# Removal of Nickel from Plating Wastewater Using the Magnetic Flocculant PG-M

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## ABSTRACT

In this study, a new kind of magnetic particle functionalized biopolymer (PG-M) was applied to remove nickel from plating wastewater. The key parameters of pH, adsorption time, the mass of adsorbent, and shaking speed were investigated to optimize conditions. Batch experiments were conducted with actual samples collected from a manufacturer having an initial nickel concentration of 143.73 mg/L at pH 5. The highest removal efficiency of $Ni^{2+}$ ions was greater than 99% when 1 g/L of the PG-M material was added to the solution (pH=10) and stirred at 200 rpm for 20 min. The

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desorption of this adsorbent was performed in a 0.1 M solution of HCl and the removal efficiency of $Ni^{2+}$ ions unchanged after nine cycles. The $Ni^{2+}$-loaded PG-M magnetic flocculant was easily separated from the solution by an external magnet.

*Keywords: Heavy metal; nickel; adsorption; PG-M.*

## 1. INTRODUCTION

Water sources contaminated by numerous industrial activities are becoming a global environmental problem because they contain biodegradable and persistent substances such as organic compounds, suspended solids, oils, bacteria, viruses, and a variety of heavy metals [1–6] These toxins from industrial wastewater adversely affect ecosystems and accumulate in aquatic organisms, flora, fauna, and human beings through the food chain without external expression [7–11,12-17]. Therefore, they are called silent poisons and considered to cause various dangerous diseases.

Nickel (Ni) is a crucial micronutrient, as well as an activator of some enzymes for plants and organisms [3,9,18]. However, depending on the dose of Ni uptake in the human body, it can be the cause of skin allergies, vertigo, asthma, chronic bronchitis, birth defects, fibrosis, and cancer, and significantly reduce the functions of the blood, immune, lung, and cardiovascular systems [1,3–10]. Ni is a popular heavy metal which is applied in manufacturing stainless steel, coins, jewelry, batteries, valves, paints, and kitchen and bathroom wares [1,3,10,19]. When Ni is used as a plating surface, products become tougher, lighter, anti-oxidative, and thermally stable [3,9]. Thus, concomitant with the development of the plating industry, wastewater needs to be treated to remove heavy metals according to standards before being released into water bodies.

Different techniques such as chemical precipitation, coagulation-flocculation, flotation, ion-exchange, adsorption, membrane filtration, and electrochemical treatment have been applied for the removal of heavy metal ions from industrial wastewater [1,7–11,20-25], but primarily the adsorption, ion exchange, and membrane filtration methods are used in studies of the treatment of heavy metal wastewater due to their high efficiency [26-30]. In this study, the combination of flocculation and adsorption was used to investigate the $Ni^{2+}$ removal capacity of an environmentally friendly material, i.e., PG-M, which is composed of two main ingredients— magnetic $Fe_3O_4$ particles and a biodegradable polymer flocculant. The $Fe_3O_4$ component plays an important role allowing the $Ni^{2+}$ ion to be easily and simply separated from aqueous solutions using magnets.

The objectives of this research are to investigate the influence of pH, contact time, the mass of absorbent, and shaking speed for $Ni^{2+}$ removal from plating wastewater, and the regeneration capacity of the PG-M particles. The Vietnamese National Technical Regulation on Industrial Wastewater for Ni is 0.2–0.5 mg/L [31]. In this research, the equilibrium concentration of Ni was demonstrated to be reduced below the current regulatory standard.

## 2. EXPERIMENTAL

### 2.1 Reagents and Chemicals

The PG-M particles were purchased from Nippon-Glu Co. Ltd, Osaka, Japan. All chemicals were of analytical grade and used as received.

$Ni^{2+}$ solutions used throughout this study were collected from the wastewater produced at the Shower and Bathroom Equipment Manufactory - Branch Lixil Viet Nam Co. Ltd in Quang Nam Province, Viet Nam.

