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Application of raw and biochared *Moringa oleifera* seed powder for the removal of nitrobenzene from aqueous solutions

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ABSTRACT

Low cost and locally available *Moringa* seed powder as a potential biosorbent was tested for its effectiveness in the removal of nitrobenzene (NB) from aqueous solution. Biochared *Moringa oleifera* seed powder was also used to compare its performance in the uptake of NB from aqueous solution. Fourier transform infrared spectroscopy fingerprint region of the biochared *M. oleifera* seed powder was clearer as compared to the raw. Pores observed by the scanning electron microscopy analysis were found to be 0.84 and 1.23 $cm^3 g^{-1}$ (by BET analysis) for the raw and biochared *M. oleifera* seed powder, respectively. The carbon elemental analysis by energy-dispersive X-ray spectroscopy was 80 and 70% for the raw and biochared *M. oleifera* seed powder, respectively. The removal efficiencies of the two sorbents were evaluated using factors such as solution pH, biosorbent dosage, contact time and initial NB concentration. A basic pH of 11 was found to be optimum for the uptake of NB for both sorbents. The sorption equilibration time of NB at 25°C was about 50 min, and the optimal NB removal efficiency was achieved with a dosage of 12.5 g L^{-1}. The pseudo-second-order was found to fit the kinetic data better with the calculated sorption capacity of NB of 0.084 and 0.071 mg g^{-1} onto the raw and biochared *M. oleifera* seed powder sorbent. The limit of detection and limit of quantification values for NB determination by HPLC-UV were found to be 11.54 and 38.46 μg L^{-1}, respectively.

Keywords: Biosorption; *Moringa oleifera*; Biochar; Nitrobenzene

1. Introduction

Nitrobenzene (NB) is widely used in the manufacturing of dyes, pesticides, explosives and paper and textile [1,2]. However, the release of NB from these industries into the environment has drawn considerable attention due to its toxicity, persistence and accumulation in the food chain. Nitroaromatic compounds (NACs) are commonly found in the subsurface soil and pose a potential threat to human health [3]. Therefore, a variety of wastewater treatment technologies such as adsorption [4], biodegradation [5] and oxidation processes [6] have been employed for the purification of NACs contaminated water. Due to high costs and environmental side effects of the chemical coagulant compounds such as aluminium and iron salts, there has been an increase in interest in the use of organic coagulants derived from plant material [7].

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Biomass, which is abundant in nature and produced in large quantities as a by-product or waste from agricultural activities could be used to make biosorbents for environmental remediation [8]. The use of biosorbents for the uptake of pollutants from aqueous medium was previously reported e.g. metal removal with biosorbents was reviewed by Veglio and Beolchini [9], and Wang and Chen [10].

Amongst other plant materials, powder form of *Moringa oleifera* seed has been proven to be one of the most effective and viable replacement of various chemical coagulants [11,12]. *Moringa*, the only genus belonging to the *Moringaceae* family, consists of 14 species [13]. Raw *M. oleifera* seed powder has been used extensively for the removal of various pollutants from wastewaters e.g. orange 7 dye [14], chromium [15] and copper [16]. However, most of the studies in literature have focused on metal ion remediation. Use have been made of the functional groups as a result of the presence of various amino acids, fatty acids, vitamins, glucosinolates and phenolics (flavonoids, anthocyanins, proanthocyanidins and cinnamates) [16]. In order to improve the sorption capacity, the *M. oleifera* seed powder has been chemically modified with different chemicals like alginate [17] and acetic anhydride [18].

Physical transformation of raw *M. oleifera* seed powder into biochar is receiving great research attention due to its potential in agronomic and environmental applications [19]. In this process, the generation of pores take place via selective elimination of the more reactive carbon and further gasification leading to the production of activated carbon with high porosity [20]. The cost of the activated carbon prepared from biomaterials is lower compared with that of commercial activated carbon [21].

In this work, factors affecting the biosorption of NB by the locally available, low cost and eco-friendly *M. oleifera* seed powder were investigated. Uptake performance of NB by biochar obtained by direct pyrolysis of *M. oleifera* seed powder was also investigated and compared with the raw material. Characterization of the raw and biochared *M. oleifera* seed powder was done by Brunauer–Emmett–Teller (BET) surface area analysis, Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and zeta potential and energy dispersive X-ray spectroscopy (EDS).

2. Materials and methods

2.1. Chemicals and materials

NB (≥99%) was bought from Sigma-Aldrich (Johannesburg, South Africa) and acetonitrile (99.9%) was obtained from Sigma-Aldrich (Steinhein, Germany).

