

# Performance Comparison of Chemically Modified Sugarcane Bagasse for Removing Cd(II) in Water Environment

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**Abstracts:** This paper evaluates the adsorption capacity of chemically sugarcane bagasses with sodium hydroxide (SHS), citric acid (CAS), tartaric acid (TAS) and unmodified sugarcane bagasse (SB) for cadmium adsorption in water environment. The results prove adsorption capacity for Cd (II) increases after chemical modification and the adsorption fits perfectly with the Langmuir isotherm. CAS had the highest maximum adsorption capacity of 45.45 mg/g followed by TAS with 38.46 mg/g and SHS with 29.41 at optimum pH 5.0 and 120 minutes equilibrium time while 1 g SB removed 18.8 mg Cd (II) in the same conditions. The kinetics study of the process followed a pseudo-second-order rate expression, that indicated a strong interaction between the biosorbents and adsorbate. The sugarcane bagasse and modified sugarcane bagasse were characterized by scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) analysis. The chemical modification was confirmed by the presence of carboxyl and esters groups created at  $1,738\text{ cm}^{-1}$ . The estimation of acid groups in modified materials shows the enhancement of this group after modification. On the other hand, desorption studies showed the high leaching of cadmium ion from the biosorbent leading to the efficient re-utilization of materials.

**Keywords:** Cadmium; chemical modification; citric acid; sugarcane bagasse

## 1 Introduction

Because of the highly toxic impacts of Cd (II) and biosphere, its removal from water environment has become a great concern from environmental perspective [1]. Cd (II) is highly hazardous due to its non-degradable and persistent. Cadmium enters the aquatic system via various industrial activities like electroplating, battery manufacturing, leather tanning, etc. [2]. Numerous methodologies have been developed for remediation, including chemical precipitation [3], biosorption [4], electrolytic recovery, membrane [5], adsorption on minerals and activated carbon [6], etc. Besides the advantages of these technologies, there are several adverse effects such as the high cost of materials used in ion exchange or membrane filtration, which makes such solutions uneconomical for developing countries [7]. During wastewater treatment process, chemical precipitation and coagulation also can remove Cd (II), on the other hand, they generate a concentrated sludge, which yields a secondary disposal problem [8]. Moreover, at low Cd (II) concentration, i.e., 100 mg/L or below, some of these methods become too costly or ineffective [9-10]. For this reason, it is important to study for the alternative technology for Cd (II) removal while not exceeding excessive costs.

Agricultural wastes are viable alternative materials since they may be used for Cd (II) contaminated waters even at low concentration, with advantages like (i) local availability and low-cost, (ii) high efficiency (iii) easy operation and (iv) Cd (II) recovery [11]. The main components of lignocellulosic materials from waste-to-product approach are cellulose, hemicelluloses and lignin. Functional groups including hydroxyl, carboxyl, esters amino, alcohols, carbonyl, amido, sulphur and acetamide presented on the structure of lignocellulosic materials can interact with heavy metal ions through hydrogen bonding, complexation, and

other interactions [12]. However, reported low-cost adsorbents also have waxes, pectines, dust and other impurities, which adds to the hydrophobic character and decrease the active surface area of these adsorbents which reduce the adsorption performance of materials [13]. In general, chemically modified agricultural waste materials express higher adsorption capacity than unmodified equivalents. Some chemical methods to modify cellulose materials from agricultural wastes were studied using acids or bases to change the surface of materials, using several agents such as hydrogen peroxide and EDTA to oxidize cellulose [14]. The aim of this paper is to compare the performance of chemically modified methods of sugarcane bagasse as an alternative material for Cd (II) removal from water environment by using sodium hydroxide (SHS), citric acid (CAS) and tartaric acid (TAS).

## 2 Materials and Methods

### 2.1 Preparation of Adsorbent Materials

The chemical modification of sugarcane bagasse was prepared following to the similar method described by Leyva et al., 2012 [15]. Firstly, SB was washed thoroughly in distilled water to remove all sugar residues and dust particles from freshly SB and then dried at 105°C for 24 hours. The material was crushed and sieved to the size ranged from 0.1-0.5 mm. Then, SB was mixed with 0.1 M sodium hydroxide for 2 hours at 150 rpm before being washed with distilled water and neutralization. The product was next dried in the oven at 60°C for 4 hours until dry. This product is denoted as SHS. After that, the treated SB was stirred for 2 hours with 1.0 M citric acid and 1.0 M tartaric acid with the weight ratio 1:3. The products, SB loaded with citric acid (CAS) and SB loaded with tartaric acid (TAS) were filtered then dried at 70°C for 6 hours slowly raised temperature to 120°C for 2 hours. Then, the modified SB was washed by distilled water to clean up excess acid and any other soluble substances until neutral pH and dried at 80°C within 24 hours before being used as adsorbent.

### 2.2 Characterization Studies

The microstructure and surface morphology of the adsorbent samples were characterized by a 10 kV HITACHI S-4800 NIHE scanning electron microscope (SEM). The functional groups of adsorbents were obtained using FT-IR model 410 JASCO (Japan).

### 2.3 Estimation of Acid Groups in Modified Sugarcane Bagasse

The estimation of the acidic groups in the adsorbents was used the methylene blue absorption method [16-17]. The 500 ml methylene blue solution with concentration of 50 ppm was treated by modified SB for 2 hours. The modified SB was filtered and the residual solution was determined the absorbance at  $\lambda_{max}$  of 664.5 nm using a Techcomp UV-Vis Spectrophotometer.

### 2.4 Adsorption Study

The rate and equilibrium data were obtained through adsorption studies conducted in batch at room temperature (25°C). The batch studies were carried out by mixing 0.1 g of adsorbent with 50 mL of solution with concentration between 10-250 mg/L. The optimal pH for adsorption was determined in the pH range of 2.0-7.0 by using 0.02 M HCl or 0.02 M NaOH for the adjustment.  $\text{NaNO}_3$  0.1M was added to produce an ionic strength of approximately 0.02 M in the suspensions. The samples were shaken with varying time intervals (10-180 minutes) at 150 rpm to monitor the equilibrium time. At the end, the mixture was filtered and the aqueous phase concentration of Cd (II) was determined by Atomic Absorption Spectrometry (AAS). Each analyzed in duplicate and the average results were used for evaluation.

