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# Adsorption of Cr(VI) ions by HCl-Modified Sugarcane Leaves as a Low-Cost Adsorbent

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## Abstract

The Cr(VI) effluent wastewater is a major source of environmental pollution. The Cr(VI) is more toxic at lower concentrations than Cr(III) due to carcinogenic and teratogenic effects. Agricultural waste materials have been used for treatment of wastewater. In this work, the potential of HCl-modified sugarcane leaves were used as an adsorbent for the hexavalent chromium removal in the batch adsorption process. The various experimental conditions such as pH (2-5), contact time (5-360 min), initial Cr(VI) concentration (10-50 mg/L), and temperature (20-40°C) were evaluated. The experimental results showed that the Cr(VI) adsorption increased with contact time and initial Cr(VI) concentration. The adsorption attained the equilibrium at 240 min. The maximum Cr(VI) adsorption occurred at pH 2. The kinetics of Cr(VI) adsorption was described using pseudo-first-order and pseudo-second-order kinetic models. The kinetic adsorption data were fitted well by the pseudo-second-order kinetic model. The equilibrium adsorption data were analyzed using the Langmuir and Freundlich isotherm. The equilibrium of Cr(VI) adsorption data were better fitted by the Langmuir isotherm, and the maximum adsorption capacity was 26.67 mg/g at 30°C. Thermodynamic parameters such as  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  for the adsorption showed that the adsorption was spontaneous and endothermic. This study indicated that the low-cost acid-modified adsorbent is an effective adsorbent for the hexavalent chromium removal in aqueous solution.

**Keywords:** adsorption, Cr(VI), low-cost adsorbent, agricultural waste

## 1. Introduction

Cr(VI) is a very toxic pollutant in the environment due to its high solubility in water [1]. The industries that discharge wastewater containing chromium include fertilizer, electroplating, mining processing, metal processing, tanning, paints, battery and domestic plumbing materials [2]. Many methods have applied for the Cr(VI) removal from wastewater, such as ion exchange, chemical precipitation, reverse osmosis, membrane filtration, and adsorption. However, by considering the prohibitive cost, long operation time and possible production of secondary toxic compounds [3], adsorption is the preferred method and gives the best results as it can be used to remove various pollutants.

Agricultural materials comprise of functional groups in the structure of lignin, cellulose, hemicellulose, ligno-humic, proteins, starch and polysaccharides. The uses of agricultural waste products are preferred for the environment because they are abundant in nature, readily available and cheaper in prices [4].

Many researchers have reported for the low cost and alternative adsorbents. For example, Adigun et al. (2020) [5] have used sugarcane leaves for the removal of  $\text{Ni}^{2+}$ ,  $\text{Cr}^{3+}$  and  $\text{Co}^{2+}$  ions from polluted water. Moreover, chemically modified plant wastes exhibit higher adsorption capacity than unmodified forms. Gupta and Rastogi (2009) [6] found that the biosorption capacities of raw and HCl-treated algae were 31 and 35.2 mg Cr(VI) per g of dry adsorbent, respectively. Puzkarewicz and Kaleta (2019) [7] reported that HCl-modified activated carbon (WDHCl) was more effective for Cr(VI) adsorption than  $\text{HNO}_3$ -modified (WD $\text{HNO}_3$ ), and unmodified (WD) activated carbon. However, there is no published paper available on the use of HCl-modified sugarcane leaves for Cr(VI) removal.

The objective of this proposed work was to study the adsorption efficiency of HCl-modified sugarcane-leaf adsorbent for the Cr(VI) removal. The equilibrium adsorption

data were analyzed by the Langmuir and Freundlich adsorption isotherms model. The results obtained can be applied to a batch design for the Cr(VI) removal in effluent wastewater.