Deionized water was obtained from Milli-Q ultrapure water (Millipore, Billerica, Massachusetts, USA). pH measurements were done on a 766 Calimatic pH meter equipped with a Shott N61 pH electrode from Knick (Berlin, Germany). For mechanical agitation, a Wisecube Fuzzy Control System from Wisd Laboratory Instruments was used at 100 rpm at a fixed temperature of 25°C. A Rotofix 32A Centrifuge from Hettich Lab Technology (Tuttlingen, Germany) was used to separate the NB solution from the sorbents, and was set at 2,500 rpm.

2.2. HPLC conditions and preparation of solutions

A Bischoff HPLC with a UV detector set at 254 nm with an Ascentis@ RP-Amide column (25 cm × 4.6 mm × 5 μm) was used to quantify the NB. The mobile phase composition was acenotnitrile/water (65/35, v/v) with the flow rate maintained at 1 mL min^{-1} in isocratic mode and the sample injection volume of 50 μL was used.

A 100-mg L^{-1} stock solution of NB was prepared by dissolving the appropriate volume in 50/50, v/v acetonitrile/water solution. A 10-mg L^{-1} NB working solution was then prepared from the stock solution and the same diluent, acetonitrile/water (50/50, v/v) was used to top up to the mark.

2.3. Biosorbent preparation

M. oleifera seeds were collected from a farm in Lebowakgomo in Limpopo Province, South Africa (24.3050°S, 29.5650°E). *M. oleifera* seeds were dried in sunlight for 3 d (average temperature was 26°C). The dehusked *M. oleifera* seeds were then washed several times with distilled water to remove all dirt. The cleaned *M. oleifera* seeds were oven dried at 80°C for 3 h. The seeds were powdered in mortar and pestle and sieved through a 2 mm mesh. Direct pyrolysis was used for the preparation of biochar from *M. oleifera* seeds. The heating process was carried out in the absence of air after purging with nitrogen for 10 min. The *M. oleifera* seed powder was biochared in a muffle furnace at 200°C for 2 h, and the average pyrolysis yield of biochar was 48.9% by mass. After biocharing, the material was repeatedly washed with distilled water.

2.4. Characterization

Through a FEI Quanta 200 ESEM scanning electron microscopy equipped with EDS, the surface morphological features of the raw and biochared *M. oleifera* seed powder were explored and elemental composi-

tions determined. The samples were mounted on a black double-sided carbon tape attached to a sample platform. To avoid charging, the samples were coated with gold palladium using a sputter coater Baltec Scutter SCD 050 to a thickness of approximately 30 nm. Fourier transform infrared spectra were recorded in the frequency range of 400–4,000 cm^{-1} using a Tensor 27 Bruker FTIR spectrophotometer (Ettlingen, Germany). Zeta potentials were measured with the Zeta-Meter 3.0 system (Malvern ZS-90).

2.5. Swelling studies

The swelling behaviour was investigated by immersion of 1.5 g of *M. oleifera* seed powder (raw and biochared) in 25 mL of distilled water at 25°C for 3 d until swelling equilibrium was achieved. Elongated times were used (3 d) to make sure equilibrium was reached. The equilibrium times are normally shorter; in orders of few hours e.g. Ijarotimi et al. [22] who equilibrated the *M. oleifera* seed flour for 30 min. The sorbent weight increase allowed the calculation of the swelling percentage using Eq. (1) where W_s and W_d are the weights of the swollen and dry sorbent samples (in g), respectively.

$$\text{Swelling ratio } (\%) = \frac{(W_s - W_d)}{W_d} \times 100 \quad (1)$$

2.6. Batch adsorption studies

A typical batch adsorption was done by adding the dried biosorbent (raw and biochared *M. oleifera* seed powder) into a solution of NB under specific experimental conditions. The effect of pH was investigated using 0.2 M NaOH and/HCl to adjust the pH of the samples to acidic, neutral and basic conditions. The effect of biosorbent loading was studied using various dosages of biosorbents (1.0, 2.50, 6.25, 12.50, 18.75, 50.0 and 100.0 g L^{-1}). Contact time was investigated at different time levels (1, 2, 5, 10, 15, 20, 30, 45 and 90 min). The effect of concentration was also examined at different levels (1.0, 0.25, 0.5, 0.8, 1.0, 1.5, 2.0 and 3.0 mg L^{-1}).