### 2.2 Adsorption Studies

Before a series of adsorption and desorption investigations were conducted, the wastewater samples were obtained from the factory and subsequently filtered through a 20–25 μm filter paper to remove suspended solids. The pH of the solution was measured by a pH meter, and the concentrations of various heavy metals were analyzed by an atomic absorption spectrometer (AAS). $Na_2CO_3$ was used for pH adjustment. Adsorption studies (Fig. 1) were performed by changing different parameters such as contact time, pH, adsorbent dose, and shaking speed in a 50-mL aliquot of the sample containing 143.73 mg/L of $Ni^{2+}$ ions in a beaker at room temperature. Each previously optimized parameter was chosen for the next experiment. Time was varied from 10 to 150 min while $Ni^{2+}$ solutions were shaken with the PG-M particles to test the effect of time on adsorption. Different pH
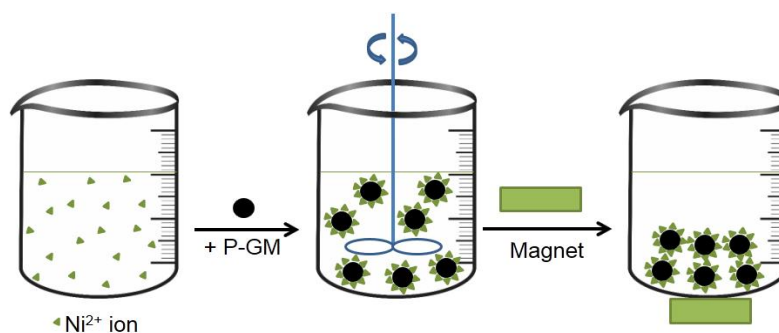
**Fig. 1. Schematic diagram of Ni$^{2+}$ ions removed using the PG-M sorbent**

values from 5.0 to 10.0 were tested to determine the optimal pH for the highest efficiency. To determine the effect of adsorbent dose, the mass of the PG-M particles added into Ni$^{2+}$ solutions ranged from 0.2 g/L to 20 g/L. All previously optimized parameters were chosen for the final shaking speed experiment in which Ni$^{2+}$ solutions were shaken at speeds from 100 to 1000 rpm. After each adsorption experiment, a magnet with a magnetic field strength of 3500–4000 Oe was placed at the bottom of the beaker to attract the PG-M particles (Fig. 1) before determining the concentration of the Ni$^{2+}$ ion.

The percent of Ni$^{2+}$ removal (removal efficiency (%)) and the amount of Ni$^{2+}$ adsorbed were determined by Eqs. 1 and 2, respectively:

$$H = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}$$

$$q_e = \frac{C_0 - C_e}{M} \times V \tag{2}$$

where $C_0$ and $C_e$ are the initial and equilibrium concentrations of Ni$^{2+}$ ions (mg/L), $M$ is the mass of adsorbent (g), $V$ is the volume of sample (L), and $q_e$ is the amount of Ni$^{2+}$ ions adsorbed per mass of absorbent (mg/g).

## 2.3 Recovery Studies

Regeneration of the adsorbent in water treatment is a crucial consideration because it controls the economy of water treatment technology. Not only can regeneration save the cost of the adsorbent dose, but also affects the removal efficiency. In the regeneration process, the adsorption capacity of the adsorbent is restored, and valuable components present are recovered. The adsorption of Ni$^{2+}$ depended on high pH value. The desorption of Ni$^{2+}$ was easily achieved by controlling the pH of the solution; the addition of

HCl at low pH was effective for efficient desorption. In many studies, the optimal HCl solution for efficient desorption was tested, and it was determined that the percentage of desorption of the PG-M particles increased as the concentration of HCl ranged from 0.05 M–0.1 M HCl [32-36]. Hence, in this study, 0.1 M HCl was chosen for the desorption of the PG-M particles.

Desorption studies were conducted by mixing Ni-loaded PG-M particles with 10 mL of 0.1 M HCl. PG-M regeneration and Ni$^{2+}$ re-adsorption experiments were performed in 12 consecutive cycles. For each cycle, a 50 mL Ni$^{2+}$ solution was adsorbed by 1 g/L of PG-M particles for 20 min and subsequently desorbed with 10 mL of 0.1 M HCl for 1 hour to reach equilibrium. After each adsorption-desorption cycle, the PG-M was washed thoroughly with ultrapure water to reach neutrality and establish good conditions for adsorption in the next cycle.

## 3. RESULTS AND DISCUSSION

### 3.1 Chemical Analysis

Ni, Cu, Zn, Cd, Pb, and Cr ions were found in the plating wastewater, and Ni$^{2+}$ ions were determined to be present at the highest concentration. The pH of the sample was 5. The results of the chemical analysis are given in Table 1. In this work, only experiments of Ni removal using the PG-M magnetic flocculant were investigated.

