

Effect of electrodeposition reactor type on nickel recovery from electroplating wastewater

Djaenudin^a, Diana Rahayuning Wulan^a, Hari Rom Hariyadi^a

^aResearch Center for Chemistry, Indonesian Institute of Sciences, Jl. Cicitu Bandung 40135, Indonesia

Abstract

Nickel recovery from synthetic electroplating wastewater using electrodeposition reactor has been investigated. The experiment was conducted in batch system using two types of electrodeposition reactors, partitioned reactors using water hyacinth leaf and single chamber reactor, a copper plate cathode size, graphite anode and applied DC voltage of 5V. The goal of this research was to obtain the best reactor type for nickel electrodeposition from NiSO₄ solution. Factors analyzed in the study were the change in pH, conductivity, electric current, cathode mass and nickel concentration in the catholyte. The electrodeposition was carried out during 4 hours. The initial concentration of nickel in the catholyte contained 2,402.19 mg/L. The results showed that the partitioned reactor using of water hyacinth leaf performed better than the single chamber reactor. The partitioned reactor using water hyacinth leaf decreased concentration of nickel in catholyte to 1756.19 mg/L and had the current efficiency of 88.17% with the specific energy of 5.2 kwh/kg nickel.

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Keywords: Nickel electrodeposition; partitioned reactor; single chamber reactor; water hyacinth leaf

1. Introduction

Nickel is a heavy metal widely used in the industries. More than 3000 nickel alloys are used for industrial application^{13, 18}, namely: stainless steels in the automotive industry as the biggest user, Monel (a 66% nickel - 32% copper alloy), nickel-electroplating (metallic coating), nickel-cadmium-battery, Raney-nickel (the catalyst in the hydrogenation of fats and oils), mixed magnetic and magnetic tape, nickel electrodes and filler wires, acrylic ester synthesis, surgical and dental prosthesis, pigment paint, coins, electronics, ceramics and glass.

Nickel in small amounts is important for human body, but when it presents in large amounts it may generate lung cancer, nose cancer, larynx cancer, prostate cancer, kidney damage, loss of balance, respiration failure, birth defects,

asthma, chronic bronchitis and liver damage¹. In environmental issues, nickel existence in water body also raises awareness; therefore local government defines the limit for nickel in wastewater. Based on the Wastewater Quality Standard (Annex I Regulation of Environmental Minister 5/2014), the nickel content in the effluent must not exceed 1 mg/L for the metal plating industry and 0.2 mg/L for non-specific wastewater.

Some previous researchers have conducted nickel removal technology from industrial wastewater, such as electrodeposition studies using single chamber electrolytic reactor^{3, 4, 5, 6, 8, 9, 10, 11, 12, 14, 15, 20, 21, 22, 23, 24} and electrolytic membrane reactor (partitioned reactor)¹⁷.

The research by Isdiriayani et al.¹⁴ using 500-mL single chamber electrodeposition reactor and titanium plates as anode and cathode, set the voltage input of 3 V and addition of 60 g/L Na₂SO₄, 6 g/L MgSO₄ and 36 g/L H₃BO₃, during 1 hour produced 0.07 grams of nickel metal deposit (from initial nickel concentration 12.5 g/L) and current efficiency of 70% and the energy specific of 3 kwh/kg nickel. The partitioned reactor study¹⁷, using electrolytic membrane reactor, PE 203 ion-exchange membrane, titanium anode and stainless steel AISI 316 cathode with 4 V DC-voltage input, during 2 hours had reduced 94.17% of nickel (initial nickel concentration 70 g /L) with current efficiency of 97.15% and the specific energy of 5 kWh/kg nickel. The partitioned reactor seems perform better than single chamber reactor. However, the performance comparison between partitioned to single chamber reactor at the same operating conditions has not yet been conducted.

