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Removal of silica from rice straw by using alkaline hydrogen peroxide solution in a fixed bed column

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Abstract

This paper investigates the efficiency of alkaline hydrogen peroxide (AHP) solution to remove silica from rice straw in a fixed-bed column. Characterization of rice straw was performed by using Fourier transforms infrared spectroscopy (FTIR), and scanning electron microscopy (SEM) techniques. The experiments were operated with different bed heights (12 and 7 cm), influent H_2O_2 concentrations (2, 4, 6, 8 and 10 %) using constant flow rates (2 mL/min) in order to obtain experimental breakthrough curves. The maximum silica removal was observed 3.0575 mg/g at 8% of AHP influent concentration at 12 cm bed depth. To evaluate the column performance, Adams–Bohart model and Thomas model were used. To analyzed the Adams–Bohart and Thomas model parameter the value of rate constant decreases with increase of influent concentration, but increases with increasing the bed depth.

1. Introduction

Rice plant (*Oryza sativa* L.) is normally grown as an *annual plant*, although in tropical areas it can survive as a perennial plant which has rice straw as raw materials. It is a high potential by product from paddy field due to the large production worldwide. Current global production of rice straw is 731 tons simultaneously allocated itself as the second largest crop after wheat [1]. The current uses of rice straw are in burning activity, fertilizer composting, mulching, paper and fuel production, single cell protein and bedding. Subsequently, rice straw can be treated with many ways to use as potential feed for animals [2]. Rice straw is commonly used as replacement for a part of forage ration and becoming a major energy source rather than nutrient source. This is because of the low nutrients content of rice straw as a barrier to be directly feed to animal. The rice straw mainly contains high amount of silica and lignin [3]. Lignin limits the quality of rice straw having a large by degree of ester bonding between lignin and hemicelluloses that can be breakable with chemical treatment such as concentrated alkaline agents. Some chemical treatments are needed to remove lignin for optimum carbohydrate utilization like alkali, steam explosion, grinding ammonium fiber treatment to increase enzymatic saccharification [4]. Silica is the main resistance on ruminal system where degradation process will substitute to silicic acid and silicon dioxide [5, 6]. High content of biogenic silica on the wall of epidermal cell layer which mainly comes from fertilizer application, irrigation and harvest time which can affect the rice straw degradation process during feed fermentation and digestion in animal gut [7]. Normally the level of silica in rice straw is about 8.3% [8] and 9-10%[9] depending on the plant location and other factors. The amount of silica present in different part of rice plant can be specified as 0.5g/ kg of polished rice, 50g/kg for rice bran, 130g/kg for rice straw, 230g/kg for rice hulls and 350g/kg for rice joints [2]. Silica can be applied in solar cells, drug delivery and biomedical field [10]. Comparison with other crops, the difference of silica content depends on the photosynthetic mechanisms of the grass and the amount of water transferred to the grass. Generally, cereal straw contains the high silica level where wheat straw (4-10%), rice straw (9-14%) and other cereals such as barley, oat and rye straw (1-6%) of silica level [11]. Silica is extremely alkali soluble and must be removed from recovery cycle especially in pulping process to avoid the mechanical error. Besides, some other studies conducted shows that the digestibility of roughages can be increase by alkali treatment where the partial solubilization of hemicellulose, lignin and silica takes place [9]. Silica act as a physical barrier which prevent bacterial attachment and inhibit the digestion of plant cell wall containing carbohydrates. To maximize the utilization of carbohydrate and sugar for biofuel and animal feed industries, silica is the key factor which contributes to resistance in degradation of rice straw [5]. Smith *et al*., (1971) reported that digestibility of organic matter decreases approximately 1% with increase in silica content of the forage [12]. In the first step, hemicellulose was solubilized by using Alkaline pretreatment (1% NaOH for 24 h) and in second step lignin was solubilized and oxidized by using alkaline/oxidative (1% NaOH and 0.3% H_2O_2 for 24 h) medium. The pretreatment is also useful in removing waxes, silica, and waterproof cutins that coats the plant tissue [13]. Delignification is not possible without complete removal of silica. This approach can significantly apply to rice straw which contains high level of silica compared to the other forage such as corn and grass.These applications normally applied in biofuel industry. Alkaline hydrogen peroxide performs well in cellulose degradation until 90% of sugar released after treatment process. For rice straw, some sugar like xylose, arabinose increased 53.4% and 16% respectively but glucose level decreased by 20.6% [14]. The result also influenced by original content of sugar in agricultural wastes. The aim of the present work is to assess the performance of fixed bed column for removal of silica from rice straw. The effects of various parameters were inspected, such as column bed depth and influent H_2O_2 concentration using a laboratory scale fixed-bed column. Adams–Bohart, Thomas models and % removal efficiency curves for the adsorption of Silica were examined to investigate the dynamic behavior of the column.

