Modified sugarcane bagasse as effective biosorbent for copper ions removal

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Abstract. In this study, sugarcane bagasse (SCB) as a cheap and effective biosorbent was used for copper ions (Cu(II)) removal and modification was performed on SCB with HCl chemical washing and mercerization with strong NaOH in order to improve the removal capability of Cu(II) from aqueous solution. The effects of three influencing parameters including pH, temperature and initial metal ion concentration on Cu(II) adsorption were investigated for both untreated and modified SCB samples (U-SCB, HCl-SCB and M-SCB). The maximum removal efficiency obtained in the experiments was 98.75% for HCl-SCB while M-SCB was 93.1% at pH 5 with an initial metal ion concentration of 10 mg L⁻¹. Four isotherm models including Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherm were used to describe the adsorption process of Cu(II) ions for each SCB sample. Among these four isotherms, the experimental data was best fitted to Langmuir isotherm with R² above 0.95. Based on the Langmuir isotherm, the maximum monolayer adsorption capacity was 0.523, 2.006 and 0.938 for U-SCB, HCl-SCB and M-SCB. It was concluded that the modification performed on SCB with HCl was able to improve the removal efficiency of Cu(II) from 71.6% up to 98.75%.

Keywords: Sugarcane bagasse, Mercerization modification, Chemical washing modification, Biosorption

1. Introduction
In recent years, various treatment processes have been developed in order to remove heavy metal pollutants from aqueous solution, including membrane filtration, adsorption, coagulation and flocculation, etc. These treatments could be conducted independently or in conjunction with other methods, such as chemical precipitation with nanofiltration or ultra-filtration [1]. Among these treatment techniques, adsorption is proven to have better and superior advantages to others in the aspects of versatility and simplicity of process, as well as being cheap and non-hazardous [2]. Recently, the trend of using eco-friendly and biological adsorbent to replace the conventional adsorbent has gaining increased attention as United Nation introduced the 17 sustainable development goals [3]. These bio-adsorbents are mainly produced using agricultural waste and their adsorption properties could be further...
enhanced with proper modification, which makes these biosorbent to be a potential alternative for conventional adsorbent.

In this research, sugarcane bagasse (SCB) was selected as the alternative and potential biosorbent for the heavy metal removal process due to its excellent adsorption capability. Moubarik & Grimi, (2015) reported that SCB was having high copper ion removal efficiency of 96%. From all previous researches, modification of SCB has shown a higher removal efficiency [5]. Hence, SCB was modified in this study and comparative study was conducted to investigate the effect of modification with hydrochloric acid (HCl) and sodium hydroxide (NaOH) on sugarcane bagasse towards the adsorption capacity, and its effectiveness in copper ions removal from aqueous solution. This research was aimed to provide an investigation on the types of modification on SCB and its relationship with each parameter (pH, temperature, initial metal ions concentration). Besides, adsorption isotherms were studied to determine the maximum adsorption capacity and favourability of SCB adsorption.

2. Methodology

2.1. Preparation of SCB as biosorbent

The SCB was boiled in distilled water for 2 hours to remove adhering organic matter and impurities. After boiling, SCB was dried in furnace at 70 °C for 24 hours and until constant weight was obtained. SCB was then shredded into smaller size by using household blender and was blended for 10 minutes at maximum speed of the blender. The SCB sample was then sieved into desired size for the experiment afterwards (<1 mm). The sample was stored in a container and kept in the cabinet where it was shaded and cool for further usage.

2.1.1. Modification of SCB by Hydrochloric Acid and Sodium Hydroxide

5 g of SCB was treated in 500 ml of 0.5M HCl for 2 hours at room temperature with stirring speed of 240 rpm [6]. Treated SCB was then filtered and washed with deionized water until the solution reached the pH value of 7. The treated SCB was then dried in furnace at 85 °C for 24 hours. Dried treated SCB was then stored in a container for further experiments. For mercerization process, similar procedures were applied with the replacement of HCl with NaOH.

2.2. Characterization of SCB samples

All SCB sample (U-SCB, HCl-SCB and M-SCB) was analysed using FTIR analysis. FTIR spectrum for each SCB samples was analysed based on the IR peak.

2.3. Evaluation of SCB performance with Batch Adsorption

The evaluation of SCB adsorption capacity and efficiency under different parameters, i.e. the effect of SCB modification, pH, initial metal ions concentration and temperature was conducted with batch adsorption experiments. Experiments were carried out by preparing copper ion stock solution and the desired concentration was obtained through dilution. After that, 0.1 g of SCB was added to the solution and the mixture was then stirred by using magnetic stirrer under 350 rpm at room temperature for 2 hours. After stirring, SCB was filtered from the mixture and the solution was then analysed using atomic adsorption spectrophotometer (AAS). The experiments were then repeated by varying pH value (3, 5, 9), temperature (40, 50, 60 °C), initial metal ion concentration (10, 30, 50 mg L⁻¹) with different types of modified SCB (U-SCB, HCl-SCB, M-SCB). The copper ion removal percentage was calculated by Eq. (1):
Heavy metal removal (%) = \frac{(C_o - C_f)}{C_o} \times 100\% \tag{1}

where $C_o$ is the initial metal ion concentration in the aqueous solution (mg L$^{-1}$) and $C_f$ is the final metal ion concentration in the aqueous solution (mg L$^{-1}$).

