Phytoremediation of Cr(VI) from Aqueous Solution by *Pistia stratiotes* L.: Efficiency and Kinetic Models

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**ABSTRACT**

Phytoremediation utilizes metal-trapping plants to recover water as the main source of contamination, *Pistia Stratiotes* L. is a hyperaccumulator plant that is considered capable of reducing hexavalent chromium levels in wastewater. This is evidenced by the results obtained on each of the variables investigated, namely the effect of contact time and the number of plants. Where, the effect of contact time on the most optimal reduction in hexavalent chromium concentration on day 10 is 22.55 mg/L with an efficiency value of 54.89%. While the effect of the number of plants on the reduction in the most optimal metal concentration was found in the first reactor with the number of plants 4, chromium concentration was 23.16 mg/L with an efficiency value of 54.89%. This means that the longer the phytoremediation process will affect the decrease in chromium levels in waste samples but has no effect on the number of plants used if the plant mass is not calculated before treatment. The recommended kinetic models for phytoremediation systems using *P. Stratiotes* L. plants are Richard's Pseudo First Order and Pseudo Second Order. However, when viewed from the prediction value and experimental data, Pseudo Second Order Kinetic Models are considered suitable to describe the phenomenon that occurs in this study, with an SSE value of 1.0042 and a reaction rate constant of 1.1662 day⁻¹ to 1.5623 day⁻¹.

**Keywords**: Chromium hexavalent, kinetic models, phytoremediation, *Pistia stratiotes* L.

1. **INTRODUCTION**

Mining and processing operations of nickel ore are regarded as one of the main industrial sectors in Indonesia, especially in eastern regions such as Sulawesi [1]. Processing nickel ore via hydrometallurgical and pyrometallurgical methods is still in significant demand, considering the comparatively moderate costs with maximum outcomes. However, both procedures have the potential to create suspended particles and heavy metal waste from nickel ore washing activities, runoff from the ore stock file area, and nickel ore leaching in the hydrometallurgical process [2].

Significantly, the environmental damage produced by heavy metals such as chromium hexavalent can dissolve in water and harm aquatic bodies [3,4]. And can injure aquatic species and disturb aquatic ecosystems. Heavy metals that accumulate in the tissues of living animals and have the ability to harm higher levels in a food chain [5]. It can also interfere with the functioning of organs, the neurological system, the respiratory system, and the reproductive system, both in people and in animals [6]. It takes substantial effort to manage waste containing heavy metals effectively. The implementation of suitable and effective waste treatment technology is one of the crucial stages in decreasing the negative impact produced by heavy metals on the surrounding environment [7–9].

Heavy metals and toxic substances can be removed by several waste treatment procedures physiologically, physically and chemically, including adsorption, ion exchange, chemical precipitation,
electrochemical processing and filtration membranes and phytoremediation [10–12]. The phytoremediation approach employs metal-trapping plants to recover water as the major source of pollution [13]. This technique is plant-based, such as plants that grow in nature as well as plants that have been genetically engineered to heal land: polluted soil and water [14]. The plant to phytoremediation technologies have the capacity to take significant quantities of heavy metals into their roots [15], withstand various metals, and have physiological characteristics to adapt to varied settings [16]. In addition, the metal detoxification phytoremediation technique for wastewater treatment is more cost-effective and ecologically benign [17]. Previous studies have demonstrated that several aquatic plants are useful for phytoremediation applications, e.g. Kiambang (Pistacia Stratiotes L.), which has been proven to be relevant for the elimination of Fe – pollutants [18].

Different from previous studies, this study used phytoremediation method with P. Stratiotes L. as a Hyperaccumulator (absorbing agent) that thrives in the Morowali Area, Central Sulawesi. In attempts to reduce the levels of chromium hexavalent (Cr-VI) heavy metals in nickel industry wastewater with several treatment variations, namely variations in the number of plants contacted to wastewater and variations in plant contact time to wastewater in the phytoremediation process. This was done to assess the ability of P. stratiotes L. (Kiambang) and the effect of research variation treatment in attempts to minimize the content of chromium hexavalent (Cr-VI) heavy metals in a nickel industry wastewater.

