

## Potential Elimination of Chromium (VI) by Chemically Biochar Derived from *Pennisetum setaceum*

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### ABSTRACT

This study consisted of a novel potential adsorbent material that could efficiently remove chromium (VI) from aqueous solutions. The optimum operating conditions were investigated including pH, agitation period. In this research, biochar derived from fountain grass (*Pennisetum setaceum*) coated with glutaraldehyde-crosslinked chitosan and treated with succinic acid to add functional groups was used to create an eco-friendly sorbent (CPES). It demonstrated that 3.0 is the ideal pH for the Cr (VI) adsorption process. The equilibrium stirring time is 120 minutes. The Langmuir and Freundlich models have been used to examine experimental data. According to the results, and the Freundlich model performed a better fit of the result than the Langmuir one. Cr (VI) has a maximum adsorption capacity of 30.96 mg/g. The Gibbs free energy change ( $\Delta G$ ), enthalpy change ( $\Delta H$ ), and entropy change ( $\Delta S$ ) thermodynamic parameters were determined. The fact that  $\Delta G$  was negative demonstrated that Cr (VI) adsorption onto the CPES adsorbent occurred spontaneously.

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### 1. Introduction

In current years, contamination of heavy metals in aqueous solutions, which mainly comes from escalating economic development such as mineral mining, metal plating, photographic industries, and battery manufacturing, is difficult to remove completely by conventional wastewater treatment systems. Studies showed that if the concentration of heavy metals exceeded the permissible limit of the World Health Organization, it would lead to many serious diseases, and threaten our health [1] - [4]. For instance, exposure to chromium may affect lung and bone, excess lead could result in brain, kidneys, and nervous system damage, while drinking water that contains hexavalent chromium is associated with lung cancer, etc [5] - [9]. Therefore, wastewater treatment should be conducted strictly and effectively to remove all the trace heavy metals that may present in the water.

Many physicochemical methods have been developed lately to eliminate heavy metal ions from water sources such as chemical precipitation, membrane, ion exchange, coagulation/flocculation, and extraction processes. These methods all proved efficiency; however, the ion exchanging, and membrane filtration technologies usually require high operating cost [4] - [10]. Although the chemical precipitation process has been used widely due to its ability to fulfill all the factors, it is not eco-friendly as it still produces a large amount of secondary solid waste that needs to be further treated [4], [11] - [13].

Adsorption, a method that could be able to combine the advantage of both using adsorbent and recycling agricultural residue, has been notably attracted attention lately. Usually, the crop residues such as rice straw; corn peel; fountain grass (*Pennisetum setaceum*) are handled by open field burning; generating biogas; feeding or bedding for animals. Among these methods, open field burning is the most common option, especially in Southern Vietnam, which could not utilize the potential nor bring more value out of the agro-waste. Moreover, due to the vast volume of agricultural residue Vietnam generates

annually (2.2 million tons in 2004), recycling crop waste to create new environmental-friendly material should be considered as an appropriate method to approach this problem. Biochar, also known as charcoal, is produced through the controlled combustion of biomass, which includes organic materials such as those found in agricultural and forestry debris. In order to form the biochar and add more functional groups onto the materials, chitosan was used to enhance the Cr (VI) removal capability of the biochar derived from *Pennisetum setaceum*.

Thus, the objective of this research is to examine the capacity of the new composite adsorbent, which was chemically formed by combining *Pennisetum setaceum* -derived biochar and chitosan, to adsorb Cr(VI) in different conditions such as pH, agitation time, and temperature. The efficiency was further analyzed by studying the adsorption isotherm.

## 2. Materials and Methods

### 2.1 Chemicals

*Pennisetum setaceum* was collected from the field in Dong Nai province, Vietnam. The raw material was then chopped into small pieces and dried at 60 °C within 1 day in the oven. Chromium standard solution (1000 mg/L) was provided by Merck Co. Sigma Aldrich Co. supplied chitosan with a deacetylation degree of 85% and a glutaraldehyde (25%) solution in water. All additional reagents utilized in this investigation were of analytical grade.