After shaking the mixture, the sorbent was separated by centrifugation at 2,500 rpm for 10 min and the concentration of NB in the supernatant was measured by HPLC-UV. Eqs. (2) and (3) were used to calculate the uptake efficiency of NB from aqueous solution.

$$\text{Extraction efficiency } (\%) = \frac{(C_o - C_e) \times 100}{C_o} \quad (2)$$

$$\text{Adsorption capacity} = \frac{(C_o - C_e)V}{m} \quad (3)$$

where C_o is the initial concentration of NB (mg L^{-1}), C_e is the amount of NB after adsorption (mg L^{-1}), V is the volume of NB solution (L) and m is the weight of the sorbent (raw or biochared *M. oleifera* seed powder) used (g).

2.7. Point of zero charge determination

For the point of zero charge (pH_{pzc}) determination, a modified method from Rivera-Utrilla et al. [23] was used: 25 mL of 0.01 M NaCl solution was placed in a vessel. Nitrogen was bubbled through the solution to stabilize the pH by preventing the dissolution of CO_2. The pH was adjusted to values between 1 and 13 by addition of 0.1 M HCl or 0.1 M NaOH solutions. 100 mg of the raw or biochared *Moringa* seed powder was added to the solution and left shaking for 24 h at 140 rpm at 25°C. The final pH was then measured and plotted against the initial pH for the determination of the pH_{pzc}.

3. Results and discussion

3.1. Characterization

The swelling results are presented in Table 1 where the raw *M. oleifera* seed powder had a swelling ration of 27.2% whilst that of the biochared *M. oleifera* seed powder was 14.2%. The raw material had almost double the swelling capability as compared to the biochared because of the various functional groups which were absent in the biochared, as the FTIR result later showed. The initial rapid increase in the swelling of the polymeric sorbent synthesized by Anirudhan et al. [24] was attributed to the presence of the hydrophilic –COOH. The surface characterization of the biosorbents shown in Table 1 indicated the high porosity of the biochared sorbent as compared to the raw one.

The morphologies of raw and biochared *M. oleifera* seed powder were investigated by SEM analysis (Fig. 1(a) and (b)). The SEM micrographs showed an amorphous and heterogeneous nature of *M. oleifera* seed powder with clear, porous characteristic on the surfaces and the development of voids. The presence of a porous surface meant an increased surface area and this translated to an increased NB sorption capacity as this increased the mass transfer.

FTIR was used to investigate the functional groups present on the *M. oleifera* seed powder sorbents. The two spectra of *M. oleifera* seed powder (raw and

Table 1
Physical characteristics of the biosorbents

Moringa powder biosorbent	Surface area ($m^2\ g^{-1}$)	Specific volume ($cm^3\ g^{-1}$)	Swelling ratio (%)
Raw	6.3	0.84	27.2
Biochared	12.6	1.23	14.2

biochared) are shown in Fig. 1(c). The broad peak seen on the raw sorbent at around 3,430 cm^{-1} indicated the presence of hydroxyl group (–OH) stretching. There was a great reduction of the hydroxyl group (–OH) stretching frequency for the biochared sorbent probably due to the elimination of moisture and –OH groups of the proteins from the biochared *M. oleifera* seed powder during biocharing. The absorption peaks at 2,920 and 2,851 cm^{-1} were due to the C–H stretching off –C=O and/or $–CH_3$ of functional groups. The bands corresponding to the carbonyl group (–COO) of the proteins and other organic compounds in *Moringa* seed powder were detected at around 1,750 cm^{-1}. The band centred at 1,600 cm^{-1} was assigned to the molecular vibration of ring stretching in C=C probably due to the presence of organic compounds in the *Moringa* seed powder. This band was intense for the raw materials and was subdued in the biochared sorbent. Biochar is a solid residue of biomass incomplete combustion or pyrolysis, which is produced alongside two other by-products, bio-oil and syngas [25]. As such, the spectrum of the biochared *M. oleifera* seed powder was observed to be cleaner in the fingerprint region. The FTIR band shifts at 3,450, 1,750 and 1,600 cm^{-1} discussed above might also be due to denaturation of proteins at high temperatures.

