

The Effect of The Removal of Hemicellulose from Sugarcane Bagasse on The Biosorption of Fe²⁺ from Potable Water

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Abstract: *Even though certain ions are essential to human health and development, the World Health Organization states that their existence in larger quantities is concerning because of their negative effects on public health. The Biosorption process has, however, been demonstrated to be an effective technique in removing heavy metals from contaminated water using agricultural biomasses. These biomasses, which are usually utilized as fuels for energy or discarded in landfills, lead to air and land pollution. Sugarcane bagasse consists of cellulose, hemicellulose, and lignin; which are highly valued components in various industries. Therefore, the aim of this study was to remove/extract hemicellulose from sugarcane bagasse through acid pretreatment (0.5% - 2.5% H₂SO₄) and further explore the efficacy of the modified biosorbent in the removal of Fe²⁺ from potable water. Based on the pretreatment of 2.5% H₂SO₄, the content of hemicellulose of 24.3% decreased to 13.63%, and the surface area and pore size of the natural sugarcane bagasse, which were respectively 0.904 cm³/g and 56.33 Å; increased to 1.233 cm³/g and 99.10 Å after acid pretreatments. Batch experiments were carried out on various operating parameters pH (2-7), Fe²⁺ metal concentration (1 - 30 mg/L), and biosorbent dose (1- 6 g). The highest percentage removal of Fe²⁺ ions, based on 1 g of the biosorbents, was found to be 32.2% for the natural and 58.79% for the modified biosorbent (2.5% H₂SO₄). The adsorption isotherms results indicated that the experimental data for the biosorption of Fe²⁺ ions fitted well with the Langmuir isotherm with maximum monolayer adsorption capacities of 0.770 mg/g for the natural and 5.743 mg/g for the modified (2.5% H₂SO₄) biosorbents. These results indicated that an ion exchange process mediated the homogenous interaction between Fe²⁺ ions and active hydroxyl and carbonyl functional groups present on the surface of the biosorbents. Based on the findings of this study, the removal of the hemicellulose resulted in an increased surface area, leading to an increased percentage removal of the Fe²⁺ ions. Therefore, the modified biosorbent has a high potential of being an alternative agricultural biosorbent in removing Fe²⁺ ions from contaminated water.*

Keywords: *Biosorption, Isotherms, Water treatment, Agricultural biomass*

1. Introduction

Contamination of potable water with heavy metals is of great concern due to their toxicity. According to [1] exposure to heavy metals have serious health consequences, such as stunted growth and damage to the body's organs. To reduce human and environmental exposure to these hazardous metals, the South African National Standard (SANS) states that Fe²⁺ concentrations in potable water must not be more than 0.04 mg/L. If Fe²⁺ ions concentration exceeds these permitted levels, it may have physiological impacts on human health. High concentrations of heavy metals have, nevertheless, been found in several drinking water samples. According to [2], increasing Fe²⁺ concentration in potable water may have been caused by various water pipe types, pipe aging, stagnation of treated water in reservoirs, and other factors. There are numerous conventional technologies (ion exchange, chemical precipitation, and reverse osmosis) for removing these heavy metals, these methods are, however, disadvantaged by their high costs. The biosorption method has therefore emerged as an effective and

affordable approach to remove heavy metals in potable water [3, 4]. Sugarcane bagasse was the chosen biosorbent in this present study to remove Fe^{2+} ions from potable water. Sugarcane bagasse contains 42% cellulose, 33.5% hemicellulose, and 20% lignin [5]. The biosorption capacity of lignocellulosic material can be increased by physical and chemical modification of the biosorbents [6]. Various pretreatments have been applied to different lignocellulosic matrices to increase accessible surface areas or selectively remove hemicellulose and lignin from the lignocellulosic matrix [7]. Diluted acidic and alkali pretreatments lead to disruption of lignocellulosic cell walls by dissolving lignin and hemicellulose by hydrolyzing uronic and acetic acid esters and by swelling cellulose [8]. This, in turn, results in an increased surface area that leads to increased adsorption capacity. This study was aimed at valorizing bagasse by removing hemicellulose through acid pretreatment for removing Fe^{2+} from potable water. The effect of various process parameters such as initial concentration of Fe^{2+} ; pH; and biosorbent dose were investigated using batch experiments.