Due to PE-203 cost, the membrane may replace by natural permeable membrane, e.g. leaf of the water hyacinth (*Eichhornia crassipes*), which abundant in Indonesia and sometimes classified as harmful plant for aquatic body. One of the important membrane characters is its pore size¹⁹.

In this experiment, water hyacinth leaf was used as partition membrane between the anode and cathode chamber. Water hyacinth leaf was selected as bio-membrane due to its fiber/cellulose¹⁶, which contains 64.51% cellulose acetate which is usually used as a raw material in the synthetic membranes manufacture. Moreover, water hyacinth leaf is thick enough so not be easily torn and more permeable that allow the ions exchanged through its pores. Pore size of the water hyacinth leaf surface is 6.158 nm⁷.

This research aims to compare the performance of single chamber reactor to partitioned reactor in the electrodeposition system of nickel removal from NiSO₄ solution as artificial electroplating wastewater.

2. Material and Method

The experiment performed at Environmental Laboratory - Research Center for Chemistry, Bandung. The reactor applied on this research was cylindrical flexy-glass with 500-mL working volume as single chamber reactor and assembled those two reactors separated by 5 cm-diameter water hyacinth leaf as membrane as partitioned reactor, as set up on Fig. 1. The distance between the anode and the cathode in partitioned reactor was set on 6 cm.

On the partitioned reactor, 0.2 M H₂SO₄ anolyte and 2402.19 mg Ni/L NiSO₄.6H₂O catholyte (artificial wastewater) were applied. On the single chamber reactor, solution of 2402.19 mg Ni/L NiSO₄.6H₂O mixed and function as anolyte and catholyte. Both reactor types using 0.4 mm graphite plate 4 cm x 10 cm as anode and 0.4 mm copper plate 4 cm x 10 cm as cathode. Both electrodes dipped into the electrolyte solution as deep as 6 cm. The observation of experimental carried out during 4 hours at room temperature (25 – 30°C).

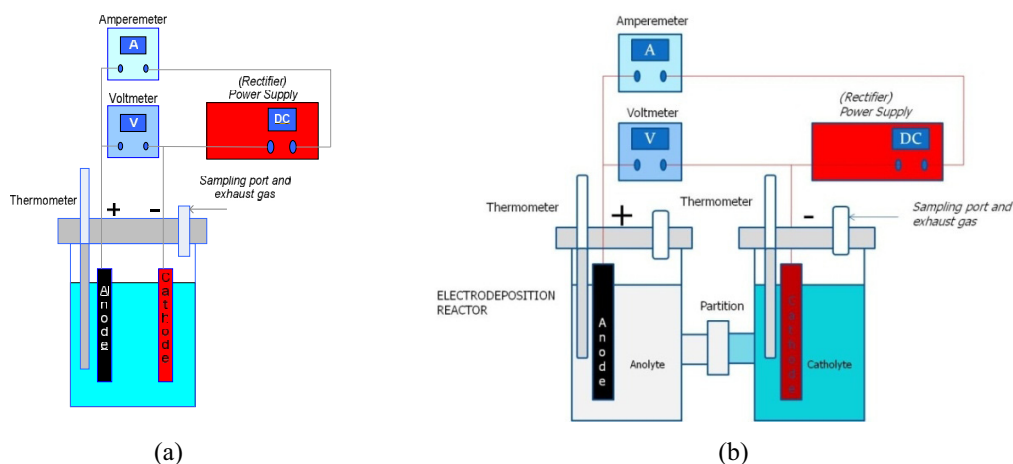


Fig. 1. Experimental set up of single chamber reactor (a) and partitioned reactor using water hyacinth leaf (b).