Cadmium retained in the adsorbent phase; the amount was calculated using Eq. (1):

$$Q = \frac{(C_0 - C_e) \times V}{W} \quad (1)$$

where  $C_0$  and  $C_e$  are the Cd (II) concentration measured before and after adsorption (mg/L),  $V$  the volume of aqueous solution (L), and  $W$  is dry weight of SB (g).

The efficiency of adsorption of Cd (II) adsorption by the absorbents can be computed by using Eq. (2):

$$\text{Adsorption (\%)} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

### 2.5 Desorption Study

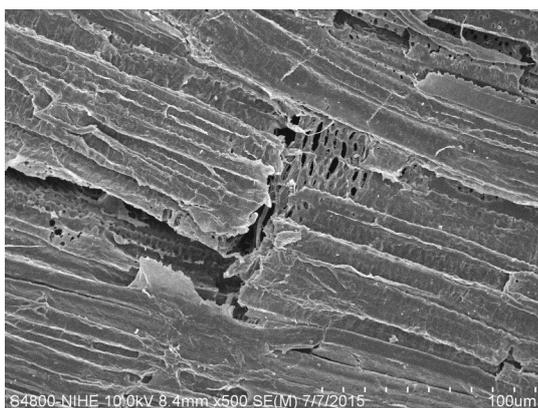
Desorption of the Cd (II) from each of the saturated materials was implemented by shaking them with 50 ml of 1 M HNO<sub>3</sub> at 35°C for 120 minutes. The Cd (II) of the desorbed acid solutions were estimated using ICP plasma spectrometers model Optima 7300DV of Perkin Elma (USA).

## 3 Results and Discussion

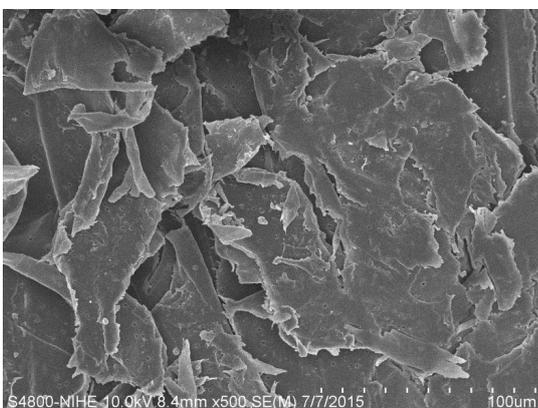
### 3.1 Characterization Studies

#### 3.1.1 SEM Analysis

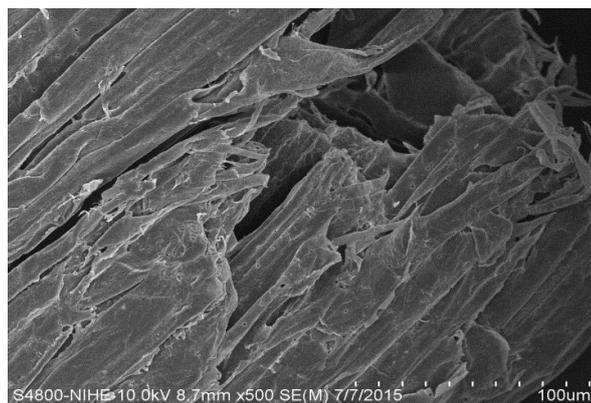
The SEM images of unmodified and modified sugarcane bagasse are shown in Figs. 1, 2, 3 and 4. It can be seen that all the samples had similar morphological characteristics such as porous structure and overlapping fiber layers which responsible for physical adsorption. As shown in Fig. 1, the surface of the unmodified sugarcane bagasse was observed to be covered by impurities and amorphous cellulose. In Figs. 2, 3 and 4, there is appearance of gaps between the fibers and the removal of amorphous cellulose which showed a potential feasibility for Cd (II) to be adsorbed [2]. This may be because pretreatment with base removed residual lignin as the result of breaking down the fiber bundles into the finer filaments which increased the effective surface area and surface charge [18].



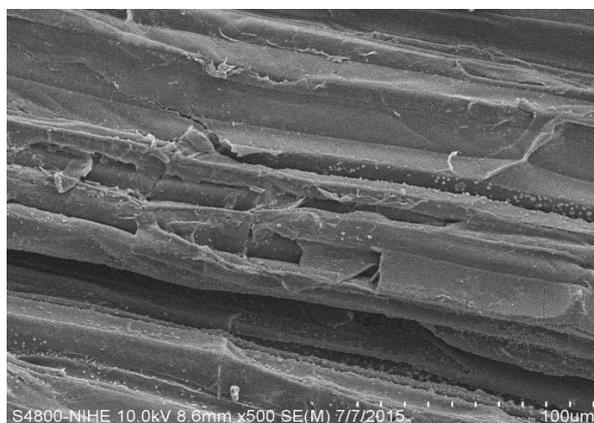
**Figure 1:** SEM image of unmodified sugarcane bagasse (SB) (Magnification: 500x)