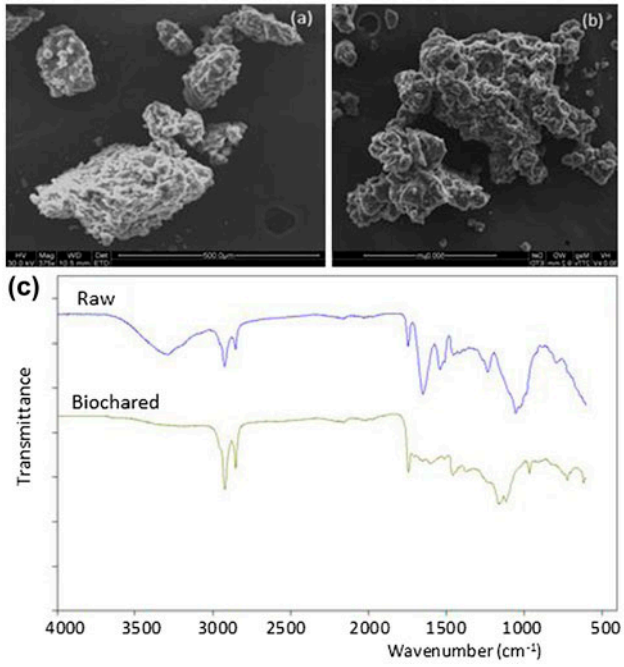

Fig. 1. SEM micrographs of (a) raw, (b) biochared *Moringa* seed and (c) FTIR of *Moringa* seed powder.

EDS was used to study the elemental composition of the *Moringa* seed powder (Fig. 2). Raw and biochared *Moringa* seed powder were dominated by carbon and moderate content of O, P, S and K were also present. Biochar is a carbonaceous material containing 65–90% carbon [26]. In the present study, the biochared sorbent had 80% carbon content, an increase from 70% for the raw sorbent. This increase has been reported by other researchers. For instance, Jouiad et al. [27] biochared date palm and Rhodes grass and

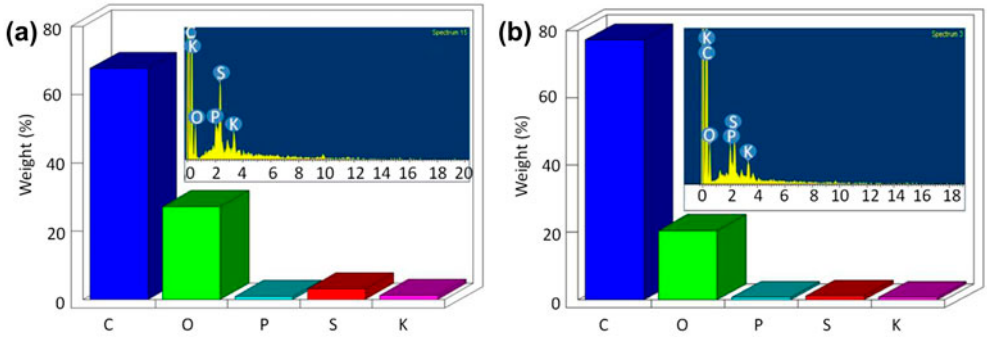

Fig. 2. Elemental composition of (a) raw and (b) biochared (inserts are the respective EDS spectra).

obtained a carbon content increase of 45.4–60.9% and 42.5–56.7%, respectively. Zhang et al. [28] also observed an increase in the fixed carbon content from 15.75 to 21.25% as the pyrolysis temperature was increased. In a research done by Břendová et al. [29], the elemental analysis done on the biochars of maize and meadow grass biomass, the content of carbon was also observed to increase.

The zeta potential of the *M. oleifera* seed powder was also determined. This surface property depends on the type and surface density of ionizable or polar functional groups on the *M. oleifera* seed powder. The zeta potential for the raw and biochared *M. oleifera* seed powder was 1.69 and 10.5 mV, respectively. The zeta potential of the biochared *M. oleifera* seed powder was quite high which indicated the absence of negatively charged functional groups on the surface which were present on the surface of the raw *M. oleifera* seed powder. This was in agreement with the findings of Gai et al. [19] who observed a decrease in the polar functional groups with an increase in pyrolysis temperature. Narrow peaks of the zeta potential (graphs not presented) indicated the high chemical homogeneity of the tested samples.

