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Sorption of Ibuprofen by chemically treated maize cob

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ABSTRACT

Potable water availability has been drastically reduced because of the indiscriminate discharge of pharmaceuticals into rivers and surrounding areas. Polluted water disrupts aquatic life and affects human health. This study investigated the potential of using NaOH-activated maize cobs for removing Ibuprofen (IBP) from a synthetic solution. The sorption capacity of the base-treated maize cob (BMC) and untreated maize cob (UMC) was compared. Batch adsorption experiments were conducted using several parameters, including a range of pH values (2–10), contact time (1–100 min), initial concentration (15–60 mg/L) and temperatures (25–65 °C). Ibuprofen's highest sorption capacity (44.92 mg/g) was obtained with BMC at pH 8.0, whilst the adsorption by UMC was 41.81 mg/g at pH 7.99. The sorption trend by both BMC and UMC indicated that the uptake of Ibuprofen increased at initial concentrations of 34.77 and 28.66 mg/g, respectively. The non-linear form of the Freundlich isotherm model best fits with the experimental results, describing the favorability of chemical interactions between IBP and both adsorbents. The removal time was fast, and the adsorption kinetics was based mainly on the pseudo-first-order model with capacities of 45.96 mg/g for BMC and 42.30 mg/g for UMC. The negative ΔG^{o} and ΔH° values proved that the adsorption process was spontaneous and exothermic, with maximum capacities of 44.07 and 40.33 mg/g obtained at 25 °C by BMC and UMC, respectively. The chemically treated BMC showed better sorption than the UMC. Batch studies showed that the overall maximum sorption capacities were 91.07% and 90.67% for BMC and UMC respectively. This research showed that maize cobs can be used as an adsorbent for removing Ibuprofen from solutions.

1. Introduction

Pharmaceutical drugs are an evolving set of contaminants in hospital and domestic wastewater (D., 2020). These drugs are complex structures comprise of active elements that help to minimize the negative effects on animals and humans. Current technologies are ineffective in removing these pollutants because they are only partially removed at wastewater treatment plants (P.M. Kumar et al., 2019; R. Kumar et al., 2019). Consequently, there is evidence of the drugs in the ground and drinking water (P.M. Kumar et al., 2019). These toxic pollutants in water are considered unsafe even at low concentrations (Ahmed et al., 2015). Therefore, efficient water purification methods are required to safely remove pharmaceuticals from the environment.

Ibuprofen is consumed worldwide because of its therapeutic applications (Mestre et al., 2007; Fadzail and Hasan, 2021). It is an anti-inflammatory drug used in the treatment of various disorders, fever and pain (Bushra and Aslam, 2010). It is highly soluble in organic solvents but less soluble in water (Mestre et al., 2007). In most cases, Ibuprofen has been detected in wastewater treatment plant (WWTPs) effluents at concentrations ranging from nanograms to micrograms per liter (Mlunguza et al., 2019). The World Health organisation (WHO) has shown that the concentration in the surface water in Finland, France and Germany was 65, 120, and 530 ng/L, respectively (Mlunguza et al., 2019). Even though these concentrations are very low, numerous studies have detected Ibuprofen. Quero-Pastor et al. (2014) (Quero-Pastor et al., 2014) reported 0.05 to 0.28 mg/L concentrations in surface water. Ismail et al. (2013) (Ismail et al., 2013) developed a method to extract seven pharmaceutical pollutants and found Ibuprofen in wastewater. The concentration of Ibuprofen was the highest at 3.4 mg/L compared with the other pharmaceuticals. Contaminants in water are accumulative. The extent of pharmaceutical drugs in the environment is not fully known due to the absence of sensitive instrumentation such as liquid

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chromatography coupled with quadrupole time of flight mass spectrometry. The costs associated with running this technology are also prohibitive (Madikizela et al., 2017).

Different strategies such as physical degradation, UV treatment, chlorination and photochemical processes, oxidation and adsorption are used to remedy Ibuprofen (Singh et al., 2021). Many mechanisms for ibuprofen uptake on adsorbents are available, including hydrophobic, hydrogen bond, electrostatic, cation exchange and π-π interactions (Singh et al., 2021). Various materials have been used to remove Ibuprofen from the environment using adsorption. Fadzail et al. 2021 (Fadzail and Hasan, 2021) used activated carbon from *Dillenia indica* peels, and their activated carbon showed an uptake of 7.5075 mg/g. Hanibali et al. (2020) (Hanbali et al., 2020) showed that carbon nanotubes could be used to uptake Ibuprofen with a percentage removal that ranged from 61.5 to 98.4%. Another study on the uptake of Ibuprofen by natural clay under equilibrium parameters such as the effect of pH, function of time, and effect of concentrations showed that Ibuprofen was adsorbed with a maximum uptake of 37 mg/g (Khazri et al., 2016). Several cost-effective experiments have been developed using non-hazardous agricultural waste materials to adsorb ibuprofen. These materials are inexpensive and eco-friendly and are good alternatives to chemical methods. Maize cobs are disposed of and burned in open fields or left in areas or landfills where they create human health and safety concerns and constitute a challenge to the environmental (Otitolaiye et al., 2021).

Maize cobs are lignocellulosic and can be harnessed for energy through combustion (Sharma et al., 2019), minimizing environmental waste and providing a platform to convert large stockpiles of maize cob into energy. This could address the issue of health and safety and environmental challenges of managing agricultural waste (Otitolaiye et al., 2021). However, these approaches cannot effectively reduce the large stockpiles of maize cob generated annually in many countries. The rugged nature of the maize cob can be used in filtration applications because it can absorb or adsorb minerals (Sharma et al., 2019). Especially when the cob is crushed, it becomes a good filtration sieve for removing mud from murky water. Hence this makes the material a good adsorbent for toxins or pollutant uptake using adsorption. Almost all maize produce waste which is the cob (Opeolu et al., 2009). Hence, this study used it as a potential material for removing ibuprofen from synthetic water. It represents an alternative way to use the generated waste and contributes to methods of reducing waste.

Kategile and Frederiksen (1979) (Kategile and Frederiksen, 1979) studied the level of NaOH treatment and volume on the nutritional value of maize cobs. Singh et al. (1989) (Singh et al., 1989) assessed the base treatment for biodegradation of corn cob by *Aspergillus*. The eeffect of NaOH pre-treatment of maize cobs was investigated for saccharification by *Penicillium* cellulase by Sahare et al. (2012) (Sahare et al., 2012). Currently, there are no studies where alkaline (NaOH) treated maize cob has been used for the adsorption of Ibuprofen. Various reagents, such as NaOH, H_2SO_4, KOH etc., have been used as chemical activators of biomass. The activation controls the pore volume and porosity (Medhat et al., 2021). Treatment of agricultural materials by strong to mild oxidizing agents has also been shown to increase the oxygen-containing functional groups like carboxyl carbonyl (-C=O) and (-COOH) on the adsorbent surfaces and ultimately improves the adsorption capacity of the adsorbent (Gupta and Saleh, 2013). Therefore, many researchers have used chemically treated biomaterials to remove pollutants from water. Medhat et al. (2021) (Medhat et al., 2021) used modified maize cob with potassium hydroxide and ammonium sulfate to remove methylene blue dye. Their results indicated that potassium hydroxide-treated adsorbent had a higher surface area than the ammonium sulfate adsorbent. Siipa et al. (2018) (Siipola et al., 2018) have shown that activation with a strong base (KOH) can produce highly microporous pine bark.

Hence in this work, base-treated maize cob (BMC) sorbent was chosen by treating the untreated maize Cob (UMC) with 0.1 M sodium hydroxide (NaOH) to increase removal efficiency. Pre-adsorption characterization was conducted using Scanning Electron Microscopy (SEM), thermogravimetric analyzer (TGA) and surface chemistry by FTIR. The sorption capacities of BMC and UMC were compared.