**Figure 2:** SEM image of sodium hydroxide sugarcane bagasse (SHS) (Magnification: 500x)



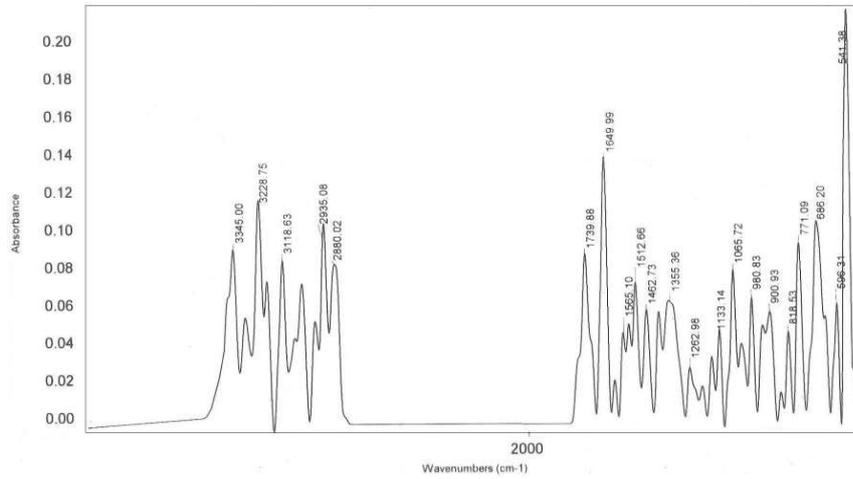
**Figure 3:** SEM image of citric acid sugarcane bagasse (CAS) (Magnification: 500x)



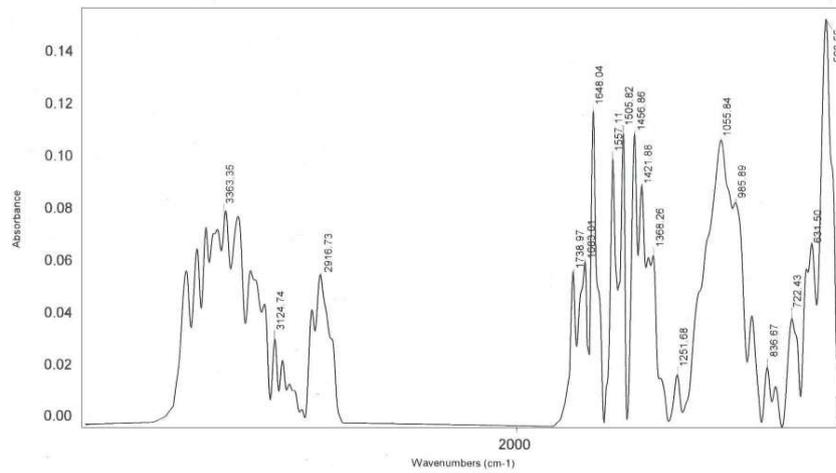
**Figure 4:** SEM image of tartaric acid sugarcane bagasse (TAS) (Magnification: 500x)

### 3.1.2 FTIR Analysis

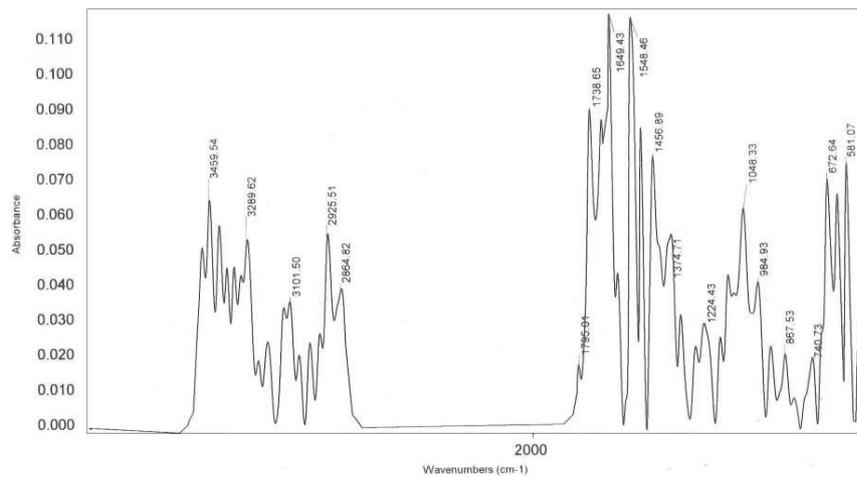
The FTIR spectra of modified sugarcane bagasse samples are shown in Figs. 5, 6, 7 and 8. As observed in all the samples, the peaks observed at  $3363\text{ cm}^{-1}$  and  $1648\text{ cm}^{-1}$  can be assigned to hydroxyl group and carbonyl group respectively. The strong band at  $1058.73\text{ cm}^{-1}$  is indicated to C-O stretching in cellulose, hemicelluloses, and lignin or C-O-C stretching in cellulose and hemicelluloses [19]. Compared to the spectra of unmodified sugarcane bagasse, the spectra of SHS, CAS, TAS give evidence of important ester bands presence at  $1738.97\text{ cm}^{-1}$  for SHS,  $1738.65\text{ cm}^{-1}$  for CAS and at  $1740\text{ cm}^{-1}$  for TAS. The bands at  $1738\text{-}1740\text{ cm}^{-1}$  are indicative of absorption by carbonyl bonds as carboxyl and esters which play an important role in cadmium adsorption. It is suggested that citric acid and tartaric acid modification create an esterification between citric acid, tartaric acid and cellulosic hydroxyl groups in SB to form an ester linkage [13]. The increase of carboxylic content of the SB surface during esterification process was leading to a significant increase in the adsorption of Cd (II).



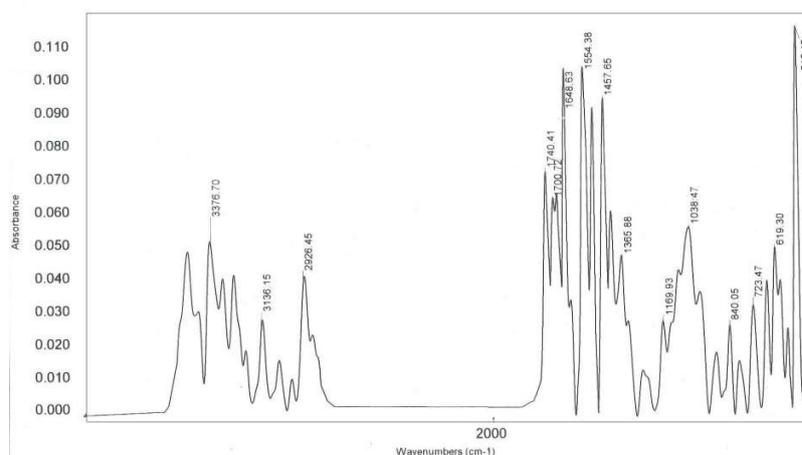
**Figure 5:** IR spectra of unmodified sugarcane bagasse (SB)



