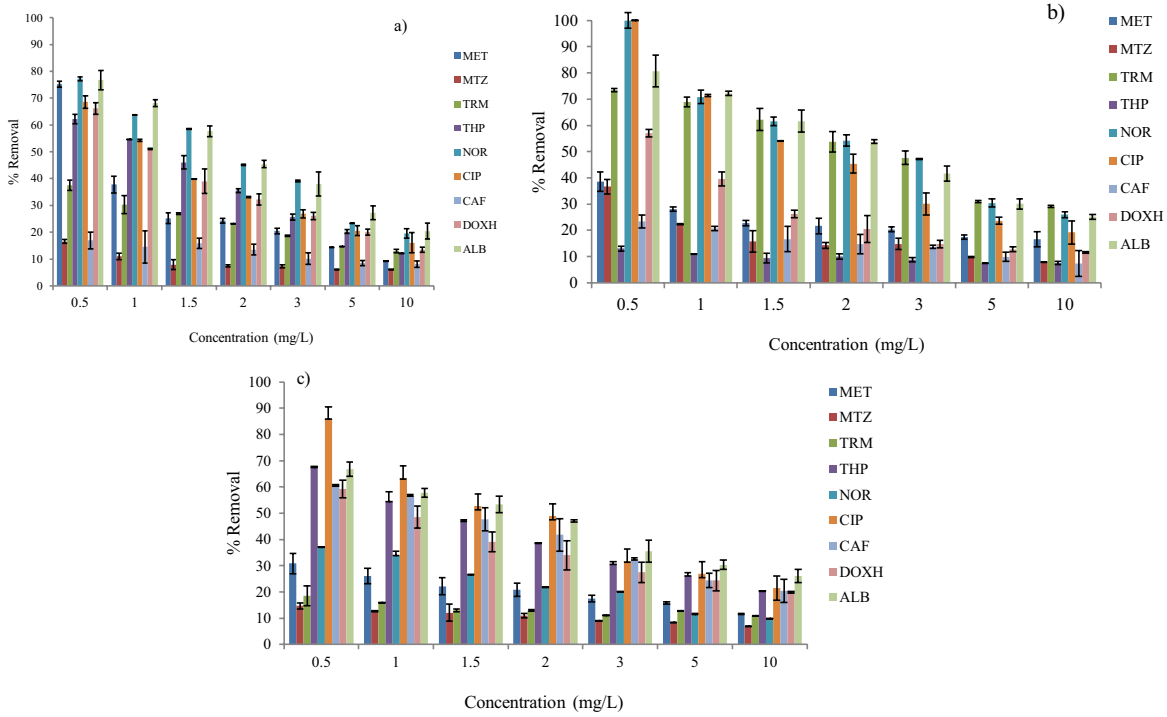


Fig. 6. Effect of initial concentration on the removal of pharmaceuticals by (a) seed cake, (b) husk and (c) water-soluble protein. Other parameters were maintained constant (i.e., adsorbent dosage of 40 mg, a sample volume of 30 mL, agitation speed of 250 rpm, the contact time of 80 min, sample pH of 5.5 and at room temperature).

Table 1
Physico-chemical properties of selected pharmaceuticals

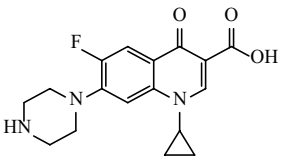
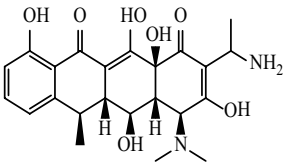
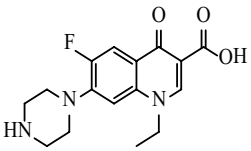
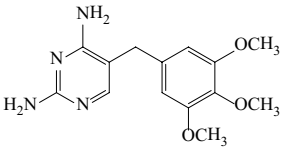
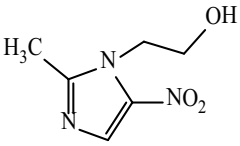
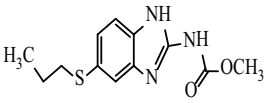
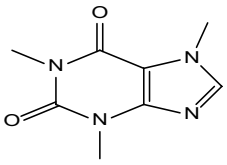
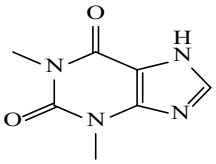
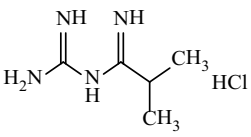
Therapeutic class	Structure of the compound	pK_a	$\log K_{ow}$	Water solubility (mg/L)	References
Ciprofloxacin (CIP)		5.9/8.9	0.28	1,010	[25,26]
Doxycycline Hyclate (DOXH)		–2.20	–0.72	630	[25]
Norfloxacin (NOR)		6.2/8.2	–0.1	1,350	[25,26]
Trimethoprim (TRM)		7.2	0.91	400	[27]
Metronidazole (MTZ)		15.44	–0.15	592	[25]
Albendazole (ALB)		9.51	3.22	20	[25]
Caffeine		10.4	–0.07	11,308	[28]
Theophylline (THP)		8.81	–0.9	22,900	[29]
Metformin (MET)		12.33	–0.92	1,380	[29]