3.2. Point of zero charge determination and effect of pH

In order to understand the adsorption mechanism of the sorption of NB onto *M. oleifera* seed powder, it was necessary to determine the pH_{pzc} (Fig. 3(a)). Due to the removal of some functional groups during biocharing, the pH_{pzc} of the biochared *M. oleifera* was lower than that of the raw one, 6.9 and 4.1, respectively. The result was close to the one obtained by Junior et al. [30] who obtained a pH_{pzc} of 4.4 for the raw *Moringa* powder. Therefore, at $pH > pH_{pzc}$ of the sorbents, the total surface charge was negative leading to the increased removal degree of NB due to the electrostatic force of attraction. Thus, the adsorption of NB was favoured at pH values above the pH_{pzc}. Electron accepting nitro group created a partial positive charge on the benzene ring of the NB. The deactivated ring was assumed to be the part which participated in the binding to both raw and biochared *M. oleifera* sorbents as the maximum sorption was determined to be in basic pH. Fig. 3(b) is a result of the experiment which was carried out to determine the pH value which gave the maximum removal efficiency of NB. It was observed that pH 11 gave the optimum performance which was in agreement with the pH_{pzc} determination. Pan and Guan [31] also found the maximum adsorption of NB in the basic region (12.6–14.0) when they used modified activated sludge sorbent where the removal efficiency of NB was about 75%. In another research by Wang et al. [32], both biosorbents (maize stem and rice stem) performed similarly and NB was completely removed when treated at $pH > 7$. However, in this work, as the benzene ring was deactivated, the nitro group became a reservoir of the negative charge which probably was used to interact with the positive surface of the sorbent at low pH.

3.3. Effect of dosage

The dependence of dosage on the adsorption of NB on *M. oleifera* seed powder (raw and biochared) is shown in Fig. 4. From 1.0 to 100.0 g L^{-1}, an increase in the dosage of adsorbent yielded a corresponding increase in the amount of NB adsorbed onto the surface of the adsorbents since there were more sites for adsorption. Non-significant increase was observed when the adsorbent doses were increased beyond 12.5 g L^{-1}. This suggested that the maximum adsorption was attained with 12.5 g L^{-1} for both raw and biochared *M. oleifera* seed powder. The small increase in percentage removal after biosorbent dosage of 12.5 g L^{-1} might have been due to particle aggregation arising from an increased use of biosorbent quantity.

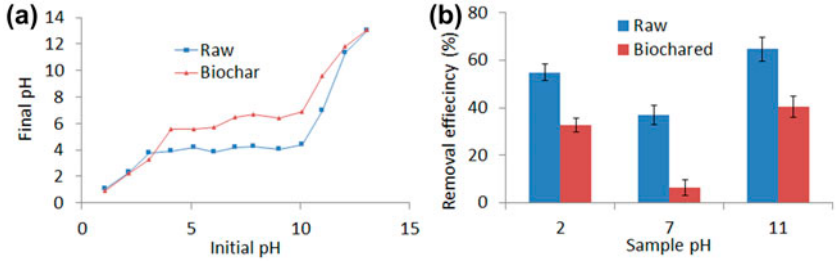

Fig. 3. (a) Point of zero charge determination of *M. oleifera* seed powder (raw and biochared) and (b) effects of pH on adsorption of NB from aqueous solutions (temperature = 25°C, adsorbent dose = 12.5 g L^{-1}, contact time = 30 min and initial NB concentration = 1 mg L^{-1}).

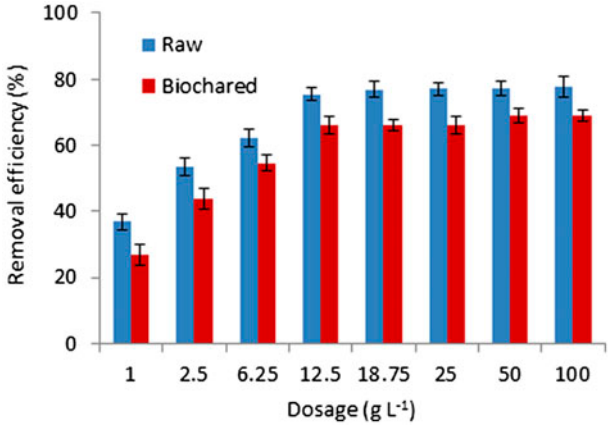

Fig. 4. Effect of sorbent dosage for the biosorption of NB from aqueous solutions (temperature = 25°C, sample pH 11, contact time = 30 min and initial NB concentration = 2 mg L^{-1}).

The formation of the aggregates was observed to reduce the total number of sorption sites available for biosorption and increased the diffusional path lengths.

