TRENDS IN SCIENCES, 2023; 20(2): 6221 RESEARCH ARTICLE
https://doi.org/10.48048/tis.2023.6221

# Sugarcane Bagasse and Corn Stalk Biomass as a Potential Sorbent for the Removal of Pb(II) and Cd(II) from Aqueous Solutions

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*Received: 9 October 2022, Revised: 15 November 2022, Accepted: 16 December 2022, Published: 20 December 2022*

## Abstract

Heavy metal pollution in the water supply is a serious environmental problem that affects human health around the world. The goal of this study was to investigate the adsorption behaviour of sugarcane bagasse (SB) and corn stalk (CS) biomass for Pb(II) and Cd(II) removal from metal-contaminated water. When the doses of biomass were increased in solutions containing Pb(II) and Cd(II), the SB and CS showed a trend of increasing metal removal efficiency. The removal efficiency of biomass for Pb(II) decreased as the pH of the solution increased from 5.0 to 7.0, with an optimum pH range of 5 to 6. However, pH has little influence on the removal efficiency of biomass for Cd(II). Adsorption equilibrium is reached in about 15 min. Adsorption for at least four cycles improves Pb(II) removal efficiency (up to 98 %) in solutions containing only Pb(II). The best fitness of the adsorption isotherm to Freundlich suggests multilayer adsorption of metal ions onto CS. Higher $q_{max}$ and $K_f$ suggest that SB and CS have a greater affinity for Pb(II) than for Cd(II). Pb(II) adsorption potential was found in biomass derived from SB and CS, but it was less effective as a Cd(II) adsorbent. For application in environmental clean-up, we suggest further study on the structural modification of biomass to enhance its metal removal capacity, the regeneration of biomass for better results, and field trials for practical application.

**Keywords:** Cadmium, Lead, Adsorption, Agricultural residues, Sorbent

## Introduction

Heavy metal contamination is becoming a problem that is of increasing great concern due to its adverse effects on the environment around the world [1]. Toxic heavy metal ions enter aquatic bodies as a result of a variety of human activities, including mining, ore refining, fertiliser industries, tanneries, batteries, paper industries, and pesticides [2]. Among the various heavy metal pollutants, cadmium (Cd), lead (Pb), mercury (Hg), arsenic (As), and chromium (Cr) comprise the 5 priority metals that are of the most public health significance because of their high degree of toxicity [3]. Of these, Cd has the most precarious long-term effects on human health, causing choking, abdominal pain, anaemia, renal dysfunction, and diarrhoea. Cadmium has also been listed as a carcinogen by the US EPA [4]. Cd and Pb are classified as non-essential heavy metals-meaning that they have no established biological functions in the growth, metabolism, or development of different organs in living organisms and are capable of causing death or illness if taken into the body, even at very low concentrations [5,6].

Heavy metals are unique toxicants since they are non-biodegradable and bioaccumulative in nature [1]. Hence, the removal of heavy metals from contaminated wastewater is necessary before discharge. Nowadays, a plethora of physicochemical and biological methods have been used to remove heavy metals from wastewater. Existing treatment techniques include chemical precipitation, ion exchange, adsorption, membrane filtration, reverse osmosis, solvent extraction, coagulation-flocculation, flotation, and electrochemical treatments [7,8]. Many techniques suffer from high capital and operational costs. Among commonly used techniques, adsorption seems to surpass all others in terms of cost-effectiveness, ease of operation [8], reduction of biological and chemical sludge (as secondary waste for further treatment), metal recovery, and adsorbent regeneration [9]. Adsorption is defined as the mass transport of any substance from either a gas or liquid state to a solid surface, which gets bound to it by physical and/or chemical interactions [10]. At present, carbon foam, activated carbon, zeolite, clay minerals, organic polymers, biochar, waste materials (e.g., fly ash, reused sanding wastes, biomass), water treatment residuals, clinoptilolite carbon nanotubes, and manganese oxides are the absorbents that have been employed for heavy metal ion removal

[8-9]. However, the most widely used adsorbents are relatively expensive. For this reason, searching for low-cost alternatives for adsorbents is of research interest.

Agricultural waste materials seem to be potential biosorbents for sequestering heavy metal ions from aqueous solutions because of their being economical and eco-friendly. Agricultural by-products, particularly those containing cellulose, show potential metal biosorption capacity [2]. Currently, there are extensive studies to assess various types of low-cost agricultural waste materials, either in their natural form or after physical or chemical modification, for sequestering heavy metals. Examples of agricultural waste that can be used for adsorption applications include rice husks [11], peels of jackfruit [12], ground shells of hazelnut and almond [13], sawdust [14], tea waste [15], activated weed (*Salvinia cucullata*) carbon [16], coconut husks [17], bagasse, paddy husk, corn cob, wheat bran, peanut skin, and human hair [18], bamboo activated carbon [19], modified corncobs [20], and modified cassava waste [21], lemon peel [22], durian peel [23], and coconut coir [24].