**Figure 6:** IR spectra of sodium hydroxide sugarcane bagasse (SHS)



**Figure 7:** IR spectra of citric acid sugarcane bagasse (CAS)



**Figure 8:** IR spectra of tartaric acid sugarcane bagasse (TAS)

### 3.2 Estimation of Acid Groups in Modified Sugarcane Bagasse

The amount of methylene blue adsorbed on the materials is shown in Tab. 1. Modification of cellulose in sugarcane bagasse leads to a generation of carboxyl groups. It was observed that there was a small change in the number of carboxyl groups between natural sugarcane bagasse and sodium hydroxyl, 0.67 mEq/g and 0.72 mEq/g, respectively. This shows that the esterification has not taken place in the sodium hydroxide modification process. In contrast, after organic acid modification, a large number of acidic groups was presented in the citric acid modification (1.024 mEq/g) while tartaric acid modification contained 1.008 mEq/g acidic groups. This difference can be explained due to the number of carboxyl groups in the structure of the organic acids used to modify sugarcane bagasse. Citric acid has a higher carboxyl group number (three groups), which leads to a higher amount of -COOH groups and may lead to a significant increase in the adsorption of Cd (II). This result also matches with the FTIR spectra.

**Table 1:** Number of acid groups in modified sugarcane bagasse

Adsorbent	Concentration of methylene blue (mg/L)	qe (mg/g)	qe (mmol/g)	-COOH (mEq/g)
SB	13.22	21.69	0.67	0.67
SHS	11.85	23.05	0.72	0.72
CAS	2.22	32.69	1.02	1.02
TAS	2.73	32.18	1.00	1.00

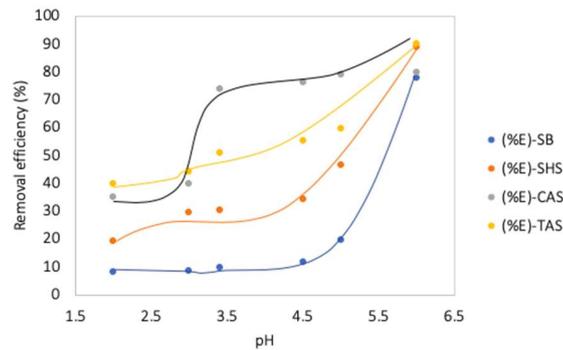
SB-unmodified sugarcane bagasse; SHS-sodium hydroxide sugarcane bagasse; CAS-citric acid sugarcane bagasse; TAS-tartaric acid sugarcane bagasse

### 3.3 Adsorption Studies

#### 3.3.1 Effect of pH

The experiments were carried out for pH values ranging from 2 to 5. In this range, Cd (II) removal can be related only to adsorption because chemical precipitation of the cadmium hydroxide occurs at pH above 5. The results depicted in Tab. 2 show that the Cd (II) removal capacity increase when pH values increase. When pH of the solution changed from 2 to 6, the Cd (II) removal efficiency changed from 8.3 mg/g to 22.38 mg/g with SB, 19.41 mg/g to 46.72 mg/g with SHS, 35.07 mg/g to 78.94 mg/g with CAS, and 39.08 mg/g to 59.73 mg/g with TAS. The decrease in Cd (II) removal as the pH decreases can be due to the basis

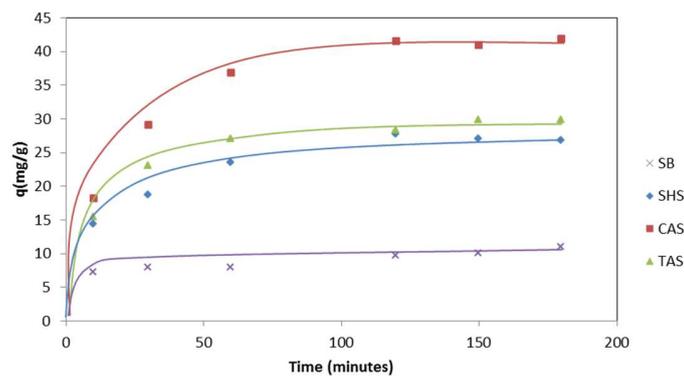
of an increase in competition between protons and Cd (II) for the surface areas and by the increase in the positive surface charge. This may reduce the number of binding sites available for the adsorption of Cd (II) [20]. Cd (II) was effectively adsorbed at about pH 5.0 for all adsorbents. Therefore, the optimum pH for the adsorption Cd (II) was 5.0. From the result of Fig. 9, it is clear that at lower pH, the adsorption of Cd (II) studied is drastically reduced.



**Figure 9:** Effect of pH on Cd (II) removal efficiency (%E) by chemically modified SB. SB-unmodified sugarcane bagasse; SHS-sodium hydroxide sugarcane bagasse; CAS-citric acid sugarcane bagasse; TAS-tartaric acid sugarcane bagasse

### 3.3.2 Effect of Contact Time

The effect of time on the Cd (II) removal was investigated at different types of chemically modified SB, with solution of 100 mg/L concentration, and at the pH at 5.0. The removal of Cd (II) versus time is shown in Fig. 10. The amount of adsorption capacity of SB, SHS, CAS and TAS increased with time and after 120 minutes, reached a constant value. Hence, the 120 minutes was assumed as equilibrium time. While increasing the contact time, the active sites on the chemically modified SBs were filled and the adsorption was stable.