2. MATERIAL AND METHOD
2.1. MATERIAL
The materials used in this study were 1,5 – diphenylcarbazide (Merck, Germany), Destillated water, Ortho – phosphoric acid 85 % (Merck, Germany), Sulfuric Acid 0.2 N (Merck, Germany), Acetone as a solvent of diphenylcarbazide reagent (Merck, Germany) and tissues, Kiambang (Pistia stratiotes L.) as a phytoremediation plant was collected from Wosu District, Morowali, Central Sulawesi. The artificial wastewater containing potassium dichromate of 50 mg/L was prepared by mixing potassium dichromate and destillated water.

2.2. PLANTS ACCLIMATIZATION
A total of seven reactors were prepared for batch operation. The reactor model used in this experiment is a batch reactor model made of plastic with a size of 140 x 110 x 50 mm as schematically in Figure 1 with single zone. The reactor is then filled with water to a height of 100 mm and allowed to stand for 6 days until the plants have new shoots and look lush.

![Figure 1. Schematically reactor model.](image)

2.3. CHROMIUM REMOVAL
Wastewater samples are poured as much as ± 5 Liters into the prepared reactor. Slowly put P. stratiotes L into the reactors to vary the number of plants in contact with wastewater samples, then put the plants to cover the surface of the wastewater in the pond for variations in plant contact time to waste. Effluent samples were taken daily for 10 days for hexavalent chromium analysis.

2.4. EXPERIMENTAL ANALYSIS
Total chrome content in wastewater samples were analyzed using SNI 6989.71 : 2009. Chromium content in plants was analyzed in roots and leaves. Analysis of chromium in
wastewater can use a visible spectrophotometer with a wavelength of 430 nm. The efficiency of chromium hexavalent removal can be determined by comparing the chromium levels before and after the removal in Eq. 1

\[
% \text{efficiency} = \frac{C_0 - C_t}{C_0} \times 100\% \tag{1}
\]

\(C_0\) is Initial concentration of chromium hexavalent in wastewater samples. \(C_t\) is the final concentration of chromium in the sample [7].

2.5. KINETICS STUDIES

Kinetic model of phyto remediation process using \(P\) \textit{Stratiotes} \textit{L}. plant is the most significant factor in influencing the efficiency, effectiveness and natural behavior of aquatic plants during the process of removing heavy metals in water or soil [19]. In addition, kinetic modeling in a process is one of the main components in comprehending a phenomena that happens in a system [20].

In this investigation using Richard’s pseudo – first – order (PFO) and pseudo – second – order (PSO) kinetic models in line with the kinetic model given by Kamalu et al. [21] which has been matched with the verification and experimental outcomes of this study. This kinetic model is developed by researching the absorption process of plant heavy metals beginning from the roots and accumulating them in their tissues, then being degraded by plant enzymes [22–24]. To solve such systems, it is recommended to use differential equations as illustrated in equations (2) and (3).

Pseudo First Order kinetic model:

\[
q = q_m - (q_m - q_0) e^{k_1(t_0 - t)} \tag{2}
\]

Pseudo Second Order kinetic model

\[
q = \frac{q_0 - q_m(q_m - q_0)}{1 - (q_m - q_0) e^{k_2(t_0 - t)}} \tag{3}
\]

Where,

\(q\) = metal concentration at time \(t\), mg/L
\(q_m\) = maximum concentration of absorbed metal, mg/L
\(q_0\) = initial metal concentration, mg/L

\(k_1\) = PFO kinetic rate constant, \(\text{day}^{-1}\)
\(k_2\) = PSO kinetic rate constant, \(\text{mg/L} \cdot \text{day}\)
\(t\) = sampling time, day
\(t_0\) = initial sampling time, day