Thailand is one of the world's leading agricultural producers. A large amount of agricultural waste is generated every year. The use of fire to clear land to remove excess biomass is widespread in Thailand, causing the premature death of approximately 32,200 people in 2019 [25]. Treating agricultural waste as non-waste serves national interests, reduces agricultural waste, reduces greenhouse gas emissions, and lowers healthcare costs, and reduces economic losses from morbidity and mortality imposed by PM2.5 emissions due to agricultural leftover burning [25]. Sugarcane bagasse (SB) and corn stalk (CS) agricultural waste were selected in this study because both are readily available and abundant. The purpose of this research is to determine whether SB and CS can be used as adsorbents to remove Cd(II) and Pb(II) from contaminated water under different conditions such as biomass doses, pH, contact time, and adsorption cycles. Finding suitable adsorbent materials for purifying available, unsafe water is not easy and remains a challenge. Possibly, SB and CS might become good alternatives and environmentally friendly options in water filtration and purification systems in rural areas.

## Materials and methods

### Raw materials and biomass preparation

After being collected from agricultural farms in Kamphaeng Saen District, Nakhon Pathom Province, SB and CS (without leaves and leaf sheath) were cut into pieces approximately 5 - 10 cm long. The raw materials of SB and CS were washed thoroughly 3 - 4 times with distilled water, dried at 70 °C in an oven for 5 days, and ground into fine particles with the help of an electric grinder. The grounded particles were filtered through a sieve with a size of 500 microns in diameter, after which they were stored in a zip-lock plastic bag and preserved in a desiccant jar for subsequent studies in experiments I - IV.

### Experiment I: Influence of the types of biomass and their doses

The test for binary solutions containing Pb(II) and Cd(II) ions was prepared in conical flasks by dissolving $Pb(NO_3)_2$ (Ajax Finechem) (prepared to be 1,000 mg Pb/L stock solution) and $CdCl_2{\cdot}2.5H_2O$ (Ajax Finechem) (prepared to be 1000 mg Cd/L stock solution) in deionized water in triplicate for each concentration (mg/L): 0 Pb + 0 Cd (control), 0 Pb + 0.7 Cd, 0 Pb + 1.4 Cd, 0 Pb + 2.8 Cd, 6 Pb + 0 Cd, 6 Pb + 0.7 Cd, 6 Pb + 1.4 Cd, 6 Pb + 2.8 Cd, 12 Pb + 0 Cd, 12 Pb + 0.7 Cd, 12 Pb + 1.4 Cd, 12 Pb + 2.8 Cd, 24 Pb + 0 Cd, 24 Pb + 0.7 Cd, 24 Pb + 1.4 Cd, 24 Pb + 2.8 Cd. The pH of each solution was adjusted by adding 1 M HCl (Merck) and 1 M NaOH (Merck). To screen for the optimum concentrations of a mixture of Pb(II) and Cd(II) solutions for maximum removal efficiency by SB and CS, 0.5 g (1 % w/v) of biomass was added individually into each 50 mL solution containing Pb(II) and Cd(II) in a conical flask. In a conical flask, 50 mL of an aqueous solution containing Pb(II) and Cd(II) was used as a control to see if heavy metal ions in the aqueous solution precipitated or not. All flasks of the treatment and control were shaken simultaneously using a rotatory shaker at a speed of 120 rpm for 60 min at 25 ± 2 °C. Then, 15 mL of each mixture of Pb(II) and Cd(II) was transferred to a centrifuge tube, centrifuged at 5000 rpm for 5 min, and filtered out precipitates with Whatman No. 42 filter paper (washed with 2 % nitric acid for 1 min before usage). Finally, the filtrate was collected for analysis of residual heavy metal content with a Flame Atomic Absorption Spectrophotometer (FAAS) (PerkinElmer, AAnalyst 200). The experiment was repeated using 1.0 g (2 % w/v) and 2.0 g (4 % w/v) of the biomass, respectively.

### Experiment II: Influence of the solution pH

In this experiment, we chose a mixture of 6 mg/L Pb(II) and 0.7 mg/L Cd(II) solution as the test solution (with a dose of 4 % w/v biomass) because this concentration showed the optimum removal efficiency in experiment I. The test solution was prepared in conical flasks in triplicate for each pH value i.e., 5.0, 5.5, 6.0, 6.5, and 7.0. To find the optimal solution pH, we added 2.0 g (4 % w/v) of SB and CS separately into every 50 mL of different solution pH in a conical flask. After the biomass was added, all flasks of a mixture of Pb(II) and Cd(II) solution were shaken simultaneously on a rotatory shaker at a speed of 120 rpm for 60 min at ambient temperature. Then, 15 mL of each mixture of Pb(II) and Cd(II) solution was transferred to a centrifuge tube, and centrifuged at 5000 rpm for 5 min, after which the precipitates were filtered out with Whatman No. 42 filter paper (washed with 2 % nitric acid for 1 min before usage). Finally, the filtrate was collected for analysing of the residual heavy content with FAAS.

### Experiment III: Influence of the contact time of biomass

To test the influence of contact time on metal removal efficiency, we chose a dose of 2.0 g (4 % w/v) of SB and CS for this experiment because this dose gave the optimum metal removal efficiency based on experiment I. The mixture of 6 mg/L Pb (II) and 0.7 mg/L Cd (II) solutions were prepared in conical flasks in triplicate for each contact time, i.e., 5, 15, 30, 45, 60, 75, and 90 min, with pH adjusted to 6.0. First, we added each type of biomass separately into every 50 mL of the mixture of Pb(II) and Cd(II) solution at different contact times in a conical flask. After each biomass was added, all flasks of a mixture of Pb(II) and Cd(II) solution were shaken simultaneously using a rotatory shaker at a speed of 120 rpm at ambient temperature. The agitated samples were collected at 5, 15, 30, 45, 60, 75, and 90 min of contact. Then, 15 mL of each mixture of Pb(II) and Cd(II) solution was transferred to a centrifuge tube, and centrifuged at 5000 rpm for 5 min, after which the precipitates were filtered out with Whatman No. 42 filter paper (washed with 2 % nitric acid for 1 min before usage). Finally, the filtrate was collected for analysing of the residual heavy metal content with FAAS.