### 2.2 Adsorbent preparation

Several past research utilized the same approach to prepare the materials. [14], [15]. *Pennisetum setaceum* was calcinated for four hours at 500 °C in a furnace. After leaving the collected coal to cool to constant temperature, it was ground and sieved to 0.015mm. In 24 hours, the materials were thoroughly mixed with H<sub>3</sub>PO<sub>4</sub> (1:3) subsequently regenerated in a microwave at 450 W for 10 minutes. A mixture of 10 g of -chitosan, 1 g of -biochar, and 240 mL of acid acetic (7%) was soaked overnight and afterward dropped into 200 mL of an alkaline coagulating solution (H<sub>2</sub>O:methanol:NaOH = 4:5:1, w/w) to produce extremely inflated spherical beads. The process of crosslinking was carried out by pouring 200 mL of wet beads into a glass beaker containing glutaraldehyde solution. The final beads (CPES) were rinsed many times with distilled water to eliminate any remaining glutaraldehyde and dried at 70 oC for 24 hours.

### 2.3 Batch adsorption studies

Experiments on adsorption were conducted using the batch equilibration method. Prepared was a stock solution comprising 1000 mg/L. In duplicate, batch adsorption tests were conducted by combining 2 g/ L of adsorbent with 100 mL of solution. At 30oC, the contents were vigorously agitated with an orbital shaker incubator at 200 rpm and 30oC. The solution was then filtered, and the concentration of residual chromium was measured using an Atomic Absorption Spectrophotometer. The pH was measured with a Horiba pH meter. With 2 g/ L of adsorbent and a temperature of 318oC and a stirring rate of 200 rpm, the effect of agitation duration was determined. Using buffers, the influence of pH on the adsorption of Cr (VI) was investigated over the pH range of 1.0 to 7.0. The amount of Cr(VI) adsorbed was calculated according to the following equation:

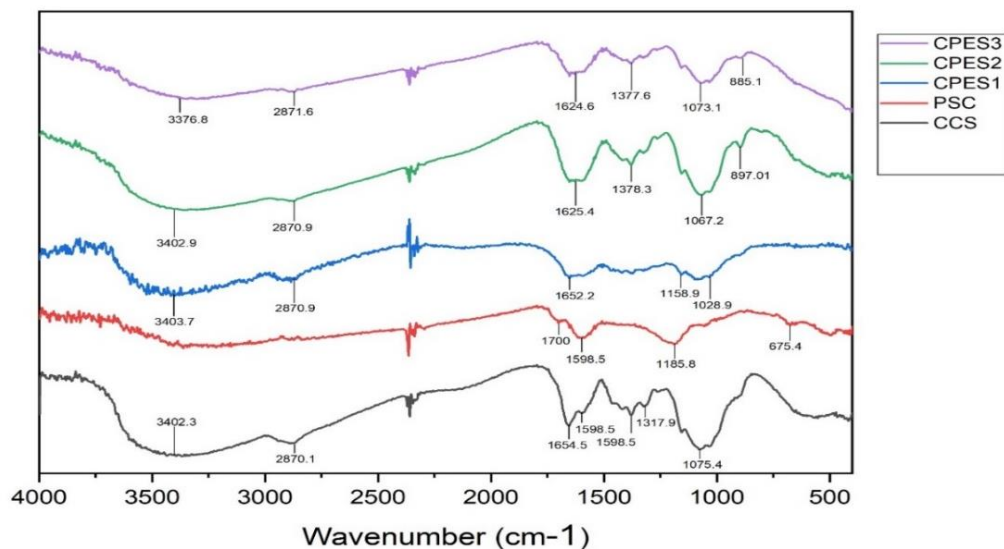
$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (1)$$

where  $q_e$  is the amount of Cr(VI) adsorbed onto CPES (mg/g),  $C_0$  and  $C_e$  are the Cr (VI) concentrations in the solution initially and at equilibrium (mg/ L), respectively,  $V$  is the volume of the solution (L), and  $m$  is the mass of adsorbent used (g).