2. Materials and Methods

2.1. Preparation of fixed bed from rice straw

Rice straw was collected from a cultivated area near FELCRA Seberang, Perak, Malaysia. It was thoroughly washed with de-mineralized water (DMW) several times to remove the dirt. Washed material cut into small pieces and placedin an oven at 60 ˚C for 72 h to remove all the moisture content.Dried material was crushed, grounded and sieved to desired mesh size ranges from 500µm – 1mm. Finally, the prepared material was packed in to the column by using compactor with constant weight for the removal of silica

2.2. Characterization of rice straw before and after silica removal

FTIR spectra of rice straw before and after removal of silica contents were recorded using a Thermo Scientific NICOLET 6700 apparatus in the region of 650-4000 cm-1 at a resolution of ± 4.0 cm-1. SEM images were recorded to find the change in the surface morphology of rice straw before and after removal of silica contents by Zeiss SUPRA 55 scanning electron microscope.

2.3. Alkaline Hydrogen Peroxide Solution preparation

Hydrogen Peroxide, H_2O_2 was obtained from QRec^{TM}, ICHEM Solution SdnBhd and used in all pretreatment experimental works. Different concentration of Alkaline Hydrogen Peroxide (2%, 4%, 6%, 8% and 10%) was taken to get the maximum silica removal. Sodium Hydroxide (NaOH) was procured from same supplier and used for pH adjustment up to 11.6 to get the alkaline condition. DMW was used throughout the study.

2.4. Column Procedure

Continuous-flow sorption investigations were operated in a stainless steel column. The column with an internal diameter of 7 and 12 cm in length was used in this work. At the base of column, a 0.5 mm stainless sieve was fixed and pursued by glass wool. In order to provide a uniform inlet flow of the solution into the column, a 7 and 12 cm high layer of rice straw was placed at the column base.

2.5. Experimental procedure

Column was packed with 170 and 200 grams of rice straw to obtain a particular bed height up to 7 and 12 cm of bed depth. pH of column materials was adjusted up to the desired level by adding acid (HCl) and base (NaOH). Constant flow rate of column solution was adjusted by using electronic pump. Varied influent concentrations (0, 2, 4, 6, 8 and 10 %) were passed through the column at a flow rate of 2 mL/min. Effluent was collected at regular time intervals to determine the concentration of silica and it continued until there no further silica dissolution was observed. The adsorption capacity of the rice straw was determined by using the silica concentration in the effluent. UV Visible Spectrometer (GBC AVANTA GF 5000 Model) was used to determine the silica concentration in collected samples at different time intervals.

2.6. Column data analysis

For the evaluation of Sorption column response, two factors are mainly responsible time for breakthrough appearance and the shape of the breakthrough curve [15]. Breakthrough curve is an important parameter to spectacle the performance of fixed-bed column. The breakthrough point was the point where effluent concentration (Ct) from the column was about 0.1% of the influent concentration (C_0). The point of column exhaustion was the point where the effluent concentration reaches 95% [15]. The breakthrough curve was represented by Ct/C_0 as a function of time/volume of the effluent for a given bed depth. The column was analyzed for the adsorption of Silicate ions at various concentrations i.e. 2, 4, 6, 8 and 10%. Bed depth was kept 7 and 12 cm for each concentration. Q was the volumetric flow rate (mL/min), which can be calculated by following equation: [16, 17]

$$V_{eff} = Q\, t_{total} \qquad (1)$$

The value of the total mass of metal adsorbed, q_{total} (mg):

$$q_{total} = Q / 1000 \int_{t=0}^{t=total} C_{ad}\, t \qquad (2)$$

Equilibrium metal uptake or maximum capacity of the column: q_{eq} (mg/g), which can be calculated as the following:

$$q_{eq} = q_{total}/m \qquad (3)$$

where, m was the dry weight of adsorbent in the column (g).

Total amount of adsorbed silica in the column (m_{total}) is calculated using following equation (Kundu and Gupta, 2005) [18]:

$$m_{total} = C_0 Q t_{total} \times 1000 \qquad (4)$$

The % removal of bisilicate ions can be obtained from Eq.

$$\%Y = q_{total} / m_{total} \times 100 \qquad (5)$$

The removal efficiency of bisilicate ions was given by:

$$\%\ \text{Removal efficiency} = C_0 - C_t/C_0 \times 100 \qquad (6)$$

where, C_0 and C_t are the original and residual silica concentrations in solution, respectively.