The aim was to investigate the capability of maize cob to adsorb IBP in an aqueous solution. The study's objectives were (I) to characterize the untreated maize cob to determine if the adsorbent has functional groups that can interact with IBP and determine the adsorbent thermal stability, (2) to modify the maize cob to increase the adsorption capacity, and (3) to compare the adsorption capacity of the untreated and base treated maize cob.

2. Material and experimental

2.1. Material

Agricultural waste maize cob is used as an adsorbent in this study. The cobs were collected from a local market waste into polyester bags in Vanderbijlpark, South Africa. Sodium hydroxide (NaOH) pallets (98.5% AR grade) and hydrochloric acid (HCl-32% AR grade) were purchased from ACE laboratories (Johannesburg, South Africa). Ibuprofen (>98% purity) was purchased from Sigma-Aldrich (Kempton Park, South Africa). All reagents were used without purification.

2.2. Experimental

2.2.1. Preparation of the adsorbent

Untreated maize cob (UMC) was washed thoroughly with ultrapure water to remove all surface dust and dried at 70 °C for 24 h. After that, it was cut into pieces and pulverized into a fine powder. Further preparation of the adsorbent followed that of Thabede et al. 2020 (P.M. Thabede et al., 2020) with some modifications. The treatment of UMC was achieved by weighing 15 g then mixed with 150 mL of 0.1 M NaOH in a 500 mL beaker. The mixture was stirred between 200 and 250 rpm for 6 h at room temperature. After 6 h, the adsorbent was rinsed with ultrapure water to remove the NaOH. The adsorbent was dried at 50 °C. The dried powder was named base-treated maize cob (BMC) and used for further studies.

2.2.2. Batch experiments

The sorption of Ibuprofen by BMC and UMC adsorbents was performed in a batch experiment on a Labcon shaker with a speed of 300 rpm using capped sample vials under ambient temperature. Exactly 0.3 g of BMC was poured into 100 mL sample vials that contained 60 mL of 500 mg/L Ibuprofen solutions of varying pH ranges of 2, 4, 6,8 and 10, followed by agitation for 60 min. The pH was adjusted using aqueous solutions of 0.5 mol/L HCl or 0.5 mol/L NaOH. Time effect was carried out at 1, 5, 10, 20, 60, 80 and 100 min intervals. The concentration effect was studied at initial concentrations of 15, 30, 45, 60 and 75 mg/L for 60 min. Temperature effect was investigated at 25, 35, 45, 55 and 65 °C for 60 min. The solid phase was separated from the solution using the filtration method. Determination of point of zero charge (pHpzc) by BMC and UMC was conducted using 0.3 g of the adsorbent which was added to 60 mL KNO_3 solution (1 M). pH of the solutions was adjusted from 1 to 9 (pHi) then equilibrated at room temperature for 24 h. The final pH (denoted pHf) of the solution was measured.

Sorption of Ibuprofen was calculated by the equations below:

$$\frac{q_e = (C_o - C_e)V}{m} \quad (1)$$

$$\frac{\text{Removal}(\%) = (C_o - C_e)X100}{C_o} \quad (2)$$

where q (mg/g) indicates the quantity of Ibuprofen per gram, C_o and C_e are initial and equilibrium concentrations of Ibuprofen in solution (mg/

L), respectively, m is the mass of BMC and UMC and V for volume (L) for Ibuprofen.

2.2.3. Desorption method

The reusability and regeneration of BMC and UMC were determined using 0.3 g of the pre-loaded adsorbent. The adsorbed IBP was removed from the surface of the adsorbents by agitating twice in 20 mL of 0.2 M HCl at 200 rpm for 60 min and then rinsed several times with ultra-pure water at 200 rpm for 60 min before reuse.

2.2.4. Characterization techniques

Fourier Transform Infrared (FTIR) spectrometer was used to analyze the surface functional groups on BMC and UMC before ibuprofen adsorption using a PerkinElmer Fourier 4000 Nicolet FTIR/FTNIR spectrometer, spectrum 400. Morphological images of BMC and UMC were taken with a Nova Nano SEM 200 from FEI operated at 10.0 KV. Thermal analyses were done using a TGA 4000 thermogravimetric analyzer from Perkin Elmer using nitrogen between 30 and 900 ℃ at a heating rate of 10 ℃/min. The Brunauer Emmett Teller (BET) was used to determine the surface area with Micrometrics TriStar II 3020 BET v3.02 with nitrogen as the adsorptive gas. A pH meter purchased from Hach was used to measure the solution's pH. The concentration of Ibuprofen was determined by spectroscopy with a Perkin-Elmer Lambda 25 with the visible range using a slit of 1.0 and width of 0.1 that collects spectra from 180 to 1100 nm UV and visible range.

3. Results and discussion

3.1. Characterization

3.1.1. FTIR analysis

Fig. 1 shows the results for FT-IR spectra of BMC and UMC absorbance. The peaks at 3340 and 3320 cm^{-1} are due to the O—H stretch. A peak associated with the C—H stretch of CH_2 and CH_3 on BMC was observed at 2915 cm^{-1} (P.M. Thabede et al., 2020; Tong et al., 2018), whilst on UMC, it was observed at 2904 cm^{-1} with doublet peaks. A small band at 1735 cm^{-1} on UMC was assigned to the ketonic group (C=O) (Shooto et al., 2019) and disappeared on the BMC. Two small sharp peaks at 1627 and 1593 cm^{-1} on BMC are due to the C=O bend and NH_2 of the amide (Poiana et al., 2015; Siddiqui and Chaudhry, 2018). On UMC, the C=O bend is observed at 1626 and 1596 cm^{-1} for the amide group. Bands between 1422 and 1370 cm^{-1} are related to lignin and hemicellulose on both BMC and UMC (P.M. Thabede et al., 2020), suggesting a reaction between the adsorbent and adsorbate. These peaks were reduced on BMC. The UMC peak at 1245 cm^{-1} is due to the C—O group and shifted to 1235 cm^{-1} on BMC (Husseien et al., 2009). Another peak at 1035 cm^{-1} associated with C—OH was observed on BMC and shifted to 1032 cm^{-1} on UMC (Matos et al., 2017). The spectral variations propose the interaction of functional groups of the sorption process (Islam et al., 2017).

3.1.2. Thermal analysis measurements

Fig. 2(a)-(b) shows the thermalgravimetric analysis (TGA) and its derivative (DTA) plots for the BMC and UMC adsorbents. Thermal analysis is usually carried out to determine the thermal behavior, temperature profile, degradation pathways, and material characteristics under oxidative thermal conditions (Otitolaiye et al., 2021). TG plots of both BMC and UMC indicate several step losses of mass from room temperature to 800 °C. BMC in Fig 2(a) shows the first stage of loss of adsorbed water of 8% from 29 to 120 °C (Shooto and Thabede, 2022). In the second stage, the major weight loss of 70% between 278 and 403 °C is attributed to the degradation of lignocellulosic materials (hemicelluloses, cellulose and lignin) including the loss of volatile matter (Otitolaiye et al., 2021). The last step is assigned to the residual of the BMC between 407 and 761 °C. Two main decomposition peaks at 68 °C and 377 °C are observed on DTA, including a small peak at 336 °C for BMC. Fig. 2(b) shows the TGA and DTA of UMC. A similar pattern is observed whereby two main decomposition steps have taken place. The first weight loss due to water is between 24 and 129 °C with dehydration of water of 6%. Afterwards, UMC experienced more significant weight loss between 219 and 387 °C due to devolatilization (thermal degradation of hemicellulose, cellulose, and lignin) with 63% mass loss. There are two small peaks at 254 and 317 °C, possibly due to the decomposition of other bio-sorbent materials. The remaining weight loss resulted in flattening as characterized by the tailing between 388 and 751 °C, indicating the complete degradation of UMC. The degradation path for the TGA combustion of UMC was examined through the DTA, as marked by the red peaks. The four peaks associated with the derivative are at 90, 254, 317 and 364 °C.