### 3.2 Effect of Contact Time

The removal efficiency was affected by the contact time; therefore, it was investigated from 0 to 150 min (Fig. 2). After 0.5 g of PG-M particles were added to 50 mL of the sample at an initial pH of 5, the solution was shaken at 300 rpm to determine adsorption performance. A sharp

increase in the uptake rate of $Ni^{2+}$ ions was observed in the first 20 min during which approximately 70% of $Ni^{2+}$ ions were removed. After this time, the removal efficiency remained stable. Therefore, it was concluded that the adsorption of $Ni^{2+}$ ions on the surface of the PG-M sorbent occurred in a single simple step, meaning that in the first stage of the adsorption process, the $Ni^{2+}$ ions rapidly occupied the active surface of the PG-M particles in a random manner. Hence, the rate of uptake was high. As time lapsed, the surface of the PG-M particles became saturated, after which the rate of adsorption slowed and stabilized. At the equilibrium state, the removal efficiency of $Ni^{2+}$ ions was 69.54% in 20 min. Therefore, an optimized time of 20 min was used to examine the adsorption performance further.

**Table 1. Different metal ion concentrations and the pH of the plating wastewater effluent**

| No. | Parameters | Unit | Value |
| --- | --- | --- | --- |
| 1 | $Ni^{2+}$ | mg/L | 143.73 |
| 2 | $Cu^{2+}$ | mg/L | 17.76 |
| 3 | $Zn^{2+}$ | mg/L | 10.80 |
| 4 | $Cr^{6+}$ | mg/L | 18.11 |
| 5 | $Pb^{2+}$ | mg/L | detection limit |
| 6 | $Cd^{2+}$ | mg/L | detection limit |
| 7 | pH | - | 5.0 |

## 3.3 Effect of pH

The pH was the most important factor in the adsorption process because it influences the functional groups on the surface of the adsorbent and regulates the Ni speciation at different pH levels [2,30,31,35]. A 0.5 g mass of PG-M particles was added to 50 mL of sample for 20 min at 300 rpm. The effect of pH on the removal of $Ni^{2+}$ ions is illustrated (Fig. 3) as pH varied from 5 to 10. The adsorption efficiency increased gradually from pH 5 to pH 7, increased dramatically between pH 7 to pH 8, and continued to increase slightly from pH 8 to pH 10. At pH 10, the concentration of $Ni^{2+}$ ions in solution was the lowest compared to the other pH values. The explanation for this observation follows. When the pH of the aqueous solution was less than 7 (pKa of PG-M) [36], Ni existed primarily in the form of $Ni^{2+}$ ions. Concomitantly, in the solution at pH less than 7, more of the carboxylic acid functional groups (-COOH) on the surface of the PG-M particles are postulated to be in the unionized form, so it was more difficult to adsorb the positively charged $Ni^{2+}$ ions on the

surface of the adsorbent. When the pH value was greater than 7, two factors influenced recovery. Firstly, in this condition, the hydroxide $Ni(OH)_2$ can be formed easily in solution, which, was easily attracted to the surface of the adsorbent. In this case, PG-M look like coagulant. Secondly, the carboxylic acid functional groups on the surface of the PG-M particles were negatively charged due to ionization to the carboxylate ion (-COO–) at high pH [2,35]. The $Ni^{2+}$ ions in solution were attracted to the surface of the adsorbent by electrostatic forces. Therefore, pH 10 was used for the subsequent experiments.

## 3.4 Effect of Adsorbent Dose

The adsorbent dose was an economic factor in the adsorption process. If the dose of the PG-M particles was insufficient, it could not absorb the $Ni^{2+}$ ions completely in aqueous solution. Conversely, excessive use of the adsorbent would not improve the $Ni^{2+}$ ion removal efficiency after the adsorption process reached the saturation state but would increase the cost. In this experiment, the amount of adsorbent was varied from 0.2 to 20 g/L. A 50-mL aliquot of the sample with the initial pH adjusted to 10 was shaken at 300 rpm for 20 min. As the dose of the PG-M particles increased, the removal efficiency of $Ni^{2+}$ ions from solution increased, and the adsorbed amount of $Ni^{2+}$ ions decreased (Fig. 4). After an initial increase, the percentage of $Ni^{2+}$ ions removed remained nearly constant at a dose greater than 2 g/L of the PG-M sorbent. In this case, the level of $Ni^{2+}$ removed (98.32%) was recorded at a dose of 1 g/L of the PG-M particles which corresponds to 0.05 g of adsorbent added to the 50-mL aliquot and was determined to provide sufficient material and efficient adsorption. This dosage was used for further studies.

