Adsorption studies of removal chromium from electroplating artificial wastewater using activated carbon

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Abstract. The batch removal of Cr ion from electroplating artificial wastewater by coconut shell activated carbon (adsorbent) was investigated. The influence of contact time, metal concentration, the dosage of adsorbent and granular size of the removal process was investigated. Metal concentration was analyzed by Atomic Absorption Spectrophotometer (AAS) method. The experiment result presented indicated that the process follows second-order rate mechanism and the data fits the Freundlich adsorption isotherm. The maximum adsorption of granular size was 0.70 mm at an initial concentration of 50% and the adsorption capacity was 0.8619 mg adsorbent/adsorbent. Adsorption studies confirmed that adsorbent effectively adsorption Cr ion in artificial wastewater.

1. Introduction
Chromium (Cr) is one of the element from heavy metals. Chromium pollution within environmental has now become attention because of its toxicity towards ecosystem [1]. It is known very toxic metal to humans and animals due to its carcinogenic nature. Cr is mostly produced from electroplating industrial waste as the main material used in metal plating activities is Cr solution. Chromium exits in the aquatic environmental mainly in two stable oxidation states, Cr(III) and Cr (VI) and have different chemical, biological and environment properties [2]. In general, Cr (VI) is more toxic than Cr(III). Cr(VI) effects human psikology, accumulates in the food chain and causes severe health problems ranging from simple skin irritation to lung carcinoma [3].

Several methods are utilized to remove chromium ions including chemical precipitation, ion-exchange, adsorption, membrane filtration, electrochemical treatment technologies. Among these, adsorption is the most promising technique because many reports have appeared on the development of low cost, renewable and environmentally friendly materials. Adsorption processes are widely used to remove chromium ions in wastewater. Heavy metal adsorption by coconut shell activated carbon has been commonly applied in industrial waste and chromium waste treatment [4]. In this research, the activated adsorbent developed from coconut shell because has known that the pore structure and surface chemical of coconut shell activated carbon effective be used to elimination chromium.

According to the ability of coconut shell in heavy metal accumulation, this study will discuss chromium ion adsorption efficiency in electroplating artificial waste which the adsorption model and kinetics figured later on by Langmuir and Freundlich mathematical equation.
2. Material and Methods
This study was run in water remediation laboratory, department of environmental engineering ITS which divided into four batches that are adsorbent preparation and characterization, reagent preparation, initial experiment, and the study itself

2.1. Materials
The adsorbent used in this study was a coconut shell, artificial wastewater using potassium dichromate, sulfuric acid (H₂SO₄) for adjusted the pH.

2.2 Adsorbent Preparation.
The adsorbent was originally made from coconut shell which has been carbonated, crushed and sieved to a size range of 1.70mm; 2.0mm and 2.36 mm (8, 10 and 12 mesh). Subsequently, Each size was activated by H₂SO₄ 4M for 24 hours in a room temperature which then the carbons were washed with distilled water to remove the sulfat acid to a normal pH 6 and water was evaporated at 105 °C in an oven for 24 hours and ready for use.

2.3 Adsorbent Preparation.
Adsorbent characterization has undergone both physically and chemically. Physical check including durability and density which consist of true bulk and apparent density, while the chemical check is done by an scanning electron microscope SEM-EDX method (Philips XL30 FEG) to figure on morphology (surficial shape) and substances that contained within it.

2.4 Adsorbate
A stock solution of artificial wastewater was prepared by K₂Cr₂O₇ in deionized water and acidified by an H₂SO₄ solution at pH 3.0. The stock Cr solution was diluted using aquadest to different chromium ion concentration from 50% and 75% for adsorption experiments.