3.1.3. SEM images

The general textural changes of BMC and UMC are shown in Fig. 3 (a)-(d). The low-magnification SEM images of BMC in Fig. 3(a) show cavities and grooves. The higher magnification in Fig. 3(b) shows a

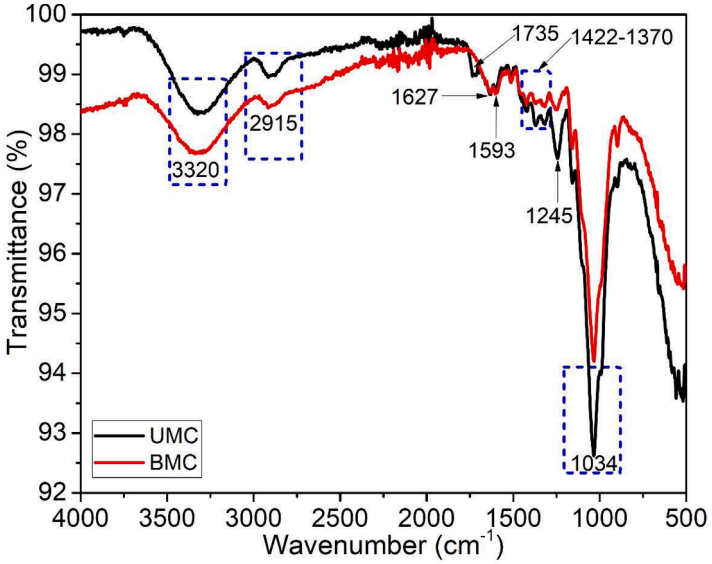

Fig. 1. IR spectra for BMC and UMC adsorbents.

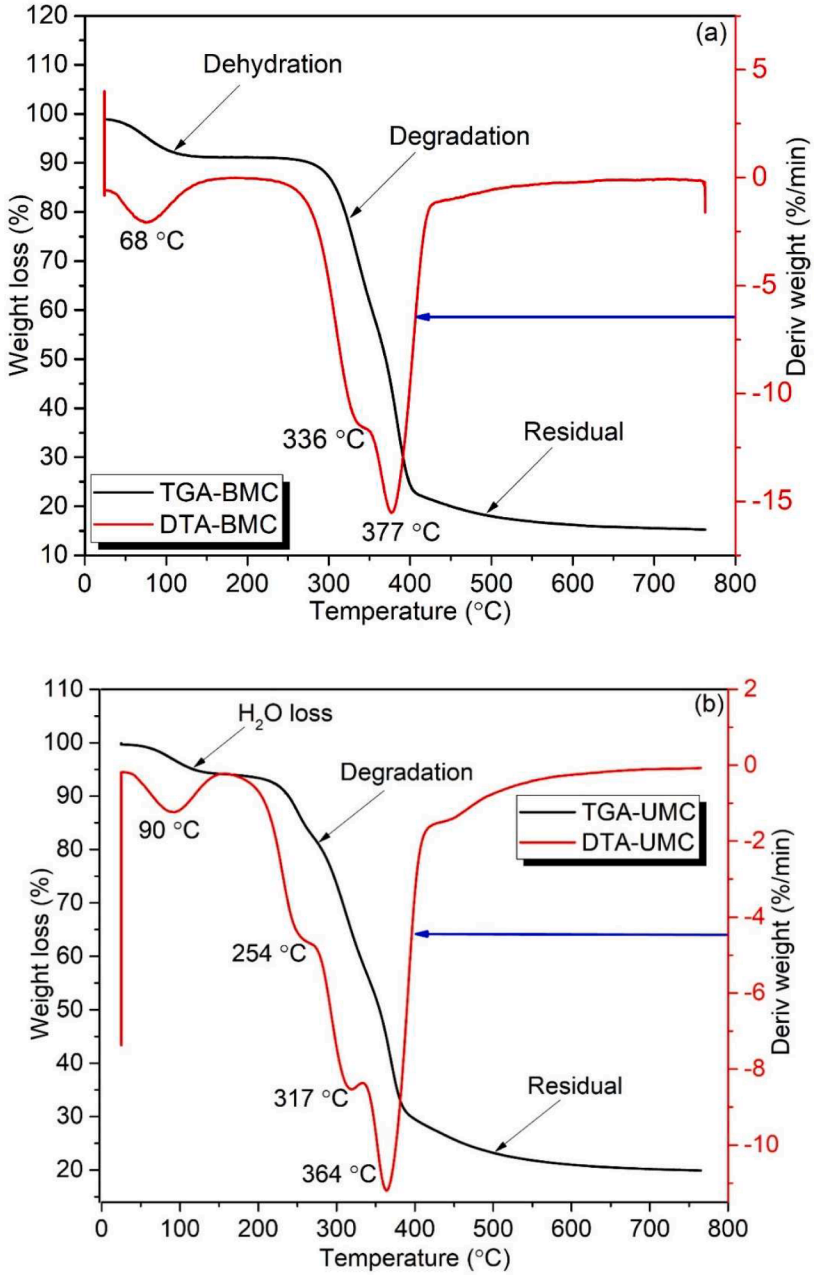

Fig. 2. TGA and DTA profiles for (a) BMC and (b) UMC adsorbents.

porous BMC with more cavities and a net-like morphology. This could be due to the partial destruction of the micropore walls and the formation of surface defects (Saucier et al., 2015; Thabede et al., 2021). The roughness is typical of plant-based materials. However, the UMC surface in Fig 3(c-d) is compact with a smooth texture and no cavities. Therefore, the base treatment process on the maize cob shows significant morphological modification, which is anticipated to trap and adsorb the Ibuprofen.

3.1.4. Porosity property

The porosity of chemically treated and untreated maize cob was examined using low-temperature nitrogen adsorption-desorption measurements at 77 K. Table 1 shows the structural parameter obtained from the experimental data. It can be observed that the base-treated maize cob has significant micropores characterized by a high specific surface area of 3.208 m^2/g compared with the untreated maize cob with a surface area of 1.145 m^2/g. These data show that the base treatment of the maize cob changed its porous structure.

3.1.5. Effect of point zero charge on Ibuprofen uptake

The pHpzc is a significant aspect that indicates the linear range of pH sensitivity and shows active surface centers and surface sorption ability (Bosacka et al., 2022). The results for pHpzc are indicated in Fig. 4, showing a pHpzc of 6.75 for BMC and 5.35 for UMC. The treatment of UMC with a base introduced hydroxyl groups and increased the pHpzc. The base treatment of BMC increased the pH to 6.75 (Bosacka et al., 2022).

3.2. Adsorption

3.2.1. Effect of pH on Ibuprofen uptake

In sorption studies, pH is important in removing solution contaminants (Boukhemkhem and Rida, 2017). The influence of pH on the sorption of Ibuprofen by BMC and UMC was evaluated. Fig. 5 indicates