The change of pH, electric current, cathode weight and nickel concentration in the catholyte were analyzed during operation time. The dissolved nickel removal, current efficiency and specific energy would be selected as indicators of optimum process. The pH was measured by Sanwa pH-meter, while voltage and electric current by AVO-meter (amperemeter was connected in series with the current circuit while the voltmeter connected in parallel) and the electric conductivity by conductivitymeter. Nickel deposit on cathode was calculated by gravimetric method using equation (1) below

$$m_{\text{nickel deposition}} = m_t - m_0 \quad (1)$$

where m_0 is the initial cathode weight (kg) and m_t is the end cathode weight (kg)²⁵. The characteristic of the metal deposit on cathode was analyzed using X-Ray Diffraction Spectroscopy (XRD). Nickel ion concentrations were observed using Atomic Absorption Spectrophotometer (AAS)^{2, 27}, whereas calculation of nickel concentration decreasing was using equation below²⁵

$$R(\%) = \frac{(C_0 - C_t)}{C_0} \times 100\% \quad (2)$$

where C_0 is the initial Ni^{2+} concentration (mg/L) and C_t is Ni^{2+} concentration at the end of process (mg/L).

Sampling ports were made on the top of the reactor which also served as gas vent, since gas formation was occurred during process. The rectifier was used to convert AC into DC input which was connected to the anode and cathode of electrodeposition reactor. The DC voltage input was 5V.

3. Result and Discussion

3.1. Nickel Content Reduction

After 4 hours operation of electrodeposition reactor, dissolved nickel concentration in catholyte solution of both reactors-type tend to decrease, as shown in Table 1.

Table 1. Decrease of nickel concentration in catholyte

Reactor Type	Nickel Concentration (mg/L)		Nickel concentration decrease (%)
	Initial	End	
Single chamber reactor	2402.19	1875.50	21.925
Partitioned reactor using water hyacinth leaf	2402.19	1756.19	26.892

Table 1. shows that nickel concentration still exceed the standards of electroplating plating industries wastewater quality. The efficiency of nickel concentration removal on both reactors-type did not show significant result. To increase the removal efficiency of nickel concentration, adding a supporting electrolyte in the catholyte, increasing electrical potential and increase the processing time could be an alternative choice.

Nevertheless, the partitioned reactor using water hyacinth leaf showed more effective than the single chamber reactor for nickel elimination from wastewater solution. On the both reactors type, common reduction reactions occurred at cathode are $\text{Ni}^{2+} + 2e^- \rightarrow \text{Ni}$; $2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^-$ and oxidation reaction at anode is $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4e^-$. On the single chamber reactor, hydrogen ion (H^+) was produced at the anode that would ease directly flow to the cathode and produced hydrogen as the reaction $2\text{H}^+ + 2e^- \rightarrow \text{H}_2$. That condition would increase gas bubbles of H_2 that disturbed nickel deposition on cathode, as shown on Fig. 2(a). Illustration of nickel deposit on the cathode of both reactors type can be observed on Fig. 2.

