

Adsorption of Chromium (Cr^{+6}) Using Durian Peel

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Abstract. This study investigates chromium (Cr^{+6}) adsorption in an aqueous solution using durian peel. All experiments were conducted in a batch experiment. Adsorption factors consisted of pH, contact time and initial Cr^{+6} concentration. Langmuir and Freundlich isotherms were used to study the adsorption mechanism and determine the maximum adsorption capacity. Moreover, pseudo-first and second order were used to explain the kinetic adsorption mechanism. Finally, the desorption process was studied to evaluate suitable management of spent adsorbent. The results show the appropriate condition of Cr^{+6} adsorption using durian peel (DP) as pH2, contact time 30 min and initial Cr^{+6} concentration 75 mg/l. Langmuir isotherm and pseudo second order were well fitted with experimental data, so they were used to explain the adsorption mechanism. The maximum adsorption capacity was 10.67 mg/g. The desorption efficiency was 63.78% for 1 M HCl. All results indicate that DP is an alternative efficient adsorbent and its utilization represents an eco-friendly alternative that can be applied for use in agricultural waste management.

Keywords: adsorption, chromium (Cr^{+6}), durian peel

1. Introduction

Chromium is widely used in electroplating, leather tanning, metal finishing and chromate preparation. Chromium exists in two stable oxidation states Cr^{+3} and Cr^{+6} . The Cr^{+6} state is of particular concern because of its toxicity [1]. Cr^{+6} is highly toxic and ingestion results in maladies such as nausea, vomiting, severe diarrhea, and hemorrhage [2]. Conventional methods have been used to remove Cr^{+6} from industrial wastewater including reduction, precipitation, ion-exchange, and reverse osmosis [3]. Among these methods adsorption is one of the most economically favorable and technically feasible methods [4]. In recent years, adsorptive techniques have been used to investigate the effective removal of large quantities of Cr^{+6} from wastewater using low cost adsorbents and focusing on various industrial wastes, agricultural byproducts and biological materials [5]. Durian peel is a significant agricultural industry waste. Each year, a substantial amount of waste peel is produced. If it is not properly managed, it could become an environmental problem on its own [6]. Previous research has shown that the peel consists of holo-cellulose, hemi-cellulose and lignin, indicating the feasibility for removing toxic metal ions or enriching trace elements from aqueous solutions due to the presence of various interesting functional groups on the cellulose [7]. Thus, the utilization of durian peel offers an alternative eco-friendly waste management tool that doesn't allow any more released Cr^{+6} into the environment. In the experiment, the adsorption factors of pH, contact time and initial Cr^{+6} concentrations were investigated. Langmuir and Freundlich isotherms were used to study the adsorption mechanism and determine the maximum adsorption capacity. Moreover, pseudo-first order and pseudo-second order were used to study the kinetics mechanism. Finally, the desorption process was studied to determine a suitable method for spent durian peel management.

2. Methodology

2.1. DP preparation

DP was collected from fruit shops in Maharakham province, Thailand. They were mixed and cut into 1 cm × 1 cm pieces. They were washed with distilled water and dried in the oven at 105°C for 24 hrs. Then, they were ground into a 125 - 250 μm fine substance. The substance was washed with distilled water until the pH was constant, and then it was dried in an oven. The adsorption of Cr⁺⁶ was performed by batch technique.

2.2. Synthetic wastewater preparation

Aqueous solutions of Cr⁺⁶ were prepared by dissolving K₂Cr₂O₇ (s) in distilled water and then diluting to get the desired concentrations. Cr⁺⁶ concentrations were measured by Atomic Adsorption Spectrophotometer (AAS) (Shimadzu AA-670; 283.3 nm) using respective standard solutions to calibrate the instrument.