## 2. Material and Methods

### 2.1 Preparation of adsorbent

Sugarcane leaves were obtained in a sugarcane plantation from Khok Samrong District, Lopburi Province, Thailand. The sugarcane leaves were cut to 1-2 inches, washed with tap water and dried in a hot air oven. The dried adsorbent was powdered and sieved particle size to 150-300  $\mu\text{m}$ . The dried adsorbent was soaked in 3.0 M HCl with the 1:1 ratio (mg:mL) for 24 h, then dried in a hot air oven and stored in a desiccator until used [7].

### 2.2 Preparation of adsorbate

A Cr(VI) stock solution of 1000 mg/L was prepared by dissolving 2.827 g of potassium dichromate (AR) in 1 L of deionized water. The pH of Cr(VI) solution was adjusted to 2-5 with 0.1 M HCl or 0.1 M NaOH. All the reagents were analytical grade.

### 2.3 Characterization of adsorbent

FTIR spectra (500-4,000  $\text{cm}^{-1}$ ) of adsorbent before and after Cr(VI) adsorption.

### 2.4 Adsorption study

To study the adsorption behavior of agricultural waste adsorbent, the effects of adsorption such as pH (2-5), contact time (5-360 min), initial Cr(VI) concentration (10-50 mg/L), and temperature (20-40°C) were investigated. The batch adsorption experiments were carried out using 0.1 g of adsorbent with 150 mL of Cr(VI) solution in 250-mL Erlenmeyer flasks. The mixture was agitated by the orbital shaker with agitation speed of 200 rpm. At the predetermined time, the supernatant was collected and the concentration of Cr(VI) remained was then examined using UV-visible spectrophotometer ( $\lambda_{\text{max}} = 540 \text{ nm}$ ) [8].

The percent adsorption and amount of the Cr (VI) adsorption were calculated as Equation (1) and (2), respectively.

$$\% \text{ adsorption} = \frac{(C_o - C_e) \times 100}{C_o} \quad (1)$$

$$q_t = \frac{(C_o - C_t)V}{W} \quad (2)$$

where  $C_o$  (mg/L) is initial Cr(VI) concentration,  $C_t$  (mg/L) is the concentration at any time,  $q_t$  (mg/g) is the amount adsorbed at any time,  $V$ (L) is the volume of the solution, and  $W$ (g) is the mass of adsorbent.

### 3. Adsorption Isotherm

#### 3.1 The Langmuir isotherm

The Langmuir isotherm in a linear form is represented as follows [1]:

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

where  $C_e$  (mg/L) is the equilibrium concentration,  $q_e$  (mg/g) is the amount adsorbed at equilibrium,  $K_L$  is the Langmuir constant, and  $q_{\max}$  (mg/g) is the maximum adsorption capacity.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless separation factor ( $R_L$ ) which is defined by:

$$R_L = \frac{1}{(1 + K_L C_o)} \quad (4)$$

#### 3.2 The Freundlich isotherm

The Freundlich isotherm in a linear form is represented as follows [2]:

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \quad (5)$$

where  $K_F$  (L/g) is the adsorption capacity, and  $\frac{1}{n}$  is the adsorption intensity.

## 4. Adsorption Kinetics

#### 4.1 The pseudo-first order kinetic

The pseudo-first order kinetic model in a linear form is written as follows [1]:

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (6)$$

where  $k_1$  (1/min) is the rate constant of pseudo-first, and  $q_t$  (mg/g) is the amount adsorbed at any time (min).

#### 4.2 The pseudo-second order kinetic

The pseudo-second order kinetic model in a linear form is written as follows [1]:

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

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

## 5. Thermodynamic parameter of adsorption

Thermodynamic parameters such as the Gibbs free energy change ( $\Delta G$ ), enthalpy change ( $\Delta H$ ) and entropy change ( $\Delta S$ ) were determined. The Gibbs free energy change ( $\Delta G$ ) in the adsorption process can be expressed as follows:

$$\Delta G = -RT \ln K_c \quad (8)$$

where  $K_c$  ( $K_c = q_e / C_e$ ) is the equilibrium constant,  $R$  is the gas constant and  $T$  is the absolute temperature.