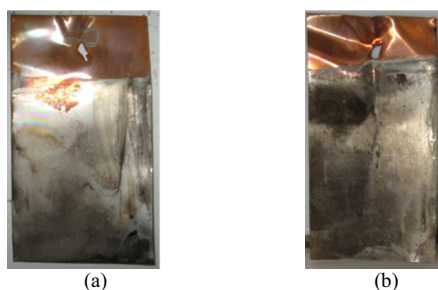
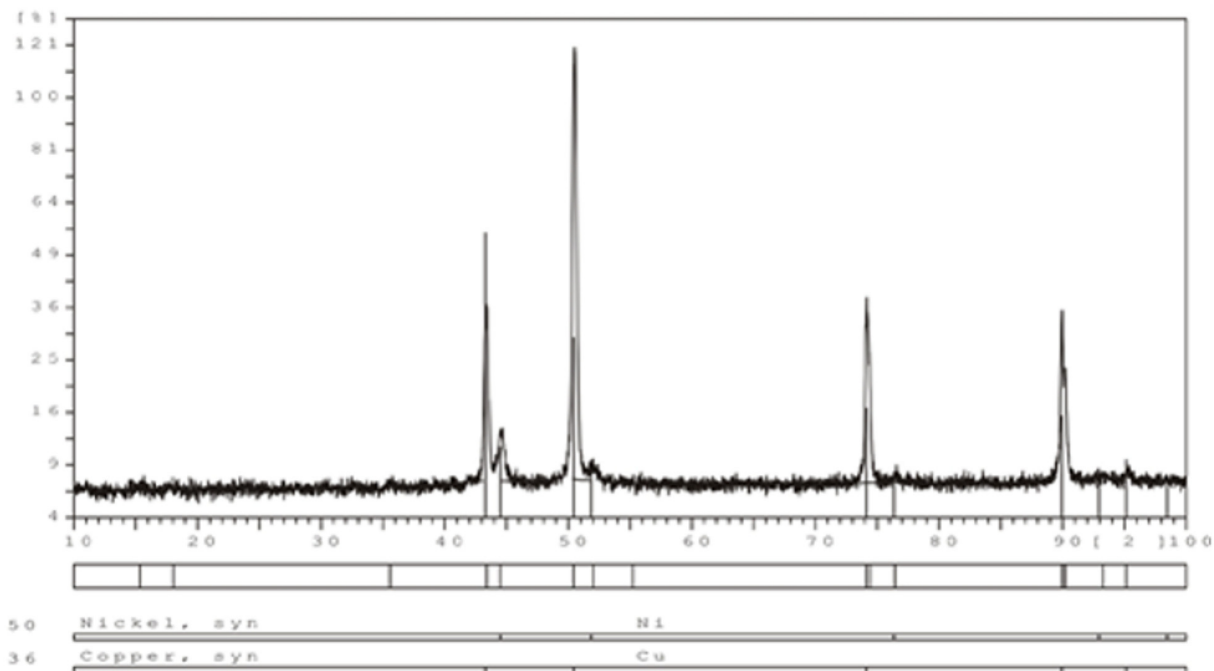


Fig. 2. Nickel deposit on the cathode of single chamber reactor (a) and partitioned reactor using water hyacinth leaf (b)

To identify the deposit composition, deposited metal on cathode was analyzed using X-Ray Diffraction Spectroscopy (XRD). Spectrum resulted by XRD analysis of deposit samples is shown on Fig. 3. These spectrums are quite similar to the spectrum of pure nickel metal. Thus, it can be concluded that the electrodeposition product is pure nickel.