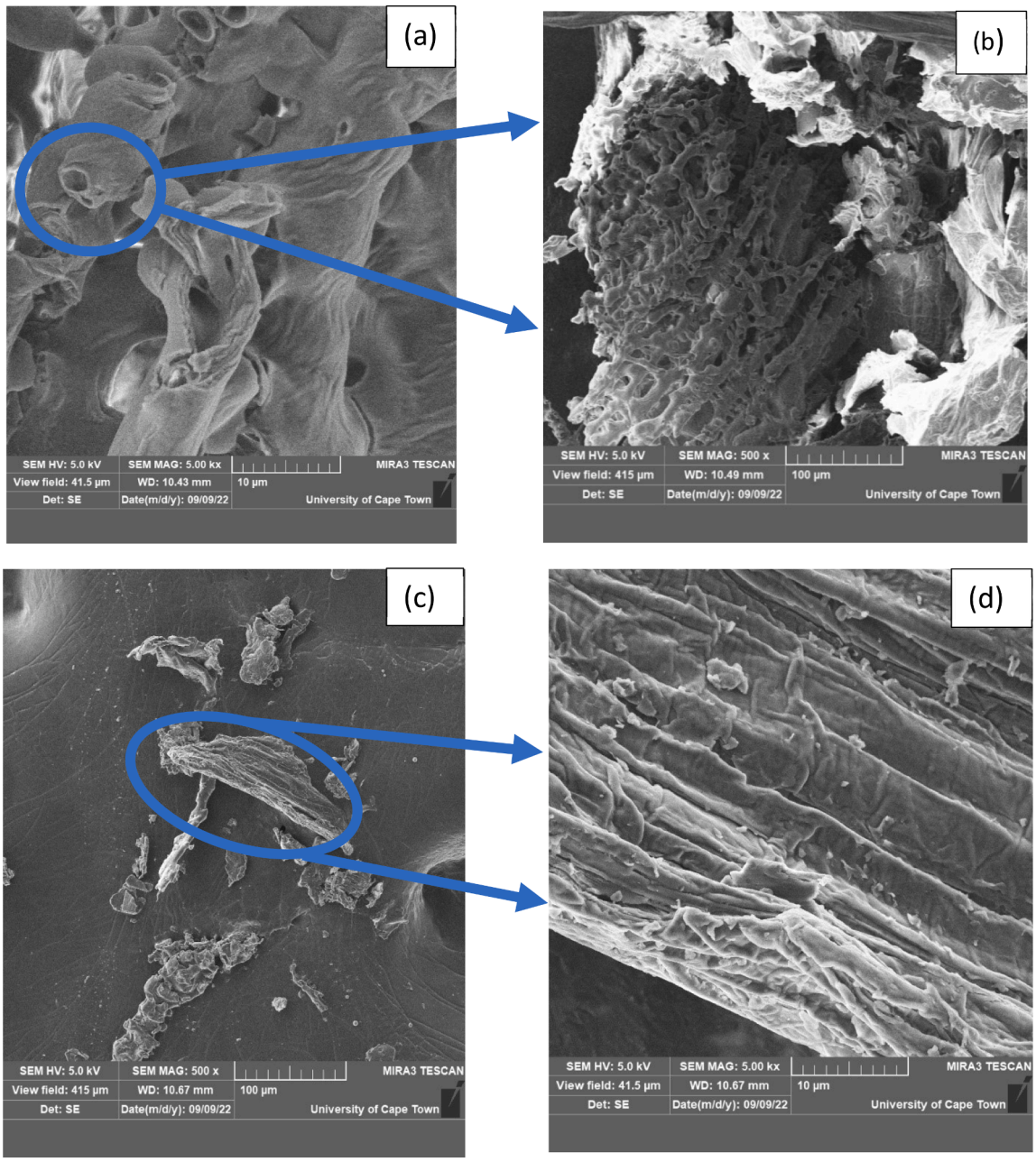

Fig. 3. Images for (a)-(b) BMC and (c)-(d) UMC adsorbents.

Table 1
Structural parameter obtained from nitrogen sorption.

Sample Name	BET(m^2/g)
UMC	1.145
BMC	3.208

that the sorption capacity increases as the pH rises for both adsorbents. The uptake of Ibuprofen by BMC increases from pH 2 to 8, and a total of 44.92 mg/g was observed at pH 8.02. Beyond pH 8, the sorption capacity by BMC decreases. A similar trend is observed in UMC, whereby the adsorption capacity increases between pH 2 and 8, with the highest sorption of 41.84 mg/g observed at pH 7.99. After that, the pH decreases. The adsorption capacity is low at lower pH and increases with increasing pH because active sites are charged with H^+ ions. This increases the repulsive forces of the adsorbent surface (Shah et al., 2022). Therefore, there is an electrostatic attraction at the basic medium between the adsorbents and the adsorbate, hence higher sorption capacities.

3.2.2. *Effect of time on Ibuprofen uptake*

The rate at which Ibuprofen is removed from an aqueous solution is essential and is assessed to determine the efficiency of the BMC and UMC adsorbents. Fig. 6 shows the removal of Ibuprofen at different contact times (1, 5, 10, 20, 60, 80 and 100 min) with 0.3 g for each adsorbent that contained 60 mL of 500 mg/L ibuprofen solution agitated at 200 rpm. The removal of ibuprofen increases as time increases, then progressively reaches equilibrium on both BMC and UMC adsorbents. The rate removal of Ibuprofen by BMC is rapid, so equilibrium was reached after 20 min. The uptake of Ibuprofen by BMC indicated a maximum capacity of 45.96 mg/g. The ibuprofen uptake by UMC is slower than BMC, which reached equilibrium after 60 min with maximum sorption

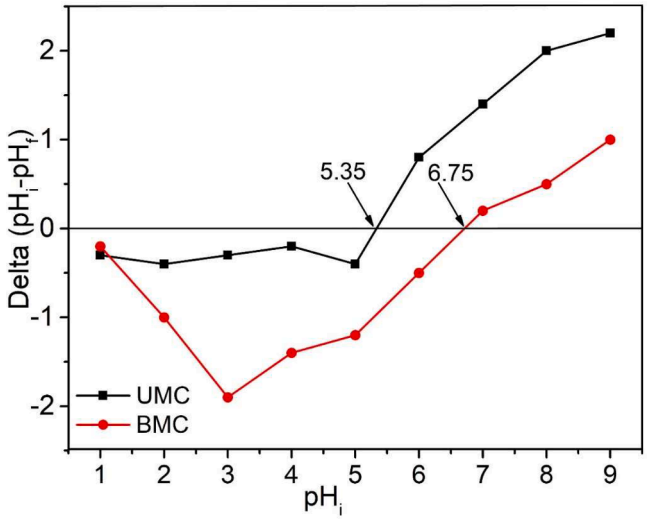

Fig. 4. pHpzc for the BMC and UMC adsorbents.

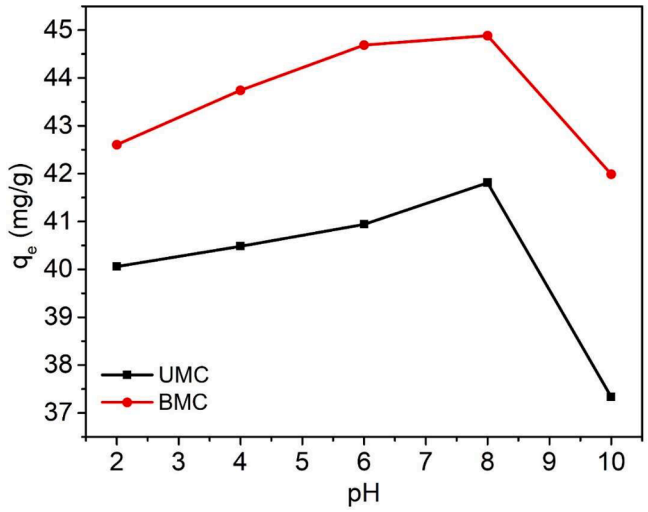

Fig. 5. Effect of pH for the BMC and UMC adsorbents.

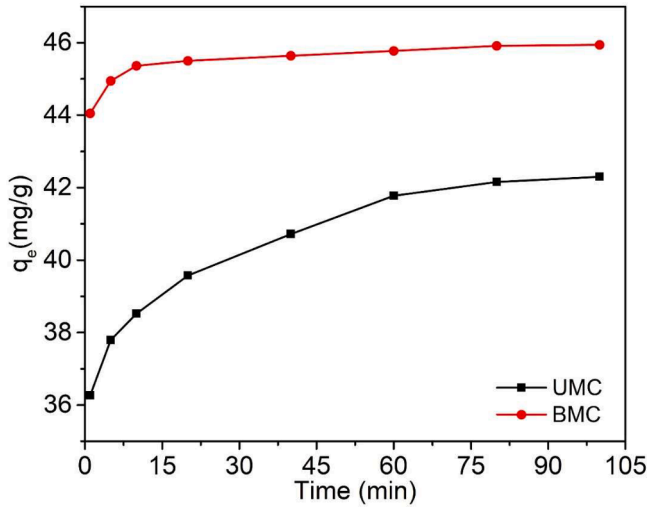

Fig. 6. Effect of contact time for the BMC and UMC adsorbents.

obtained at 42.30 mg/g. The maximum sorption capacities were observed at 80 min for both BMC and UMC. The fast sorption is due to the availability of active sites on both BMC and UMC adsorbents (Shooto et al., 2019). With time the uptake of Ibuprofen gradually becomes constant, indicating the non-availability of sorption sites (Hafshejani et al., 2015).