### Experiment IV: Influence of adsorption cycles

To investigate the effect of the number of adsorption cycles on metal removal efficiency, the residual heavy metal solution filtrate from the earlier cycle of adsorption was used as the starting heavy metal concentration for the next cycle of adsorption. Due to SB and CS demonstrating the most suitable adsorbent for Pb removal from the first 3 experiments, a single solution of Pb(II) was used for testing the influence of adsorption cycles on removal efficiency. In the first cycle of adsorption, 24 mg/L Pb(II) solutions were prepared in conical flasks in triplicate, with pH adjusted to 6.0. Then, 6.0 g (4 % w/v) of SB and CS were added separately into every 150 mL of the Pb(II) solution in a conical flask. After adding SB or CS biomass, all flasks of Pb(II) solution were shaken simultaneously using a rotatory shaker at a speed of 120 rpm for 15 min (optimum adsorption time from experiment III) at ambient temperature. Later, the Pb(II) solution mixed with biomass was collected and divided into 2 batches. The first batch of the mixture (10 mL) filtered out the precipitates with Whatman No. 42 filter paper, and then the filtrate was collected for analysis of the residual Pb(II) content with FAAS. The second batch or the remaining mixture was filtered with Whatman No. 1 (washed with 2 % nitric acid prior to usage) in a Büchner funnel, and then the filtrate was measured in its remaining volume and transferred to a new conical flask for use as the starting Pb(II) solution in subsequent cycles of adsorption. To keep the biomass constant at 4 % w/v in every cycle of adsorption, the new weight of biomass added in the subsequent cycles of adsorption was varied depending on the remaining volume of the solution filtrate from the earlier filtration through the filter paper No. 1. All the steps as explained in the first cycle of adsorption were repeated 6 times. Using the same standard concentration curve, the final filtrate from each cycle of adsorption was analysed for residual Pb(II).

### Calculation method of removal efficiency

The removal efficiency of heavy metals was calculated from the initial and final concentrations of heavy metals calculated according to Ayub *et al*. [26] by using the following formula (1):

$$\text{Removal efficiency (\%)} = \frac{(C_i - C_e)}{C_i} \times 100 \qquad (1)$$

where $C_i$ and $C_e$ are the initial and equilibrium concentrations (mg/L) in the solution, respectively.

### Isotherm model

Adsorption isotherms are used to describe the relationship between the amount of the adsorbate (metal ions) adsorbed by the SB and CS biomass ($q_e$) and the concentration of the residual adsorbate in the aqueous solution after the system reaches equilibrium concentration ($C_e$) at a constant temperature. The equilibrium adsorption experiments were carried out with binary solutions containing Pb(II) and Cd(II) at initial metal concentrations ($C_i$) ranging from 6 to 24 mg/L Pb(II) and 0.7 to 2.8 mg/L Cd(II), with 2 g of biomass in

50 mL of solution and pH of 6. The adsorption capacity ($q_e$) at equilibrium was calculated according to Ayub *et al*. [26] by using the following expression (2):

$$q_e = \frac{C_i - C_e}{W} \times V \tag{2}$$

where $q_e$ is the adsorption capacity (mg/g), $C_i$ and $C_e$ are the initial and equilibrium concentrations (mg/L) of metal ions, respectively. V and W represent the solution volume (L) and mass (g) of the adsorbent, respectively.

The data derived from the adsorption of heavy metal ions were modelled using Langmuir and Freundlich isotherms to explain the equilibrium adsorption characteristics by using the following expression:

The Langmuir's isotherm (3):

$$\frac{1}{q_e} = \frac{1}{K_L q_{max}} \cdot \frac{1}{C_e} + \frac{1}{q_{max}} \tag{3}$$

where $q_{max}$ is the maximum adsorption capacity (mg/g) and $K_L$ (L/mg) is the Langmuir's isotherm constant (the binding affinity between metal ions and adsorbent).

The Freundlich's isotherm (4):

$$\text{Log } q_e = \text{Log } K_f + \frac{1}{n}\text{Log}C_e \tag{4}$$

where $K_f$ represents the Freundlich's constant and the adsorption capacity, and 1/n is the adsorption intensity (favorable adsorption process: $0.1 < 1/n < 0.5$ and unfavorable adsorption process: $1/n > 2$).

### Statistical analyses

The experiment was set up in replicates, and all data were the means of triplicate (n = 3). The removal efficiency was subjected to full factorial ANOVA followed by Fisher's Least Significant Difference (LSD) at a significance level of 0.05. Statistical analyses were performed using SPSS Version 18.0 Statistical Software Package (SPSS Corporation).

## Results and discussion

Factors influence metal ion sorption, including the nature of the biosorbents, the pH of the solution, the nature of metal ions [27], temperature, surface area to volume ratio, biomass concentration, initial metal ion concentration, and metal affinity to biosorbent [28]. In this study, biomass was used for the removal of Pb(II) and Cd(II) ions from binary and single solutions. The effect of different parameters, such as types of biomass and their doses, initial concentrations of metal aqueous solution, solution pH, contact time, and adsorption cycles, on the removal efficiency of the biomass was evaluated.

