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Effective Treatment of Pharmaceutical Waste Water Through Adsorption Using Sugarcane Bagasse Derived Cellulose Nanocrystal as an Innovative Adsorbent

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Abstract

This study investigates the production of cellulose nanocrystals (CNCs) from sugarcane bagasse and evaluates their adsorption performance for the removal of metronidazole (MNZ) from aqueous solutions. CNCs were synthesized through acid hydrolysis and characterized for use as an adsorbent. Batch adsorption experiments were conducted to assess the interaction between MNZ and CNCs under varying conditions. Equilibrium data were analyzed using Langmuir and Freundlich isotherm models, with the Freundlich model demonstrating a superior fit ($R^2 = 0.8818$), indicating multilayer adsorption on a heterogeneous surface. Kinetic modeling revealed that the adsorption process followed a pseudo-second-order model ($R^2 = 0.9972$), suggesting that chemisorption is the dominant mechanism. Thermodynamic parameters, including Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS), were calculated to understand the nature of the adsorption. Negative ΔG values at all examined temperatures confirmed the spontaneous nature of the process, while positive ΔH values indicated that adsorption was endothermic and favored at elevated temperatures. The results collectively demonstrate that sugarcane bagasse-derived CNCs exhibit promising adsorption capabilities for MNZ, combining favorable kinetics, thermodynamics, and equilibrium behavior. This work underscores the potential of agricultural waste valorization for the development of cost-effective and sustainable adsorbents for pharmaceutical pollutant removal in water treatment applications.

Keywords: Cellulose Nanocrystals; Sugarcane Bagasse; Metronidazole Adsorption; Adsorption Isotherms; Pseudo-second-order Kinetics; Thermodynamic Parameters

INTRODUCTION

Water is a valuable resource that dominates the earth's surface. However, the increasing population and industry growth have created a large demand for water, while the amount of water available has stayed the same (hassanzadel, 2018). The discharge of pharmaceutical-based effluent into water resources has become a growing global concern over a past few decades. This pollution caused the release of pharmaceutical products into the environment through various means, such as hospitals and other sources. The presence of these compounds in the environment can cause harmful effect on both humans and animals.

Water is very important in the pharmaceutical industries and it is use in many different ways, from handling raw materials to drug purification. As a result of that, wastewater is produced during drug synthesis in pharmaceuticals (Zhan *et al.*, 2019). This wastewater can contain organic solvents and various pharmaceutical intermediates including nitrosamines which are carcinogenic, and harmful to human health. Therefore, it is important to treat pharmaceutical wastewater in order to maintain health stability.

Adsorption is a common method in wastewater treatment because it is cost-effective and easy to design. However, the adsorption process is affected by the nature of the adsorbate (the suSBtances that is to be adsorbed) and its suSBtituent groups (attached group). In addition, its active sites on the adsorbent affect adsorption capacity and the removal mechanism. These factors have the powerful effect on the adsorption process (Yenisoy *et al.,* 2004). Among many processes of removal, adsorption has the most potential efficiency, less energy, high selectivity and easy to be operated. Additionally, it can separate different chemical compounds (Adebowale *et al.,* 2015). Adsorption treats wastewater in which pharmaceutical molecules, attached to an adsorbent surface by means of physical and chemical properties. Thus it is paramount to have low cost adsorbents. For this reason, it is important to use less cost adsorbents by using agricultural waste products such as sugarcane bagasse etc. In recent years, a large number of less cost adsorbents have been used to remove water pollutant from wastewater such as cucumber peels, meranti sawdust, durian leaf powder, watermelon peels, etc. (Ali *et al.,* 2017).

The use of agricultural waste material is an economy and effective way to remove pollutants from pharmaceutical wastewater. This method reduces the need for expensive materials and disposal of agricultural waste, while also helping the environment. Furthermore, agricultural waste is readily available and cost- effective, making it an appealing option for wastewater treatment. Finally, many studies have demonstrated the effectiveness of agricultural waste materials in removing all unwanted materials produce from wastewater (Gupta *et al.,* 2015).

Cellulose is the indigestible part of a plant organic polymer on earth and is a major structural component of plant cell walls (Isogai, 2014). Structurally, cellulose is a homo polysaccharide that link together, by beta-1-4-glycosidic linkage. Nano celluloses are molecules with a width of 3 – 10 nm and several microns in length depending on the origin (Isogai 2014).Research on "Nano cellulose" has increased greatly and for the next three decades it is expected to continue to grow (Milanez *et al.,* 2013).