2. Materials and methods

2.1 Materials and Chemicals

All the materials and reagents used were of analytical grade with sulphuric acid and sodium hydroxide purchased from the Sigma Aldrich Chemical Company. De-ionized water was used for the preparation of all samples. Sugarcane bagasse was collected from the Illovo sugar mill in Umkomaas Area in Durban, South Africa. The bagasse was firstly washed and air-dried using Gunt Hamburg CE 130 air-convection drier, set at 30°C and air velocity of 1 m/s. The dried bagasse was subsequently broken down into particle sizes of 200 μm . A portion of the dried bagasse was added into 5 beakers (each containing 1000 ml of pretreatment solutions (0.5; 1; 1.5; 2 and 2.5% H_2SO_4)) and allowed to soak for 24 h, thereafter filtered. The solid residues were thoroughly washed with deionized water until neutral pH was obtained for the filtrates, then air-dried using an air convention drier (Gunt Hamburg CE 130). To replicate the concentration of heavy metals in potable water, synthetic solutions of Fe^{2+} were prepared by adding the specific mass of ferrous sulphate heptahydrate salt ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) into 1000 mL of deionized water. The synthetic solutions were thoroughly agitated using Cole-Parmer Stuart Orbital Shaker (SSL1). For the concentration experiments, Fe^{2+} solutions were obtained by diluting the stock solutions to varying concentrations of Fe^{2+} .

2.1.1 Biosorption Experiments

Batch experiment studies were conducted to study the effect of the natural and acid-modified sugarcane bagasse on the removal of Fe^{2+} from potable water. The effect of biosorbent dose was studied by agitating 100 ml of 1 mg/L Fe^{2+} solution containing different doses of natural and acid-modified biosorbents (0.2 to 1.4 g) for 60 mins at 25°C using an orbital shaker (model SSL1) set at 160 rpm. The effect of initial concentration was investigated by respectively adding 1 g of the natural and acid-modified biosorbents to 100 ml of varying Fe^{2+} concentrations (1 – 30 mg/L). For pH variation, both the natural and acid-modified biosorbents were subjected to Fe^{2+} solutions of 1 mg/L of various pH (2 – 7), at a constant biosorbent dose of 1 g, contact time of 60 mins, and agitation speed of 160 rpm. An Orion Star A215pH/ conductivity meter (electrode: Orion 8157 BNUMD Ross Ultra pH/ATC Triode) was used to measure pH. The solution pH was adjusted using 1.0 M NaOH and 1.0 M H_2SO_4 . All biosorption experiments were carried out in triplicates, and an Atomic Absorption Spectrometer (AAS-Perkin Elmer, AAnalyst 400 model) was used to analyze the final Fe^{2+} concentration after the experiments. The percent removal of Fe^{2+} was calculated using equation (1).

$$\% \text{ Removal} = \frac{C_o - C_e}{C_o} * 100\% \quad (1)$$

Where C_o (mg/L) is the initial concentration and C_e (mg/L) is the concentration at equilibrium.

2.1.2 Adsorption Isotherms

The two most used isotherm models were chosen for this present study (Langmuir and Freundlich). In the Langmuir isotherm (equation 2) metals are adsorbed through homogenous interaction in a single layer of the

molecule. The dimensionless separation factor (R_L) (equation 3) can also be used to evaluate the favorability of the biosorption process. The Freundlich isotherm (equation 4) is based on the assumption that biosorption occurs through multilayer or heterogeneous surfaces with various adsorption sites [9].

$$\frac{C_e}{q_e} = \frac{1}{q_{max}} C_e + \frac{1}{q_{max}K_L} \quad (2)$$

$$R_L = \frac{1}{(1 + K_L C_o)} \quad (3)$$

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_f \quad (4)$$

Where C_e (mg/L) is the concentration at equilibrium; q_e (mg/g) is the adsorption capacity, q_{max} (mg/g) is the maximum adsorption capacity, K_L (L/mg) is the Langmuir adsorption constant, K_f and n are the Freundlich constant.