### Influence of the types of biomass and their doses

Overall, SB and CS showed a trend of increasing metal removal efficiency when increasing the doses of the biomass (Figs. not shown). We only used 2 optimum concentrations of binary solutions containing Pb(II) and Cd(II) in this experiment: low initial concentrations (6 mg/L Pb + 0.7 mg/L Cd) and high initial concentrations (24 mg/L Pb + 2.8 mg/L Cd), with 3 biomass doses of 1, 2 and 4 % w/v. The metal removal efficiencies of SB and CS for Pb(II) and Cd(II) removal from binary solutions at low and high initial concentrations are shown in **Figure 1**.

In binary solutions, CS removed more Pb(II) than SB in all doses of biomass at low and high initial concentrations (except at 2 % w/v) (**Figures 1(A)** and **1(C)**). CS had no greater removal efficiency than SB for Cd(II) at low metal concentrations, but at high initial concentrations, CS adsorbed Cd(II) better than SB in all doses of biomass (except at 2 % w/v) (**Figure 1(D)**). When the removal efficiency of CS at low and high initial metal concentrations was compared using a 4 % w/v dose of biomass, CS at low metal concentrations removed more metal than CS at high metal concentrations for Pb(II) (79 % vs. 69 %) and Cd(II) (34 % vs. 29 %), respectively. SB performed better at low metal concentrations than at high metal concentrations for Pb(II) (65 % vs. 40 %) and Cd(II) (24 % vs. 23 %), respectively (**Figure 1**).

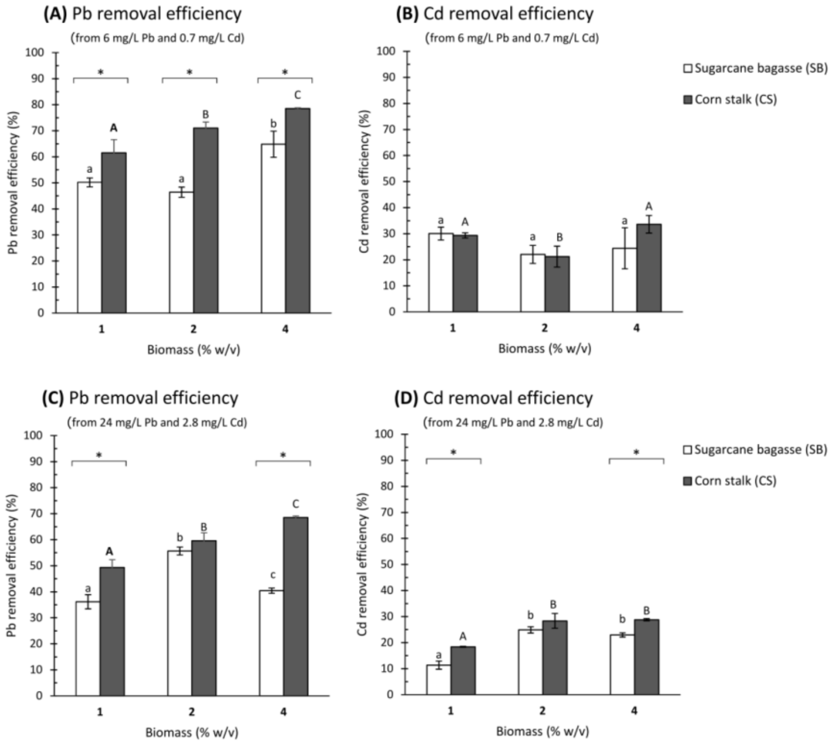


**Figure 1** Comparison of metal removal efficiency of SB and CS from the binary solutions at pH 6 and an adsorption time of 60 min. The lowercase letters showed a statistically significant difference ($p < 0.05$) when different dosages of SB were used (ANOVA followed by LSD); the uppercase letters showed a statistically significant difference ($p < 0.05$) when different doses of CS were used (ANOVA followed by LSD); *****The mean values were statistically different ($p < 0.05$) by using a t-test.