3.2.3. *Effect of concentration on Ibuprofen uptake*

In the uptake of Ibuprofen from an aqueous solution, the initial concentration is a very important parameter to determine the performance of adsorbents towards its successful large-scale application (Show et al., 2021). Comparative sorption by BMC and UMC was conducted at various concentrations (15, 30, 45, 60 and 75 mg/L) for 60 min at 25 ℃ (Fig. 7). The trend indicates that Ibuprofen uptake increases with an increase in initial concentration of both BMC and UMC and a greater increase is observed at higher concentrations. This is ascribed to greater chances of collision between Ibuprofen and the surface of the adsorbent at the initial concentration of 75 mg/L. It may also be due to the higher concentration gradient, which acts as a driving force to overcome resistance to the mass transfer of metal ions between the aqueous and solid phases (Akpomie et al., 2015; Aichour et al., 2019; Novais et al., 2019). Diagboya and Dikio (2018) (Diagboya and Dikio, 2018) also made a similar observation and indicated that this type of trend indicates multilayer adsorption, which agrees with the Freundlich isotherm. Furthermore, better sorption at high concentrations is attributed to the reduced repulsive forces during the adsorption process as concentration increases, resulting in improved sorption (Tong et al., 2018). Increased sorption of Ibuprofen on BMC is also due to high surface area and availability of active sites after chemical treatment (Tong et al., 2018). The maximum sorption of Ibuprofen by BMC and UMC is 34.77 and 28.66 mg/g, respectively.

3.2.4. *Effect of temperature on ibuprofen uptake*

The effect of temperature (25, 35, 45, 55 and 65 ℃) for 60 min with the agitated speed at 200 rpm with 500 mg/L of Ibuprofen by BMC and UMC is illustrated in Fig. 8. The plots of BMC and UMC showed high temperature affects adsorption process negatively. The adsorption capacities of BMC and UMC decrease as the temperature rises. Sorption capacity decreases between 25 and 65 ℃. The maximum sorption capacity of 44.07 and 40.33 mg/g was observed at 25 ℃ by BMC and UMC, respectively. This may be due to a decrease in the specific surface area available for Ibuprofen resulting from overlapping adsorption sites, which increase the diffusion path length for Ibuprofen (Akpomie et al., 2015). Similar trends were obtained when determining the adsorption

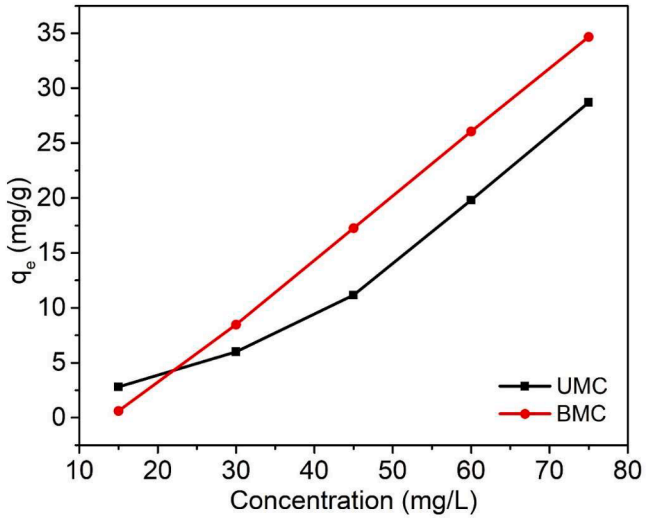

Fig. 7. Effect of concentration for BMC and UMC adsorbents.

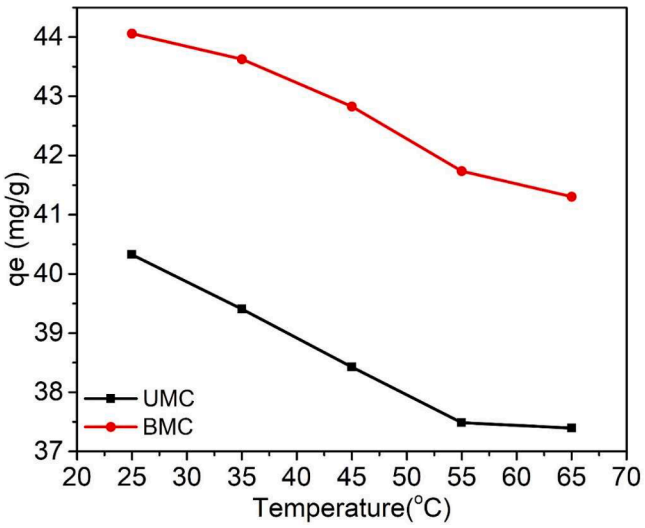

Fig. 8. The effect of temperature for BMC and UMC adsorbents.

capacity of bentonite polyurea formaldehyde for ibuprofen uptake by Majeed et al. (2018) (Majeed et al., 2018). The decrease indicates the destabilization of the physical forces involved (Cortes-Arriagada, 2021). Also, this could likely mean that the increased temperature might have broken the bonding between the ibuprofen molecules, leading to a decreased degree of aggregation (Gomez-Aviles et al., 2021).

3.2.5. Adsorption isotherms

Sorption isotherms indicate Ibuprofen distribution between the liquid and the surface of the solid phase (Oba et al., 2021). Isotherms in this study are achieved by nonlinear regression using computer software for data estimation. Table 2 mainly shows both BMC and UMC adsorbents fit the Freundlich model. This means the process is formed by multilayers of heterogeneous distributions (Bernal et al., 2018). Zhang et al. (2018) (Li and Zhang, 2018) showed that energy decreases exponentially and stays constant when adsorption reaches equilibrium. Also, the system is ascribed to the competition between the adsorbate and solvent, meaning the adsorption enthalpy is unstable. The RMSE and MPSD data for Ibuprofen onto BMC and UMC indicates that the lowest error values were observed in the Freundlich model.

3.2.6. Thermodynamic modeling

Thermodynamics indicates the energy variations between the adsorbent and adsorbate (Thabede et al., 2021). Temperature changes are measured employing enthalpy (ΔH°), entropy (ΔS°) and Gibbs free energy (ΔG°) and are shown in Table 3. To determine the thermodynamic parameters, the temperature values were converted to Kelvin units: 298, 308, 318, 328 and 338 K. ΔG° values ranged from −14.08 to −22.27 kJ/mol for BMC and −22.89 to −31.78 kJ/mol for UMC. The values decreased with increasing adsorption temperature, suggesting

Table 2
Isotherms for ibuprofen on BMC and UMC adsorbents.

Isotherms		BMC UMC
Langmuir	Q_o (mgg^{-1})	38.02 22.10
	b (Lmg^{-1})	1.5274 1.352
	R^2	0.9559 0.9431
	RMSE	10.55 8.57
	MPSD	24.81 13.71
Freundlich	1/n	11.74 9.74
	k_f ($mg^{(1-n)}$ L^n g^{-1})	0.652 0.588
	R^2	0.9943 0.9971
	RMSE	1.45 2.78
	MPSD	4.21 3.12
Experimental (q_e) (mg/g)		34.77 28.66

Table 3
Thermodynamic results for Ibuprofen on BMC and UMC adsorbents.