3. Results and discussion

3.1. Characterization

Surface morphology of rice straw before and after silica removal is shown in Fig.1a and 1b, respectively. As shown in Fig. 1a, the surface of crushedrice straw is boorishand havinggrooves and furrows. After removal of silica with chemical treatment of AHP, the surface of rice straw (Fig. 1b) appears to be highly cave like and porous structure and has been changed which is entirely different from the crude rice straw, authenticating the removal of silica on the surface of rice straw.

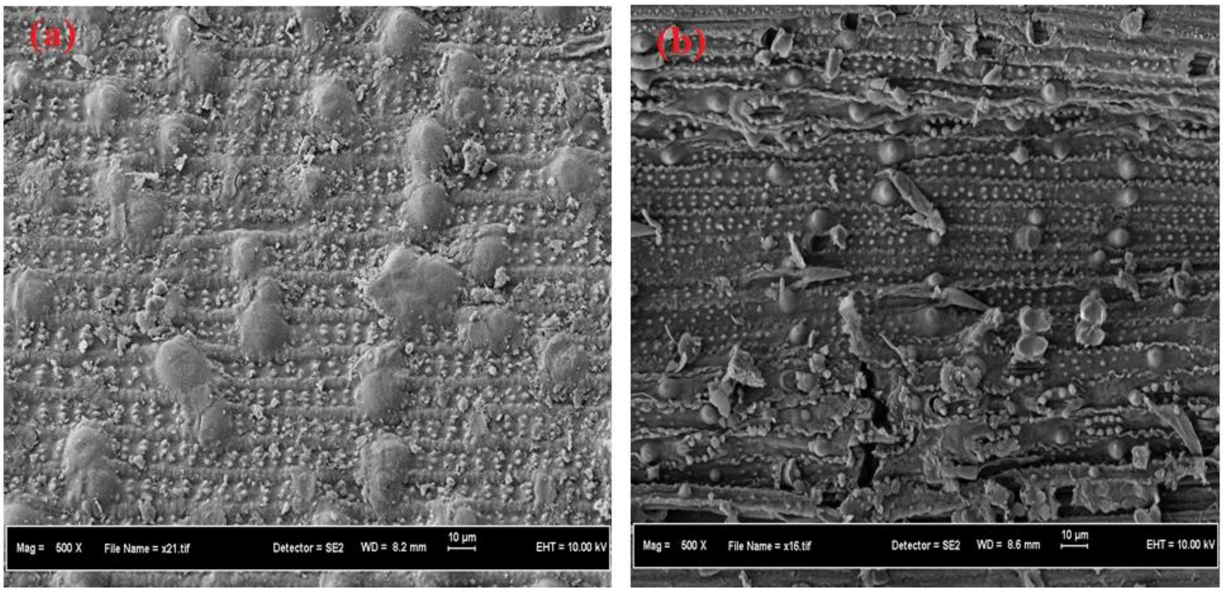


Figure 1. SEM Images of (a) rice straw before silica removal (b) AHPtreated rice straw after silica removal

The FTIR analysis was taken for the qualitative determination of the main functional groups present on the surface of rice straw. The FTIR spectra of rice straw are shown in Fig. 2a and b. The broad band appears around 3327.58 cm^{-1} was mainly ascribed to symmetrical stretching variations of silanol OH groups (SiO–H) and adsorbed water, respectively, whereas the peak appeared at 2918.30 cm^{-1} was assigned to the aliphatic CH groups and sharp band at 2850 cm^{-1} appears due to the C–H stretching. The peak appear at 1637.52 cm^{-1} belonged to H–O–H bending [19]. The peak obtained at 1430.47 cm^{-1} corresponds to the CH_2 bending vibration. The peaks in the region from 1384.61-1319.16 cm^{-1} may be attributed to the O–H bending or C–H bending vibrations. The strong band at 1034.63 cm−1 cm^{-1} is due to Si–O–Si asymmetry stretching which clearly confirms the presence of silica. Two sharp peaks at 789.59 and 719.46 cm−1, assigned to the Si–O symmetric stretching and bending, respectively [20, 21]. From the Fig. 2b, these two peaks are absent which confirmed the removal of silica from the AHP chemically treated rice straw.