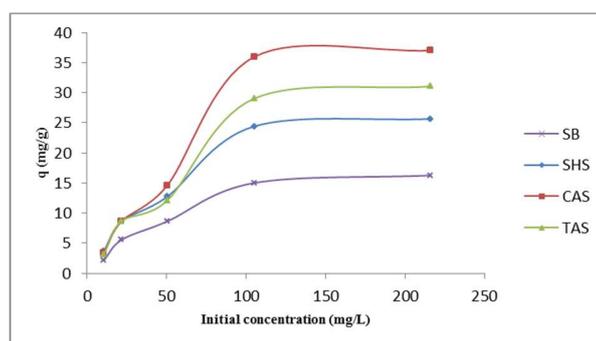


**Figure 10:** Effect of time on Cd (II) uptake by chemically modified SB. SB-unmodified sugarcane bagasse; SHS-sodium hydroxide sugarcane bagasse; CAS-citric acid sugarcane bagasse; TAS-tartaric acid sugarcane bagasse

### 3.3.3 Effect of Initial Cd (II) Concentration

The effect of the initial Cd (II) concentration on the Cd (II) adsorption capacity is shown in Fig. 11. It was observed that the amount of CD (II) ions adsorbed by adsorbents-based SB increased with increasing

initial Cd (II) concentration. For example, when the initial Cd (II) concentration increased from 10 to 100 mg/L, the Cd (II) adsorption capacity of SHS, CAS and TAS increased from 3.72 to 24.4 mg/g, from 3.35 to 35.95 mg/g and 3.15 to 29.02 mg/g, respectively. However, when the initial Cd (II) concentration was changed from 100 to 200 mg/L, the Cd (II) adsorption capacity was unchanged probably because of the adsorbents were saturated. This indicates that the Cd (II) uptake was highly dependent on the initial Cd (II) concentration in solution. At low Cd (II) concentration, the adsorption capacity was significant increase due to the low ratio between the number of moles of Cd (II) in solution and the available surface area of adsorbents. At higher concentration, binding sites were less available and hence Cd (II) removal was dependent on the initial concentration of solution. This confirms that the structure of the pores and the active functional group of the materials are well suited for adsorption of cadmium. Moreover, a low concentration was beneficial for cadmium removal from water.



**Figure 11:** Effect of initial Cd (II) concentration uptake by modified SB. SB-unmodified sugarcane bagasse; SHS-sodium hydroxyl sugarcane bagasse; CAS-citric acid sugarcane bagasse; TAS-tartaric acid sugarcane bagasse

### 3.4 Adsorption Isotherms

Adsorption isotherm models had been used to express the distribution of Cd (II) ions between the solid phase (adsorbent) and liquid phase (solution) when equilibrium was reached. The Freundlich and Langmuir isotherm models had been widely used to describe the interaction between Cd (II) ions in solution and adsorbents. The Langmuir isotherm assumes that the adsorption process takes place at specific homogeneous by monolayer adsorption. The Langmuir isotherm [21] can be expressed by Eq. (3):

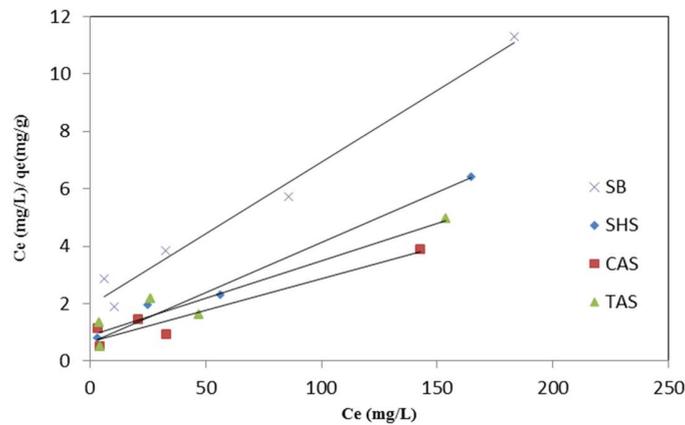
$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_a q_m} \quad (3)$$

where  $C_e$  (mg/L) is the equilibrium concentration;  $q_e$  (mg/g) the amount of cadmium adsorbed at equilibrium,  $q_m$  (mg/g) the adsorption for a complete monolayer;  $K_a$  (L/mg) is the adsorption equilibrium constant. When  $C_e/q_e$  is plotted against  $C_e$  and the data are regressed linearly,  $q_m$  and  $K_a$  constants are calculated from the slope and the intercept. The linear form of the Freundlich isotherm [6] is given by Eq. (4):

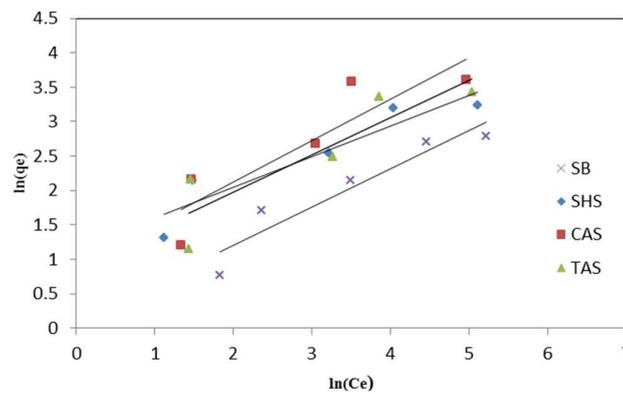
$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

The constant  $K_F$  (mg/g) is related to the adsorption capacity of adsorbents;  $1/n$  is related to the surface heterogeneity. When  $\log q_e$  is plotted against  $\log C_e$ ,  $1/n$  and  $K_F$  can be determined from the slope and intercept [6].

The Langmuir and Freundlich isotherms were plotted as a function of different types of SB, from the Fig. 12 and Fig. 13, the result of both isotherm models (in Tab. 2) calculated the isotherm constants and correlation coefficients. From the result of the Fig. 12 and Fig. 13, the Langmuir model fitted the results better than the Freundlich model ( $R^2 < 0.9$ ) for both phases with the correlation coefficient ( $R^2 = 0.98$  for SHS, 0.91 for CAS and 0.92 for TAS). This result demonstrates the formation of monolayer coverage of cadmium molecule at outer surface of the chemically modified SB.