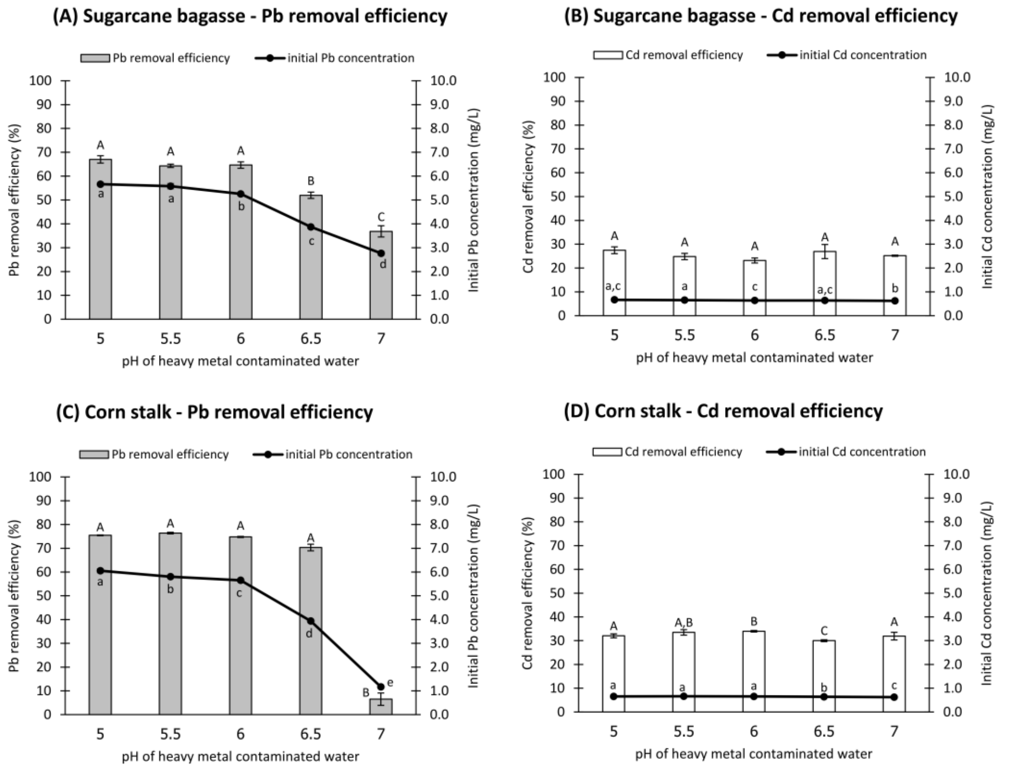
Biosorption is a highly efficient and selective process that takes place regardless of cellular metabolism [29]. The process of metal biosorption typically requires a solid adsorbent that can bind metal ions by physical attractive forces, ion exchange, or chemical binding [30]. Agricultural waste, including SB and CS, contains abundant cellulose and is a well-known low-cost adsorbent of toxic pollutants [31-33]. SB is typically composed of cellulose (40 - 50 %), hemicellulose (25 - 35 %), and lignin (15 - 35 %), whereas CS contains cellulose (35 - 50 %), lignin (5 - 34 %), and petosan (20 - 41 %), according to Akhgül *et al*. [34]. The pollutant removal capacity of biosorbents relies not only on their chemical composition but also on their morphological organisation [35]. The irregular structure and the different levels of porosity in the sorbent materials help to facilitate the biosorption of heavy metal ions [36]. Overall, CS demonstrated better removal efficiencies for Pb(II) and Cd(II) than SB. This suggests that CS contains a higher proportion of cellulose and other functional groups (i.e., acetamido groups, carbonyl, phenolic, polysaccharides, amine, carboxyl groups, and esters) to promote metal chelation [2] or a more adsorptive surface in its biomass than SB. A high number of hydroxyl groups contained in cellulose can provide binding sites for heavy metal ions during the adsorption process. However, such an interaction between hydroxyl groups and heavy metal ions is rather weak [37]. To enhance adsorption ability, specific functional groups should be introduced onto the adsorptive surface of the biosorbents before their application in removing heavy metal ions from wastewater, together with an increase in biomass doses.

### Influence of the solution pH

The different pH values of binary solutions had an effect on the removal efficiency of Pb(II) and Cd(II) by SB and CS, as well as the initial metal concentration, in our study. **Figure 2** sums up the effect of the pH values from weakly acidic to neutral solutions (i.e., 5.0, 5.5, 6.0, 6.5, 7.0) containing 6 mg/L Pb and 0.7 mg/L Cd (low concentrations of metal solution) on the metal removal efficiency of 4 % w/v biomass. In general, the Pb(II) removal efficiency of SB and CS and initial Pb(II) concentration decreased with an increase in the solution pH (Figs. 2A and C), whereas an increase in the solution pH had a slight impact on Cd(II) removal efficiency and initial Cd(II) concentration that is to say, an increase in the solution pH did not result in higher Cd(II) removal efficiency of either type of biomass (**Figures 2(B)** and **2(D)**).

The optimum pH value for the maximum removal efficiency for Pb(II) by SB and CS was the same at pH 5 - 6 (**Figures 2(A)** and **2(C)**). SB had removal efficiencies of 65 % for Pb(II) and 25 % for Cd(II) at pH 5 - 6, whereas CS had removal efficiencies of 76 % for Pb(II) and 33 % for Cd(II) at pH 5 - 6.

The removal of metal ions from the aqueous solution by adsorption depends on the pH of the solution as it affects the surface charge of the adsorbent, the degree of ionization, and the chemical properties of the adsorbent [38]. In this study, it was seen that SB and CS exhibited a pH-dependent binding trend from pH 5 - 7 with optimum binding occurring around pH 5 - 6. The maximum removal efficiency for Pb(II) was at low pH (pH 5) and the lowest removal efficiency for Pb(II) was at high pH (pH 7) (**Figures 2(A)** and **2(C))**. By contrast, SB and CS did not exhibit any different removal efficiency for Cd(II) at all when the solution pH changed and remained steadily lower than that for Pb(II) throughout the experiment (**Figures 2(B)** and **2(D)**). The adsorption of Cd ions behaves as pH-independent like some other metal ions such as $Ag^+$ and $Hg^{2+,}$ and $AuCl^{4-}$ that form a strong covalent complex with biosorbents, with minimal effect on pH [39].