Determination of the kinetic model is based on the application of adsorption kinetics with nonlinear optimization using an error function to assess the adequacy of the model employed, in addition to the standard error value used to assure the quality of the data fitted to the model [25]. This research uses an error function, specifically Sum Square Error (SSE). SSE is one of the most widely reported error functions in isotherm modeling [26]. The smallest value of the error function is used as a criterion that states the best model because it has the minimum error value between the experimental results and the predicted values [27]. This function can be represented by the following expression:

\[
SSE = \sum_{i=1}^{n} (q_{t, \text{experiment}} - q_{t, \text{prediction}})^2 \tag{4}
\]

Where, \(q_{t, \text{experiment}}\) is the concentration of chromium hexavalent obtained based on the experiments that have been carried out. Meanwhile, \(q_{t, \text{predicted}}\) is concentration of chromium hexavalent calculated from the isotherm model used.

3. RESULTS AND DISCUSSION

The experiments of chromium hexavalent removal in wastewater nickel industry using reactors with batch systems shown Figure 1. It begins with the stage of acclimation of plants for seven days. This stage is carried out as a time of plant adaptation to the planting media and the surrounding environment.

3.1. EFFECT OF CONTACT TIME ON CHROMIUM HEXAVALENT REMOVAL

In this experiment, chromium hexavalent removal was carried out in terms of contact time of \(P.\) \textit{stratiotes} \textit{L.} as hyperaccumulator plants. A total of ten \(P.\) \textit{stratiotes} \textit{L.} plants were put in the reactor for 10 days with an initial concentration of wastewater of 50...
mg/L and a capacity in each reactor of 5 Liters.

**Figure 2.** Effect of contact time on chromium hexavalent removal.

**Figure 3.** Effect of the number of plants on chromium hexavalent removal.

Figure 2 indicated that there was a drop in chromium hexavalent levels beginning from day 2, which was about 24.076 mg/L. The process of absorption or translocalization of heavy metal compounds carried out by *P Stratiotes* L plants progressed slowly until achieving the most ideal absorption values on day 10, namely 22.55 mg/L.

The potential to absorb heavy metals by this plant is believed to be maximal until the plant exhibits morphological changes marked by yellowing of the leaves and plants in a wilted state or sinking to the bottom of the reactor. Slowly but steadily, this plant reduces hexavalent chromium levels over 50%.

### 3.2. EFFECT OF THE NUMBER OF PLANTS ON CHROMIUM HEXAVALENT REMOVAL

The effect of the number of plants in the removal of chromium hexavalent levels is regarded important with the purpose of understanding the appropriate number of plants to reduce chromium levels in nickel industry wastewater.

A total of three reactors were created with variations in the amount of various plants in each reactor, the first reactor was filled with 4 plants, the second reactor was filled with 6 plants and the third reactor was filled with 8 plants with an observation duration of 8 days. The starting concentration of waste is 50 mg/L with the total volume in each reactor being 5 liters.

**Figure 3** showed that there was a decline in chromium hexavalent levels in the first reactor successively from the first day to the final day, respectively 26.32 mg/L, 25.73 mg/L, 25.89 mg/L, 25.73 mg/L, 25.36 mg/L, 24.40 mg/L, and 23.16 mg/L. Meanwhile, in the second reactor acquired the results of a drop in chromium levels in water samples successively, namely 27.98 mg/L, 27.13 mg/L, 26.52 mg/L, 25.88 mg/L, 25.49 mg/L, 24.76 mg/L, 23.79 mg/L, and 24.27 mg/L. While in the third reactor exhibited a reduction in chromium hexavalent levels from the first day to the final day, namely 27.84 mg/L, 26.28 mg/L, 26.21 mg/L, 25.80 mg/L, 25.76 mg/L, 24.96 mg/L, 23.99 mg/L, and 24.27 mg/L. When compared to the most ideal decline in levels occurred on day 8 for the three reactors, although the lowest decrease in distillated water chromium levels was reported in the first reactor with a final concentration of 23.16 mg/L. The drop in chromium levels in each reactor was not considerable, this was attributed to limited sunlight intake in phytoremediation plant medium, resulting in the metal absorption process not working...
properly. In addition, the unmeasured plant mass at the beginning of the phytoremediation process impacts the absorption of chromium hexavalent metal in the sample, even when the number of plants has been distinguished [11].