Although the term "nanocellulose" can refer to a variety of cellulose nanomaterials such as nanofibrilliated cellulose (NCF), Microfibrilliated cellulose (MFC), Cellulose nanocrystal (CNC), Bacterial cellulose (BC), etc. Each of these materials has its own unique set of dimensions and properties. For example, CNCs are needle-like in shape and have diameters ranging from 5-10nm and lengths on the order of 100 to 200 (chemical & Eng. new news, 2014). Nanocellulose is regenerated from bio molecule with large specific surface area. Some characteristics, such as surface charge and dimensions, depend on the cellulose origin. For specific applications it have been approved that nanocellulose must be chemically changed to a useful materials (Hassanzedah and Masoumeh, 2018).

The functional groups of the nanocellulose can bind to a wide range of molecule including all the organic molecule, antibodies and drugs. These results can be used in several fields of industries such as food packaging, pharmacy, wastewater treatment, cosmetics, etc.

(Mahfoudhi and Boufi 2017; Suopajarvi *et al.,2014 ;* Suopajarvi *et al.,* 2013; Laitinen *et al.*, 2014; Barazzouk and Daneault 2012).

It appears that the use of agricultural waste specifically sugarcane bagasse as a sorbent for pharmaceutical effluents has not been study in details. The use of agricultural waste as pharmaceutical sorbent has the potential to benefit both the environment and the agriculture parts. Not only could also provide an additional source of revenue for farmers by allowing them sell their agricultural waste. This could be a win-win solution for both the environment and agricultural sector.

In order to improve the efficiency of water purification using agricultural waste, such as sugarcane bagasse, it is important to further investigate the kinetics, equilibrium isotherm and thermodynamic parameters of the adsorption process.

MATERIALS AND METHODS

Chemicals

All the chemicals and reagents used in this research were of analytical grade. In addition, the laboratory equipment's used were of analytical grade.

Preparation of Sugarcane Bagasse

Fresh Sugarcane Bagasse was collected from sugarcane selling market in area of Gombe State. The Sugarcane Bagasse was washed and sized reduced in a clean mortar and pestle, and shade dried.

Extraction of ∝ -cellulose

A 500 g of the size reduced Sugarcane Bagasse was weighed using electrical weighing balance and transferred into a stainless steel container. A 2%w/v of sodium hydroxide solution prepared was measured and added to the 500 g of the sample above in the container and stirred well to wet the sample. Followed by placed in a hot water bath set at 80 °C and left for 4 hours to remove all the lignin. The mixture was filtered using cloth sieve and washed excessively with excess water and filtered again. The marc was placed in a container, treated with 1:1 dilution of sodium hypochlorite solution (for bleaching) at 95 °C for 30mins on a water bath. The material was also filtered and washed excessively using sieve cloth and sufficient water, it was placed back into the stainless steel container and 17.5%w/v of sodium hydroxide solution (2.0 L) was added while stirring and this was placed on a water bath set at 80 °C for 1 hour to obtain α-cellulose. The resulting material was also washed with water, filtered and bleached with 1:1 dilution of sodium hypochlorite (700 mL) in a water bath set at 80 °C for a maximum of 15 minutes. This was further filtered with sieve cloth, and washed with sufficient water up to five times where it was tested neutral to litmus paper and then pressed into a big lump followed by reduction into small lumps which were dried at 60 °C for 60 minutes in a hot air oven.

Preparation of Nano-Crystalline Cellulose (Hydrolysis of α -Cellulose)

The method reported by Ohwoavworhua *et al.,* (2005) was used with little modifications. The α-cellulose obtained above (37g) was weighed and treated with 2.5N hydrochloric acid solution at boiling temperature for 40 minutes in a glass beaker. The hot acid mixture was then poured into excess tap water in a bucket and stirred vigorously. This was allowed to stand for 18h, the resulting material which sediment at the bottom was filtered with sieve cloth, washed vigorously (until tested neutral to litmus paper) and processed into a small lumps which were dried in a hot air oven at 60 °C for 60 minutes. The per cent yield was calculated and the Nano cellulose obtained was labelled as Cellulose Nano Crystals (SB-CNC). This was placed in a desiccator. The SB-CNC obtained was sized reduced using porcelain mortar and pestle and the fractions were passed through sieve no. 60. The percentage yield was calculated.

Percentage Yield of SB-CNC:

Percentage yield was calculated using the formula below;-

$$\% \text{ Yield} = W / W_o \times 100 \ldots (1)$$

Where; W_o = Initial weight of raw waste paper.

W = Weight of dried hydrolysed cellulose.

Adsorption Test

Preparation of Standard Solutions

Analytical grade Metronidazole (an antibiotics drug) was obtained from a Pharmaceutical laboratory, Gombe State University. A stock solution of drug concentration 1000 mg/l was prepared by dissolving 1g of powdered drug in 1L of distilled water. Using molar concentration formula;

$$C_1V_1 = C_2V_2 \ldots (2)$$

Where, C_1 = concentration of stock solution

C_2 = concentration of dilute solution

V_1 = volume of taken from stock solution

V_2 = final volume of dilute solution

The actual concentration of the dilute solution was determined using UV-visible Spectrophotometer.