**Figure 12:** The linear Langmuir model applied on chemically modified SB. SB-unmodified sugarcane bagasse; SHS-sodium hydroxyl sugarcane bagasse; CAS-citric acid sugarcane bagasse; TAS-tartaric acid sugarcane bagasse



**Figure 13:** The linear Freundlich model applied on chemically modified SB. SB-unmodified sugarcane bagasse; SHS-sodium hydroxyl sugarcane bagasse; CAS- citric acid sugarcane bagasse; TAS-tartaric acid sugarcane bagasse

**Table 2:** Parameters of the Freundlich and Langmuir adsorption isotherm for chemically modified SB

Adsorbents	Langmuir			Freundlich		
	$q_m(\text{mg/g})$	$b(\text{L/mg})$	$R^2$	$K_F(\text{mg/g})$	$n$	$R^2$
SB	18.821	0.430	0.901	3.193	2.253	0.877
SHS	29.412	0.052	0.984	3.194	2.252	0.815
CAS	45.453	0.034	0.912	2.511	1.667	0.870
TAS	38.462	0.033	0.925	2.445	1.858	0.791

SB-unmodified sugarcane bagasse; SHS-sodium hydroxyl sugarcane bagasse; CAS-citric acid sugarcane bagasse; TAS-tartaric acid sugarcane bagasse

According to the  $q_m$  values listed in Tab. 2 and from the Langmuir isotherm model, unmodified SB had the lowest adsorption capacities estimated at 18.8 mg/g. Adsorption capacity of Cd (II) depends on physico-chemical properties of the adsorbent’s surface. SHS (29.4 mg/g) had a higher adsorption capacity than SB, which may be explained because of the higher amount of hydroxyl groups or pores structure in

the material after modification. Moreover, bases also increase the adsorption efficiency due to negatively charged hydroxyl anions. Hydroxyl ions charge the surface of the adsorbent negatively, improving the binding between materials and metal ions. Furthermore, pretreatment with base removed residual lignin resulting in the breakdown of fiber bundles into finer filaments, which increase the effective surface area and surface charge [18].

Overall, CAS was found to have the highest adsorption capacity ( $q_m$ ) (45.45 mg/g), followed by TAS with 38.46 mg/g. Carboxyl groups appearing in TAS and CAS play an important role in cadmium adsorption. The more acidic groups present in CAS and TAS, which were found in the FTIR and methylene blue study, enhances the higher adsorption capacity and thus removal efficiency. The higher number of acidic groups in the two types of materials can be explained because base treatment may also increase the number of hydroxyl groups by cracking the crosslinking in the cellulose structure. These new hydroxyl groups as well as the primary hydroxyl groups had appropriate porous in cellulosic fraction to be esterified with citric acid and tartaric acid. In other word, in this treatment stage, some extra carboxyl groups in cellulose may be bound by enriched in hydroxyl, that can further enhance the cation uptake ability of SB [15]. The more carboxyl groups present in the organic acid, the more carboxylic groups can be inserted into cellulose molecules. Based on this assumption, sugarcane bagasse modified with citric acid may be more effective for enhancing the cation exchange capacity than sugarcane bagasse modified with tartaric acid.

From Tab. 2, the  $n$  values from application of the Freundlich isotherm model lie between 1 and 10 indicating that the Cd (II) ions were favourably adsorbed by the biosorbents. The interaction of metal ions and biosorbents was further evaluated by the separation factor ( $R_L$ ).  $R_L$  is a dimensionless constant separation factor, an equilibrium parameter derived from the Langmuir model. The  $R_L$  was defined by Hall et al. (1966) [22] and is expressed in Eq. (5):

$$R_L = \frac{1}{1 + bC} \quad (5)$$

The  $R_L$  values indicate whether the isotherm is favorable ( $0 < R_L < 1$ ), unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ) or irreversible ( $R_L = 0$ ). The  $R_L$  values of all adsorbents onto biosorbents are in the range of 0-1, suggesting that the adsorption of metal ions was favorable.

The maximum adsorption capacity ( $q_m$ ) of SHS, CAS and TAS for Cd (II) was compared with other low-cost adsorbents presented in Tab. 3. The difference in adsorption capacity can be related to the difference in physical and chemical characteristics of the adsorbents. Compared with others, a number of modifying agents have been used to improve the adsorption capacity of agricultural wastes. Sodium hydroxide has been applied on several different materials such as *Juniper fiber*, *Rice husk*, *Saw dust* [23-25] and *Sugarcane bagasse* (in this study). However, these other studies report a different Cd (II) removal efficiency. This may be attributed to the assumption that the surface change and surface morphology were different for different materials. Saw dust modified with NaOH was reported to have the highest adsorption capacity. However, a comparison of the maximum adsorption capacity of CAS and TAS for cadmium with other biosorbents suggests an obvious advantage of the present sugarcane bagasse when chemically modified.

**Table 3:** Comparison of maximum adsorption capacity in various low-cost adsorbents

Adsorbent	Modifying agent(s)	$q_{max}$ (mg/g)	Reference
Modified pine bark	Sodium hydroxide	11.20	[4]
Corn cob	Nitric acid	19.30	[26]
Juniper fiber	Sodium hydroxide	29.54	[23]
	Sodium hydroxide	20.24	[24]
Rice husk	Sodium hydroxide	20.24	[24]
	Sodium hydrocarbonate	16.18	
	Epichlorhydrin	11.12	

Orange peels	Nitric acid	13.70	[27]
Saw dust	Sodium hydroxide	73.62	[25]
Sugarcane bagasse	Sodium hydroxide	29.41	in this study
Sugarcane bagasse	Citric acid	45.45	in this study
Sugarcane bagasse	Tartaric acid	38.46	in this study

### 3.5 Kinetic Studies

The adsorption kinetic data of Cd (II) measured on SHS, CAS and TAS were investigated in terms of pseudo first-order, pseudo-second-order and intraparticle diffusion models. The pseudo first-order equation and the pseudo-second-order Eq. (28) are based on equilibrium adsorption, as given in Eq. (6) and Eq. (7):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (6)$$

where  $q_e$  and  $q_t$  are the amounts of cadmium adsorbed (mg/g) at equilibrium and at time  $t$  (min), respectively and  $k_1$  is the rate constant for adsorption (1/min).