2.1.3 Adsorption Kinetic Models

The pseudo-first-kinetic model (given by equation 5) assumes that metal ions only adsorb on one sorption site onto the surface of the biosorbent while the Pseudo-second-order model (Eq. (6)) assumes that the biosorption occurs through chemisorption adsorption [10].

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{q_e} t + \frac{1}{K_2 q_e^2} \quad (6)$$

Where q_e and q_t (mg/g) are adsorption capacities at equilibrium and at time t respectively; k_1 (min^{-1}) is the pseudo-first-order-adsorption rate constant. K_2 is the pseudo-second-order rate constant ($\text{g/mg}\cdot\text{min}$).

2.2 Characterization Studies

Characterization of the natural and modified sugarcane bagasse was performed using Fourier Transform Infrared Spectroscopy (Perkin Elmer with wavenumber of $400 - 4000\text{cm}^{-1}$) to identify functional groups on the biosorbent.

3. Results and Discussion

3.1 Biosorption Studies

3.1.1. Effect of pH Variation

The effect of pH is presented in Fig. 1a shows that the removal of Fe^{2+} ions was very low at a pH of 2 -3, but as the pH of the solution was increased from 3 to 7, the percentage removal of Fe^{2+} when using natural sugarcane bagasse increased from 0.23% to 99.2%. The overall trend from Fig 1a for both natural and modified biosorbents in the biosorption of Fe^{2+} is that it performs better at a neutral pH of 7 with removal between 95 to 99.95%.

3.1.2 Effect of Adsorbent Dosage

It can be noted from Fig.1b that the amount of Fe^{2+} removed increased with an increase in biosorbent dose for both the natural and modified biosorbents. A percentage removal of 3.3% and 22.3% Fe^{2+} was obtained using 0.2 and 1 g of natural sugarcane bagasse. No appreciable biosorption was observed for biosorbent doses above 1 g for both the natural and acid-modified biosorbents. The percentage of Fe^{2+} removed increased from 12.82 to 34.51% for 0.5% H_2SO_4 and 20.87 to 58.79% for 2.5% H_2SO_4 . The highest removal of Fe^{2+} removal of 58.79% was obtained at the dosage of 1g of 2.5% H_2SO_4 .

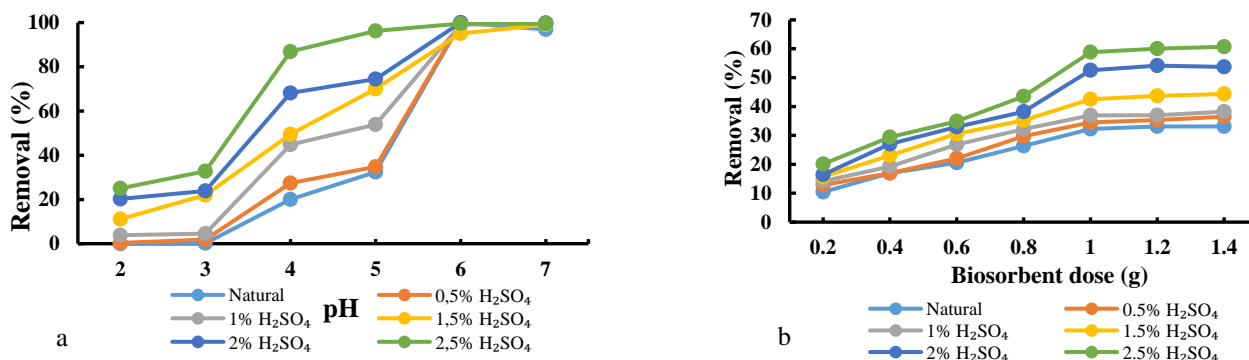


Fig. 1 a,b: The effect of (a) pH and (b) biosorbent dose - on the removal of Fe²⁺.