Batch Adsorption Experiment

Adsorption tests were conducted using metronidazole stock solution (500 mg L^{1}). The stock solution was diluted to 50, 100, 150, 200, 250 mg L^{1} for the adsorption tests.

Effect of adsorbent dosage

The effect of adsorbent dose on the adsorption of MNZ was investigated by adding varying quantities of SB-CNC (0.5, 1.5, 2.0, 2.5 and 3g) into the flask having 100mL of MNZ solution (50 mg L^{1}) at normal pH and room temperature. The samples were shaken continuously at 200rpm for 60 minutes and the adsorbent was filtered out of the MNZ solution using a Whiteman filter paper. UV-Vis spectrophotometer (Shimadzu, double beam, UV1800, Japan) was used to determine the MNZ concentration in the spectrophotometric mode.

Effect of pH

To determine the effect of pH on the adsorption of MNZ, SB-CNCs (2.0 g) were mixed with 100 mL of MNZ (50 mg L^{1}) solution at initial pH of 3, 5, 7, 9 and 10. MNZ solutions have an initial pH of 4.8, which were adjusted to the desired pH using sodium hydroxide (0.1 M) and hydrochloric acid (0.1 M) aqueous solution, and were confirmed by pH meter. The solution was shaken in an incubator shaker at room temperature at 200 rpm for 60 minutes.

Effect of contact time

To study the rate of adsorption and find the equilibrium period, batch adsorption kinetics study was carried out. In this experiment, 2.0g of adsorbent was mixed with 100 mL each of 50mgL^{1} of MNZ solutions and the solutions were shaken for 60 minutes at room temperature. Samples were taken from the solution at 30, 60, 90, 120 and 150 minutes intervals and were detected with UV-Vis spectrophotometer. Adsorption capacities at a specific time q_t (mg g^1) were computed using equation (5)

$$Qe = \left(\frac{Co - Ce}{Ce}\right) * t \ldots (5)$$

Where, "C_t" represents the MTZ concentration at a specific time "t"

Effect of initial concentration and temperature

To study the effect of temperature and initial concentration, batch adsorption experiment of MNZ onto the adsorbent SB-CNC was conducted in a 250 ml airtight Erlenmeyer flask containing 100 ml of known concentration of the MNZ solution and an accurately weighed amount of the optimum adsorbent dosage of 2g (Polycarp, 2018). The mixtures in the flasks were agitated on an orbital shaker operating at a constant speed of 200 rpm. The effect of initial MTZ concentration (50,100,150,200,250 mg/l), and temperature (298, 303, 313, 323 & 333 K) was evaluated. The flask containing the samples were withdrawn from the shaker at a predetermined time interval (60 minutes), filtered and the final concentration of the MNZ in the supernatant solutions was analysed using the UV-visible spectrophotometer (Polycarp, 2018). The amount of equilibrium uptake of the MNZ was determined using:

$$q_e = \frac{(C_o - C_e)V}{M} \ldots (6)$$

$$\%MTZ\ Removal = \frac{(C_o - C_e)V}{M}\ X\ 100 \ldots (7)$$

Where q_e is the amount of MNZ taken up by the adsorbent at equilibrium (mg/g), C_o is the initial MNZ concentration (mg/l), C_e is the MNZ concentration at equilibrium (mg/l), M is the mass of the adsorbent (g), and V is the volume of the solution, (L).

Equilibrium Adsorption Experiment

Equilibrium adsorption experiments were conducted at room temperature. Predetermined volume of MNZ solution was added to 250 ml stoppered Erlenmeyer flasks containing an appropriate mass of SB - CNC powder and agitated on mechanical shaker at 200 rpm. Portions of residual MNZ samples were removed from the flasks periodically and filter. The absorbance of the residual MNZ was read at the maximum wave length of 665nm for MNZ as scanned using UV spectrophotometer.

The kinetics experiments data was conducted by similar to those for batch adsorption for the effect of contact time. The adsorption kinetic data was assessed using the models: Pseudo First Order and Pseudo Second Order Kinetics Equations as stated in equation 8 and 9 respectively.

$$\mathrm{Ln}(q_e - q_t) = lnq_e - k_1 t \ldots (8)$$

Here, q_e and q_t signify the amount of pollutant adsorbed per unit mass on the adsorbent at equilibrium and various time intervals t, respectively. The pseudo-first-order adsorption rate constant is denoted as k_1 (min^-1). By plotting ln(q_e - q_t) against time t, k_1 and calculated q_e can be obtained from the slope and intercept, respectively (Hammari *et al.,* 2024)

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e} \ldots (9)$$

Here, k_2 represents the pseudo-second-order adsorption rate constant (g/mg·min), and qe is the amount of dye adsorbed (mg/g) at equilibrium.