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

where  $k_2$  is the rate constant of second-order adsorption (g/mg.min).

The intra-particle diffusion model was tested to identify the diffusion mechanism. It is an empirically observed functional relationship, common to most adsorption processes, where uptake varies almost proportionally with  $t^{1/2}$  rather than with the contact time  $t$ :

where  $C$  is the intercept,  $k_p$  ( $\mu\text{g/g h}^{1/2}$ ) is the intra-particle diffusion rate constant.

By comparing  $R^2$  in Tab. 4, it is observed that the pseudo-second order model fits the experimental data with higher  $R^2$  values (0.98 to 0.99) than the pseudo-first order  $R^2$  values (0.807 to 0.897). In addition, the values of  $q_e$  obtained from the pseudo second order model are closer to the experimental results than  $q_e$  obtained from the pseudo-first-order model. These results indicate that the adsorption of Cd (II) onto these modified sugarcane bagasses followed the second order kinetic equation. This demonstrates that the cadmium interaction with adsorbent materials was controlled by chemical adsorption.

The intra-particle diffusion model rate constant,  $k_p$  is obtained from the slope of the straight line of  $q_t$  versus  $t^{1/2}$ . The calculated values of  $k_p$  of SB ( $2.66 \text{ mg/g.min}^{1/2}$ ) and CAS ( $2.19 \text{ mg/g.min}^{1/2}$ ) higher than that of SHS ( $1.27 \text{ mg/g.min}^{1/2}$ ) and TAS ( $1.28 \text{ mg/g.min}^{1/2}$ ), which shows that the SB and CAS have more intraparticle diffusion than SHS and TAS. The  $R^2$  values of the intra-particle diffusion model were lower than those obtained from the pseudo-second-order kinetic model.

**Table 4:** Adsorption kinetic model parameters for modified sugarcane bagasse

Parameter	SB	SHS	CAS	TAS
<b>Pseudo first order kinetic model</b>				
$k_1$ ( $\text{min}^{-1}$ )	0.001	0.02	0.004	0.002
$R^2$	0.97	0.81	0.85	0.81
$q_m$	11.88	13.46	29.04	26.18
<b>Pseudo second order kinetic model</b>				
$k_2$ ( $\text{g mg}^{-1} \text{min}^{-1}$ )	0.06	0.003	0.001	0.002
$h_0$ ( $\text{mg}/(\text{g min})$ )	7.93	3.02	2.99	2.88
$R^2$	0.98	0.99	0.99	0.99
$q_m$ (mg/g)	11.36	29.41	47.61	32.25

<b>Intraparticle diffusion model</b>				
$k_p$ (mg/g.min <sup>1/2</sup> )	2.66	1.27	2.19	1.28
$R^2$	0.94	0.90	0.88	0.86

SB-unmodified sugarcane bagasse; SHS-sodium hydroxyl sugarcane bagasse; CAS-citric acid sugarcane bagasse; TAS-tartaric acid sugarcane bagasse

### 3.6 Desorption Study

During desorption, the Cd (II) ions are replaced by H<sup>+</sup> ions from the eluting acid. It is clear seen from Tab. 5 that during desorption, almost all the metal ions adsorbed in SHS, TAS and CAS are replaced by H<sup>+</sup> ions from the eluting acid while in SB, only 30.9% of Cd (II) was desorbed in acid solution. This difference can be explained by the functional groups involved to the cellulose-cadmium ion binding. The lower percentage of desorption is assumed to be related to the lower binding between -COO- and Cd (II). The metal ion removal may be due to phenol groups which cannot be desorbed in acid solution. The higher percentage of desorption in SHS, TAS and CAS indicates a higher amount of hydroxyl groups. This desorbed percentage was also considered satisfactory for a possible re-utilization of the chemically modified SB for new adsorption cycle.

**Table 5:** Desorption of Cd (II) on different materials

Adsorbents	Adsorbed		Desorbed (%)
	(mg/g)	(%)	
SB	19.5	37.0	30.9
SHS	25.1	23.0	71.7
CAS	36.1	33.0	85.5
TAS	31.2	28.0	82.8

SB-unmodified sugarcane bagasse; SHS-sodium hydroxyl sugarcane bagasse; CAS-citric acid sugarcane bagasse; TAS-tartaric acid sugarcane bagasse

### 4 Conclusions

Results from this paper highlight the feasibility of modification of sugarcane bagasse with three types of chemicals, i.e., sodium hydroxide, citric acid and tartaric acid, to enhance the Cd (II) removal efficiency in aqueous solution. Estimation of acid groups in chemically modified SB indicates that modification of cellulose in sugarcane bagasse leads to a generation of carboxyl groups with the largest number of acidic groups was presented in the citric acid modification (1.024 mEq/g) followed by tartaric acid modification contained 1.008 mEq/g acidic groups. The modification was confirmed by Fourier transform infrared spectroscopy, which demonstrates the increase of adsorption sites. The chemical treatment results in an improvement of the adsorbent properties of the studied materials. CAS has the highest maximum adsorption capacities of 45.45 mg/g followed by TAS with 38.46 mg/g and SHS with 29.41 at optimum pH 5.0 and 120 minutes equilibrium time while SB's adsorption capacity is 18.8 mg/g. The surface area of chemically modified SBs was relatively high, with well-developed pores. The equilibrium data were fitted to Langmuir isotherms. The adsorption kinetics was found to follow closely the second-order kinetic model. On the other hand, desorption studies show the high leaching of cadmium ion from the biosorbent leading to the efficient re-utilization of materials.