2.5 Batch Adsorption Study
Batch process has undergone with 6 paddles jar test which is 6cm long and 2.5cm wide and rotational velocity that can also be manually controlled. Isotherm adsorption experiment was done with 100ml of the sample and 50%; 75%; and 100% of concentration, an adsorbent mass ranging from 0.5-8.0gr with a granular size of 2.36mm; 2.00mm; 1.70mm, and agitated at a constant temperature of 25°C Mixing rate of 100 rpm for 90 minutes. Kinetic adsorption check varied by contact period of 0.5; 1; 2; 4; and 6 hours to figure chromium concentration change rate before filtered by filter paper [5]. The equilibrated solution was analyzed to AAS (Atomic Absorption Spectrophotometer) method. The difference between the initial and final lead concentration was used to calculate the amount of chromium ion adsorbed.

2.6 Langmuir dan Freundlich Isotherm Adsorption Model
Wastewater Chromium adsorption mechanism was theoretically explained as follows:

\[
q_e = \frac{x}{m} = q_{maks} \frac{K_L C_e}{1 + K_L C_e} \quad (1) \text{ Langmuir Equation}
\]

\[
\frac{C_e}{q_e} = \frac{1}{q_{maks} K_L} + \frac{C_e}{q_{maks}} \quad (2)
\]

Where, Cₑ is the equilibrium Cr concentration (mg L⁻¹), Qₑ is the amount adsorbed at equilibrium (mg g⁻¹) Q maks and Kₛₐₖ are Langmuir constants related to maximum adsorpsi capacity and energy of adsorpsi.

\[
q_e = \frac{x}{m} K_f C_e^{1/n} \quad (3) \text{ Freundlich Langmuir}
\]

\[
\ln q_e = \log K_f + \frac{1}{n} \ln C_e \quad (4)
\]
Where, $C_e$ is the equilibrium Cr concentration (mg L$^{-1}$), $K_f$ and $n$ are Freundlich constant incorporating all in factors adsorption capacity, and indication of favorability of Cr adsorption onto adsorbed.

### 2.7 Adsorption Kinetics

Pseudo-first-orde (Lagurren) dan pseudo-second-orde [6] has been used to identify chromium adsorption mechanism developed within activated carbon.

$$\ln(q_e - q_t) = \ln(q_e) - \frac{K_1}{2.303} t$$  \hspace{1cm} (5) Pseudo-first-orde

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e t}$$  \hspace{1cm} (6) pseudo-second-orde

### 3. Material and Methods

#### 3.1 Adsorption Kinetics

One of the Physical-chemical characteristics of adsorbent that affect adsorption rate and capacity was pore size which needs to be relatively larger than the size of adsorbate. Coconut shell has plentiful of both micro and macro pores which promote effective adsorption.

| Characteristic | Result   |
|---------------|----------|
| Physical Durability | 1.78%    |
| Density       |          |
| a. True Bulk Density |          |
| Granular size (2.36 mm) | 0.7233 g/ml |
| Granular size (2.00 mm) | 0.7236 g/ml |
| Granular size (1.75 mm) | 0.7235 g/ml |
| b. Apparent Density |          |
| Granular size (2.36 mm) | 0.5385 g/ml |
| Granular size (2.00 mm) | 0.5389 g/ml |
| Granular size (1.75 mm) | 0.5392 g/ml |

According to physical characteristic check, coconut shell indicates physical durability percentage lower than 2% which is effective and appropriate as chromium ion adsorbent. 24 hours of activation process gave its pores cleaning and larger size. SEM analysis indicates the transformation in pores before and after the activation. H$_2$SO$_4$ has known to be effective in dissolving any impurities that attached. EDX exhibit any substances on activated carbon which contained carbon, calcium, oxygen, silicate, and potassium.

![Figure 1](image1.png)

Figure 1. Coconut shell characteristic before adsorption (a) 2.36 mm particle size, (b) 2.00 mm particle size, (c) 1.70 mm particle size.

| Component       | Percentage (%) |
|-----------------|----------------|
|                 |                |

Table 2. Coconut Shell Activated Carbon Composition
3.2 Adsorbent Size

Adsorbent size is one factor that affects the adsorption process because it defines the surface area, in which the more surface area it has the faster the adsorption rate [7]. To discover chromium removal efficiency, the experiment uses varied adsorbent size which divided into 2.36mm; 2.00mm; and 1.75mm and other condition that support the process were pH of 3, the temperature of 25°C, rotational speed of 100rpm and 100%; 75%; 50% of chromium concentration solution.