Table 2
Adsorption isotherms parameters

Adsorbent	Analyte	Langmuir parameters				Freundlich parameters		
		q_{max} (mg/g)	K_L (L/mg)	R_L (L/mg)	R^2	K_f ((mg/g)/(mg/L)$^{1/n}$)	n	R^2
Seed cake	MET	54.6	0.33	0.55	0.9332	15.4	2.31	0.9379
	MTZ	44.8	0.12	0.62	0.8900	3.94	1.07	0.916
	TRM	115	0.20	0.59	0.8919	20.9	1.72	0.9897
	THP	159	0.58	0.48	0.9899	59.2	2.44	0.9246
	NOR	370	0.33	0.55	0.8860	100	2.14	0.9428
	CIP	286	0.42	0.52	0.9516	91.3	2.38	0.9741
	CAF	116	0.11	0.62	0.8031	11.9	1.39	0.9859
	DOXH	53.5	0.57	0.48	0.9850	16.3	1.94	0.9702
	ALB	53.5	0.57	0.48	0.9600	32.4	1.81	0.9853
Seed husk	MET	111	0.11	0.62	0.9013	10.8	1.23	0.9885
	MTZ	76.3	0.15	0.61	0.8627	8.30	1.50	0.9181
	TRM	256	0.21	0.58	0.8766	46.1	1.64	0.9677
	THP	6.3	0.75	0.44	0.8191	12.9	1.26	0.9944
	NOR	526	0.25	0.57	0.8623	118	1.98	0.9733
	CIP	313	0.57	0.48	0.9218	124	2.92	0.9370
	CAF	83.3	0.22	0.58	0.9705	15.4	1.66	0.9924
	DOXH	49.0	0.26	0.57	0.8131	11.9	2.19	0.9234
	ALB	192	0.21	0.58	0.9082	34.8	1.67	0.9771
Water-soluble protein	MET	112	0.09	0.63	0.9531	9.60	1.28	0.9931
	MTZ	65.4	0.07	0.64	0.7248	4.40	1.06	0.9785
	TRM	132	0.08	0.63	0.8332	10.4	1.21	0.9926
	THP	333	0.19	0.59	0.9345	56.1	1.58	0.9600
	NOR	192	0.26	0.57	0.7819	44.6	1.83	0.9003
	CIP	400	0.34	0.54	0.9453	104	1.93	0.9211
	CAF	244	0.18	0.60	0.9284	4.60	1.50	0.9622
	DOXH	106	0.16	0.60	0.9318	14.8	1.45	0.9667
	ALB	256	0.11	0.62	0.8685	28.8	1.35	0.9765

in river water collected from Kebena River (R_1) and Akaki River (R_2), Addis Ababa, Ethiopia. None of the target analytes were detected in the water samples. Percent removal of the adsorbents was evaluated after spiking 30 mL of river water sample with 0.5 mg/L standard mixture solutions of the target pharmaceuticals (Table 4). The range of removal efficiency obtained was 10.4%–77.5%, 8.50%–75.4% and 10.5%–88.5% for *Moringa* seed cake, husk and water-soluble protein, respectively and more than half of the pharmaceutical compound shows >50% removal efficiency. Thus, variations are attributed with the K_{ow} values of the pharmaceutical (Table 1) which explains the polar or non-polar nature of the compounds and their affinity either to the adsorbent or towards the solution. Most polar compounds were poorly adsorbed on the biosorbents. There was a moderate reduced removal of the pharmaceuticals in the spiked real water sample compared to deionized water sample. Matrix effects in the sample could have caused this decrease.

4. Conclusions

Natural adsorbents from *M. oleifera* seed were studied for their effectiveness in removing multi-class pharmaceuticals from water. Batch experiments were conducted under different ranges of parameters such as sample pH (3–11), contact time (10–200 min) and initial concentration (0.5–10 mg/L) of target compounds were optimized by varying one parameter at a time while keeping the other constant. The studied adsorbents (seed cake, seed husk and water-soluble protein) have promising removal efficiency for the removal of multi-class pharmaceuticals. The adsorption of the analytes was found to fit the Freundlich adsorption model indicating monolayer sorption with a heterogeneous energetic distribution of active sites. The adsorption process in the present study followed the pseudo-second-order model indicating chemisorption as the rate-limiting step. Finally, these *M. oleifera* adsorbents were used to remove pharmaceuticals from real water and found