3.4. Effect of the contact time and kinetic modelling

The uptake of NB by the *M. oleifera* seed powder (raw and biochared) was examined at different time intervals and the results are shown in Fig. 5. It was observed that, during the first 50 min of the experiment, the concentration of NB adsorbed on both the raw and biochared *M. oleifera* seed powder increased with time. After 50 min, no further appreciable biosorption was observed. Thus, 50 min was taken as the optimum contact time and was used in subsequent experiments. In general, longer extraction times of NACs have been reported in literature, e.g. Fu et al. [33] used bamboo charcoal@$ZnCl_2$ and Yang et al. [34] used vermicompost-biochar and obtained optimal sorption times of 3 and 24 h, respectively.

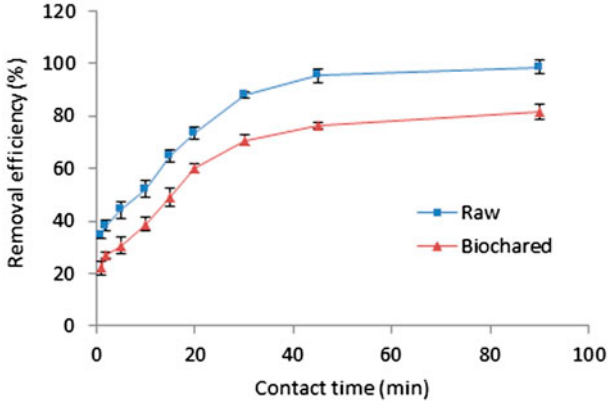

Fig. 5. Effect of contact time for the biosorption of NB from aqueous solutions (temperature = 25°C, sample pH 11, adsorbent dose = 12.5 g L^{-1} and initial NB concentration = 1 mg L^{-1}).

For kinetic modelling, the data from the effect of contact time was used. Two most commonly used models; pseudo-first-order and pseudo-second-order were used in their linearized forms, Eqs. (4) and (5), respectively:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

where q_e (mg g^{-1}) represents the equilibrium sorption capacity and q_t (mg g^{-1}) the instantaneous sorption capacity at time t (min). The first- and second-order rate constants are k_1 (min^{-1}) and k_2 (g mg min^{-1}), respectively. Table 2 summarizes the most important constants for pseudo-first-order and pseudo-second-order models. Based on the correlation coefficients ($R^2 > 0.98$), the pseudo-second-order model fitted the data better than the pseudo-first-order. Again, the pseudo-second-order model was seen to model the kinetic data better as $q_{e,cal}$ (0.084 and 0.071 mg g^{-1} for raw and biochared *M. oleifera* seed powder, respectively) was closer to $q_{e,exp}$ (0.08 and 0.05 mg g^{-1} for raw and biochared *M. oleifera* seed powder, respectively). The adsorption kinetics study was also used to understand the mechanism of adsorption reactions. The pseudo-second-order kinetic model is based on the assumption that the rate-limiting step may be chemisorption involving hydrogen bonding between NB and the *M. oleifera* seed powder sorbent.

3.5. Effect of initial concentration and adsorption modelling

The influence of the initial concentration of NB sorption onto *M. oleifera* seed powder is shown in Fig. 6. At the initial stages of biosorption process, the biosorption capacity increased rapidly. High sorption capacities were observed with higher initial NB concentrations. It was explained by the equilibrium shift in either monolayer (Langmuir) or multilayer (Freundlich) adsorption [35]. The higher concentration of NB caused the increasing aqueous NB gradient at the surface of adsorbent, hence resulting in the higher binding affinity possibility on the active sorption sites and adsorption capacity [36]. At low NB concentration, the active sorption sites of the biosorbent were

Table 2
Kinetic model parameters for NB adsorption on *M. oleifera* seed powder

	Pseudo-first-order			Pseudo-second-order		
Moringa sorbent	k_1 (min^{-1})	q_e (mg g^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	q_e (mg g^{-1})	R^2
Raw	0.018	2.70	0.542	1.88	0.084	0.991
Biochared	0.006	13.0	0.705	1.73	0.071	0.988

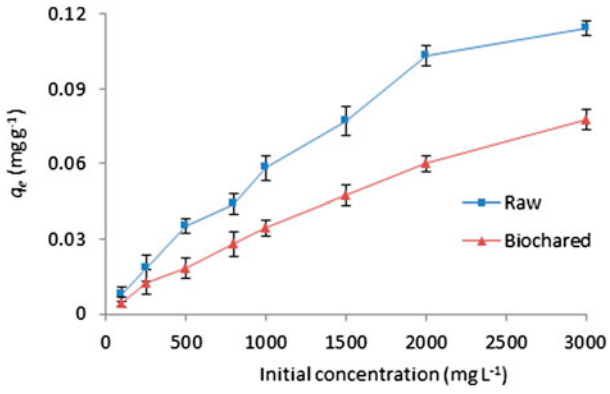

Fig. 6. Effect of initial concentration on adsorption of NB onto *M. oleifera* seed powder (temperature = 25°C, sample pH 11, adsorbent dose = 12.5 g L^{-1} and contact time = 50 min).

not saturated and the NB removal efficiency was therefore increased with more occupation of the sites.