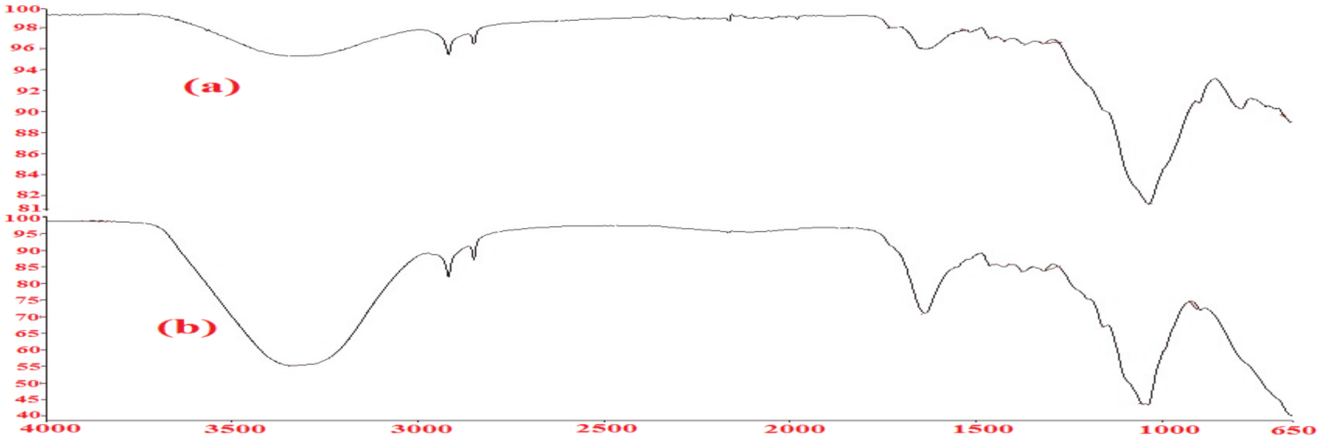


Figure 2. FTIR spectra of (a) rice straw before silica removal (b) AHPtreated rice straw after silica removal

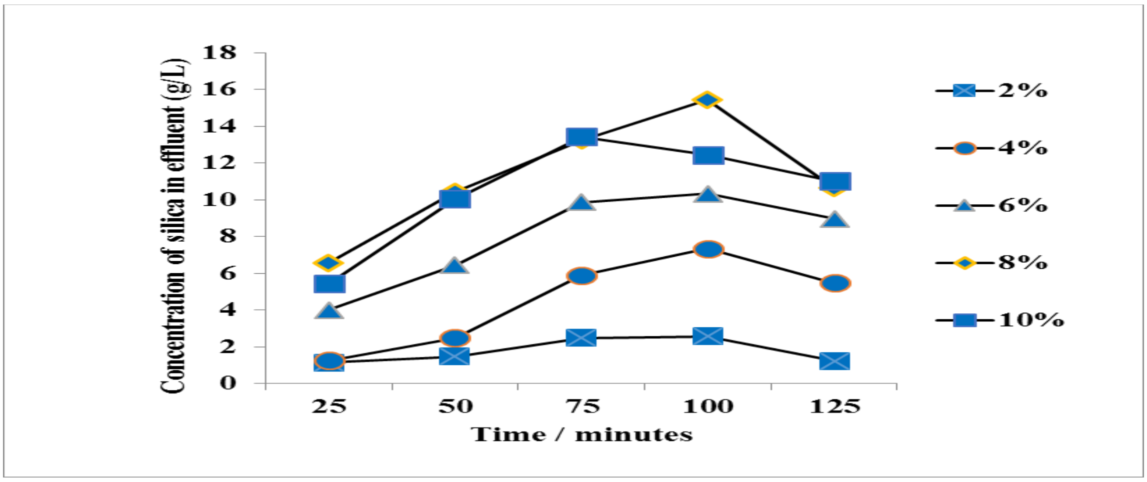
3.2. Effect of AHP concentration on % removal efficiency

The sorption column data and desorption of silica for bed depth of 7 and 12 cm were evaluated and presented in Tables 1.