2.3. Effects of adsorption parameters

The effects of pH (2.0 – 7.0), contact time (0, 5, 10, 15, 30, 60, 120, 240 and 360 min) and initial Cr⁺⁶ concentration (5, 25, 50, 75 and 100 mg/l) were investigated. The initial pH adjustments were carried out either by 0.1 M HCl or 0.1 M NaOH. Samples were taken at certain time intervals, filtered through Whatman GF/A for removing the suspended biomass and analyzed for residual Cr⁺⁶ concentration. The Cr⁺⁶ concentration in the supernatant solution was determined using AAS.

The removal efficiency of metal ion was calculated from,

$$\% \text{ Removal} = ((C_0 - C_e) / C_0) \times 100 \quad (1)$$

where C₀ and C_e are the initial and equilibrium Cr⁺⁶ concentration (mg/l).

2.4. Kinetic study [8]

The Pseudo first-order and second-order kinetic models are the most popular models used to study the biosorption kinetics of heavy metals and to quantify the extent of uptake in biosorption kinetics. In order to investigate the mechanism of biosorption and potential rate controlling steps, the pseudo first and second-order kinetic models were used. The pseudo first-order rate expression is:

$$\log(q_e - q_t) = \log q_e - (K_1/2.303) t \quad (2)$$

Linear plots of log(q_e - q_t) versus t indicate the applicability of this model Eq. (2). The pseudo second-order kinetic model is expressed as:

$$t/q_t = 1/K_2 q_e^2 + t/q_e \quad (3)$$

If the pseudo second-order kinetics is applicable, the plot of t/q_t versus t should give a linear relationship.

2.5. Adsorption isotherm [9]

Adsorption equilibrium data were fitted to the Langmuir and Freundlich isotherm. Langmuir isotherm is based on the monolayer adsorption of chromium ions on the surface of carbon sites and is expressed in the linear form as

$$C_e/q_e = (1/q_m b) + (1/q_m) C \quad (4)$$

where C_e is the equilibrium concentration (mg/l) and q_e the amount adsorbed at equilibrium (mg/g). The Langmuir constants q_m (mg/g) represent the monolayer adsorption capacity and b (l/mg) relates the heat of adsorption. Freundlich isotherm describes the heterogeneous surface energies by multilayer adsorption and is expressed in linear form as

$$\ln q_e = \ln K_f + (1/n) \ln C \quad (5)$$

where K_f indicates adsorption capacity (mg/g) and 1/n an empirical parameter related to the intensity of adsorption, which varies with the heterogeneity of the adsorbent. For values in the range 0.1 < 1/n < 1, adsorption is favorable. The greater the values of K_f better is the favorability of adsorption.

2.6. Desorption

Metal elution is of crucial importance for the reusability of exhausted adsorbent and the recovery of adsorbed metals. In the desorption process, 0.5 g of applied DP for Cr⁺⁶ adsorption in the appropriate condition were leached by using 0.1, 0.5 and 1 M HCl 50 ml. The mixtures were shaken at an agitation speed 150 rpm and a temperature at room temperature for a contact time 30 min. Samples were filtered through a Whatman GF/A for removal of the suspended biomass and analyzed for Cr⁺⁶ concentration using AAS. The desorption capacity was determined by

$$D = \frac{\{(C_0 - C_e) - C_d\}}{(C_0 - C_e)} \times 100 \quad (6)$$

Where, D is desorption efficiency (%) and C_d is the eluted Cr⁺⁶ concentration (mg/l).

3. Results and Discussion

3.1. Effects of pH

Effects of pH on the uptake capacities of Cr⁺⁶ on DP were investigated. Experimental studies were carried out at room temperature with an initial Cr⁺⁶ concentration of 25 mg/l using an adsorbent dosage (adsorbent size 125 - 250 μm) of 10 g/l, and an agitation speed of 150 rpm for 30 min. Moreover, because hydroxide ions (OH⁻ ions) in the solution can bind with Cr⁺⁶ ions to form hydroxide complexes, the system pH should not exceed 7 (2.0 – 7.0). The adsorption results are shown in Figure 1. In Figure 1, the results show that the Cr⁺⁶ adsorption efficiency was very high at low pH and decreased with an increase of pH. At low pH, the biosorbent is positively charged due to protonation on the surface of the DP and dichromate ions of Cr₂O₇²⁻, HCrO₄⁻, CrO₄⁻, and HCrO₇⁻ as an anion leading to an electrostatic attraction between them [10]. As pH increases, deprotonation starts and thereby results in a decrease of adsorption capacity. The maximum value of Cr⁺⁶ adsorption efficiency occurred at pH 2.0.