Parameters	BMC	UMC
ΔH^o (kJ mol^{-1})	−1.67	−4.30
ΔS^o (kJ $mol^{-1}K^{-1}$)	1.70	4.90
ΔG^o (kJ mol^{-1}) 298 K	−22.11	−31.78
308 K	−21.34	−29.45
318 K	−20.54	−27.98
328 K	−16.66	−24.68
338 K	−14.32	−22.89

that the sorption decreased with a temperature rise. This decrease in ΔG° value is due to increased freedom which might have enhanced desorption rather than adsorption at high temperatures (Rani and Sud, 2015). The (ΔH°) results for the sorption of Ibuprofen on BMC and UMC were negative, whereas the entropy (ΔS°) values were positive on both adsorbents. This indicates that the adsorption reaction is feasible and exothermic with negative ΔG° and ΔH° and positive value for ΔS° (Singh et al., 2021).

3.2.7. Adsorption kinetics

The rate of binding of Ibuprofen on BMC and UMC was evaluated by adsorption kinetics which also assisted in gaining insight into the sorption process. The kinetic mechanisms for the adsorbents uptake of Ibuprofen were determined by pseudo-first-order (PFO), pseudo-second-order (PSO), and intraparticle diffusion, as shown in Table 3. The parameters in Table 4 fit PFO, meaning the uptake of Ibuprofen occurred due to electrostatic interactions and sorption sites (P.M. Thabede et al., 2020).

3.2.8. Data analysis

Non-linear equation (Eq. (3)) and (Eq. (4)) is for Pseudo-First Order (PFO) and Pseudo-Second Order (PSO) estimated model respectively. Ibuprofen adsorbed *qe (mg/g)* with *(qt)* quantities at a time *(t)*. Rate constants k_1 and k_2 for PFO and PSO, respectively.

$$q_e = q_t\left(1 - e^{-k_1 t}\right) \tag{3}$$

$$q_e = \frac{1 + k_2 q_e t}{k_2 q_e^2 t} \tag{4}$$

(q_t) and *(k_i)* rate parameters calculated using software (KyPlot). *(k_i)* parameter *($g\ g^{-1}\ min^{1/2}$)* used for intra-particle diffusion (IPD) control stage in Eq.5 and *C* is ibuprofen concentration onto BMC an UMC.

$$q_t = k_i\left(t^{1/2}\right) + C \tag{5}$$

Eq. (6) and Eq. (7) represent the adsorption isotherms calculated by Langmuir and Freundlich, respectively. *(Q_o)*-maximum sorption capacity *(mg/g)* for both BMC and UMC. *(b)* is the solute-surface interaction energy parameter, kf is Freundlich isotherm, and 1/n is linearity.

Table 4
Kinetics for ibuprofen on BMC and UMC adsorbents.

Models		BMC	UMC
PFO	q_e	15.19	13.88
	k_1	3.39	2.27
	R^2	0.9982	0.9974
PSO	q_e	13.44	18.63
	k_2	1.019	1.011
	R^2	0.8882	0.7872
IPD	C	12.78	8.33
	k_i	1.11	1.89
	R^2	0.8123	0.8461
EPA*	%	24.86	29.24
ESA**	%	75.14	70.76
Experimental (q_e)		45.96	42.30

$$q_e = \frac{Q_0 b C_e}{1 + bC_e} \tag{6}$$

$$q_e = k_f C_e^{1/n} \tag{7}$$

(K_c) is equilibrium constant used in Eq. (8). Thermodynamic parameters (entropy change) -(ΔS^o), (enthalpy change) -(ΔH^o) estimated by using Eq. (9) and (ΔG^o) for spontaneity of the adsorption process determined by using Eq (10). Temperature *(T)* in Kelvin.

$$K_c = \frac{q_e}{C_e} \tag{8}$$

$$ln\ K_c = -\frac{\Delta H^o}{RT} - \frac{\Delta S^o}{R} \tag{9}$$

$$\Delta G^o = -RT \ln K_c \tag{10}$$

3.2.9. Error determination

The estimation of the accuracy for the isotherm models was obtained by using two error functions, namely, the (RMSE) root mean square error (Dirbaz and Roosta, 2018) and the (MPSD) Marquart's percentage standard deviation (Demirbas et al., 2008), as shown in Eqs. (11) and 12, respectively. Where *qe,exp* denotes the experimental removal uptake, *qe, cal* is the calculated removal uptake. *p* and *N* represent the number of parameters and data points, respectively.

$$RMSE = \sqrt{\frac{1}{N-p}\sum_{i=1}^{N}\left(q_{e,\ exp} - q_{e,\ cal}\right)^2} \tag{11}$$

$$MPSD = 100\sqrt{\frac{1}{N-p}\sum_{i=1}^{N}\left(\frac{q_{e,\ exp} - q_{e,\ cal}}{q_{e,\ exp}}\right)^2} \tag{12}$$

3.2.10. Regeneration study

Reusability is a parameter that shows the efficiency and cost-effectiveness of the adsorbent (Bhadra et al., 2017). In this study, we have carried out desorption investigations of Ibuprofen as indicated in Fig. 10. The recyclability of BMC and UMC in IBP adsorption was determined up to five cycles after washing the used adsorbents with 0.2 M HCl and water. The highest recovery was found to be 91% and 80% for UMC and BMC, respectively.

4. Comparative study

Base-treated maize cob (BMC) adsorption capacity for the uptake of Ibuprofen was compared with other sorbents, as indicated in Table 5. This study showed a higher performance of BMC of Ibuprofen. Therefore, BMC is a cost-effective material for the uptake of Ibuprofen in solution.

Table 5
Base-treated maize cob compared with other sorbent materials for ibuprofen uptake.

Adsorbents	$q_{(max)}$ (mg/g) Ibuprofen	References
Activated carbon cloth	491.9	(Bhadra et al., 2017)
Mesoporous MOF	206.5	(Guedidi et al., 2017)
Activated carbon	17.0	(Van Tran et al., 2019)
Base-treated maize cob	**45.96**	**This study**
Functionalized plasma	13.76	(Sahin et al., 2020)
Sugarcane	11.90	(Al-Yousef et al., 2021)
Olive waste cake	9.09	(P. Chakraborty et al., 2018)
Modified aluminum mineral	7.61	(Baccar et al., 2012)
Montmorillonite	6.10	(Dwivedi et al., 2011)
Wood apple biochar	5.00	(Behera et al., 2012)
Nano-clay composite	3.78	(P. Chakraborty et al., 2018)
Molecularly imprinted polymer	2.01	(Rafati et al., 2019)

5. Adsorption mechanism

Sorption capacities for several adsorbents of Ibuprofen are based on physicochemical characteristics, namely, surface functional groups, porosity and surface area (Husseien et al., 2009). FTIR spectra of most adsorbents showed peaks greater than 3200 cm^{-1} for (OH), C—H band from 2900 to 2960 cm^{-1}, C=O for ester, ketone from 1700 to 1780 cm^{-1}, C=C band between 1600 and 1690 cm^{-1} and C—O peak around 1300 and 1090 cm^{-1}. Participation by functional groups throughout ibuprofen adsorption is obtained through band intensity of peaks, widening of peaks and appearance/disappearance, as well as shifting of peaks from low to high wavenumber and vice-versa (Oba et al., 2021). Many researchers have studied ibuprofen uptake using various adsorbents. Some mechanisms include; electrostatic, hydrophobic (Van der Waals, π-π and electron donor-acceptor) interaction and hydrogen bonding (Oba et al., 2021). Fig. 9 shows some of the mechanisms for Ibuprofen sorption on BMC and UMC. These pointers indicate a successful ibuprofen sorption onto the adsorbent.