Data used for describing the isotherm was obtained by fixing the mass of adsorbent, time, volume and pH of adsorbent, the experiment is similar to those of batch adsorption. The equilibrium adsorption data was evaluated using Langmuir and Freundlich isotherms as stated in equations 10 and 11 respectively.

$$\frac{C_e}{q_e} = \frac{1}{q_m k_l} + \frac{C_e}{q_m} \ldots (10)$$

The Langmuir isotherm model quantifies the adsorption process by considering the equilibrium amount of dye adsorbed (qe) in relation to the maximum adsorption capacity (qm) when saturation is reached. Ce denotes the equilibrium dye concentration, and kl represents the Langmuir constant, which is associated with the strength of dye binding to the adsorbent surface.

$$Logq_e = LogK_f + \frac{1}{n} LogC_e \ldots (11)$$

In this equation, Kf represents the Freundlich constant, a measure of adsorption capacity, while n signifies the intensity of adsorption. The value of n holds particular significance:

n = 1 corresponds to linear adsorption

n < 1 implies a chemical process

n > 1 indicates a physical process (Hammari *et al.,* 2020).

Investigating the thermodynamics is crucial to determine whether the adsorption process is favorable. The thermodynamic parameters—free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°)—play a crucial role in assessing heat changes during the adsorption process. These parameters are calculated using the following equations: (Abubakar *et al.,* 2025)

$$k_e = \frac{qe}{C_e} \ldots (12)$$

$$lnk_e = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \ldots (13)$$

$$\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ \ldots (14)$$

Here, 'Ke' stands for the equilibrium constant, 'qe' represents the amount of pollutant adsorbed in mg on the adsorbent per dm^3 of the solution at equilibrium, 'Ce' is the equilibrium concentration of pollutant in the solution (mg/L). 'R' is the universal gas constant (8.314 J/mol K), and 'T' is the temperature in Kelvin. 'ΔH' and 'ΔS' parameters are calculated from the slope and intercept of the plot of ln(ke) versus 1/t.

RESULTS AND DISCUSSION

Batch Adsorption Study

Effect of Initial Concentration on Adsorption

The results of initial concentrations of MNZ adsorption onto SB-CNC from 50 to 250 mg/L are shown below;

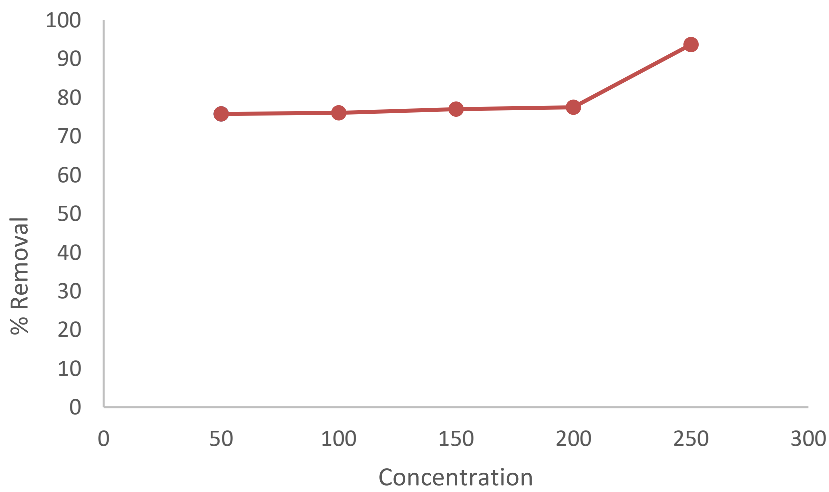

Figure1. Effect of concentration on adsorption of metronidazole

The result indicated that the percentage removal of MNZ by the SB - CNC material increased slightly with increased in concentration of the adsorbate. For example, the percentage of MNZ removed at 50mg/L, 100mg/L, 150mg/L, 200mg/L, and 250mg/L was 75.76%, 76.00%, 76.95%, 77.47%, and 93.66% respectively. These results demonstrated that higher concentrations of MNZ in the adsorbate solution lead to higher rates of adsorption onto the SB-CNC. The reason for this trend can be explained by the concentration gradient which can be attributed to mass transfer phenomenon or diffusion, which was driven by the concentration gradient between the adsorbent and the adsorbate. At a low initial concentration of 50mg/L, the adsorbent sites were easily saturated by adsorbate molecules. On the other hand, at a higher initial concentration of 250mg/L the adsorbent - adsorbate adsorption ratio was higher because there were a greater number of adsorbate molecules available for adsorption. The higher adsorption capacity at the higher initial concentration can be attributed to the increase adsorbent-adsorbate interaction due to the higher number of adsorbate molecules available for adsorption. This interaction may be related to the ionic interactions between the adsorbent and adsorbate (Patil *et al.,* 2011).