3.1.3 Effect Initial Concentration

The efficiency of both the natural and modified biosorbents decreased with an increase in initial Fe²⁺ concentration as depicted in Fig. 2. The efficacy of the modified biosorbent increased as the concentration of the acid pretreatment increased but decreased when the initial Fe²⁺ concentration increased from 1 to 30 mg/L. The percentage removal of Fe²⁺ adsorbed by the natural sugarcane bagasse decreased from 50% to 4.6% when the initial concentration was 1 and 30 mg/L, respectively. The percentage removal of Fe²⁺ for the 0.5% H₂SO₄ biosorbent was 57.25% at 1 mg/L and decreased to 11.53% at 30 mg/L. The most efficient modified biosorbent was that of 2.5% H₂SO₄ with 75.93% Fe²⁺ adsorbed at the initial concentration of 1 mg/L and 17.73% at the initial concentration of 30 mg/L (Fig. 2).

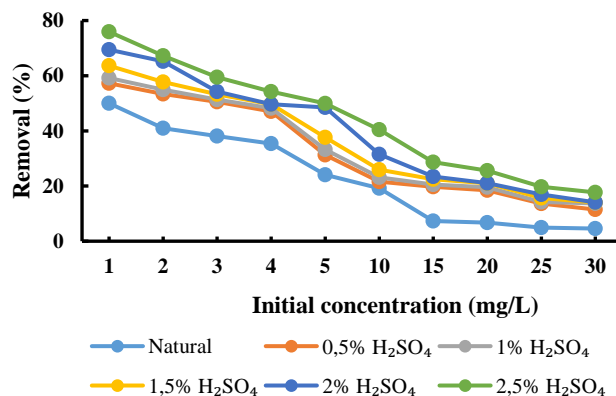


Fig. 2: The effect of initial concentration on the removal of Fe²⁺ using natural and Acid-Modified Biosorbents

3.2 Adsorption Kinetics and Isotherms

The values of the maximal uptake adsorption capacities (q_{\max} (mg/g)) and the energy of the biosorption (K_L (L/mg)) were calculated using the linear plots of $\frac{C_e}{q_e}$ vs C_e . Results obtained for the Langmuir and Freundlich isotherms are exhibited in Table 1.

TABLE I: The Freundlich and Langmuir isotherms parameters for the natural and acid-modified biosorbents

	FREUNDLICH MODEL				LANGMUIR MODEL			
	K_f (mg/g)	n	$1/n$	R^2	K_L (L/mg)	q_{max} (mg/g)	R^2	R_L
Natural	0.852	5.577	0.179	0.471	0.066	0.770	0.981	0.938
0.5% H ₂ SO ₄	1.058	2.496	0.401	0.921	3.700	4.435	0.974	0.213
1% H ₂ SO ₄	1.100	2.398	0.417	0.941	3.805	4.433	0.965	0.208
1.5% H ₂ SO ₄	1.206	2.413	0.414	0.959	3.330	4.647	0.981	0.231
2% H ₂ SO ₄	1.396	2.581	0.387	0.958	2.409	4.645	0.995	0.293
2.5% H ₂ SO ₄	1.423	3.101	0.322	0.975	4.587	5.743	0.994	0.279

For the Langmuir isotherm, the maximal adsorption capacity (q_{max}) and adsorption energy K_L for the natural sugarcane bagasse were determined to be 0.770 mg/g and 0.066 L/mg, respectively. The q_{max} increased from 4.435 mg/g at 0.5% H₂SO₄ to 5.743% at 2.5% H₂SO₄, while the adsorption energy (K_L) increased from 3.7 to 4.59 L/mg as the pretreatment concentration increased from 0.5% H₂SO₄ to 2.5% H₂SO₄. Among the range of acid pretreatment concentrations, 2.5% H₂SO₄ had the highest adsorption capacity of 5.743 mg/g and R^2 of 0.994. The sorption capacity and correlation factor for the natural sugarcane bagasse for the Freundlich model were 5.57 mg/g and 0.471, respectively. Though the Freundlich model is regarded as favorable when the value of $1/n$ is between 0 and 1, and unfavorable when the value of $1/n$ is greater than 1, the values of the R^2 are very low (>0.95) making the Freundlich isotherm unfavorable in this case. Therefore, the Langmuir model provided an excellent fit for the adsorption isotherm, as shown by the q_{max} , R^2 , and R_L parameters of the Langmuir isotherm. The results of R_L ranging between 0 and 1, show that the adsorption of Fe²⁺ onto the natural and acid-modified sugarcane bagasse was favorable.