**Figure 4.** Efficiency of the number of plants on chromium hexavalent removal.

### 3.3. EFFICIENCY OF CHROMIUM HEXAVALENT REMOVAL

The capacity of heavy metal absorption carried out by *P. stratiotes* L. is quite excellent and this plant can be categorized as a hyperaccumulator plant in the phytoremediation process [24]. This can happen because the metal content in the water body will be transferred by plants with transport networks [28], particularly xylem and phloem which are then routed to specific areas of the plant [23,29]. Based on the test results, the efficiency level of the phytoremediation method with *P. stratiotes* L. showed quite good results, where the measurement of the efficiency of the phytoremediation process in the variation of treatment of the number of plants contacted to wastewater showed the lowest efficiency value, namely in second reactor on the first observation day with an efficiency value of 44.05% and the highest efficiency value in first reactor on the last observation day with a value efficiency of 53.69%. Meanwhile, the variation in the treatment of plant contact time with wastewater (Figure 5) indicated the lowest efficiency value, that is on the first observation day with an efficiency value of 51.84% and the maximum efficiency value on the final observation day with an efficiency value of 54.89%.

**Figure 5.** Efficiency of contact time on chromium hexavalent removal.

Determination of the efficiency of phytoremediation technique using *P. stratiotes* L as a hyperaccumulator plant seeks to discover the variables or impacts of different procedures carried out in this research to obtain the desired outcomes. Based on the efficiency values obtained from both treatment variations, it can be observed that the best results are produced from changes in the number of plants as much as 6 and the duration of observation period for 8 days.

### 3.4. KINETICS OF PHYTOREMEDIATION PROCESS

The kinetic model is helpful for examining the mass transfer rate of metals from a medium to plant tissues [30]. On top of that, the kinetic research gives relevant information on the design and optimization of biological treatment technologies at a big scale [19].

the kinetic characteristics of numerous heavy metal removals using accumulator plants are given in Tables 1 and 2. Whereas, the uptake rate constant (k) for the plants is an essential parameter for measuring the metal uptake performance by plants [31]. After running
using both recommended kinetic models, the $k$ value obtained ranged from 0.0012 day$^{-1}$ to 1.7176 day$^{-1}$ with maximum concentration value of chromium hexavalent that is trapped in the range of 23.264 mg/L to 48.95474 mg/L and the minimum value of SSE 1.0042 in second reactor variations in the number of plants. Based on the data obtained in this study, it shows that the number of plants and contact time do not significantly influence the reaction rate constant value. Meanwhile, the concentration of hexavalent chromium absorbed relies on the contact time necessary for plants to absorb the heavy metal to its maximum limit. Based on the SSE values obtained in the kinetic model of phytoremediation of heavy metals using P. Stratiotes plants. L in reducing the concentration of hexavalent chromium metal in wastewater, the two models that have been proposed in this study show that there is a very good model match between experimental data and predicted data from the proposed kinetic model. This is indicated by the acquisition of a small SSE value. The SSE value obtained reflects the amount of the discrepancy between the value predicted by the model and the actual value from the data. Therefore, the lower the SSE value (closer to 0) in a research, the greater the compatibility between the kinetic model and the description of the system used.