The Langmuir isotherm (Eq. (6)) was used to model the adsorption data and to determine whether the mechanism of adsorption was chemisorption. From the Langmuir isotherm equation, the value of b of the raw sorbent was higher than that of the biochared material (Table 3) indicating the affinity of binding sites for NB (0.0145 vs. 0.0015). However, in both cases b lied between zero and one, suggesting that the adsorption of NB onto *M. oleifera* seed powder sorbent was favourable.

$$\frac{1}{q_e} = \frac{1}{q_m b C_e} + \frac{1}{q_m} \tag{6}$$

The favourability of the sorption process was also to be measured by a dimensionless separation parameter R_L, which can be calculated by Eq. (7). Since R_L values for both the raw (0.986) and biochared (0.999) *M. oleifera* seed powder, respectively, fell in the range of 0–1, the sorption of NB onto these sorbents was concluded to be favourable.

$$R_L = \frac{1}{1 + bC_o} \tag{7}$$

To ascertain whether the sorption was physisorption, the adsorption data was modelled by the Freundlich data, Eq. (8). The constant n is the empirical parameter related to the intensity of adsorption, which varies with the heterogeneity of the material. When $1/n$ values are in the range $0.1 < 1/n < 1$, the adsorption process is favourable, which was the case in this work.

The statistical parameter chi-squared (χ^2) (Eq. (9)) was used to quantify the degree of variation of the calculated from the experimental sorption capacity, $q_{m,cal}$ and $q_{m,exp}$, respectively. Since the deviation was smaller for the Langmuir isotherm model (1.5×10^{-5} and 1.2×10^{-2}) as compared to the Freundlich isotherm (0.51 and 6.15) (Table 3), the former was concluded to be the best.

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{8}$$

$$\chi^2 = \sum \frac{(q_{e,exp} - q_{e,cal})^2}{q_{e,cal}} \tag{9}$$

3.6. Method validation and application

A series of calibration standard solutions were made (a linear range of 50–500 μg L^{-1} was used). All standard solutions were stored in a refrigerator at 4°C

Table 3
Constant parameters for the adsorption models for the adsorption of NB onto *M. oleifera* seed powder

	Langmuir constants					Freundlich constants			
Sorbent	q_m (mg g^{-1})	R_L	b (mg^{-1})	R^2	χ^2	K_F (mg g^{-1})	n	R^2	χ^2
Raw *Moringa oleifera*	0.0811	0.986	0.0145	0.944	1.5×10^{-5}	0.0097	3.12	0.950	0.51
Biochared *Moringa oleifera*	0.0816	0.999	0.0015	0.948	1.2×10^{-2}	0.0004	1.45	0.978	6.15

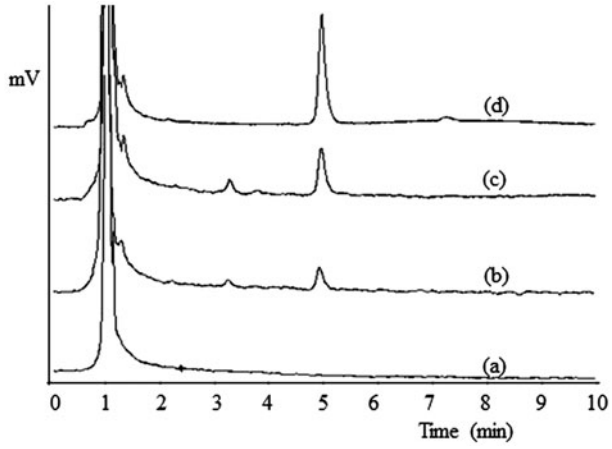

Fig. 7. Chromatogram of (a) unspiked, (b) 0.5 mg L^{-1} spiked, (c) 1.0 mg L^{-1} spiked wastewater sample subjected to biochared *M. oleifera* seed powder and (d) 1.0 mg L^{-1} NB standard solution.

when not in use. The calibration curve found was $y = 0.1838x + 7.3464$ (where x is the NB concentration and y the instrument response) and a good correlation was obtained ($R^2 = 0.9923$).