Also enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) changes can be estimated by the following equation:

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (9)$$

where  $\Delta H$  and  $\Delta S$  can be determined respectively by the slope and intercept of the linear plot between  $\ln K_c$  and  $1/T$ .



(a) before Cr(VI) adsorption



(b) after Cr(VI) adsorption

**Figure 1** FTIR of adsorbent before (a) and after (b) Cr(VI) adsorption

## 6. Results and discussion

### 6.1 FTIR study

FTIR analysis results of adsorbent before and after Cr(VI) adsorption are observed in Figure 1. The broad band observed in the region of 3,100-3,400  $\text{cm}^{-1}$  related to O-H stretching vibrations groups because of the existence of lignin, cellulose, and pectin [9, 10].

The bands observed in the region of 2,850 and 3,000  $\text{cm}^{-1}$  are attributed to the C-H and C-O stretching vibrations [11]. The band observed in the region of 1,450-1,600  $\text{cm}^{-1}$

and 1,630-1,680  $\text{cm}^{-1}$  are attributed to the C=C aromatic ring and C=O stretching [12]. The peak observed at 1736.42  $\text{cm}^{-1}$  is ester C=O group [5]. The bands around 1,016-1,101  $\text{cm}^{-1}$  are attributed to C-O bonds indicating several bands in cellulose and xylose [13].

After Cr(VI) adsorption at pH 2, the peaks at 2,918.01, 2,850.17, 1,736.42, 1,676.92, 1,036.23  $\text{cm}^{-1}$  shifted to 2,917.02, 2,849.22, 1735.43, 1,676.55, 1,033.98  $\text{cm}^{-1}$  in the chromium loaded adsorbent. Therefore, the hydroxyl and carboxylic

groups presented in the adsorbent could bind with Cr(VI).

## 6.2 Effect of pH

The effect of the initial solution pH on the Cr(VI) adsorption was examined in the pH range of 2.0 to 5.0 at the initial Cr(VI) concentration of 10 mg/L, and the percentage of adsorption was shown in Figure 2.

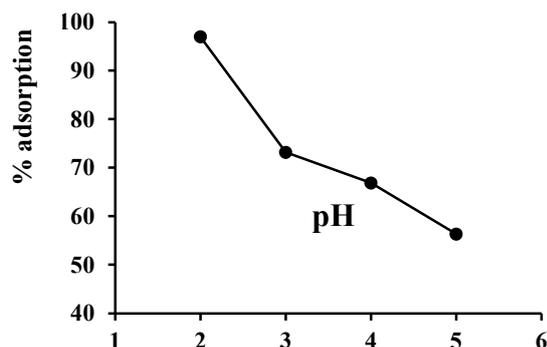
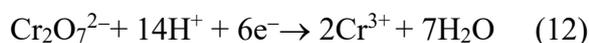
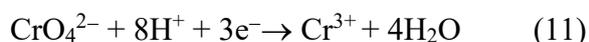
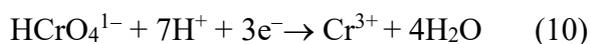


Figure 2 Effect of pH on Cr(VI) adsorption

The solution pH, one of the most important parameters, affects not only the surface charge of the adsorbent, the degree of ionization of functional groups on adsorbent surface, but also the solution adsorbate chemistry. In aqueous solution, the Cr(VI) coexists in five different forms of oxyanions in aqueous medium:  $\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{HCr}_2\text{O}_7^-$ ,  $\text{H}_2\text{CrO}_4$ ,  $\text{HCrO}_4^-$ , and  $\text{CrO}_4^{2-}$  [4]. Under acidic medium,  $\text{HCrO}_4^-$  is the major species of Cr(VI). In Figure 2, the Cr(VI) adsorption decreased with increasing pH from 2.0 to 5.0. The optimum removal efficiency for Cr(VI) reached 96.97% at pH 2.0.

At pH 2.0, the negatively charged oxyanion as  $\text{HCrO}_4^-$  ion can be adsorbed because of electrostatic attraction with positive charges on adsorbent [14]. Moreover, Cr(VI) ions have high redox potential under acidic conditions and they may be reduced to Cr(III) ions as the Equation (10), (11) and (12) [15].