**(A) Sugarcane bagasse - Pb removal efficiency**

**(B) Sugarcane bagasse - Cd removal efficiency**

**(C) Corn stalk - Pb removal efficiency**

**(D) Corn stalk - Cd removal efficiency**

**Figure 2** The influence of pH in the mixed metal solutions on the metal removal efficiency and initial metal concentration from the binary solutions containing 6 mg/L of Pb and 0.7 mg/L of Cd by 4% w/v SB (A and B) and CS (C and D), with a 60-min absorption time. The data were plotted by using Mean ± SD (n = 3); The different lowercase letters indicate a significant difference in initial metal concentrations ($p < 0.05$) according to the LSD test; The different uppercase letters indicate a significant difference in metal removal efficiency ($p < 0.05$) according to the LSD test.

Overall, metal adsorption by biosorbents increases with an increase in solution pH to pH 6 [38,40]. At low pH, there is a high concentration of $H^+$, which has high mobility with respect to metal ions, and competition between $H^+$ and metal ions reduces its adsorption. On the other hand, adsorption also increases as the solution pH rises due to a lower number of $H^+$ and a greater number of surface ligands with negative charges [41]. This trend seems to be counter to our finding where the maximum removal efficiency was seen at a low solution pH but similar to the result reported by Jalali and Aboulghazi [42] that showed the optimum pH for the maximum Pb and Cd adsorption was 5. It means that, outside the optimum range of pH, metal removal efficiency is lower. A plausible explanation is that the solubility of metal in a solution decreases with increasing pH, resulting in fewer free metal ions for adsorption due to metal precipitation [43]. To meet optimal treatment efficiency, the pH of metal-contaminated water adjusted to 5 or 6 needs to be adjusted back to the pH of most usable water, which is somewhere between 6.5 and 8.5 [44] when applied in practice.

**Influence of the contact time of biomass**

The influence of different contact times of SB and CS on removal efficiency for Pb(II) and Cd(II) at a dose of 4 % w/v is shown in **Figure 3**. Once again, SB and CS were confirmed to have higher Pb removal efficiency than Cd removal efficiency across different contact times (**Figures 3(A)** and **3(B)**). In general, SB shows a steady removal efficiency for Pb(II) across different contact times (**Figure 3A**); a significant increase in removal efficiency for Cd(II) was seen at 15 min, then remained steady until 75 min, and finally gained its highest peak at 90 min (**Figure 3(A)**). By contrast, CS showed an increasing trend of removal efficiency for Pb(II) when contact time increased (15 - 60 min) and an increasing trend of removal efficiency for Cd(II) when contact time increased (15 - 60 min), which then started to decrease in terms of removal efficiency for Cd(II) at 75 - 90 min (**Figure 3B**).

The pattern of contact time analysis most often shows the increased removal of heavy metals at the beginning of the process. This is caused by physical adsorption or ion exchange that occurs on the surface of the solid adsorbent. In the early stages, there are fewer vacancies for binding metal ions on the surface, and more free-binding sites are available before they diminish and stagnate [45]. In this study, the saturation curves were attained shortly after the initial stage (ca. 15 min) of adsorption for Cd(II) by SB (**Figure 3A**) and Pb(II) and Cd(II) by CS (**Figure 3(B)**), suggesting that there is a limited number of active sites available for metal binding by biomass surface. In this study, a contact time of 15 min was the optimum time duration when applying SB and CS to Pb(II) and Cd(II) removal from metal-contaminated water. Exceeding the optimum contact time is required for the maximum removal of contaminants, although it leads to a slow decrease in removal efficiency [35]. In most cases, the adsorption rate is fast at first and steadily slows down when equilibrium is reached [46]. Saeed *et al.* [47] demonstrated the 2-stage removal mechanism of metals from aqueous solutions using papaya wood as a biosorbent - the first phase is fast and quantitatively predominant, and the second is the slowest and quantitatively insignificant. In general, the coexistence of multiple metals affects the biosorption efficiency of single metals - meaning that the competition between metal species can reduce their tendency to be adsorbed on the adsorbent [42].

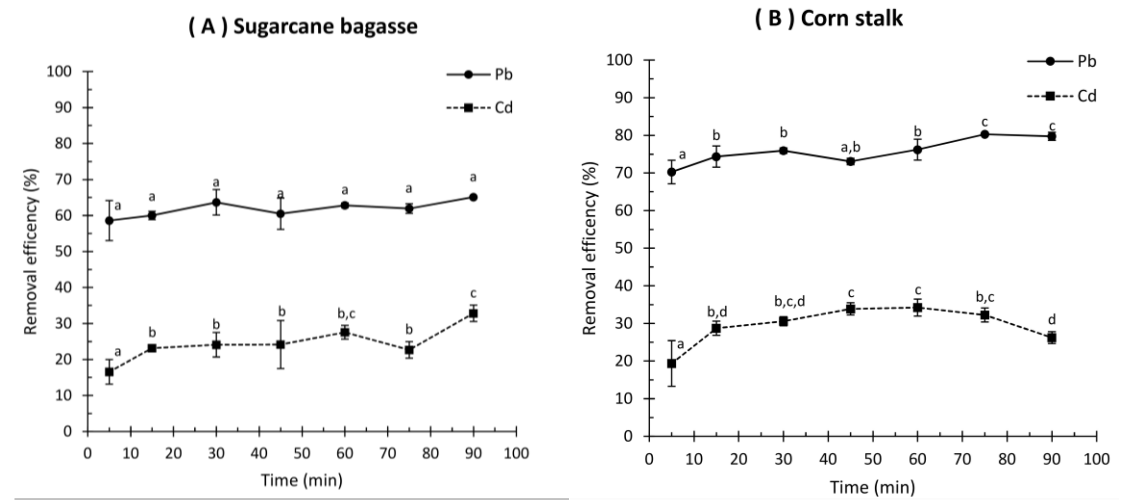


**Figure 3** Removal efficiency versus different contact times by 4% w/v SB (A) and CS (B) biomass from binary solutions containing 6 mg/L of Pb and 0.7 mg/L of Cd at pH 6. The different lowercase letters indicate a significant difference ($p < 0.05$) in metal removal efficiency among different contact times according to the LSD test. Data were presented by using Mean ± SD (n = 3).