a. Single chamber reactor

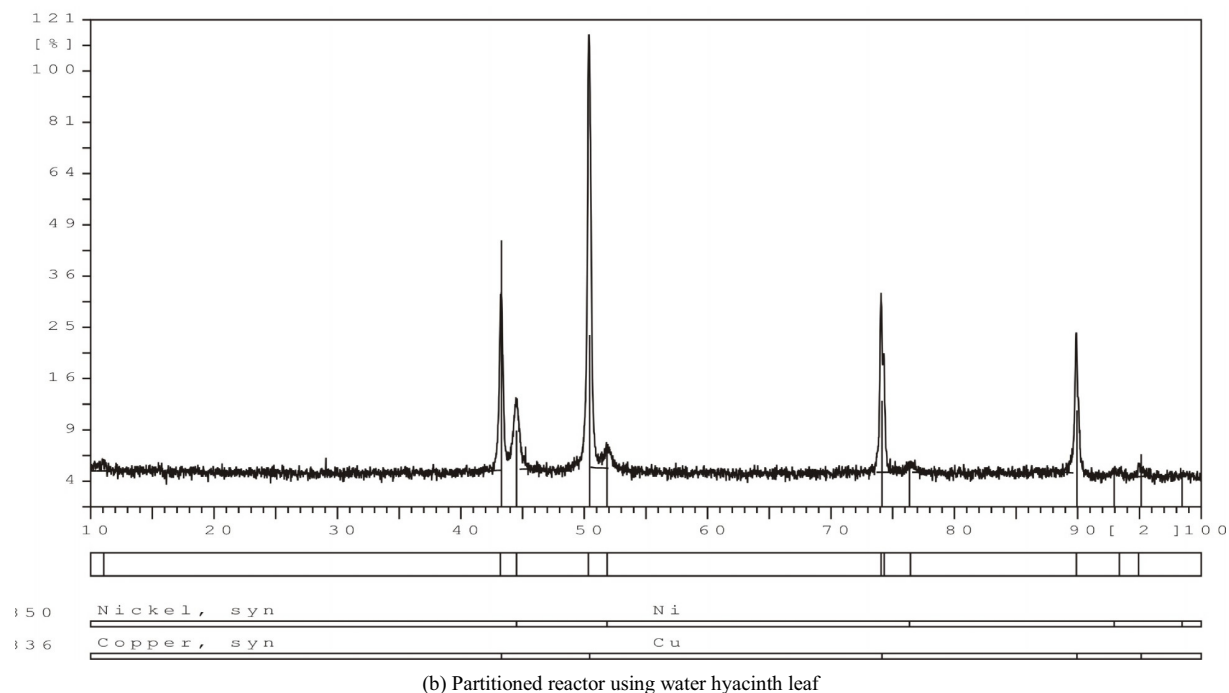


Fig. 3. XRD spectrum of electrodeposited nickel and pure nickel of both reactor type

3.2. Current Efficiency

Reduction of heavy metal content in wastewater to comply the Government Regulation becomes a mandatory for electroplating industry. Electrodeposition process may reduce the nickel concentration and produce the valuable nickel metal at the same time, and hence, may compensate the cost of wastewater treatment. Moreover, cost can be minimized by carrying out electrodeposition at high current efficiency. Current efficiency is defined as the ratio of the metal produced and the amount of metal that can be produced by the electric charge applied during electrodeposition. Based on Faraday's law, current efficiency can be written as

$$\eta = \frac{m \cdot n \cdot F}{I \cdot t \cdot A \cdot r} \quad (3)$$

where η = current efficiency; m = weight of nickel deposit; n = ionic charge of Ni^{2+} ; F = 96500; I = electric current (ampere); t = time of process (second); $A \cdot r$ = atomic weight.

To calculate current efficiency, the weight of nickel deposit on cathode could be calculated using equation (1) and the result was shown in Table 2.

Table 2. Weight of nickel deposit weight on cathode

Reactor Type	Weight of cathode (gram)		Ni deposit, m (gram)
	Initial	End	
Single chamber	4.2827	4.3584	0.0757
Partitioned reactors using water hyacinth leaf	4.3163	4.4169	0.1006

In comparison, nickel deposit on the cathode surface in single-chamber reactor (0.0757 grams) was fewer than partitioned one (0.1006 grams). This phenomenon caused by H_2 gas bubbles production on cathode surface that inhibited deposition of nickel on cathode in single chamber reactor. Mixing of anolyte and catholyte on single

chamber reactor allowed hydrogen gas bubbles resulted from reduction H^+ ions from H_2O , but not in partitioned reactor. This condition favorable to minimize the hydrogen bubbles at cathode compare to other effort as addition of boric acid or anionic surfactant in single chamber reactor¹⁵.



Fig. 4. Hydrogen bubbles formed on cathode on single chamber reactor (a) compared to clear solution on cathode compartment of partitioned reactor using water hyacinth leaf (b)

The current efficiencies of both reactors type was shown in Table 3. Table 3 shows that the partitioned reactor using water hyacinth leaf provides higher current efficiency than the single chamber reactor, i.e. 88.17%. The lower current efficiency on single chamber reactor may be caused by the utilization of electric energy for hydrogen evolution on cathode, as shown on Fig. 4.