The results obtained from the batch experiments were also fitted into the two kinetic models (pseudo-first-order and pseudo-second-orders) to kinetically explore the biosorption of Fe²⁺ onto the natural and modified biosorbents.

TABLE II: The Pseudo-first and Pseudo-second parameters for the natural and acid-modified biosorbents

	PSEUDO-FIRST-ORDER				PSEUDO-SECOND-ORDER			
	q_e (mg/g)	$q_e^{(calc)}$ (mg/g)	K_1 (min ⁻¹)	R^2	$q_e^{(exp)}$ (mg/g)	q_e (mg/g)	K_2 (g/mg.min ⁻¹)	R^2
Natural	2.437	3.805	0.055	0.838	2.437	3.458	0.012	0.887
0.5% H ₂ SO ₄	2.867	2.816	0.044	0.958	3.702	2.851	0.091	0.905
1% H ₂ SO ₄	2.922	3.267	0.056	0.951	4.975	3.992	0.011	0.926
1.5% H ₂ SO ₄	3.182	3.164	0.047	0.944	4.906	4.762	0.007	0.943
2% H ₂ SO ₄	2.451	1.924	0.056	0.981	4.573	2.885	0.031	0.972
2.5% H ₂ SO ₄	2.766	1.550	0.065	0.980	4.426	2.998	0.063	0.981

It can be seen in Table 2 that the calculated adsorption capacities, experimental adsorption capacities; and R^2 are in close proximity for both the pseudo-first-order and pseudo-second-order models, meaning that the biosorption of Fe²⁺ took place on both the homogeneous and heterogeneous surfaces of the natural and modified biosorbents experiencing physical and chemical adsorption of Fe²⁺.

3.3 Characterization studies

3.3.1 Fourier Transform Infrared Spectrometry (FTIR)

The analysis showed mainly the bonded OH groups, CH stretching vibrations at 2945-2920 cm⁻¹, C=C aromatic vibrations of lignin at 1600 and 1500 cm⁻¹ and C-O stretching vibrations at 1241 cm⁻¹. Modified samples showed a shift in some peak intensities had increased. The stretch vibrations of the C=C and C-O bonds of the acetyl ester groups found in the hemicellulose were identified as the source of the peak at 1243 cm⁻¹ on the spectra of natural and acid-modified biosorbents [11]. Due to the elimination of hemicellulose, the acid pretreatment had a significant impact on the structure of the sugarcane bagasse, as seen by the shifts in peak intensities at 832, 1206, 1240, 1348,

1522, 1743, 2848, and 3330 cm^{-1} . The hemicellulose-related peaks at 1043 and 997 cm^{-1} were also reduced. The intensities of the bands in the regions of 500–898 cm^{-1} , 1217, 1606, and 1745 cm^{-1} and (3175 - 3490 cm^{-1}) decreased for the modified biosorbents, indicating that the functional groups (carbonyl, silanol, and hydroxyl) were involved in the biosorption of Fe^{2+} .