## 6.3 Effect of contact time and adsorption kinetics

The adsorption was examined as a function of contact time (5-360 min) at initial concentration of 10 and 30 mg/L. The results of adsorption were shown in Figure 3. As seen in Figure 3, the adsorption was rapid at the first 30 min and then gradually decreased to become constant at the equilibrium time at 240 min. The rapid adsorption observed during the first stage was probably due to the abundant availability of active sites on adsorbent surface [16]. The kinetic data were analyzed by linear pseudo-first and pseudo-second order (not shown) and the parameters were calculated as shown in Table 1.

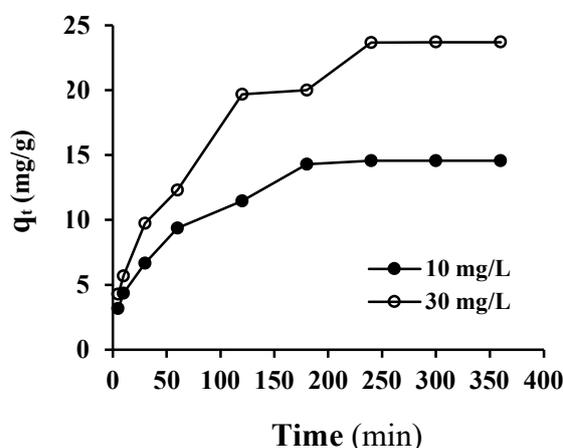


Figure 3 Effect of contact time on Cr(VI) adsorption (pH = 2,  $T_{em} = 30^\circ\text{C}$ )

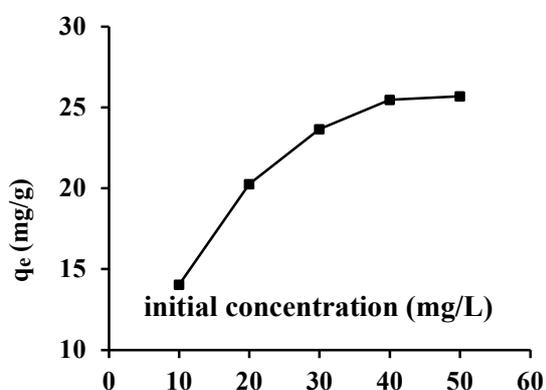
Table 1 Kinetic parameters of Cr(VI) adsorption

Kinetic models	Initial concentration (mg/L)	
	10	30
Pseudo-first order		
$q_e$ (exp) (mg/g)	14.57	23.71
$q_e$ (cal) (mg/g)	17.49	32.19
$k_1$ (1/min)	0.023	0.022
$R^2$	0.940	0.787
Pseudo-second order		
$q_e$ (cal) (mg/g)	16.10	26.88
$k_2$ (g/(mg.min))	0.001	0.001
$R^2$	0.999	0.988

From the kinetic model analysis at initial Cr(VI) concentration of 10 and 30 mg/L, the correlation coefficients ( $R^2$ ) of adsorption were 0.940 and 0.787 for pseudo-first order kinetic model and 0.999 and 0.988 for pseudo-second order kinetic models. Therefore, the adsorption was best described by pseudo-second order kinetic model. A similar result was observed in the adsorption of Cr(VI) onto *Leucaena leucocephala* Seed Shell Activated carbon [2].