## 3.5 Effect of Shaking Speed

Shaking speed also impacted the performance of the adsorption process. A 50-mL aliquot of the sample at pH 10 was mixed with 0.05 g of adsorbent (1 g/L of the PG-M particles) for 20 min. Different shaking speeds from 100 to 1000 rpm were compared. Slight fluctuations in the removal of $Ni^{2+}$ ions were observed (Fig. 5). Because the removal efficiency of $Ni^{2+}$ ions at all shaking speeds was greater than 95%, 200 rpm was selected as the optimal shaking speed to save energy when the procedure is applied in practice.
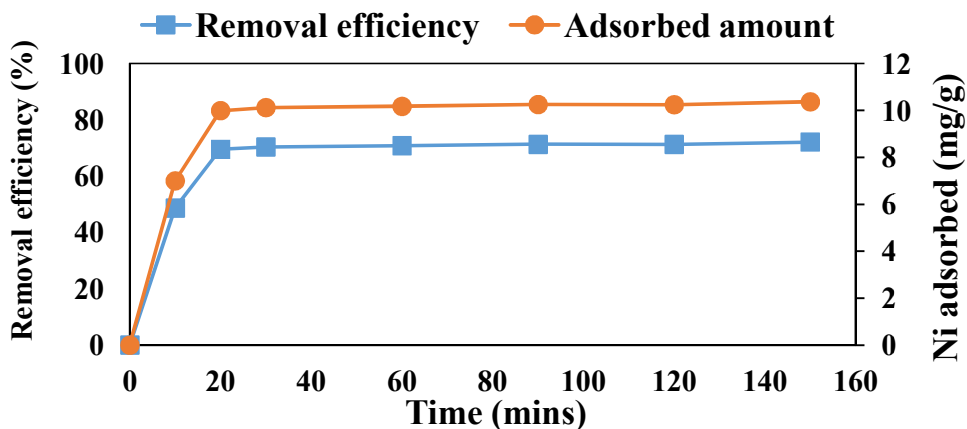
**Fig. 2. Effect of contact time on the removal efficiency of Ni²⁺ ions using the PG-M sorbent**
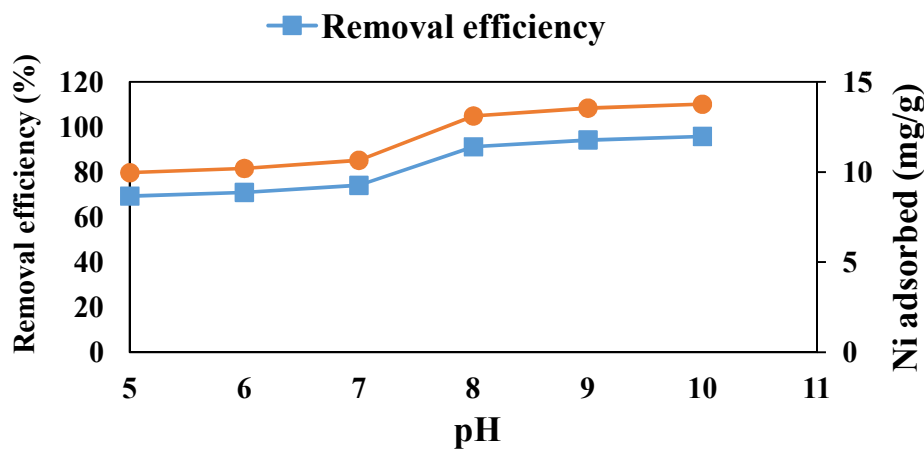


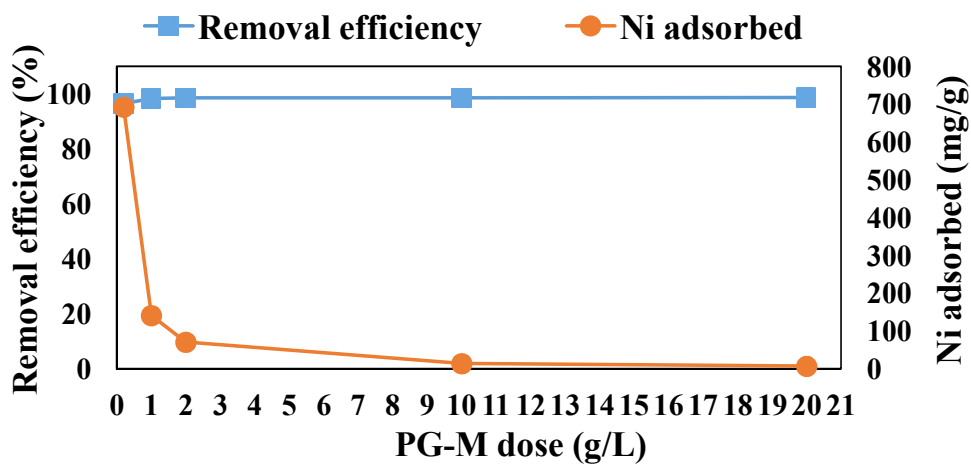**Fig. 3. Effect of pH on the adsorption of Ni²⁺ ions using the PG-M sorbent**