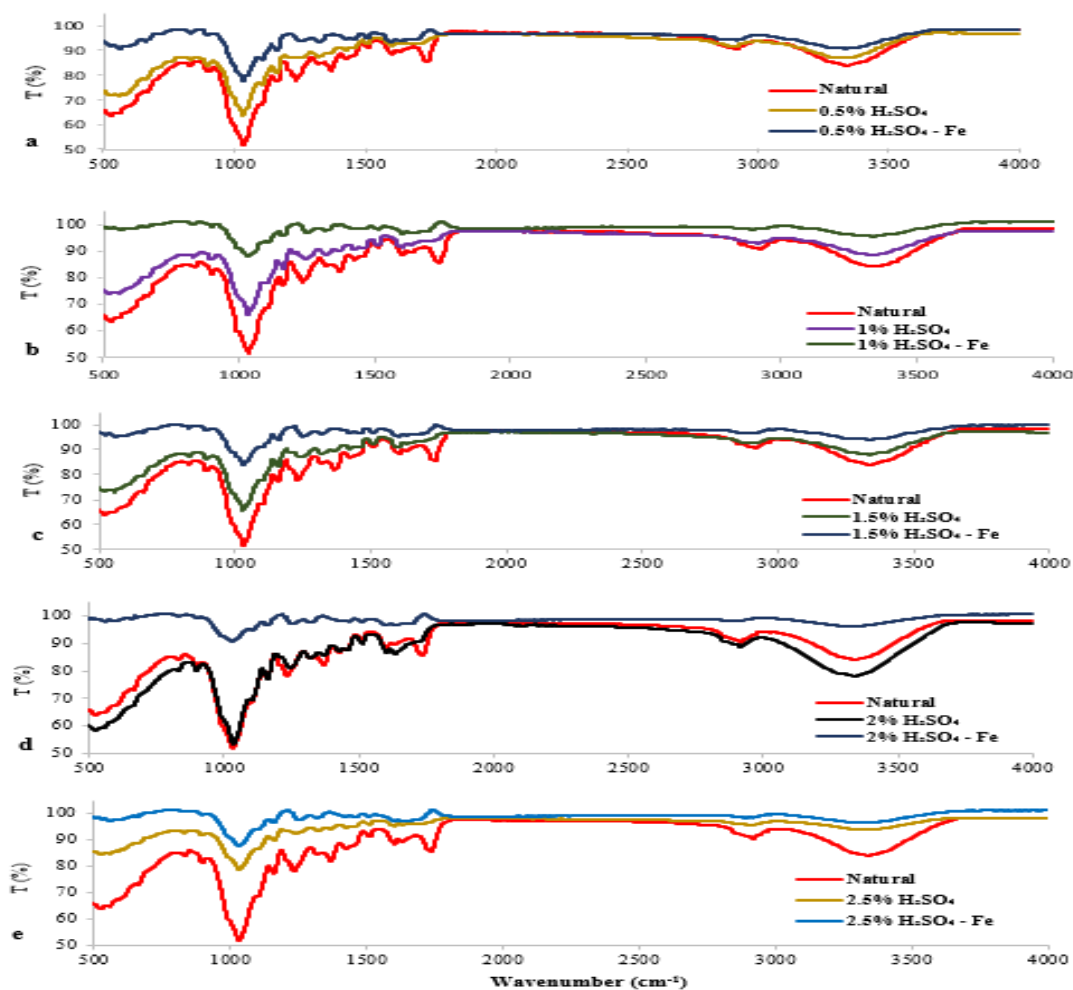


Fig. 3: The FTIR spectra of the acid pretreatment

3.3.2 Brunauer Emmett Teller Analysis

The results depicted in Table 3 are that of BET analysis for both the natural and acid-modified biosorbents. The natural sugarcane bagasse was found to have a surface area and pore size of 0.904 cm^3/g and 56.33 \AA , respectively. The surface area and pore size after acid pretreatment increased to 0.934 and 1.233 cm^3/g for 0.5% H_2SO_4 and 60.225 and 75.680 \AA for 2.5% H_2SO_4 , respectively. The loss of the amorphous components (hemicellulose) of the sugarcane bagasse due to acid pretreatment might have resulted in increased surface areas and pore sizes.

TABLE III: BET results for the natural and acid-modified biosorbents

	Surface area (cm ³ /g)	Pore size (Å)
Natural	0.904	56.330
0.5% H ₂ SO ₄	0.934	60.225
1% H ₂ SO ₄	0.950	63.589
1.5% H ₂ SO ₄	1.134	66.220
2% H ₂ SO ₄	1.184	70.240
2.5% H ₂ SO ₄	1.233	75.680

4. Conclusion

Biosorption studies were conducted on batch experiments to investigate the effect of removing hemicellulose from sugarcane bagasse, where sugarcane bagasse was chemically modified using varying concentrations of acid pretreatment. The batch experiment results showed that the chemically modified biosorbents removed a higher percentage of Fe²⁺ than the natural ones. The maximum removal of both the natural and modified biosorbents was obtained at a pH of 7, a biosorbent dose of 1 g, and an initial Fe²⁺ concentration of 1 mg/L. The equilibrium data fitted well with the Langmuir isotherm and followed a pseudo-second-order kinetic model. These results show that the acid-modified biosorbents have the potential of being an effective biosorbents for the removal of heavy metals from water.

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6. References

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