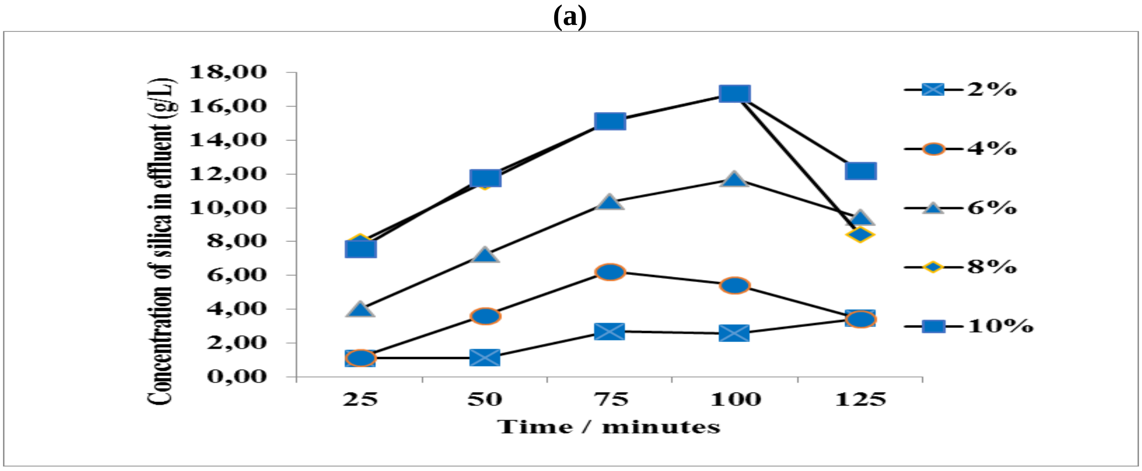
Table 1. Effect of AHP Concentrations on silica removal at 7 cm and 12 cm bed depth

Time/minutes	Concentration of AHP/%				
	2	4	6	8	10
7 cm bed depth					
25	1.143	1.255	3.999	6.577	5.433
50	1.462	2.477	6.433	10.432	10.043
75	2.477	5.877	9.877	13.232	13.423
100	2.556	7.332	10.332	15.432	12.434
125	1.233	5.464	8.976	10.666	11.008
12 cm bed depth					
25	1.09	1.13	4.01	7.99	7.59
50	1.11	3.62	7.23	11.54	11.78
75	2.67	6.24	10.36	15.16	15.13
100	2.57	5.44	11.71	16.75	16.46
125	3.46	3.42	9.43	8.43	12.22

From the Fig 3a and b, it was observed that removal of silica increases with increase in initial concentration of the AHP solution. Due to the availability of more number of hydroxyl ions in the AHP solution, uptake capacity increases with increase in initial concentration. At higher concentration, hydrogen peroxide can act as both proton donor and proton acceptor in one time [22]. Hydrogen peroxide molecules has the ability to form stronger bonds with silicon than water molecules if it acts as proton acceptor, as it provide some hydroxide radicals which enhanced the removal rates. From above discussion, hydroxyl ions may react with silica present in rice straw and forms silicic acid, $Si(OH)_4$. The mechanism shows that $Si\text{-}O^-$ sites will react with –OH sites of AHP to form silicic acid [23]. Silicic acid formation leads to the formation of large number of silicate ion through condensation process. The presence of silicate ions increases the solubility of silica which enhance the removal process. This may be ascribed to high influent concentration contributing higher driving force for the transfer process to overcome hydroxyl ions mass transfer resistance [24]. The maximum removal of RSP was 16.75 g/L at 8 % influent concentration of hydroxyl ions at 12 cm bed depth. These outcomes showed that higher influent concentrations led to higher driving force for mass transfer, thereupon the adsorbent attained saturation more quickly, which brought about reduction of exhaust time and adsorption zone length.



(a)



(b)

Figure 3. Effect of AHP Concentration on silica removal at (a) bed depth 7cm and (b) bed depth 12 cm.

3.3. Effect of contact time on removal efficiency

Effect of contact time was studied for removal of silica from rice straw by varying contact time at different concentrations. Removal efficiency of silica with varying contact time is presented in Fig. 3(a) and (b) at a constant bed depth (7cm and 12 cm, respectively). From the fig 3(a) and (b), it was observed that with increase in time, effluent concentration decreases and removal efficiency increases [25]. The increase in silica uptake capacity with increasing contact time in the fixed bed column may be due to increase in surface area, which provides more binding site for column adsorption [26]. Kumar and Gaur [27] reported that the removal of metal ions onto cynobacteria and found that % metal removal is independent of mat thickness (0.2–1.6 mm), in batch system. Furthermore, higher bed height give higher breaking or exhausting point and get longer time to become saturated. This results in longer contact time between the available active sites of adsorbent and adsorbate. A table 1 shows the removal efficiency of silica. Removal efficiency of silica increases with the increase in mass of adsorbent (rice straw). The outcome affirms that the bed depth (12 cm) provides maximum removal efficiency. Hence, the consecutive studies were carried out with optimized bed depth.

3.4. Breakthrough curve modeling

An outstanding outline of column adsorption process mainly requires prediction of the breakthrough curve for the effluent [28]. Various mathematical models for describing and analyzing the lab scale column studies are mostly used in industrial applications. For predicting the dynamic column behavior, Adams–Bohart, Thomas, Yoon and Wang models were used [29]. To evaluate the breakthrough curve modeling in fixed-bed column, Chen *et al.* investigated the adsorption of hexavalent chromium from aqueous solution onto modified corn stalk [25].