**Influence of adsorption cycles**

The removal efficiency of Pb(II) from a single solution by SB and CS biomass as a function of the number of adsorption cycles is shown in **Figure 4**. It is evident that SB and CS exhibit a similar curve of removal efficiency for Pb(II) by a new biomass sample after 6 cycles of adsorption. The removal efficiency for Pb(II) by SB and CS increased rapidly at first, then gradually throughout the experiments. The selective adsorption of Pb(II) onto the surface of SB and CS biomass increased, with more than 90 % completed over 4 successive cycles for 1 h (15 min × 4 cycles). At the end of 6 successive cycles, Pb ions were removed from the single solution by up to 98 % (**Figure 4**). Adding new biomass instead of reusing the old biomass in a mixture of metal solution and biomass over successive cycles of adsorption helps provide more binding sites for the residual metal ions. Once the saturation of the available active sites for binding pollutants is reached, the chance of collisions between adsorbent and adsorbate is decreased.

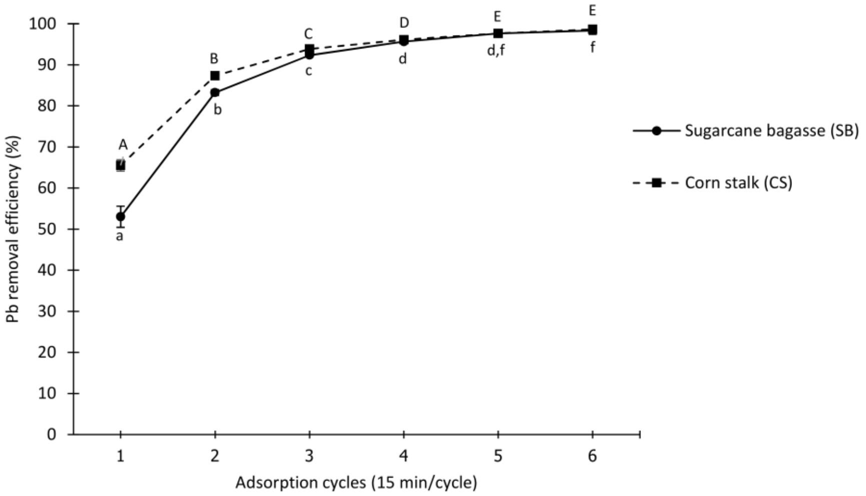


**Figure 4** The Pb removal efficiency versus absorption cycles (15 min/cycle) by 4 % w/v SB and CS biomass, with a single solution containing 24 mg/L of Pb at a pH of 6. The different letters indicate a significant difference in Pb removal efficiency ($p < 0.05$) among adsorption cycles according to the LSD test (small letters for SB; large letters for CS). Data were presented by using Mean ± SD (n = 3).

### Adsorption isotherms

Langmuir and Freundlich's isotherms are common models used in batch adsorption studies. The Langmuir adsorption model assumes that the adsorption consists entirely of a monolayer at the adsorption surface and that there is no interaction between molecules on different sites and each site can hold only 1 adsorbed molecule, whereas the Freundlich adsorption model is an empirical formula that relies on adsorption on heterogeneous surfaces [48]. In this study, the Langmuir constants ($q_{max}$ and $K_L$) and Freundlich constants ($K_f$ and 1/n) were calculated and the values are presented in **Table 1**. It was observed that the Freundlich isotherm model described the adsorption process with a high coefficient of determination ($R^2$), better than the Langmuir isotherm model for Pb(II) and Cd(II) in binary solution by CS (**Table 1**). However, the Freundlich and Langmuir isotherm models gave an unexplained low coefficient of determination ($R^2$) for Pb(II) in binary solution by SB (**Table 1**). Based on the better fitness of the adsorption process to the Freundlich than the Langmuir isotherm model in **Table 1**, multilayer coverage of Pb(II) and Cd(II) on the surface of CS, and multilayer coverage of Cd(II) on the surface of SB are predicted, and the heterogeneous surface of both types of biomass are assumed [49]. In the Freundlich model, the stronger binding sites are assumed to be occupied first, until adsorption energy is exponentially decreased when the adsorption process is being completed [50]. The adsorption capacity, $q_{max}/K_f$, indicates that the uptake of Pb(II) was higher than that of Cd(II) by CS and SB (**Table 1**).