#### 6.4 Effect of initial Cr(VI) concentration

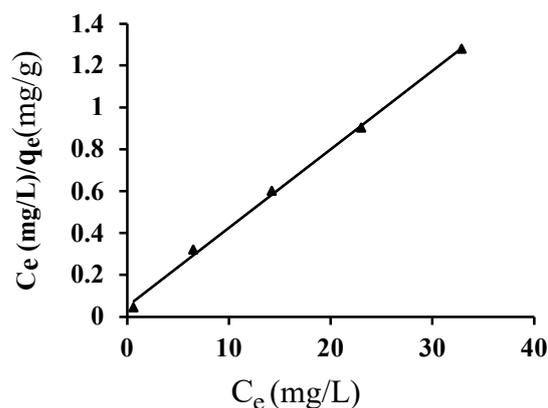
The adsorption was examined as a function of initial concentration of Cr(VI) from 10-50 mg/L at equilibrium time. The results of adsorption were shown in Figure 4. The results revealed that the adsorption capacity increased (14.04-25.69 mg/g) as the increase of Cr(VI) concentration (10-50 mg/L), and reached a saturation level at the concentration over 40 mg/L. The adsorption capacity increased because of the driving force of concentration gradient for mass transfer with the increase in initial adsorbate concentration [1].



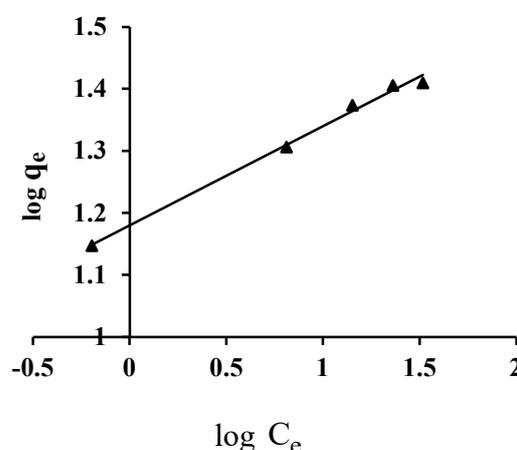
**Figure 4** Effect of initial Cr(VI) concentration on adsorption capacity

#### 6.5 Adsorption isotherm

The equilibrium data of Cr(VI) adsorption were analyzed using linear two isotherms, namely Langmuir and Freundlich isotherm. The plots of isotherms were shown in Figure 5, and the parameters were calculated in Table 2.



(a) Langmuir isotherm



(b) Freundlich isotherm

**Figure 5** Isotherms of Cr(VI) adsorption

**Table 2** Parameters of the isotherm models for Cr(VI) adsorption

Isotherm model	Values
Langmuir isotherm	
$q_{\max}$ (mg/g)	26.67
$K_L$ (L/g)	0.001
$R_L$	0.982-0.917
$R^2$	0.997
Freundlich isotherm	
$K_F$ (L/mg)	15.14
$1/n$	0.159
$R^2$	0.993

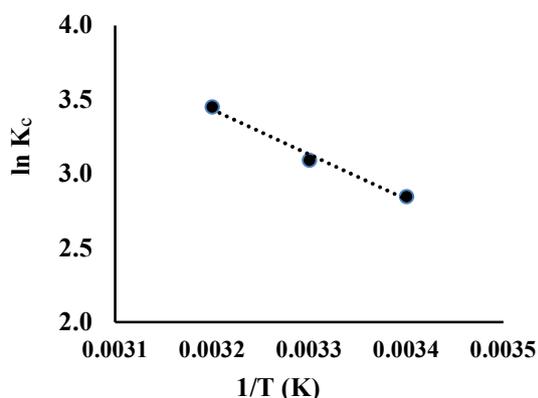
Based on the  $R^2$ , the result showed better fitting of data by the Langmuir model than by the Freundlich isotherm, and the maximum

adsorption capacity ( $Q_{\max}$ ) was 26.67 mg/g at 30°C. The adsorption isotherm data were well fitted by the Langmuir isotherm, indicating the homogeneous monolayer coverage of the adsorbate on the surface of the adsorbent. Several researchers reported similar results [14,15]. For the  $R_L$ , the value of  $0 < R_L < 1$  indicated that the Cr(VI) adsorption was favorable [14].

For Freundlich model, the value of  $1/n$  was less than 1 suggesting the favorable adsorption.