6. Conclusion

This study provides important information regarding the chemical activation of maize cob biomass for the adsorption of Ibuprofen. FTIR analysis showed hydroxyl, carbonyl, amide, and carboxyl groups were responsible for binding the Ibuprofen. SEM images showed that the base treatment process of UMC shows significant morphological modification, which contributed to the increase in the adsorption capacity of Ibuprofen. BET data of BMC indicated a high surface area of 3.208 m^2/g compared to UMC with 1.145 m^2/g. The results show that the base-treated maize cob changed its porous structure. The batch biosorption studies confirmed the pH dependency of adsorption, with the optimal pH for Ibuprofen being 8.0 for both adsorbents. The optimum time for the uptake of Ibuprofen was attained at 80 min for both BMC and UMC. The temperature increases negatively affected adsorption because as the temperature increased, the adsorption capacity decreased for BMC and UMC. The adsorption data followed the Freundlich model for both BMC and UMC, suggesting that the adsorption was heterogeneously distributed. The adsorption kinetics fitted PFO and implied that sorption was based on electrostatic interactions. Thermodynamics results indicated that the adsorption process was spontaneous and exothermic. The sorption trends for all parameters suggested that the base-treated maize cob (BMC) adsorbent performed better than the untreated maize cob (UMC) adsorbent. Ibuprofen's highest maximum sorption capacity was 45.96 and 42.30 mg/g on BMC and UMC, respectively. On the other hand, less sorption on UMC might be attributed to the presence of

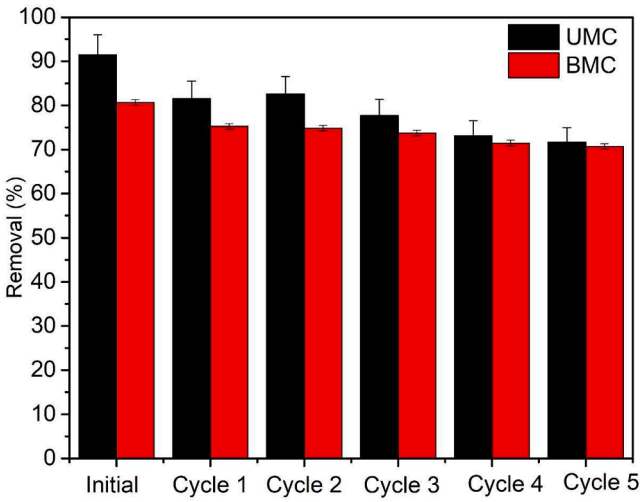

Fig. 9. Regeneration study of Ibuprofen on BMC and UMC adsorbents.

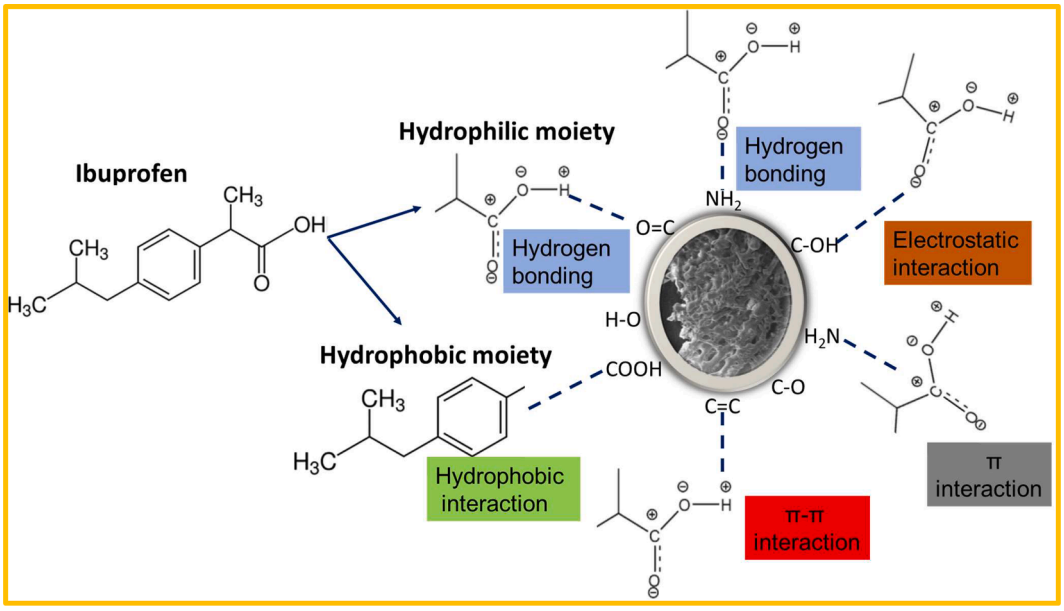

Fig. 10. Adsorption mechanism of ibuprofen on BMC and UMC adsorbents.

lignocellulosic constituents, which hampers sorption. From this study, the treatment of maize cob with sodium hydroxide was found to be suitable for the uptake of Ibuprofen in solution. The amount of ibuprofen desorbed from UMC and BMC was 91% and 80%, respectively. The residual amount that did not desorb appeared to be tightly bound to the surfaces of the adsorbents.

Declaration of Competing Interest

The corresponding authors and all other authors mentioned in this manuscript declare that they have no identified competing interests that could influence the work reported in this paper.