Table 3. Current efficiency

Reactor Type	$\frac{A^p}{N} = e$	$Q = \int I dt$ (Coulomb)	Mass of deposited nickel, m (gram)	Current Efficiency (%)
Single-chamber	29.22	375.984	0.0757	66.49
Partitioned	29.22	376.848	0.1006	88.17

3.3. Energy Consumption

The most important component of electrodeposition cost is the electric energy. Therefore, the electrodeposition cost could be minimized by reducing the energy consumption. The amount of energy required for electrodeposition process can be calculated by the following equation.

Energy specific calculated by following equation (4) :

$$E_s = \frac{V \times I \times t}{m} \quad (4)$$

where E_s = energy specific; V = applied voltage (volt); $q = I \times t$ = supplied electric charge ($= \int I dt$); I = electric current (ampere), t = reaction time (second), and m = weight of nickel deposited on cathode. The result of specific energy calculation that required for both reactors type can be seen in Table 4.

Table 4. Specific energy (E_s)

Reactor Type	V (volt)	$Q = \int I dt$ (Coulomb)	W (kwh)	Weight of deposited Ni, m (kg)	E_s (kwh/kg nickel)
Single chamber	5	375.984	0.00052222	0.0000757	6.90
Partitioned reactor using water hyacinth leaf	5	376.848	0.00052333	0.0001006	5.20

Table 4 shows that electrical energy required for nickel electrodeposition in partitioned reactor lower than in the single-chamber reactor and resulted higher current efficiency of partitioned reactor using water hyacinth leaf, as shown in Fig. 8. It means only need 5.2 kWh to get 1 kg nickel deposited in cathode. This current efficiency is higher than Ref.¹⁴ that only need 3 kWh/kg nickel, that caused by higher input of 5V in this study.

The pH value was measured during electrodeposition process. Its change would represent the process itself, as shown in Fig. 5. There were differences of initial pH value in the partitioned reactor between catholyte and anolyte solution because of separation and use of difference electrolyte solutions in anode and cathode compartments, as 0.2 M H₂SO₄ anolyte and 2402.19 mg Ni/L NiSO₄.6H₂O catholyte while in the single-chamber reactor there was only one solution with single initial pH value.

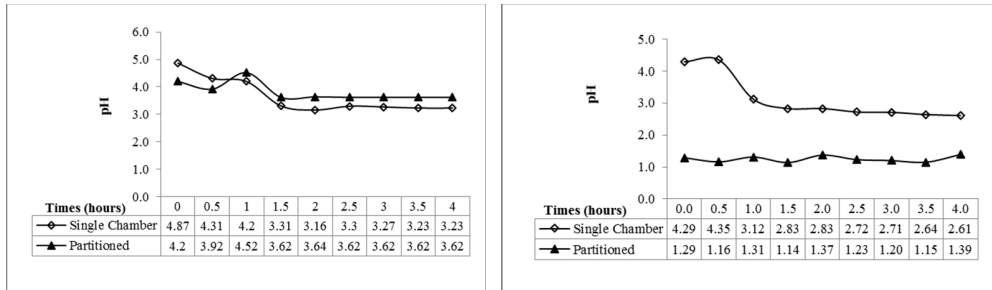


Fig. 5. Changes in pH of catholyte (left) and anolyte (right) during time reaction

Conductivity, as the indicator of electrodeposition, also measured during process. Based on Fig. 6., anolyte conductivity in partitioned reactor was higher than in the single chamber reactor, because of the anolyte in the partitioned reactor contains H₂SO₄ 0.2 M which has higher conductivity than NiSO₄ 2402.19 mg/L. It means higher conductivity has higher solution capability to conduct the ion into electrode.