Effect of Adsorbent Dosage on Adsorption

Fig.2 shows that the percentage removal of MNZ by SB - CNC changes with different amount of adsorbent. It's clear from the figure that increasing the adsorbent dose increases the adsorption efficiency of SB-CNC. Even at the lowest dose of 0.5 g, the adsorbent was able to removed most of the MNZ. This result is likely due to the fact that higher adsorbent dose provide more surface area for adsorption, as well as increase number of binding site for MNZ molecules. While increasing the adsorbent dose beyond 1.5g resulted in higher removal. This suggests that the adsorption capacity of SB - CNC increased with increased in dosage. The increased adsorption capacity of SB - CNC with increased doses can be attributed to the material's surface area and pore volume, as reported by Irfan *et al., (*2015). The increased in adsorption capacity observed at higher doses may be attributed to the fact that, as the amount of adsorbent increases, the adsorbate molecules gained more access to the available binding site (Irfan *et al.,* 2015). The results of this study are in agreement with the previous research by Khosravi *et al.* (2018), who found that increasing the adsorbent dosage led to increase removal of cephalexin from aqueous solutions. It seems that the availability of more adsorbent sites and unsaturation of the adsorbent binding sites played a significance role in this effect.

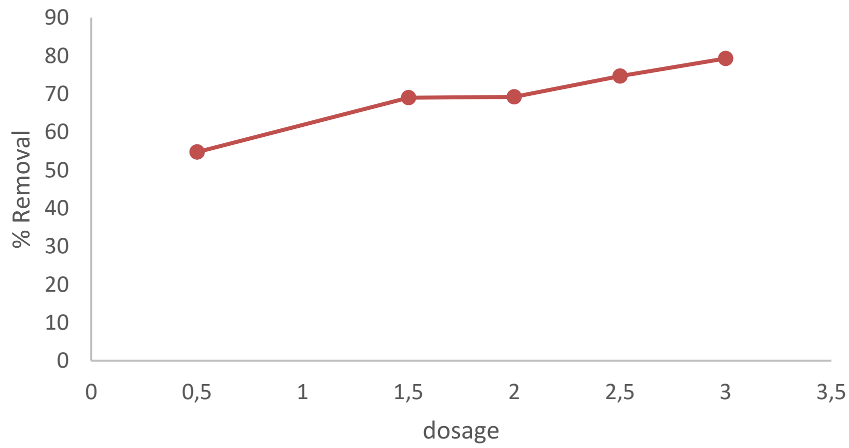

Figure 2. Effect of adsorbent dosage on adsorption of Metronidazole.

The Effect of Contact Time on adsorption

Fig. 3 shows the effect of contact time (30, 60, 90, 120 and 150 min) on the adsorption of MNZ by SB - CNC. The graph shows that the adsorption of metronidazole by SB - CNC increased with contact time and reach equilibrium at 150 minutes. This showed that the majority of the adsorption occurred after 150 minutes, and the adsorption reached equilibrium at 150 minutes (Irfan *et al.,* 2015), the poor initial adsorption is likely due to the low number of free adsorption sites available at the beginning of the process. As the adsorption progressed, the available site increases and the process goes up, then it reach to equilibrium after 150 minutes. Most of the previous studies showed that the adsorption equilibrium is usually reach in between the range of 90 -150 min (Irfan *et al.,* 2015).

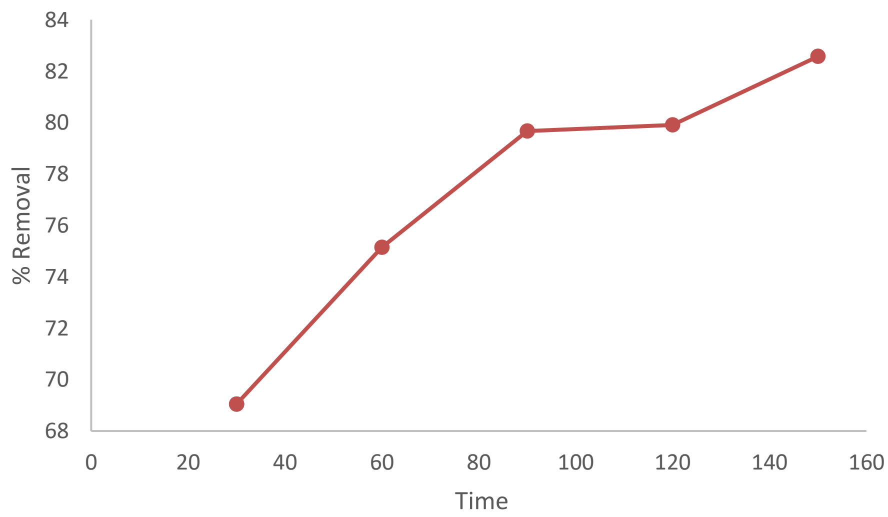

Figure3. Effect of contact time on Metronidazole adsorption

Effect of pH on adsorption

Fig.4 shows that the adsorption efficiency of SB - CNC is dependent on the pH of the solution. This shows that the adsorption efficiency increased as the pH increases. It's clear that the solution's pH influence both the solution chemistry and the surface properties of the adsorbent. These two factors, in turn, affect the adsorption process.