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References

Ahmed, M.B., Zhou, J.L., Ngo, H.H., Guo, W., 2015. Sci. Total Environ. https://doi.org/10.1016/j.scitotenv.2015.05.130.
Aichour, A., Zaghouane-Boudiaf, H., Zuki, F.B.M., Aroua, M.K., Ibbora, C.V., 2019. J. Environ. Chem. Eng. 7, 103409.
Akpomie, K.G., Dawodu, F.A., Adebowal, K.O., 2015. Alexandria Eng. J. 54, 757.
Al-Yousef, H.A., Alotaibi, B.M., Alanazi, M.M., Aouaini, F., Sellaoui, L., 2021. J. Environ. Chem. Eng. 9, 104950.
Baccar, R., Sarra, M., Bouzid, J., Feki, M., Blanquez, P., 2012. Chem. Eng. J. 211, 310.
Behera, S., Oh, S., Park, H., 2012. Int. J. Environ. Sci. Technol. 9, 85.
Bernal, V., Giraldo, L., Moreno-Pirajan, J.C., 2018. J. Carbon Res. 4, 62. https://doi.org/10.3390/c4040062.
Bhadra, B.N., Ahmed, I., Kim, S., Jhung, S.H., 2017. Adsorptive removal of Ibuprofen and diclofenac from water using metalorganic framework-derived porous carbon. Chem. Eng. J. 314, 50.
Bosacka, A., Zienkiewicz-Strzalka, M., Derylo-Marczewska, A., Chrzanowska, A., Wasilewska, M., Sternik, D., 2022. 2022. Colloids Surf. A: Physicochem. Eng. Asp. 647, 129130.
Boukhemkhem, A., Rida, K., 2017, 2017. Adsorp. Sci. Technol. 35, 753.
Bushra, R., Aslam, N., 2010. Oman Med. J 25, 155.
Chakraborty, P., Banerjee, S., Kumar, S., Sadhukhan, S., Halder, G., 2018a. Process Saf. Environ. Prot. 118, 10.
Chakraborty, P., Show, S., Banerjee, S., Halder, G., 2018b. J. Environ. Chem. Eng. 6, 5287.
Cortes-Arriagada, D., 2021. J. Mol. Liq. 325, 115229.
D. M, 2020. Juela. Sustain. Environ. Res. 30, 23.
Demirbas, E., Kobya, M., Konukman, A.E.S., 2008. J. Hazard. Mat. 154, 787.
Diagboya, P.N., Dikio, E.D., 2018. J. Clean. Prod. 180, 71.
Dirbaz, M., Roosta, A., 2018. J. Environ. Chem. Eng.
Dwivedi, A.D., Gopal, K., Jain, R., 2011. Chem. Eng. J. 168, 1279.
Fadzail, F., Hasan, M., 2021. Z. Mokhtar. IOP Conf. Ser.: Earth Environ. Sci. 646, 012031.
Gomez-Aviles, A., Sellaoui, L., Badawi, M., Bonilla-Petriciolet, A., Bedia, J., Belver, C., 2021. Chem. Eng. J. 404, 126601.
Guedidi, H., Reinert, L., Soneda, Y., Bellakhal, N., 2017. L. Duclaux. Arabian J. Chem. 10, S3584.
Gupta, V.K., Saleh, T.A., 2013. Environ. Sci. Pollut. Res. 20 (5), 2828.
Hafshejani, L.D., Nasab, S.B., Gholami, R.M., Izadpanah, M.M., Hafshejani, S.B., Bhatnagar, A., 2015. J. Mol. Liq. 211, 448.
Hanbali, G., Jodeh, S., Hamed, O., Bo, R., Khalaf, B., Qdemat, A., Samhan, S., 2020. Materials 13, 3329.
Husseien, M., Amer, A.A., Hamedallah, A.E.N., 2009. J. Anal. Appl. Pyrolysis 86, 360.
Islam, M.A., Sabar, S., Benhouria, A., Khanday, W.A., Asif, M., Hameed, B.H., 2017. J. of the Taiwan Institute of Chemical Engineers 74, 96.
Ismail, L., Osman, R., Saim, N., 2013. Malaysian J. Anal. Sci. 17, 262.
Kategile, J.A., Frederiksen, J.H., 1979. Anim. Feed Sci. Technol. 4 (1), 1.
Khazri, H., Ghorbel-Abid, I., Kalfat, R., Trabelsi-Ayadi, M., 2016. Appl. Water Sci. https://doi.org/10.1007/s13201-016-0414-3.
Kumar, P.M., Kishor, K., Mlsna, T., Pittman, C.U., Mohan, D., 2019a. Chem. Rev. 119, 673.
Kumar, R., Tscharke, B., O'Brien, J., Mueller, J.F., Wilkins, C., Padhye, L.P., 2019b. Sci. Total Environ. 658, 947.
Li, J., Zhang, K., 2018. H. Environ. Pollut. 237, 460.
Madikizela, L.M., Mdlulia, P.S., Chimuka, L., 2017. S. Afr. J. Chem. 70, 145.
Majeed, B.A.A., Muhseen, R.J., Jassim, N.J., 2018. Iraqi J. Chem. Pet. Engin. 19, 29.
Matos, T.T.S., Schultz, J., Khan, M.Y., Zanoelo, E.F., Mangrich, A.S., Araújo, B.R., Navickiene, S., Romão, L.P.C., 2017. J. Braz. Chem. Soc. 28, 1975.
Medhat, A.El-Maghrabi, Abdelghany, H.H., Menem, A., Moustafa, N.M.A., Elsayed, P.Y. M., Nada, M.A., 2021. Appl. Surf. Sci. Advances 3, 100037.
Mestre, A.S., Pires, J., Nogueira, J.M.F., 2007. A.P. Carbon 45, 1988.
Mlunguza, N.Y., Ncube, S., Mahlambi, N.P., Chimuka, L., Madikizela, L.M.J., 2019. Environ. Chem. Eng. 7, 103142.
Novais, R.M., Carvalheiras, J., Tobaldi, D.M., Seabra, M.P., Pullar, R.C., 2019. J. A. Labrincha. J. Clean. Prod. 207, 350.
Oba, S.N., Ighaloa, J.O., Aniagor, C.O., Igwegbe, C.A., 2021. Sci. Total Environ. 780, 146608.
Opeolu, B.O., Bamgbose, O., Arowolo, T.A., Adetunji, M.T., 2009. Utilization of maize (Zea mays) cob as an adsorbent for lead (II) removal from aqueous solutions and industrial effluents. Afri. J. Biotechnol. 8 (8), 1567.
Otitolaiye, V.O., Otitolaiye, D.A., Omer, F., Ubana, D., Ibrahim, A.O., Dodo, Y.A., Nyakuma, B.B., 2021. Thermal and kinetic analyses of maize cob combustion under non-isothermal and multiple heating rate thermogravimetric conditions. Pet Coal 63 (3), 694.
Poiana, M., Alexa, E., Munteanu, M.F., Gligor, R., Moigradean, D., Mateescu, C., 2015. Open Chem 13, 698.
Quero-Pastor, M.J., Garrido-Perez, M.C., Acevedo, A., Quiroga, J.M., 2014. Sci.Total Environ 466, 957.

Rafati, L., Ehrampoush, M.H., Rafati, A.A., Mokhtari, M., Mahvi, A.H., 2019. J. Environ. Health Sci. Eng. 17, 753.
Rani, S., Sud, D., 2015. Plant Soil Environ 61, 36.
Sahare, P., Singh, R.Seeta R.Laxman, Rao, Mala, 2012. Appl. Biochem. Biotechnol. 168, 1806.
Sahin, O.I., Saygi-Yalcin, B., Saloglu, D., 2020. Desalination Water Treat 179, 396.
Saucier, C., Adebayo, M.A., Lima, E.C., Cataluna, R., Thue, P.S., Prola, L.D.T., Puchana-Rosero, M.J., Machado, F.M., Pavan, F.A., Dotto, G.L., 2015. J. Hazard. Mater 289, 18.
Shah, G.M., Imran, M., Aiman, U., Iqbal, M.M., Akram, M., Javeed, H.M.R., Waqar, A., Rabbani, F., 2022. 2022. Peer J. Phys. Chem. 23.
Sharma, A., Tomer, A., Singh, J., Chhikara, B.S., 2019. Biosorption of metal toxicants and other water pollutants by Corn (Maize) plant: a comprehensive review. J. Int. Sci. Technol. 7 (2), 19.
Shooto, N.D., Thabede, P.M., 2022. Environ. Nanotechnol. Monit. Manag. 18, 100683.
Shooto, N.D., Thabede, P.M., Naidoo, E.B., 2019. South African J. Chem. Eng. 30, 15.
Show, S., Mukherjee, S., Devi, M.S., Karmakar, B., 2021. G. Process Saf. Environ. Prot. 147, 942.
Siddiqui, S.I., Chaudhry, S.A., 2018. J. Clean. Prod. 200, 996.
Siipola, V., Tamminen, T., Källi, A., Lahti, R., Romar, H., Rasa, K., Keskinen, R., Hyväluoma, J., Hannula, M., Wikberg, H., 2018. Bioresources 13, 5976.
Singh, A., Abidi, A.B., Agrawal, A.K., Darmwal, N.S., 1989. Folia Microbiol (Praha) 34 (6), 479–484. https://doi.org/10.1007/BF02814457. PMID: 2635128.
Singh, S., Kumar, V., Anil, A.G., Kapoor, D., Khasnabis, S., Pavithra, S.N., Samuel, J., Subramanian, S., Singh, J., Ramamurthy, P.C., 2021. J. Environ. Manage 300, 113569.
Thabede, P.M., Shooto, N.D., Naidoo, E.B., 2021. Asian J. Chem 33, 471.
Thabede, P.M., Shooto, N.D., Naidoo, E.B., 2020a. South African J. Chem. Eng. 33, 39.
Thabede, P.M., Shooto, N.D., Naidoo, T.X.E.B., 2020b. J. Environ. Chem. Eng. 8, 104045.
Thabede, P.M., Shooto, N.D., Xaba, T., Naidoo, E.B., 2020c. Asian J. Chem. 32, 1361.
Tong, D.S., Wu, C.W., Adebajo, M.O., Jin, G.C., Yu, W.H., Ji, S.F., Zhou, C.H., 2018. Appl. Clay Sci. 161, 256.
Van Tran, T., Nguyen, D.T.C., Le, H.T., Nguyen, O.T., Nguyen, V.H., Nguyen, T.T., Bach, L.G., Nguyen, D.T.R., 2019. Soc. Open Sci. 6, 190058.