Table 3
Adsorption kinetics parameters

Adsorbent	Analyte	Pseudo-first-order					Pseudo-second-order			
		q_e (mg/g) exp	q_e (mg/g) cal	k_1 (min^{-1})	R^2	SSE	R^2	k_2 (min^{-1})	q_e (mg/g) cal	SSE
Seed cake	MET	13.1	4.43	0.018	0.9275	3.25	0.9965	0.079	13.2	0.06
	MTZ	3.08	1.33	0.015	0.9068	0.66	0.9714	0.017	7.78	0.64
	TRM	13.6	8.09	0.016	0.6989	2.06	0.9491	0.016	15.4	0.70
	THP	36.9	15.0	0.017	0.6022	8.27	0.9242	0.012	45.9	3.41
	NOR	64.7	45.2	0.026	0.7754	7.38	0.9664	0.013	80.0	5.77
	CIP	63.3	7.87	0.034	0.8950	20.9	0.9387	0.118	7.87	1.82
	CAF	7.08	3.77	0.011	0.7721	1.24	0.9694	0.026	7.25	0.06
	DOXH	11.9	8.91	0.020	0.9494	1.11	0.9083	0.009	12.8	0.36
	ALB	20.2	5.04	0.013	0.6705	5.72	0.9971	0.074	20.4	0.07
Seed husk	MET	6.71	4.17	0.015	0.9248	0.96	0.9785	0.020	7.39	0.26
	MTZ	6.84	4.10	0.015	0.9068	1.04	0.9714	0.017	7.78	0.35
	TRM	26.6	1.12	0.001	0.1053	9.62	0.9997	0.982	25.6	0.37
	THP	7.73	3.35	0.013	0.9518	1.66	0.9906	0.053	8.06	0.13
	NOR	83.8	9.76	0.014	0.6594	27.9	0.9991	0.138	85.5	0.63
	CIP	92.4	4.32	0.008	0.2214	33.3	0.9989	0.159	94.3	0.74
	CAF	9.78	2.73	0.003	0.1519	2.66	0.9824	0.392	7.77	0.76
	DOXH	8.49	3.05	0.017	0.8188	2.06	0.9967	0.065	8.72	0.08
	ALB	21.2	7.98	0.016	0.6766	5.10	0.9967	0.038	22.3	0.41
Water-soluble protein	MET	5.33	1.66	0.008	0.3024	1.39	0.9677	0.051	5.12	0.08
	MTZ	2.75	1.30	0.012	0.7135	0.55	0.9826	0.039	2.82	0.03
	TRM	6.73	3.69	0.008	0.5890	1.15	0.9149	0.017	6.73	0.03
	THP	39.9	37.5	0.033	0.9011	0.92	0.9749	0.026	43.9	0.75
	NOR	31.1	5.56	0.002	0.0260	9.64	0.9709	0.047	18.1	4.89
	CIP	77.8	1.36	0.007	0.1332	28.9	0.9997	0.653	78.1	0.10
	CAF	25.2	1.05	0.001	0.0527	9.12	0.9996	0.769	24.3	0.34
	DOXH	8.81	3.40	0.003	0.2505	2.05	0.9991	0.269	8.19	0.24
	ALB	17.6	1.01	0.005	0.9508	6.25	0.9957	0.099	14.7	1.08

Table 4
Removal efficiency of *Moringa oleifera* seed adsorbents from real water samples

Analyte	R_t	Seed cake			Husk			Protein		
		Pure water	R_1	R_2	Pure water	R_1	R_2	Pure water	R_1	R_2
MET	1.94	75.2	62.4	58.7	38.6	35.4	33.5	30.8	28.5	30.1
MTZ	5.38	16.5	10.6	12.5	36.6	38.5	40.5	14.7	11.5	10.5
TRM	6.02	37.5	33.5	25.6	73.5	70.9	66.4	18.6	20.4	19.4
THP	6.39	62.2	65.3	55.7	13.0	10.4	8.50	67.4	59.8	65.4
NOR	7.07	77.2	68.4	70.5	98.7	82.5	76.4	37.0	30.5	38.5
CIP	7.27	68.5	64.3	50.8	96.5	87.5	70.5	86.0	80.5	88.5
CAF	7.34	16.9	11.4	10.4	23.4	20.3	25.4	60.6	56.6	60.4
DOXH	11.74	66.1	59.7	49.6	57.0	49.5	40.6	59.2	56.7	60.4
ALB	13.83	76.8	77.5	70.5	80.7	75.4	70.5	66.7	65.4	60.4

to be effective, efficient, economic and alternative adsorbents. It is recommended to work on surface modification to further increase the adsorption of the surface of the adsorbents.

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Conflict of interest

The authors declare that they have no conflict of interest.

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