## 3. Results and Discussion

### 3.1 Adsorbent specifications

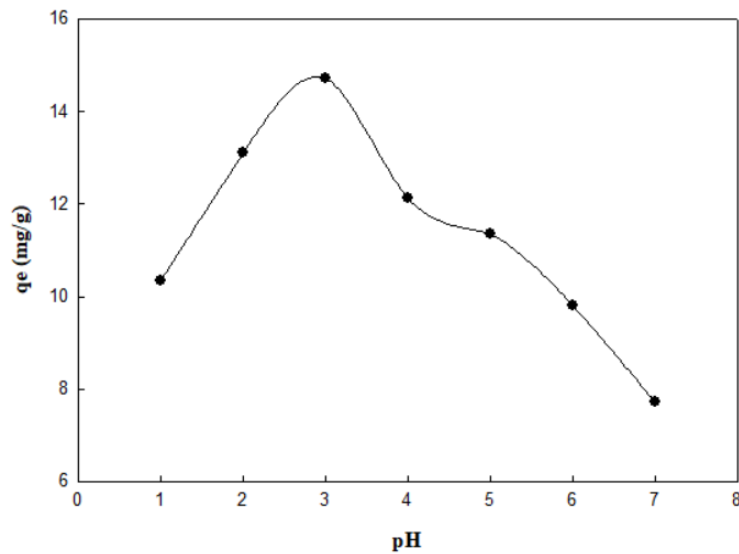
Figure 1 depicts the FTIR spectra of CCS (a) obtained with Chitosan data as at the peak 3402.3cm<sup>-1</sup> (oscillations of the O-H and N-H<sub>2</sub> bonds overlap). This peak is more evident in CPES1(c), indicating that hydrogen bonding is stronger. Furthermore, the presence of intense intensities at 1652.2cm<sup>-1</sup>, (CPES1) and 1654.5 cm<sup>-1</sup>, 1598.5 cm<sup>-1</sup> indicates the existence of a carboxylate functional group. C-H groups are demonstrated by the peaks at 1158.9 cm<sup>-1</sup> and 1028.9 cm<sup>-1</sup> in CPES1. The FTIR spectrum absorption band following adsorption of metal ions drops in intensity, indicating a shift to the low frequency bands, demonstrating a relationship between functional groups and metal oxide, as depicted in figure CPES2(d), which exhibits a weak adsorption peak of 897.01 cm<sup>-1</sup>. Changes in spectra caused by the adsorption of metal ions demonstrated that the successfully prepared materials possess the features of two materials, PSC and CCS, as well as adsorption capability. The substance contains the functional groups -OH, -COO, -NH<sub>2</sub>, -COOH, -C-H, and -CH<sub>2</sub>. As demonstrated in Figure 1, CPES3 (e), following desorption, the material tends to recover the same peaks as CPES1, whereas the intensity of the metal peaks in CPES2 has diminished.



**Figure 1.** FTIR spectra of (a) Chitosan (CCS), (b) Modified charcoal at 500°C (PSC), (c) Chitosan combined with *Pennisetum setaceum* biochar before adsorption (CPES1), (d) Chitosan combined with *Pennisetum setaceum* biochar after adsorption (CPES2), (e) Chitosan combined with *Pennisetum setaceum* biochar after desorption (CPES3)