3.2. Effects of contact time

Experiment studies were carried out at room temperature with an initial Cr⁺⁶ concentration of 25 mg/l using an adsorbent dosage (adsorbent size 125 - 250 μm) of 10 g/l at pH 2.0 and an agitation speed of 150 rpm for contact times of 0, 5, 10, 15, 30, 60, 120, 240 and 360 min. The adsorption results are shown in Figure 2. In Figure 2, it can be seen that the rate of Cr⁺⁶ adsorption increased rapidly during the initial 30 minutes. Thereafter, the removal of Cr⁺⁶ ions was almost constant. During the initial stage of sorption, a large number of vacant surface sites were available for adsorption. After a lapse of some time, the remaining vacant surface sites were more difficult to occupy due to repulsive forces between the adsorbed molecules on the solid surface and in the bulk phase or desorption [11]. The suitable contact time was 30 min in which the rate of Cr⁺⁶ adsorption was similar to the rate of Cr⁺⁶ desorption. After this time, adsorption efficiency was almost constant.

3.3. Kinetic study

The pseudo first and second order were used to investigate the adsorption mechanism. The adsorption results are shown in Table 1. The results show that the pseudo second order fitted better than the pseudo first order. It indicates that the adsorption mechanism rate was related to the chemical reaction and adsorption mechanism. The controlling steps of adsorption mechanism consisted of 2 steps. The 1st step, Cr⁺⁶ passed through the liquid phase to the film layer by bulk transport. The 2nd step, Cr⁺⁶ passed through the film layer to the surface of the adsorbent and adsorbed on the surface [8].

3.4. Effects of initial Cr⁺⁶ concentration

Effects of initial Cr⁺⁶ concentration on the removal of Cr⁺⁶ is illustrated Figure 3. Experiment studies were carried out at the room temperature with Cr⁺⁶ initial concentrations of 5, 25, 50, 75 and 100 mg/l using an adsorbent dosage (adsorption size 125 – 250 μm) of 10 g/l at pH 2.0 and an agitation speed of 150 rpm for 30 min. In Figure 3, the adsorption capacity increased with an increase in the initial Cr⁺⁶ concentration. This is because an opportunity existed for increased reaction between the adsorbent and the adsorbate [13]. In this experiment, the suitable initial Cr⁺⁶ concentration was 75 mg/l.