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## References

1. Pan, J. F., Lin, R. G., Ma, L. (2000). A review of heavy metal adsorption by marine algae. *Chinese Journal of Oceanology and Limnology*, 18(3), 260-264.
2. Pham, T. T., Nguyen, V. A., Van der Bruggen, B. (2012). Evaluation of two low cost-high performance adsorbent materials in the waste-to-product approach for the removal of pesticides from drinking water. *CLEAN-Soil, Air, Water*, 40(3), 246-253.
3. Esalah, J. O., Weber, M. E., Vera, J. H. (1999). Removal of lead from aqueous solutions by precipitation with sodium di-(n-octyl) phosphinate. *Separation and Purification Technology*, 18(1), 25-36.
4. Argun, M. E., Dursun, S., Karatas, M. (2009). Removal of Cd(II), Pb(II), Cu(II) and Ni(II) from water using modified pine bark. *Desalination*, 249(2), 519-527.
5. Canet, L., Iplide, M., Seta, P. (2002). Efficient facilitated transport of lead, cadmium, zinc, and silver across a flat-sheet-supported liquid membrane mediated by lasalocid A. *Separation Science and Technology*, 37(8), 1851-1860.
6. Ayranci, E., Hoda, N. (2005). Adsorption kinetics and isotherms of pesticides onto activated carbon-cloth. *Chemosphere*, 60(11), 1600-1607.
7. Ngah, W. S. W. (2008). Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: a review. *Bioresource Technology*, 99(10), 3935-3948.
8. Świątkowski, A., Szymański, G., Biniak, S. (1996). Adsorption from aqueous solutions of selected heavy metal cations on chemically modified activated carbon. *Fundamentals of Adsorption*, 356, 913-920.
9. Ceribasi, I. H., Yetis, U. (2001). Biosorption of Ni(ii) and Pb(ii) by Phanerochaete chrysosporium from a binary metal system-kinetics. *Water SA*, 27(1), 15-20.
10. Fosso-Kankeu, E., Mittal, H., Waanders, F., Ntwampe, I. O. (2016). Preparation and characterization of gum karaya hydrogel nanocomposite flocculant for metal ions removal from mine effluents. *International Journal of Environmental Science and Technology*, 13, 711-724.
11. Sud, D., Mahajan, G., Kaur, M. P. (2008). Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions-a review. *Bioresource Technology*, 99(14), 6017-6027.
12. Salman, M., Athar, M., Farooq, U. (2015). Biosorption of heavy metals from aqueous solutions using indigenous and modified lignocellulosic materials. *Reviews in Environmental Science and BioTechnology*, 14(2), 211-228.
13. O'Connell, D. W., Birkinshaw, C., O'Dwyer, T. F. (2008). Heavy metal adsorbents prepared from the modification of cellulose: A review. *Bioresource Technology*, 99(15), 6709-6724.
14. Wan Ngah, W. S., Hanafiah, M. A. K. M. (2008). Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review. *Bioresource Technology*, 99(10), 3935-3948.
15. Leyva-Ramos, R., Landin-Rodriguez, L. E., Leyva-Ramos, S., Medellin-Castillo, N. A. (2012). Modification of corncob with citric acid to enhance its capacity for adsorbing cadmium (II) from water solution. *Chemical Engineering Journal*, 180, 113-120.
16. Sèbe, G., Pardon, P., Pichavant, F., Grelier, S., De Jéso, B. (2004). An investigation into the use of eelgrass (*Zostera noltii*) for removal of cupric ions from dilute aqueous solutions. *Separation and Purification Technology*, 38(2), 121-127.
17. Klemm, D., Philipp, B., Heinze, T., Heinze, U., Wagenknecht, W. (2004). Introduction. *Comprehensive Cellulose Chemistry*. Wiley-VCH Verlag GmbH & Co. KGaA.
18. Suradi, S. S., Yunus, R. M., Beg, M. D. H., Yosof, Z. A. M. (2009). Influence pre-treatment on the properties of lignocellulose based biocomposite. *Proceeding of National Conference on Postgraduate Research*.
19. Shukla, S. R., Pai, R. S. (2005). Adsorption of Cu(II), Ni(II) and Zn(II) on modified jute fibres. *Bioresource Technology*, 96(13), 1430-1438.

20. Kamari, A., Yusoff, S. N. M., Abdullah, F., Putra, W. P. (2014). Biosorptive removal of Cu(II), Ni(II) and Pb(II) ions from aqueous solutions using coconut dregs residue: adsorption and characterisation studies. *Journal of Environmental Chemical Engineering*, 2(4), 1912-1919.
21. Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical Society*, 40(9), 1361-1403.
22. Hall, K. R., Eagleton, L. C., Acrivos, A., Vermeulen, T. (1966). Pore- and solid-diffusion kinetics in fixed-bed adsorption under constant-pattern conditions. *Industrial & Engineering Chemistry Fundamentals*, 5(2), 212-223.
23. Min, S. H., Han, J. S., Shin, E. W., Park, J. K. (2004). Improvement of cadmium ion removal by base treatment of juniper fiber. *Water Research*, 38(5), 1289-1295.
24. Kumar, U. B. M. (2006). Fixed bed column study for Cd(II) removal from wastewater using treated rice husk. *Journal of Hazardous Materials*, 129(1-3), 253-259.
25. Memon, S. Q., Memon, N., Shaw, S. W., Khuhawar, M. Y., Bhanger, M. I. (2007). Saw dust-a green economical sorbent for the removal of cadmium(II) ions. *Journal of Hazardous Materials*, 139(1), 116-121.
26. Ramos, R. L. Bernal-Jacome, J. L., Rodriguez, I. A. (2005). Adsorption of cadmium(II) from aqueous solution on natural and oxidized corncob. *Separation and Purification Technology*, 45(1), 41-49.
27. Lasheen, M. R., Ammar, N. S., Ibrahim, H. S. (2012). Adsorption/desorption of Cd(II), Cu(II) and Pb(II) using chemically modified orange peel: equilibrium and kinetic studies. *Solid State Sciences*, 14(2), 202-210.
28. Ho, Y. S., McKay, G. (1998). Sorption of dye from aqueous solution by peat. *Chemical Engineering Journal*, 70(2), 115-124.