**Table 1** Isotherm model constants for heavy metal adsorption using 2 g (4 % w/v) of sugarcane bagasse (SB) and corn stalk (CS) biomass in 50 mL of binary solutions containing Pb(II) and Cd(II), with pH 6.0 and contact time of 60 min.

| Adsorbent | Adsorbate | Langmuir isotherm | | | Freundlich isotherm | | |
|---|---|---|---|---|---|---|---|
| | | $q_{max}$ (mg/g) | $K_L$ (L/mg) | $R^2$ | $K_f$ | 1/n | $R^2$ |
| SB | Pb | 0.2564 | 0.2866 | 0.5261 | 0.0791 | 0.3941 | 0.3840 |
| | Cd | 0.0283 | 0.4482 | 0.8446 | 0.0085 | 0.7013 | 0.8938 |
| CS | Pb | 1.0379 | 0.0897 | 0.9507 | 0.0891 | 0.7938 | 0.9710 |
| | Cd | 0.0766 | 0.1777 | 0.9977 | 0.0114 | 0.8628 | 0.9976 |

### Comparison of SB and CS with other sorbents

A comparison of the adsorption capacities of various sorbents from the literature with the results of the present study (μmole/g) was shown in **Table 2**. As can be seen from the results, the Pb adsorption capacities of SB (i.e., 5.82) and CS (i.e., 5.24) are lower than most of the previously reported results, except for the cases of non-modified silica gel [51] and raw corn stalk [52], whereas the Cd adsorption capacities of SB (i.e., 0.15) and CS (i.e., 0.16) are very lower than most earlier studies. The differences in adsorption capacities among various sorbents come from different experimental variables such as doses of sorbents, initial concentration, solution pH, temperature, contact time, and adsorbent particle size.

**Table 2** Comparison of the adsorption capacities of various sorbents from the literature with the results of this study.

| Sorbent | Adsorption capacity for metal ion (μmole/g) | |
|---|---|---|
| | **Pb(II)** | **Cd(II)** |
| Acid red 88 [53] | 12.10 | 11.70 |
| Wheat straw [54] | 18.65* | 42.22* |
| Non-modified silica gel [51] | 3.28 | 6.05 |
| Banana peel [55] | 8.20 | 15.10 |
| Tangerine peel [56] | 7.48 | 5.78 |
| Untreated sugarcane bagasse [57] | 30.75 | - |
| Raw sugarcane bagasse [58] | 102.80 | - |
| Raw corn stalk [59] | - | 30.16* |
| Raw corn stalk [52] | 0.029 | 0.046 |
| Sugarcane bagasse (This study)<br>(condition 24Pb + 0.7Cd, mass (1 % w/v), pH 6.0) | 5.82 | 0.15 |
| Corn stalk (This study)<br>(condition 24Pb + 0.7Cd, mass (1 % w/v), pH 6.0) | 5.24 | 0.16 |

*value was evaluated from the Langmuir isotherm parameters

### Application in environmental clean-up

SB and CS agricultural waste appear to have potential as biosorbents for the removal of heavy metal ions, particularly Pb(II), from contaminated water due to their ease of availability and low cost. Other advantages of using SB and CS as biosorbent materials include a small carbon footprint, a shorter reaction time, no or low cost of equipment and operation, and easy operation. At the end of this study, we estimated the operating cost of treatment for 125 litres of contaminated water before household consumption by considering factors as shown in **Table 3**. Our study would also be valuable in wastewater treatment operations, as the vast majority of industrial wastewater contains a variety of metals and other species that must be removed before being released into the environment. Effective industrial scale-up of the system provides a wastewater treatment system that can utilise existing waste and hopefully prove versatile for a wide range of heavy metals. More research is needed on the following topics: 1) structural modification of SB and CS to improve their capacity for adsorbing Pb(II) and Cd(II) from wastewater; 2) regeneration of 2 types of biomass to provide better results and a permanent solution for biomass disposal, and 3) field trials to confirm whether SB and CS are suitable biosorbents for practical application.

**Table 3** Expenses are estimated based on producing 5 kg of biomass (2500 treatments) for adsorbing 125 L of contaminated water using 2 g (4 % w/v) of biomass.

| Cost item | Unit | Quantity | Price per unit | Total price (THB) |
|---|---|---|---|---|
| 1) Labour | Day | 2 | 300 | 600.0 |
| 2) Electricity | Unit | 240 | 4.42 | 1060.8 |
| 3) Filtration paper | Pack (100/pack) | 25 | 250 | 6250.0 |
| 4) Waste disposal | kg | 10 | 45 | 450.0 |
| | | | **Total** | 8360.8 |

As a result, the cost of treating 1 L of contaminated water is 66.8 THB.

## Conclusions

In summary, sugarcane bagasse and corn stalk are potential adsorbents for the removal of Pb and Cd ions from binary and single solutions. The adsorption process is spontaneous and is a function of the adsorbent and adsorbate concentrations, solution pH, contact time, and the number of adsorption cycles. In a binary solution system, sugarcane bagasse and corn stalk biomass exhibit better ion removal efficiency for Pb ions than Cd ions, with an optimum pH range of 5 to 6. The removal of Cd ions using sugarcane bagasse and corn stalks seemed to be pH-independent. The optimum contact time for Pb and Cd removal by sugarcane bagasse and corn stalks is 15 minutes. At least four adsorption cycles in a single solution (i.e., Pb) system help to increase the removal efficiency for Pb(II) by sugarcane bagasse and corn stalk biomass to 98 percent.

## Acknowledgments

This research project is supported by Mahidol University (Kanchanaburi Campus), Thailand. The authors would like to acknowledge Mr. Chawalit Takoon from Mahidol University - Frontier Research Facility (MU-FRF) for technically helping with heavy metal analysis.

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