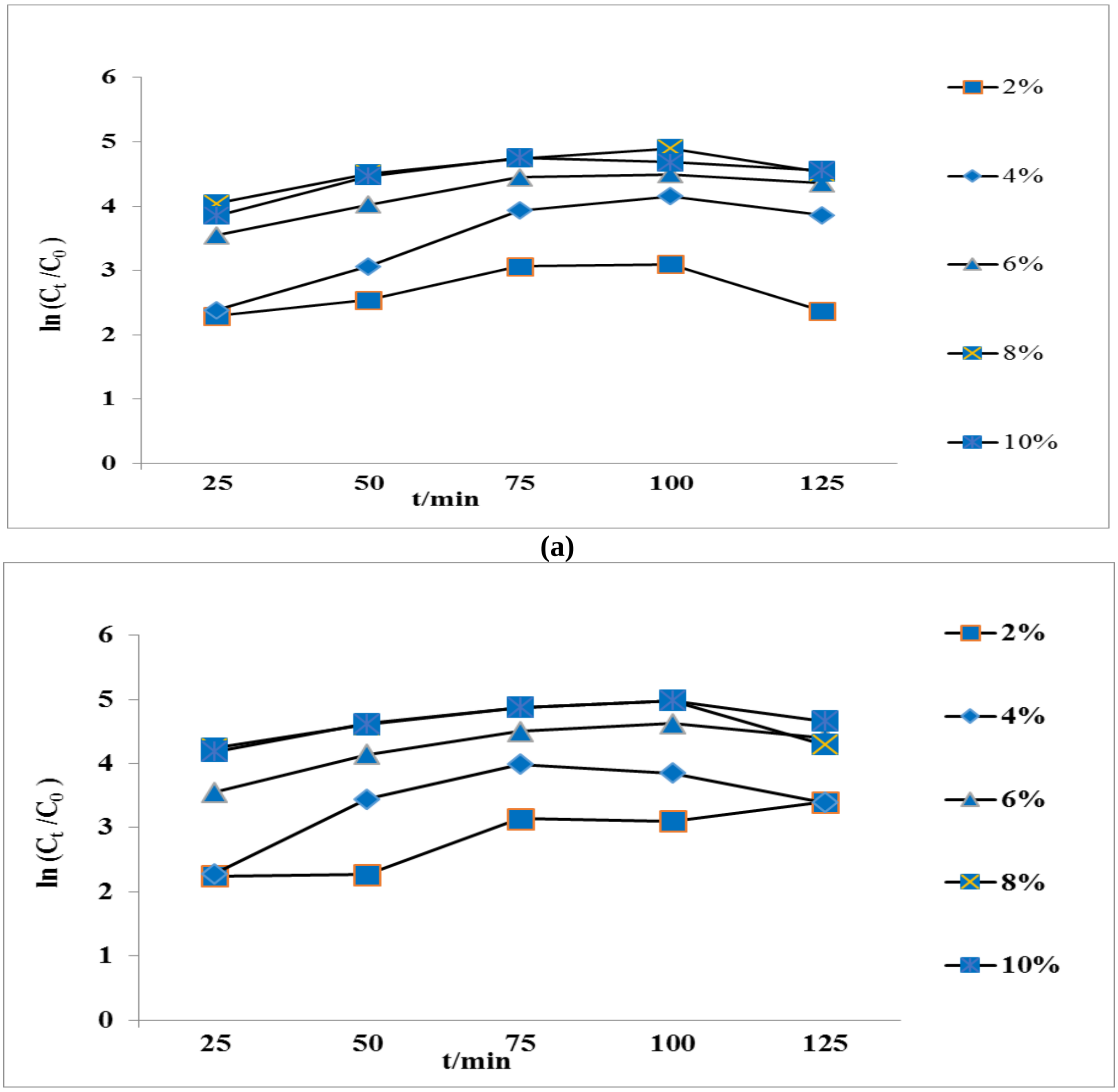
3.4.1. Adams–Bohart model

Bohart and Adams [30] described the relationship between C_t/C_0 and t in a continuous system,which is used for describing the initial part of the breakthrough curve. The expression is as follows:

$$\ln (C_t/C_0) = k_{AB}C_0t - k_{AB}N_0(Z/U_0) \qquad \textbf{(7)}$$

where C_0 and C_t are the influent and effluent concentration (g/L), k_{AB} is the kinetic constant (L/g.min), N_0 is the saturation concentration (g/L), Z is the bed depth of the fix-bed column(cm) and U_0 is the superficial velocity (cm/min) defined as the ratio of the volumetric flow rate Q (cm^3/min) to the cross-sectional area of the bed A (cm^2), k_{AB} and N_0 can be calculated from the linear plot of ln (C_t/C_0) against time (Fig. 4a and b).