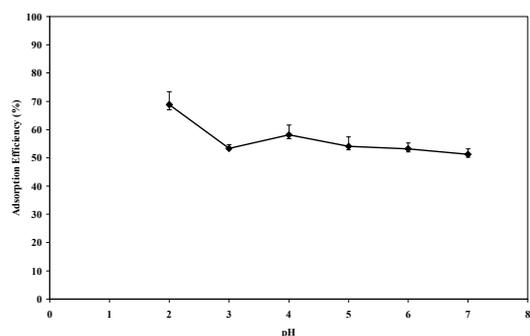


Figure 1 Effects of pH

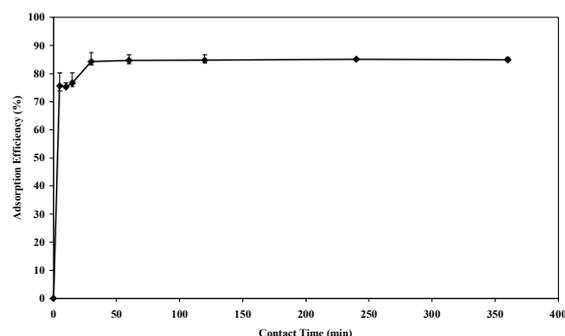


Figure 2 Effects of contact time

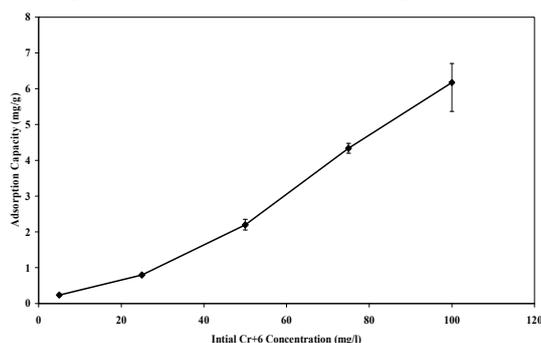


Figure 3 Effects of initial Cr+6 concentration

Table 1 Pseudo first and second order constants for adsorption of Cr⁺⁶ on DP

Adsorbent	Pseudo first order			Pseudo second order		
	q _e	K ₁	R ²	q _e	K ₂	R ²
DP	0.99	0.90	0.9875	1.97	0.52	0.9999

Table 2 Langmuir and Freundlich isotherm constants for adsorption of Cr⁺⁶ on DP

Adsorbent	Langmuir Isotherm			Frundlich Isotherm		
	q _m (mg/g)	B (l/mg)	R ²	K _f (mg/g)	1/n (-)	R ²
DP	10.67	0.011	0.979	0.34	1.97	0.9196

Table 3 Comparison of adsorption capacity of DP with the other adsorbents

Adsorbent	Adsorption capacity (mg/g)	References
Soya cake	0.28	[12]
Maize corncob	0.28	[13]
Jatropha oil cake	0.82	[13]
Sugar cane bagasse	0.63	[13]
Almond shell	0.58	[14]
DP	10.67	This study

3.5. Adsorption isotherm

The results present that the experiment data were better fitted to the Langmuir equation ($R^2 = 0.979$) than to the Fruendlich equation ($R^2 = 0.9196$). Thus, the assumption of the Langmuir equation explains that the adsorption, based on a homogeneous surface by monolayer adsorption without interaction between adsorbed

species [9], becomes more appropriate to describe this process. The contents of the Langmuir and Freundlich isotherms for Cr⁺⁶ adsorption on DP are presented in Table 2. Then, the adsorption capacity of DP was compared with the other adsorbents for Cr⁺⁶ adsorption and the results are presented in Table 3. It can be seen that the adsorption capacity is either comparable to or more than many of the other adsorbents. Therefore, it could be concluded that DP is an effective adsorbent for Cr⁺⁶ adsorption in aqueous solutions.

3.6. Desorption

In final experiment, desorption is studied to determine the spent adsorbent management. The results presented that the desorption efficiency of both adsorbents were 63.78, 65.64 and 64.03% at 0.1, 0.5 and 1 M HCl. From the result, the appropriate suitable is 0.1 M HCl which is more economically and less environmental effects than the other concentrations. This result indicated that it is possible to recovery adsorbed Cr⁺⁶ for utilization.

4. Conclusion

All adsorption factors as pH, contact time and initial Cr⁺⁶ concentration have affect to the Cr⁺⁶ adsorption on DP. The optimal condition for adsorption of Cr⁺⁶ using DP was pH 2, contact time 30 min and initial Cr⁺⁶ concentration 75 mg/l. Langmuir isotherm and pseudo second order were well fitted with experimental data, so they were used to explain the adsorption mechanism. The maximum adsorption capacity was 10.67 mg/g. Moreover, the desorption ability was 63.78% at 0.1 M HCl. All results conclude that DP is an effective adsorbent for Cr⁺⁶ contamination adsorption in wastewater. The DP utilization is an alternative for waste management or eco-friendly technique.

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