### 3.1 Effect of pH on the adsorption capacity

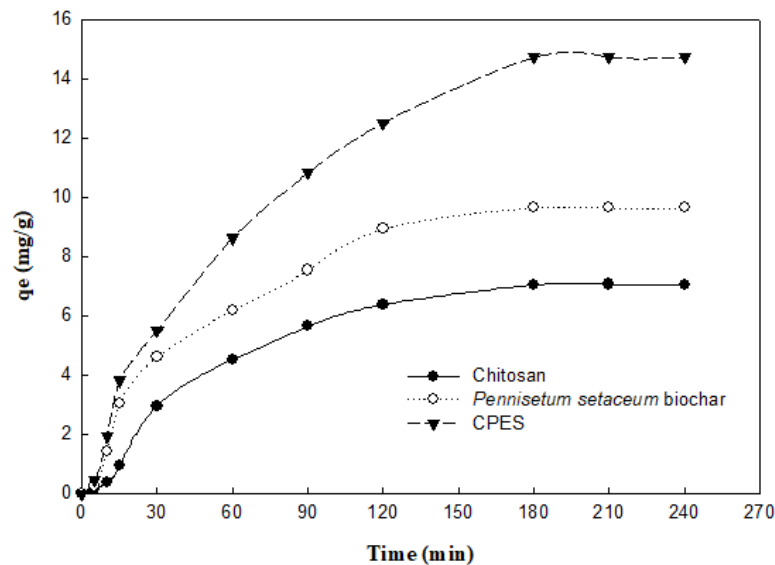
As shown in Figure 2, the experimental results indicate that CPES could adsorb a substantial amount of Cr(VI). In addition, it was observed that the extent of sorption of chromium ions by the sorbent increased with increasing acidity up to a maximum value of a pH of 3.0. The graph indicates that maximum sorption was observed at a pH of 3.0. At pH 3.0, CPES had a Cr(VI) sorption capacity of 14.1 mg/g, which decreased to 7.6 mg/g at pH 6.0. Several other authors [7], [8], [10] discovered that the adsorption of Cr(VI) on biomass increased with decreasing pH and was greatest at a pH value of 2.0. Cr(VI) exists as the oxyanion HCrO<sub>4</sub><sup>-</sup>, Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, CrO<sub>4</sub><sup>2-</sup>, Cr<sub>4</sub>O<sub>13</sub><sup>2-</sup>, and Cr<sub>3</sub>O<sub>10</sub><sup>2-</sup>. The pH decrease causes the sorbent surface to become protonated to a higher extent. At pH 3.0, the negatively charged chromate ions would interact with the positively charged functional groups of *Pennisetum setaceum* biomass more strongly, resulting in a high Cr(VI) uptake. It is known that the predominant form of Cr(VI) at pH 1.0 is the acid chromate ion species (HCrO<sub>4</sub><sup>-</sup>), and that as pH increases, the concentration of HCrO<sub>4</sub><sup>-</sup> shifts to CrO<sub>4</sub><sup>2-</sup> and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> are likely the active forms of Cr(VI) that are being sorbed by the biochar, as the sorption of Cr(VI) increased as the pH rise to 3.0. Reduction in Cr(VI) biosorption at pH values below 2.0 is likely due to a change in the chemical nature of caused by the acid's hydrolytic activity at high concentrations.



**Figure 2.** The effect of initial pH on adsorption of CPES

### 3.2 Effect of agitation time

Figure 3 depicts the effects of agitation duration on the adsorption of Cr (VI) on CPES as well as chitosan and plain Pennisetum setaceum biochar. In the initial 60 minutes, a significant absorption occurs. After 120 minutes, the adsorption equilibrium is totally attained. The optimal interaction time is therefore determined to be 120 minutes.



**Figure 3.** The effect of agitation time on adsorption of CPES

### 3.3 Adsorption isotherm and thermodynamic

The following equation described the linear form of the Freundlich model [16], [17].

$$\ln q_e = \ln K_F + (1/n) \ln C_e \quad (2)$$

where  $K_F$  is a constant indicating the relative adsorption capacity of the adsorbent ( $\text{mg}^{1-(1/n)} \text{L}^{1/n} / \text{g}$ ), and  $n$  is a constant indicating the adsorption intensity.

Table 1 lists the values of  $K_F$  and  $n$  derived from the graph of  $\ln q_e$  and  $\ln C_e$  at various temperatures. The  $n$  value reflects the trend of the adsorption process; if  $n = 1$ , linear adsorption occurs; if  $n < 1$ , the process is chemical; and if  $n > 1$ , the process is physical [18]. The correlation coefficient  $r^2$  obtained is more than 0.991, indicating the applicability of the Freundlich equation. In this study,  $n$  is determined to be between 2.38 to 2.65, which is greater than 1.0 and demonstrates the physical mechanism of metal ion adsorption on CPES. In order to reveal the adsorption behavior on the surface [19], [21], the Langmuir isotherm model was applied. The linearized Langmuir equation is:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} \left( \frac{1}{q_{max}} \right) \quad (3)$$

where  $q_{max}$  is the maximum quantity of adsorption (mg/g), and  $K_L$  is the Langmuir constant (L/mg).