As shown in Table 2, the values of k_{AB} decrease with increase of AHP influent concentration, but increases with increasing bed depth. It was demonstrated that the overall system kinetics was controlled by external mass transfer in the initial part of adsorption in the column [31, 32].



(a)

(b)

Figure 4a and b. Adam- Bohart model curve at bed depth 7 and 12cm

3.4.2. Thomas model

Thomas model [33] was considered as most simple and widely used parameter to depict the performance theory of the sorption process in fixed-bed column. The linear equation of this model can be represented as follows:

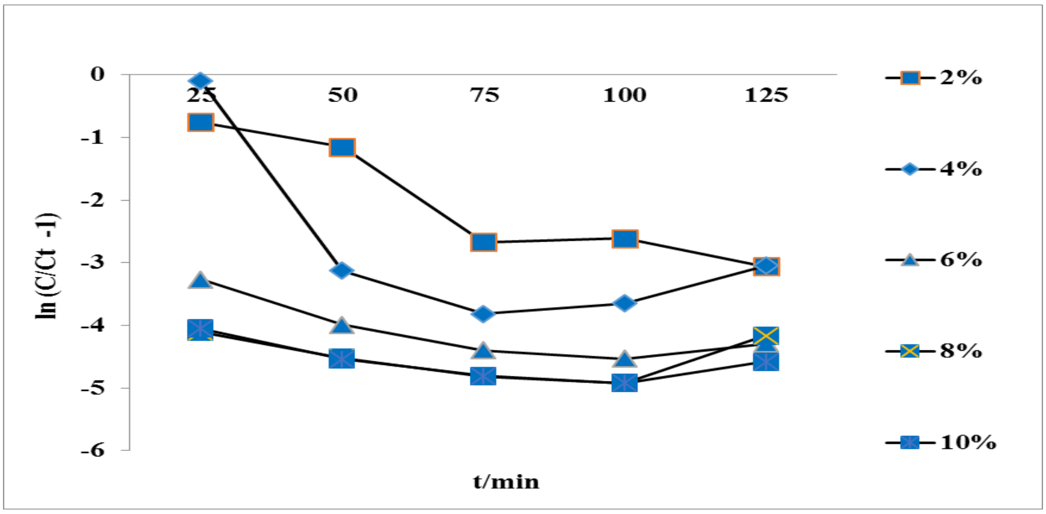
$$\ln (C_0/Ct - 1) = k_{Th}q_0m/Q - k_{Th}C_0t \qquad \textbf{(8)}$$

wherek_{Th} is the Thomas model constant (mL/min/mg), q_0 is the adsorption capacity (mg/g), and t stands for total flow time (min). The values of k_{Th} and q_0 can be determined from the linear plot of ln (C_0/C_t-1) against t (Fig. 5a and b).

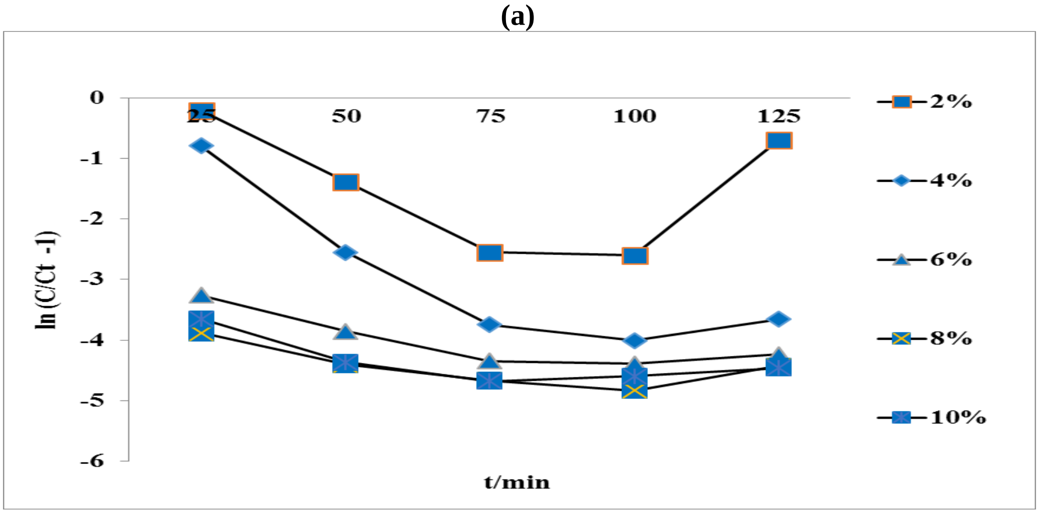
The Thomas model was suitable for adsorption process, which demonstrated that the external and internal diffusions were not the limiting step [34, 35]. From Table 3, it can be seen that with increasing bed depth from 7 cm to 12 cm, the kTh values decreases. The value of kTh decreases with increasing initial AHP influent concentration. It was also because the system kinetics was dominated by external mass transfer. Thus the higher influent concentration and bed depth would increases desorption of Silica in the column.