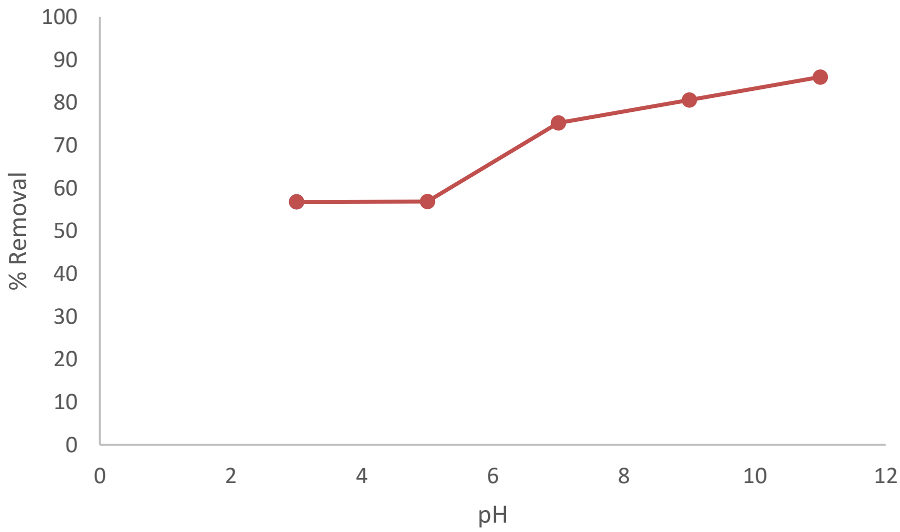

Figure4. Effect of pH on adsorption of metronidazole

This increase in efficiency at higher pH values can be explained by the concept of the pHpzc (point of zero charge). At pH values above the pHpzc, the adsorbent surface is negatively charged, which helps to repels the negatively charged MNZ molecules. However, at pH values below the pHpzc, the adsorbent surface is positively charged, which can attract the negatively charged MNZ molecules, resulting in an increase in adsorption efficiency. The results of this study suggest that the high removal efficiency of MNZ in basic conditions is due to the hydroxyl groups on the adsorbent surface. According to Legnoverde *et al.* (2014), hydroxyl groups are more active at high pH values, which allows for the adsorption of MNZ via electrostatic interactions with the positively charged surface. So, the mechanism of adsorption involves the electrostatic attraction between the positively charged adsorbent surface and the negatively charged MNZ molecules. This mechanism has been previously reported by Pouretedal and Sadegh (2014).

Effect of temperature on adsorption

Figure 5 depicts the effect of temperature of 25, 30, 40, 50, 60 ^{0}C on the adsorption of MNZ by the SB - CNC adsorbent. It's clear from the figure that the adsorption efficiency declined with increasing temperature. This could be due to the vulnerability of the adsorbate molecules and a decreased in the viscosity of the solution at higher temperatures.

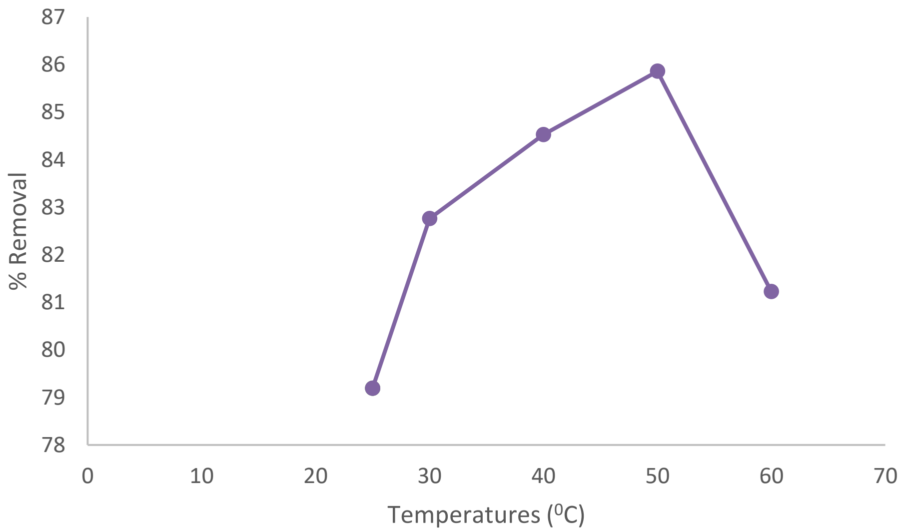

Figure5. Effect of temperature on adsorption

The increase in adsorption capacity observed when the temperature was increased from 25 ^{0}C to 50 C can be explained by the increased movement of adsorbate molecules and decreased viscosity, mentioned. However, when the temperature was increased beyond 50 C, the adsorption capacity decreased. This is likely because the adsorbent-adsorbate interactions became weaker at higher temperatures, due to the increased thermal energy of the molecules (Aluigi *et al.*, 2014; and Yagub *et al.* 2014). In general, the adsorption of organic and chemical compounds is an exothermic process, meaning that it releases heat energy to the surroundings (Yagub *et al.*, 2014). This exothermic nature of adsorption means that as the temperature decreases at 60 C, the adsorption capacity increases. So, the increase in adsorption capacity observed at lower temperatures in this study can be explained by the exothermic nature of the adsorption process.