### 6.6 Thermodynamic of adsorption

The Gibbs free energy change ( $\Delta G$ ) values were calculated at varying temperature by using equation (8). The enthalpy change ( $\Delta H$ ) and entropy change ( $\Delta S$ ) were calculated from intercept and slope of the linear plot shown in Figure 6. And, the thermodynamic parameter values were tabulated in Table 3.



**Figure 6** The plot of  $\ln K_c$  versus  $1/T$  for the adsorption of Cr(VI) on HCl-modified sugarcane leaves

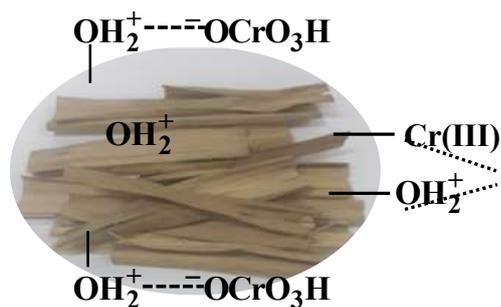
**Table 3** Thermodynamic parameters for the adsorption of Cr(VI) on HCl-modified sugarcane leaves

Tem (°C)	$K_c$	$\Delta G$ (kJ/mol)	$\Delta H$ (kJ/mol)	$\Delta S$ (J/mol K)
20	17.23	-6.93	23.00	101.99
30	22.05	-7.79		
40	31.53	-8.98		

The experiments were performed at equilibrium time using initial Cr(VI) concentration of 10 mg/L. As seen in Table 3, the values of  $\Delta G$  were -6.93, -7.79, and -8.98 kJ/mol at 20, 30 and 40°C, respectively. The negative values of  $\Delta G$  indicated that the adsorption process was spontaneous. For the enthalpy change ( $\Delta H$ ), the positive value of  $\Delta H$  was 23 kJ/mol. Therefore, the adsorption was endothermic. Moreover, if the  $\Delta H$  value lies between 2.1 and 20.9 kJ/mol, it is consistent with electrostatic interaction between adsorption sites and adsorbing ions, showing the adsorption belongs to physisorption. If the  $\Delta H$  value lies between 20.9 and 418.4 kJ/mol, it reveals the adsorption involves charge sharing or transferring from adsorbent surfaces to adsorbing ions to form coordinate bonds, which indicates the adsorption owes to chemisorption [17]. The positive value of  $\Delta S$  suggested an increase in entropy with adsorption. This occurred as a result of an increase in randomness at the solid-solution interface during the adsorption.

### 6.6 Mechanism of Cr(VI) adsorption

The surface functional groups of agricultural by-products consist of lignin, cellulose, hemicellulose, ligno-humic, proteins, starch and polysaccharides [4]. In this study, the result showed that the adsorption capacity reached maximum at pH 2.0. At pH 2, the functional groups on the adsorbent become positive charge. Therefore, the Cr(VI) adsorption mechanism (Figure 7) should be the electrostatic attraction (-----) between the positively charged surface of  $\text{OH}_2^+$  in adsorbent and  $\text{HCrO}_4^-$  in adsorbate. Moreover, Cr(VI) changed to Cr(III) in acidic solution, and the Cr(III) ions could form complexation (.....) with the lone pair electrons of oxygen on oxygen-containing groups in adsorbent.



**Figure 7** Mechanism of Cr(VI) adsorption on HCl-modified sugarcane leaves

## 7. Conclusions

In this study, the HCl-modified sugarcane leaves have been used for its application as the adsorbent for the Cr(VI) adsorption in the batch experiments under conditions of pH, contact time, and initial Cr(VI) concentration. The maximum adsorption occurred at pH 2 and equilibrium time at 300 min. The equilibrium adsorption data were better described by the Langmuir isotherm, and the maximum adsorption was 26.67 mg/g. The negative value of  $\Delta G$  indicated that the adsorption process was spontaneous. The positive value of  $\Delta H$  indicated that the adsorption process was an endothermic process. Therefore, the HCl-modified sugarcane leaves were successfully utilized as the effective adsorbent for the Cr(VI) removal from water, which could be used in wastewater treatment system.

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