In order to test the accuracy of the proposed method, real wastewater samples were spiked with NB at different concentration levels of 0.5 and 1.0 mg L^{-1}. These samples were analysed using the extraction and chromatographic procedure optimized in this work. Fig. 7 shows an example of chromatograms obtained after sorption of spiked and unspiked-NB wastewater samples by biochared *M. oleifera seed powder* together with a 1-mg L^{-1} NB standard solution. Recoveries obtained from spiked wastewater samples at different concentration levels are shown in Table 4. It was observed that, good recoveries ranging between 59 and 81% were obtained for wastewater. High precision of the instrumental analysis was obtained, as shown by RSD ($n = 3$) of 2.1–8.2%.

Table 4
Recoveries of NB from spiked real wastewater samples using *M. oleifera* seed powder ($n = 3$)

	Concentration (mg L^{-1})			
	Spiked	Found	Recovery (%)	RSD (%)
Raw	–	–	–	–
	0.5	0.41	81.0	8.2
	1.0	0.74	74.0	6.7
Biochared	–	–	–	–
	0.5	0.35	69.7	2.1
	1.0	0.58	58.8	5.4

3.7. *Comparison of* M. oleifera *seed powder with other sorbents*

In order to assess the performance of *M. oleifera* seed powder (raw and biochared) as an adsorbent for NB, a comparison with other adsorbents is given in Table 5. As can be seen, there is a wide range of adsorption capacities for the uptake of NB. This was expected as various sorption conditions were applied by different researchers. More so, different sorbents

Table 5
Uptake performance comparison of closely related sorbents

Sorbent	Target pollutant	Adsorption conditions[a]	q (mg g^{-1})	Refs.
Modified cetyltrimethylammonium bromide	NB	Sample pH ≈ 11, dosage 2 g L^{-1}, time 24 h, [NB] 150 mg L^{-1}, Temp. 25°C	24.8	[31]
Bamboo charcoal@$ZnCl_2$		Sample pH 2.0, dosage 12 g L^{-1}, time 180 min	–	[33]
Vermicompost biochar	NB	Sample pH 5.47, dosage 2 g L^{-1}, time 24 h, [NB] 20 mg L^{-1}, Temp. 25°C[b]	8.20	[34]
Phenyltrimethoxysilane@magnetite	NB	Sample pH 5.47, dosage 2 g L^{-1}, time 24 h, [NB] 1,000 mg L^{-1}, Temp. 25°C	0.45[c]	[37]
Raw *Moringa oleifera* seed powder	NB	Sample pH 11, dosage 12.5 g L^{-1}, time 50 min, [NB] 2 mg L^{-1}, Temp. 25°C	0.09	This work
Biochared *Moringa oleifera* seed powder	NB	Sample pH 11, dosage 12.5 g L^{-1}, time 50 min, [NB] 2 mg L^{-1}, Temp. 25°C	0.078	This work

[a]Sample pH, dosage, time, concentration and temperature values are given, if not, the researchers concerned did not provide.
[b]Sample pH not optimized but was only fixed at the stated value.
[c]Calculated from mmol g^{-1}.

with different surface morphologies were used. The most important finding in this work was the raw *M. oleifera* seed powder sorbent which had a superior uptake of NB as compared to the biochared material.

3.8. Toxicity of Moringa seed powder

Application of high quantity of *Moringa* seed powder in aquaculture ponds leads to mortality of fish due to the presence of toxic substances or antinutritional factors [38]. Data on toxicity *of M. oleifera* seed extract on freshwater fish are still scarce. However, studies from Al-Anizi et al. [39] indicated that the main toxicity is from the insoluble fatty acid components of *M. oleifera*. The toxicological assessments by Berger et al. [40] and Grabow et al. [41] have already indicated that there is no threat to human health in using *M. oleifera* as a primary coagulant.

4. Conclusions

Raw and biochared *M. oleifera* seed powder were successfully used as biosorbents for the removal of NB from aqueous solutions. However, the former was seen to have a better uptake capability due to the organic functional groups which were not present in the biochared material. The optimum conditions for the NB uptake were pH 7, dosage of 12.5 g L^{-1} and a contact time of 50 min. The pseudo-second-order and the Langmuir isotherm modelled the kinetic and the adsorption data better, respectively, pointing to a chemisorption type of interaction between the *M. oleifera* seed powder (raw and biochared) and NB. Owing to its low cost, high availability and biodegradable nature, this biosorbent can be considered a viable alternative for the treatment of contaminated aqueous solutions.

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