Isotherm Models

The Freundlich isotherm model is based on a heterogeneous surface with a non-uniform distribution of heat of adsorption (Abdollahzadeh *et al.* 2020).

Table 1. Equilibrium Isotherms Parameters for MNZ Removal

Models	Parameters	
Langmuir	$1/q_m$ (mg/g)	0.0003
	K_L (1/mg)	-0.0002
	R^2	0.8707
Freundlich	log KF	-0.7133
	1/ n	9.1825
	R^2	0.8818

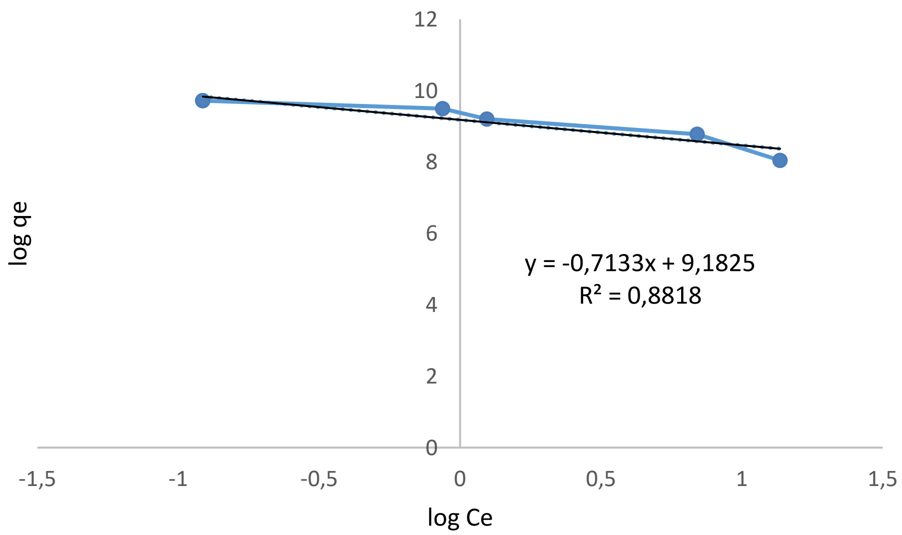

Figure 6. Freundlich Isotherm Model for Metronidazole Removal

Kinetic Models

The value of K_2 can be used to evaluate the adsorption rate. Based on the values of R^2 (0.9972), the adsorption of MNZ onto SB-CNC followed the pseudo-second-order model, indicating that chemical adsorption was the rate-limiting step in the adsorption process. Other studies have also shown that the adsorption of organic compounds onto natural and engineered adsorbents follows the pseudo-second-order model (Wang *et al.* 2009; Ashraf *et* *al.* 2013). The kinetic constants and the correlation coefficients (R^2) presented in Table 2 and Figure 7. (Al-Khalisy *et al.*,2010).

Table 2 Kinetic Model Parameters for Metronidazole Removal

Kinetic Model	Parameters	
Pseudo First Order	q_e, cal (mg/g)	7.7611
	- K_1 (min^{-1})	-0.0471
	R^2	0.8877
Pseudo Second Order	q_e, cal (mg/g)	0.0024
	K_2 (g/ mg min)	0.0003
	R^2	0.9972