2.4. Adsorption Isotherm

Adsorption isotherm was used to describe the behaviour of adsorbate uptake during equilibrium. The proposed models to describe the adsorption isotherm and to investigate the maximum adsorption capacity are Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm model [6]. Experiment for isotherm was designed with various amounts of adsorbents (0.05, 0.15, 0.2 g) in contact with 30 ml of heavy metal solution (20 mg L$^{-1}$) under pH of 5 in a beaker. The total uptake of heavy metal was calculated using mass balance equation [6] as shown in Eq.(2):

$$q_e = \frac{(C_o - C_f)V}{m} \tag{2}$$

where $q_e$ is the amount of adsorbed heavy metal per gram adsorbent at equilibrium (mg g$^{-1}$) and $C_o$ is the initial metal ions concentration while $C_f$ is the final metal ion concentration. $V$ is the total volume of aqueous solution and $m$ is the mass of adsorbent.

3. Results and Discussion

3.1. Characterization of SCB with FTIR analysis

FTIR analysis was conducted on U-SCB, HCl-SCB and M-SCB used before and after adsorption in order to examine the changes of functional groups during the adsorption process. As shown in Table 1, there was no significant changes on peak-shift observed before and after adsorption, indicating that the adsorption process of Cu(II) ions onto SCB samples has no major effect on the structure of SCB. However, multiple peak shifting was observed in the FTIR spectrum for SCB samples after adsorption. This peak shifting inferred to the interaction of metal ions with the functional group on the surface of the SCB samples. The IR band at 1605 cm$^{-1}$ and 1515 cm$^{-1}$ corresponded to the aromatic skeletal vibration in lignin, while the adsorption band at 1315 cm$^{-1}$ was ascribed to the stretch vibration of C-H in cellulose and Cl-O syringyl derivatives [7]. Besides, the peaks at 835 cm$^{-1}$ was referring to C-H stretching vibration in lignin, while the shifted peak after adsorption indicated the possibility of carboxyl and hydroxyl functional group involved in adsorption process. In other words, both carboxyl and hydroxyl groups were believed to be the main functional groups in binding Cu(II) ions onto the adsorbent [6]. As a result, it was postulated that the mechanisms like ion exchange, electrostatic attraction may be involved in this biosorption process.
Table 1 Major peak-shift in FTIR spectrum for U-SCB, HCl-SCB and M-SCB before and after adsorption

| Adsorbent | Major peak-shift in FTIR spectrum, cm⁻¹ | Corresponding functional groups                        |
|-----------|-----------------------------------------|--------------------------------------------------------|
|           | Before Adsorption | After adsorption |                                                                 |
| U-SCB     | 1604             | 1595             | Aromatic skeletal vibration                                 |
|           | 1512             | 1495             | Aromatic skeletal vibration                                 |
|           | 1315             | 1307             | Stretching vibration of C-H in cellulose                    |
|           | 833              | 827              | Stretching vibration of C-H in lignin                       |
| HCl-SCB   | 1605             | 1596             | Aromatic skeletal vibration                                 |
|           | 1512             | 1519             | Aromatic skeletal vibration                                 |
|           | 1319             | 1310             | Stretching vibration of C-H in cellulose                    |
|           | 831              | 821              | Stretching vibration of C-H in lignin                       |
| M-SCB     | 1605             | 1570             | Aromatic skeletal vibration                                 |
|           | 1513             | 1505             | Aromatic skeletal vibration                                 |
|           | 1314             | 1309             | Stretching vibration of C-H in cellulose                    |
|           | 835              | 815              | Stretching vibration of C-H in lignin                       |

3.2. Evaluation of SCB Adsorption Performance

The adsorption experiments were conducted with different interactive parameters such as pH, temperature and initial metal ions concentration to determine the optimum adsorption condition and efficiency for the removal of copper ion by SCB biosorbent.