On Figure (2) indicates chromium removal efficiency difference between all three sizes where 1.70mm promotes highest removal efficiency as it became the smallest amongst three sizes analyzed [8], the smaller the size, the higher the surface area for adsorption process.

Figure 2. Chromium Removal Efficiency Relative To Adsorbent Size And Concentration

3.3 Chromium Concentration

Chromium concentration was varied to 100%; 75%; and 50%. Variation was intended to discover how concentration affects the adsorption process. Other conditions that support the process were pH of 3, the temperature of 25°C, the rotational speed of 100rpm.

Table (3) indicates a concentration of 50% has the highest removal efficiency compared to 100% (Fig. 3). This was because lower molecular density can be absorbed easier than that with higher concentration [9].

According to Illustration (3) the higher the concentration, the less the chromium removal efficiency became. It was because higher concentration gives a higher load to adsorbent media while surface area remains the same, thus promotes saturation (saturated state) [9].
Figure 3. Removal Efficiency of Cr Concentration

Table 3. Removal Efficiency of Cr Concentration In Various Adsorbent Mass

| Concentration (%) | Removal Efficiency (%) |
|-------------------|------------------------|
|                   | In Various Adsorbent Mass (gram) |
|                   | 0.5 | 1  | 2   | 4   | 6   | 8   |
| 50                | 35.61 | 59.65 | 77.26 | 86.81 | 94.96 | 94.79 |
| 75                | 26.69 | 35.77 | 64.34 | 87.41 | 92.01 | 92.00 |
| 50                | 26.49 | 33.85 | 55.32 | 61.69 | 78.79 | 87.88 |

3.4 Adsorbent Dosage

Table (4) indicates that removal efficiency increased in accordance to adsorbent dosage added. This was because addition in adsorbent mass also promotes the enhancement of surface area and pores that bind chromium ion within adsorption process. As Figure (4) indicates an enhancement in adsorption efficiency through dosage addition only up to a certain level [10]. Figure (4) indicates saturation caused by pores that were already covered by Chromium.

Tabel 4. Cr Removal Efficiency In Dosage Variation

| Adsorbent Mass (Gram) | Removal Efficiency (%) |
|-----------------------|------------------------|
|                       | 2.36 (mm) | 2.00 (mm) | 1.75(mm) |
| 0.5                   | 29.71      | 35.61      | 49.41    |
| 1                     | 55.57      | 59.65      | 69.89    |
| 2                     | 73.27      | 77.26      | 82.38    |
| 4                     | 75.40      | 86.81      | 91.15    |
| 6                     | 87.15      | 94.96      | 97.31    |
| 8                     | 86.90      | 94.79      | 97.39    |

Figure 4. Cr Removal Efficiency In Dossage Variation

3.5 Isotherm adsorption

Chromium ion adsorption equation illustrated by Langmuir and Freundlich model. Langmuir assumes that surface area of adsorbent formed monolayer which reversible [11] whereas Freundlich stated that surface area of adsorbent formed very weak interaction which irreversible [12]. These two models give information about adsorbent maximum capacity and adsorption intensity. The Isotherm constants of Freundlich and Langmuir were calculated from the plots of Ce/qe vs Ce as depicted from Figure (5) and Log qe vs Log Ce. Respectively, and the result are listed in table (5). Results correlation of the study
and adsorption model can be discovered by (R^2) coefficient obtained. As Figure 5 the values of determination (R^2) are 0.9582 for Freundlich and 0.9183 for langmuir.