Table 2. Adam-Bohart model data using different concentration of AHP at 7 cm and 12 cm bed depth.

Concentration (%)	Q (mL/min)	Z(cm)	K_{AB}(mL/g.min)	No(g/L)
7 cm bed depth				
2	2	7	2.7294	0.1976
4	2	7	2.2792	0.3265
6	2	7	1.9003	0.5389
8	2	7	0.4163	3.0575
10	2	7	1.1327	1.0783
12 cm bed depth2	2	12	0.6158	0.6660
4	2	12	3.4926	0.1084
6	2	12	1.8135	0.3259
8	2	12	1.1787	0.5848
10	2	12	1.4102	0.4699



(a)



(b)

Figure 5a and b. Thomas model curve at bed depth 7 and 12cm

Both models indicate that the adsorption rates decreases with increase in the concentration of AHP influent solution, due to limitation of mass transfer which contribute to the slower rate. Same condition was already studied for adsorption of aluminum on BDH activated carbon, which depends on the nature of materials used.

Mass transfer limitation means that decrease of surface diffusion due to limited availability of active sites on bed surface. Particle size must be considered to reduce the mass transfer limitation.

Thomas model is actually based on a derivation from the assumption of second order Langmuir kinetics of adsorption and desorption applied and no axial dispersion considered [36]. Thomas model can be precisely fitted on any adsorption and desorption kinetics and also for mass transfer kinetics [37]. The study conducted by Martinez *et al*. [38], which successfully applied Thomas model for Selenium adsorption and desorption on two non-living biomass of aquatic weeds. Thomas model is widely used to describe the column performance [39] and also based on assumption that the rate of driving force obeys the second order reversible reaction kinetics. Adam Boharts model applied only at the initial part of the breakthrough curve. The weakness of Adam Bohart model is quite similar to Wang and Yoon model [30]. These models assumed that influent concentration of aqueous solution always higher than effluent concentration. But in this study adsorption occurs by the AHP solution which containing low Silica concentration (0.1153 g/L) compared to the silica present in the rice straw bed. Therefore, this assumption is not suitable for these models. Adam Bohart also shows limited capability especially in external mass transfer which control the speed of adsorption.

Table 3. Thomas model data using different concentration of AHP at 7 cm and 12 cm bed depth.

Concentration (%)	Q (mL/min)	Z(cm)	K(mL/min g^{-1})	q$_o$(g/mg)
7 cm bed depth				
2	2	7	5.2645	0.0005
4	2	7	5.5672	0.0017
6	2	7	2.2550	0.0173
8	2	7	0.4553	0.1123
10	2	7	1.2541	0.0389
12 cm bed depth				
2	2	12	1.9003	0.0052
4	2	12	6.2281	0.0015
6	2	12	2.1657	0.0178
8	2	12	1.3226	0.0350
10	2	12	1.6158	0.0276

Conclusions

This work investigated the efficacy of AHP solution to remove Silica from rice straw. Silica removal was carried out under fixed bed column by using the alkaline AHP solution. The highest hydroxyl ion due to AHP solution efficiently removed bisilicate ions which present in the rice straw. Removal of silica through a fixed-bed column depends on the bed depth and AHP influent concentration. The maximum adsorption capacity was found to be 3.0575 mg/g at 8% of AHP influent concentration and at 12 cm bed depth. The Thomas and Adam–Bohart models were successfully applied to anticipate the breakthrough curves, indicating that they were very suited for rice straw column design. This method is considered to be a very simple and economical method for rice straw treatment for biofuel and animal feeds industry. In general, rice straw is an environmental friendly potential biosorbent for heavy metals. But high silica content maybe one of the reasons to choose in this study. However, this work can be considered as an initial study to conclude that AHP having high potential and efficient solution for the adsorption of silica from rice straw.

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