3.2.1. Effect of pH

As shown in Fig. 1, the uptake of copper ions by U-SCB at pH 3 was shown to have moderate efficiency at 67.6%, while pH 5 had a slight improvement with 71.2% of adsorption efficiency and a negative trend was observed at a lower removal efficiency (63.2%) when the pH was further increased to 9. In addition, both HCl-SCB and M-SCB also demonstrated the same trends as U-SCB with the copper ion removal efficiency to be the highest at pH 5 and the lowest at pH 9. As for the comparison between the performances of all three SCB biosorbent, the best adsorption performance was shown by HCl-SCB with the removal percentage of 97.85%, 98.25%, and 96.35%, which had outperformed M-SCB with 87.55%, 89.05% and 86.6% at pH 3, 5 and 9, respectively. The findings from this study were in accordance with the study by Khoramzadeh et al. (2013), which showed that the removal efficiency of mercury by SCB was capped at 97.58% at pH 4.0 while further increment of pH did not increase the efficiency.
3.2.2. Effect of Temperature

The effect of temperature on Cu(II) ions removal by SCB was conducted by varying the temperature of solution between 40 °C to 60 °C, while maintaining the initial metal ion concentration for 20 mg L⁻¹, pH at 5.0 and adsorbent dosage for 0.1 g. As illustrated in Fig. 2, the findings showed that adsorption process was slightly affected by temperature for U-SCB, while the effect on HCl-SCB and M-SCB was insignificant. The Cu(II) ions removal efficiency for U-SCB at the range of 40 to 60 °C was 62.95%, 65.95% and 68.80%, respectively. The findings exhibited a proportionate correlation between temperature and adsorption efficiency by U-SCB, which is a typical trend for biosorption of metal ions from their solution [8]. This observation also implied that the adsorption process for U-SCB was endothermic and external heat was required to promote adsorbent-adsorbate interaction [9]. The removal efficiency for HCl-SCB and M-SCB was nearly constant throughout all temperatures tested, which were 97.40%, 97.95% and 97.70% for HCl-SCB, 87.65%, 87.35% and 88.20% for M-SCB, respectively. As the temperature increased, the movement of ions could lead to more heat energy supplied to the solution and this heat energy was transferred to the particles including both ions and adsorbent within the solution. The movement of ions increased rapidly which resulted in the increase of collision between the ions and the adsorbent, contributing to a faster adsorption rate than usual passive adsorption. Hence, the adsorption efficiency was shown to be greater at higher temperature.
3.2.3. Effect of Initial Metal Concentration

Based on Fig. 3, it was found that the removal efficiency for HCl-SCB at 10 mg L\(^{-1}\) reduced from 98.75% to 85.95% when the initial concentration was raised up to 50 mg L\(^{-1}\). Both U-SCB and M-SCB were showing same kind of negative trend, where it decreased from 69.1% to 48.95% for U-SCB and 93.1% to 82.4% for M-SCB when the concentration increased from 10 to 50 mg L\(^{-1}\). Thus, it was postulated that the removal efficiency of Cu(II) ions was inversely proportional to the initial Cu(II) ions concentration. The decreasing trend of adsorption efficiency with increasing initial concentration could be justified with bulk mass transfer of Cu(II) ions at the surface of adsorbent [9]. As the initial concentration increased, the amount of Cu(II) ions in the solution also increased, while the amount of adsorbent remained. Mass transfer driving force increased with the increment of Cu(II) ions, hence the active site of adsorbent could be saturated much faster and the excess metal ions were competing for the limited available active site, thus leading to a slower rate of adsorption [10].

![Fig. 3 Effect of initial ion concentration on copper ion removal efficiency by U-SCB, HCl-SCB and M-SCB](image)

3.3. Adsorption Isotherms

By comparing all isotherm models in this study, the adsorption process for U-SCB, HCl-SCB and M-SCB were best fitted to Langmuir isotherm, where the \(R^2\) for all samples were the highest among all isotherms with the value above 0.95. Based on Langmuir isotherm, the adsorption process for U-SCB, HCl-SCB and M-SCB was highly favourable. The \(q_{\text{max}}\) obtained for U-SCB was 0.523 mg g\(^{-1}\), 2.006 mg g\(^{-1}\) for HCl-SCB, and 0.938 mg g\(^{-1}\) for M-SCB, indicating that the modification on SCB has greatly improved the removal efficiency of Cu (II) ions. Besides, Temkin isotherm was also fitted nicely with the \(R^2\) above 0.8, in which the \(b_T\) computed has further proven that all the adsorption processes by different SCB were endothermic processes.
4. Conclusion
The adsorption efficiency of SCB as alternative biosorbent for copper ions removal was successfully investigated in this study. Two types of modification on SCB were performed with HCl chemical washing and mercerization with strong NaOH to improve the adsorption performance of SCB. Based on the findings, HCl-SCB performed the best among all three samples at pH 5, with the highest removal efficiency of 98.5%. The removal efficiency of U-SCB samples increased as the temperature raised until 50 °C, while further increment in temperature did not show much significant effect. The copper ions removal efficiency also demonstrated a decrease trend with increased initial ion concentration. It was shown that the adsorption process of copper ions was best fitted with the Langmuir isotherm model. Based on the data computed, the maximum adsorption capacity of U-SCB, HCl-SCB and M-SCB was 0.523, 2.006, 0.938 mg g⁻¹. Hence, it was concluded that the modified SCB have further proven its potential as alternative to commercial adsorbent in the wastewater industry.

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