Table 1. Kinetic Parameters of variation in the number of plants.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Reactor</th>
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<tbody>
<tr>
<td></td>
<td>R1</td>
</tr>
<tr>
<td><strong>Pseudo First Order</strong></td>
<td></td>
</tr>
<tr>
<td>$k$ (day$^{-1}$)</td>
<td>1.5623</td>
</tr>
<tr>
<td>$q_m$ (mg/L)</td>
<td>24.6996</td>
</tr>
<tr>
<td>SSE</td>
<td>3.7861</td>
</tr>
<tr>
<td><strong>Pseudo Second Order</strong></td>
<td></td>
</tr>
<tr>
<td>$k$ (day$^{-1}$)</td>
<td>0.0066</td>
</tr>
<tr>
<td>$q_m$ (mg/L)</td>
<td>48.8814</td>
</tr>
<tr>
<td>SSE</td>
<td>3.7861</td>
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Table 2. Kinetic Parameters of variation contact time.

<table>
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<th>Parameter</th>
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<tbody>
<tr>
<td><strong>Pseudo First Order</strong></td>
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<tr>
<td>$k$ (day$^{-1}$)</td>
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<tr>
<td>$q_m$ (mg/L)</td>
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<tr>
<td>SSE</td>
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<td><strong>Pseudo Second Order</strong></td>
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<td>$k$ (day$^{-1}$)</td>
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<td>$q_m$ (mg/L)</td>
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<td>SSE</td>
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Figure 6. Kinetic models of PFO and PSO on variation in plant numbers.

Figure 7. Kinetic models of PFO and PSO on variation of contact time.
Figures 6 and 7 illustrate comparison of PFO and PSO kinetic models with experimental results obtained from chromium hexavalent removal utilizing *P. Stratiotes L.* phytoremediation technique. It can be seen that there is a match of the model used with the experimental data. The referred to figures and tables demonstrate that there is a good fit between the experimental findings and the model predictions, as is obvious from the values of the SSE. A minimized SSE number suggests that statistical computations assessing the discrepancy between observed and predicted values are modest, thereby suggesting that the model is acceptable for application [32].

Figure 6 (a), (b) and (c) show concentration versus time plots with a comparison of concentration values predicted from the PFO suggesting that the model is acceptable for application [32]. Figure 6 (a), (b) and (c) show concentration versus time plots with a comparison of concentration values predicted from the PFO and PSO kinetic models with experimental data. Where, in Figure 6 (a) in reactor 1 with 4 plants, it indicates that the qm value of PFO is 24.69 mg/L and the qm value of PSO is 48.88 mg/L. In plot (b) for reactor 2 with the number of plants 6 shows the qm value of PFO which is 24.83 mg/L and the qm value of PSO which is 48.95 mg/L. Meanwhile, plot (c) for reactor 3 with 8 plants indicates the qm value of PFO, which is 24.95 mg/L and the qm value of PSO that is 48.87 mg/L. The difference between the predicted qm values in the PFO and PSO kinetic models for the three reactors can be seen from the plot which is significant. Based on these figures, it can be observed that the PFO kinetic model is quite suited for this system, this is because the qm value in reactor 2 is very similar to the experimental data concentration value for variations in the number of plants.

Meanwhile, Figure 7 shows a plot of concentration versus time with a comparison of concentration values from prediction findings and experimental data. Where, in this situation the variation used is a variation in contact time. From the results obtained, it can be seen that the qm value of PFO is 23.26 mg/L and the qm value of PSO is 48.69 mg/L, thus it can be seen that the PFO kinetic model is very suitable for this system. The predicted PFO qm value is quite close to the experimental data value. This is also supported by the SSE value in the PFO kinetic model being significantly smaller compared to PSO in the two variations evaluated.

4. CONCLUSION

The ability of *P. Stratiotes L.* plants to remove chromium hexavalent metal in nickel industry wastewater is proven to be able to reduce heavy metal levels by 54.89 % or 22.55 mg/L from the total initial concentration of 50 mg/L. Pseudo First Order and Pseudo Second Order Kinetic Models are considered suitable to describe the phenomenon that occurs in this study, with an SSE value of 1.0042 and a reaction rate constant of 0.0012 day\(^{-1}\) to 1.7176 day\(^{-1}\). From the qm and SSE values obtained, it can be determined that the most suitable kinetic model to utilize is the Pseudo First Order kinetic model.

REFERENCES


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