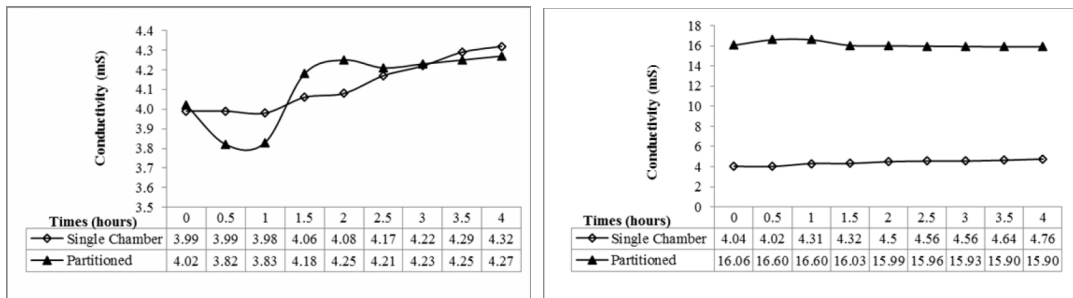


Fig. 6. Changes in conductivity of catholyte (left) and anolyte (right) during process

Electric current on the partitioned reactor using water hyacinth leaf initially low, around 12 mA and then rose sharply to 30 mA at 2.5 hours, then tend to steady around 32 mA at 4 hours as shown on Fig. 7. On the single chamber reactor, electric current initially at 25 mA and then increased slightly to 27.5 mA or tend to be flat to the end of the experiment.

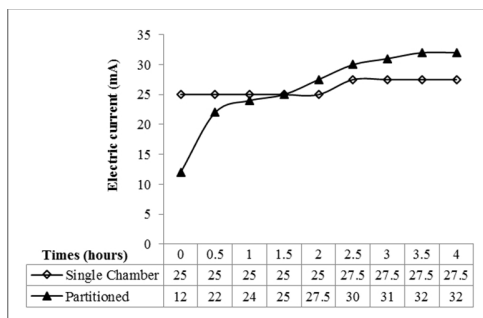


Fig. 7. Changes of the electricity current

This phenomenon was caused by the presence of the water hyacinth leaf biomembrane on partitioned reactor that having electric resistance that impede electric current at the beginning of the experiment. Then, electric current rising sharply due to the transfer of H⁺ from the anode to the cathode chamber as a result of the oxidation reaction $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ which increases the electric current. Whereas on the single chamber reactor, between the anode and cathode chamber were not partitioned by water hyacinth leaf biomembrane, so that from the beginning, the electric current is high, resulting electric current changes tend to be flat the end of the experiment despite an increase in the concentration of H⁺ due to the oxidation reaction at the anode.

Comparison of current efficiency and energy consumption for electrodeposition of nickel can be seen in Fig. 8 below. Higher current efficiency and less specific energy needed by partitioned reactor than single chamber does. Only need 5.2 kWh to treat 1 kg nickel deposited in cathode.

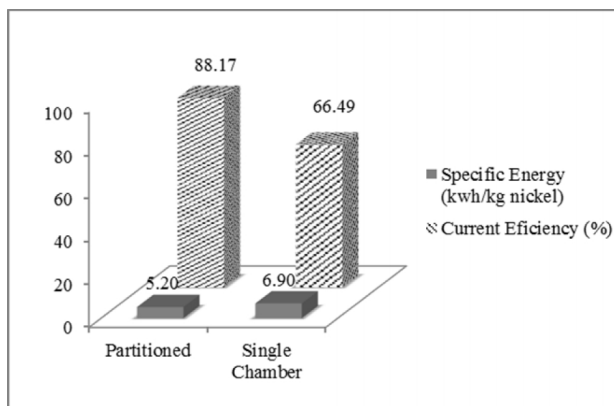


Fig. 8. Specific energy and current efficiency of nickel electrodeposition in partitioned reactor and in single chamber reactor.

4. Conclusion

The comparison between two types electrodeposition reactor has been conducted. The partitioned reactor using water hyacinth leaf in this study resulted better performance than the single chamber reactor with 26.892% nickel concentration decrease in catholyte, current efficiency of 88.17 %, and specific energy of 5.2 kWh/kg nickel. However, further research on reaction time variation could be conducted to reach higher nickel concentration removal in electrodeposition partitioned reactor.

Acknowledgements

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