The values of  $K_L$  and  $q_m$  found from the graph  $C_e/q_e$  and  $C_e$ , listed in Table 1, compares the experimental data with the ones fitted by the Langmuir equation (Equation 6) at different temperatures.

$$q_e = \frac{q L_{e max}}{1 + K_L q_{max}} \quad (4)$$

**Table 1.** The isotherm parameters of the adsorption process of Cr(VI) on the CPES at pH 3.0

| Temperature<br>(°K) | Langmuir        |                     |       | Freundlich                         |      |       |
|---------------------|-----------------|---------------------|-------|------------------------------------|------|-------|
|                     | $K_L$<br>(L/mg) | $Q_{max}$<br>(mg/g) | $R^2$ | $K_F$<br>(mg/g)(mg/L) <sup>n</sup> | $n$  | $R^2$ |
| 308                 | 0.0537          | 30.96               | 0.918 | 0.258                              | 2.47 | 0.979 |
| 313                 | 0.0559          | 28.49               | 0.955 | 0.332                              | 2.38 | 0.991 |
| 318                 | 0.0491          | 23.20               | 0.896 | 0.309                              | 2.65 | 0.959 |

The Gibbs energy ( $\Delta G$ ) (kJ/mol), the enthalpy change ( $\Delta H$ ) (kJ/mol), and the entropy change ( $\Delta S$ ) (J/mol K) of an adsorption process can be estimated by [22]

$$\Delta G = -RT \ln K_L \quad (5)$$

where  $T$  is the absolute temperature (K) and  $R$  is the universal gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>). The values of  $\Delta H$  and  $\Delta S$  can be obtained from the slope and intercept of the graph of  $\ln K_L$  against  $1/T$  based on the van't Hoff equation

$$\ln K_L = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (6)$$

**Table 2** shows the thermodynamic parameters of the adsorption process of Cr (VI) on CPES. The negative  $\Delta G$  values which indicated the metal ions adsorption on the CPES was spontaneous. The values of  $\Delta H$  and  $\Delta S$  were 27.73 and 0.188 respectively. Both of enthalpy change ( $\Delta H$ ) and entropy change value ( $\Delta S$ ) reveal the spontaneous at low temperature.

**Table 2.** The thermodynamic parameters of the adsorption of Cr(VI) on CPES at pH 3.0

| Temperature<br>(°K) | $K_c$    | $\Delta G^o$<br>(kJ/mol) | $\Delta H^o$<br>(kJ/mol.K) | $\Delta S^o$<br>(kJ/mol.K) |
|---------------------|----------|--------------------------|----------------------------|----------------------------|
| 308                 | 154978.2 | -30.6                    | 27.73                      | 0.188                      |
| 313                 | 142857   | -30.89                   |                            |                            |
| 318                 | 218470.2 | -32.5                    |                            |                            |

#### 4. Conclusions

In this study, the ability of Cr( VI) adsorption on chemically Pennisetum setaceum biochar modified with crosslinked chitosan was investigated. The optimal pH value for adsorption was 3.0. The experiment data followed Freundlich isotherm. The maximum amount of Cr (VI) adsorbed is 30.96 mg/g. The equilibrium contact time is 120 mins. The negative  $\Delta G$  values which indicated the metal ions adsorption on the ASB-CBs was spontaneous. The values of  $\Delta H$  and  $\Delta S$  were -53.8182 and -0.1682, respectively. Both of enthalpy change ( $\Delta H$ ) and entropy change value ( $\Delta S$ ) reveals the spontaneous at low temperature. This adsorbent is of low cost; its utility can be economical and can be viewed as a part of a feasible waste management strategy.

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