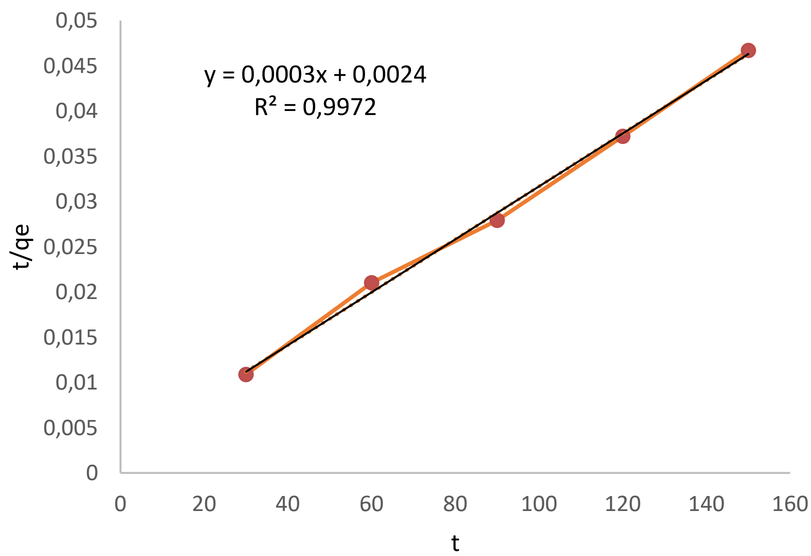

Figure 7. Pseudo Second Order Kinetic Model for Metronidazole Removal

Thermodynamics Parameters

Table 3 Thermodynamic Parameters for Metronidazole Removal

Temperature (K)	ΔG (J/mol)	ΔS (J/mol/K)	ΔH (J/mol)
298 -17397.954 303 -17689.894 313 -18273.770 58.388 1.670			
323 -18857.654			
333 -19441.534			

Thermodynamics parameters have been investigated to determine whether the adsorption phenomenon is favourable or not. $\Delta G, \Delta H, and\ \Delta S$ where obtained from the experimental by Van't Hoff plot studies at different temperatures of 298, 303, 313, 323, and 333 K. All thermodynamic parameters for MNZ onto SB - CNC are tabulated in Table 3. The ΔG values are negative as the temperature varies from 298 to 333 which indicate that MNZ adsorption reaction is spontaneous. The decrease in ΔG values with increase in temperature is an indication that MNZ adsorption on SB - CNC is favourable (Enenebeaku *et al.,* 2015). The positive value of ΔH suggests an endothermic process, which is often associated with chemisorption. The ΔS indicated the degree of randomness, the positive value of entropy increase randomness at the solid – solute interface during adsorption.

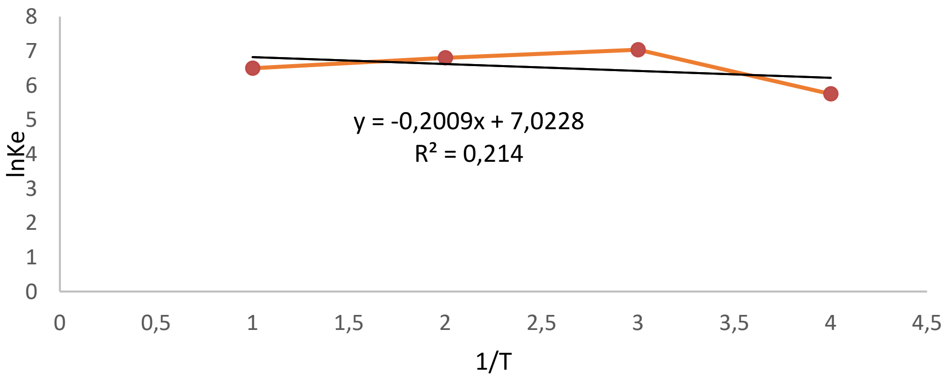

Figure 8. Thermodynamic Plot for MNZ removal

CONCLUSION

The present study investigated the adsorption behavior of metronidazole (MNZ) onto sugarcane bagasse-derived cellulose nanocrystals (SB-CNC), with a focus on evaluating its effectiveness and suitability for wastewater treatment applications. Although the percentage yield of SB-CNC was relatively low at 7.4%, limiting its economic viability on a larger scale, the material exhibited promising adsorption characteristics under optimized conditions. The adsorption process was found to be highly efficient in alkaline environments, with performance positively influenced by increasing initial MNZ concentrations, contact time, and adsorbent dosage factors that significantly enhanced the removal rate.

Kinetic analysis revealed that the adsorption of MNZ followed the pseudo-second-order model, with a high coefficient of determination ($R^2 = 0.9972$), indicating that the adsorption process is likely controlled by chemisorption involving valency forces through sharing or exchange of electrons. Furthermore, equilibrium data were best described by the Freundlich isotherm model ($R^2 = 0.8898$), suggesting a heterogeneous adsorption surface and the simultaneous occurrence of physisorption and chemisorption mechanisms.

Thermodynamic evaluations supported the spontaneity and endothermic nature of the adsorption process, as indicated by the negative values of Gibbs free energy (ΔG) and the positive values of enthalpy (ΔH) and entropy (ΔS). The positive entropy change further implied increased randomness at the solid–solution interface during MNZ adsorption.

In conclusion, despite the low material yield, SB-CNC demonstrates significant potential as an eco-friendly and sustainable adsorbent for the removal of pharmaceutical contaminants from wastewater. Its performance under favorable conditions underscores its practical applicability in water purification systems. Future research should explore strategies to improve the synthesis yield and cost-efficiency of SB-CNC, as well as assess its scalability and reusability in real wastewater matrices to further validate its environmental and economic viability.

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