| No | Diameter   | K_L  | Qm   | R^2  | K_F  | n   | R^2  |
|----|------------|------|------|------|------|-----|------|
| 1. | 8 Mesh; Cr 100% | 0.0487 | 1.0120 | 0.8285 | 0.0507 | 1.2407 | 0.8915 |
| 2. | 8 Mesh; Cr 75%  | 0.3397 | 0.5225 | 0.878 | 0.1581 | 2.4143 | 0.9452 |
| 3. | 8 Mesh; Cr 50%  | 0.0124 | 7.5758 | 0.8697 | 0.0996 | 0.9941 | 0.8797 |
| 4. | 10 Mesh; Cr 100% | 0.0796 | 1.2511 | 0.8096 | 0.0883 | 1.2142 | 0.843 |
| 5. | 10 Mesh; Cr 75%  | 0.2091 | 1.0344 | 0.9071 | 0.2034 | 1.8734 | 0.9153 |
| 6. | 10 Mesh; Cr 50%  | 0.3170 | 0.9656 | 0.9091 | 0.2187 | 1.4615 | 0.9685 |
| 7. | 12 Mesh; Cr 100% | 0.0100 | 9.2081 | 0.9183 | 0.0810 | 0.8285 | 0.9582 |
| 8. | 12 Mesh; Cr 75%  | 0.0398 | 4.4053 | 0.9354 | 0.1679 | 1.0637 | 0.9308 |
| 9. | 12 Mesh; Cr 50%  | 0.7269 | 0.8619 | 0.9022 | 0.3269 | 1.5195 | 0.9640 |

Figure 5. Freundlich Model (a) Langmuir Model (b)

Table 5 indicates the ability of coconut shell in absorbing chromium ion regarding its Langmuir model which ranging from 0.5225 to 9.2081 mg/g. Cr adsorption value from 1.70mm coconut shell was higher than 2.36mm and 2.00mm which are 1.0120mg/g and 1.2511mg/g respectively, indicating that adsorption capacity was affected by adsorbent surface area.

3.6 Kinetika Adsorpsi

Adsorption kinetics is illustrated by first-order (equation 5) and second order (equation 6). Adsorption process of chromium ion by coconut shell varied by its granular size. The analysis result of the adsorption mechanism was plotted into the charts below (Figure 6).
Figure 6. Pseudo-first order (a) and Pseudo-second order (b)

Table 6. Analysis Result of (Cr) Kinetical Reaction with Coconut Shell Adsorbent

| Adsorbent Size | Cr Concentration (%) | Pseudo-first order | Pseudo-second order |
|----------------|----------------------|--------------------|---------------------|
|                |                      | q_e                | K_1, R^2            | q_e                | K_2, R^2 |
| 8 Mesh         | 100%                 | 1,0957             | 1,3477, 0,8442      | 0,4112             | 1,9504, 0,9906 |
|                | 75%                  | 0,2109             | 1,0759, 0,9881      | 0,2668             | 8,2713, 0,9995 |
|                | 50%                  | 0,1253             | 1,0639, 0,9919      | 0,1737             | 19,6502, 0,9992 |
| 10 Mesh        | 100%                 | 0,3018             | 1,1204, 0,9978      | 0,4029             | 4,6913, 0,9988 |
|                | 75%                  | 0,0730             | 0,4072, 0,7169      | 0,2569             | 20,9644, 0,9989 |
|                | 50%                  | 0,1225             | 1,3452, 0,9906      | 0,1892             | 23,5366, 1 |
| 12 Mesh        | 100%                 | 0,1988             | 0,9718, 0,9985      | 0,3828             | 8,5229, 0,9997 |
|                | 75%                  | 0,1059             | 0,9627, 0,9976      | 0,2767             | 16,8464, 0,9997 |
|                | 50%                  | 0,0833             | 1,0066, 0,9976      | 0,1892             | 23,5460, 1 |

The result indicates that chemical adsorption has been occurred. There is a trend on chemical adsorption that refers to pseudo-second order relative to granular size and concentration.

4. Conclusion
Coconut shell activated carbon used in electroplating wastewater was proven to be effective in removing chromium (Cr) ion. The granular size and dosage of adsorbent and Cr concentration were varied in this study. The range of removal efficiency by the concentration of 50%; 75%; and 100% was 87.15%-97.31%; 87.59%-95.73%; 64.42%-87.84% respectively. Higher Freundlich coefficient of Cr adsorption was indicated at isotherm, which explained the utilization of multilayer coconut shell activated carbon correspond to the Freundlich model and pseudo-second-order.

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