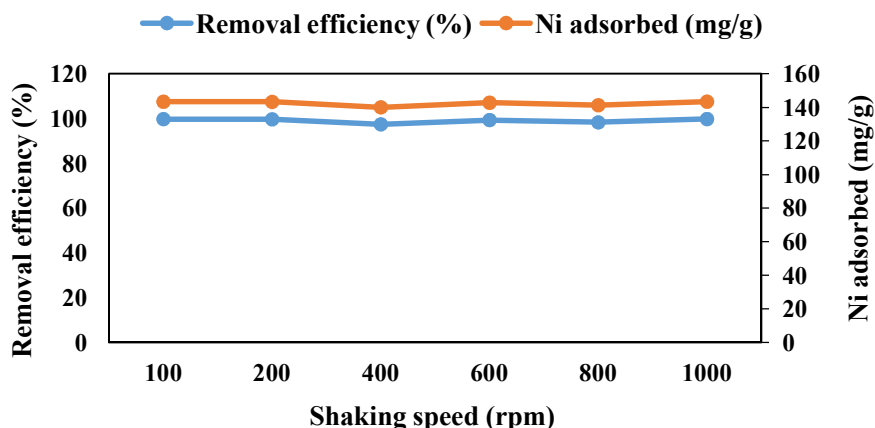**Fig. 4. Effect of the PG-M dose on the adsorption of Ni²⁺ ions**

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**Removal efficiency (%)** ─●─ **Ni adsorbed (mg/g)**

**Fig. 5. Effect of shaking speed on the removal efficiency of Ni$^{2+}$ ions using the PG-M sorbent**

## 3.6 Regeneration

For regeneration studies, successive adsorption-desorption processes were conducted for 12 cycles (Fig. 6). After each adsorption-desorption cycle, ultrapure water was applied to rinse the surface of the PG-M sorbent to remove unwanted ions. The metal removal capacity of the PG-M particles remained nearly constant for 12 cycles, which indicated that no irreversible sites existed on the surface of the PG-M sorbent. In Viet Nam, the final Ni$^{2+}$ concentration after treatment ranges from 0.2–0.5 mg/L for domestic water and nondomestic water, respectively [32]. Fe concentration was also analyzed to determine the amount of Fe dissolved during desorption with 0.1M HCl as indicated in Table 2.
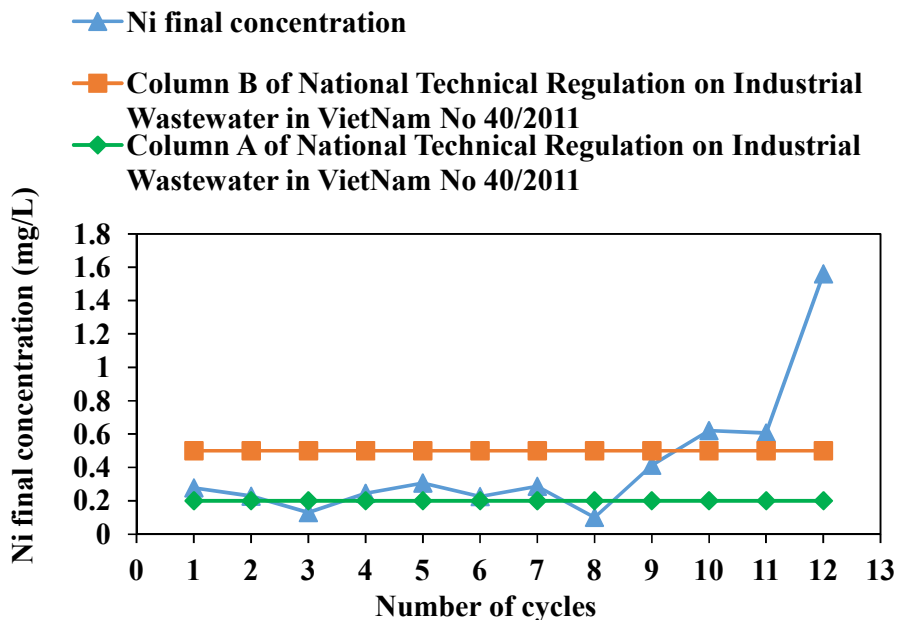
─▲─ **Ni final concentration**

─■─ **Column B of National Technical Regulation on Industrial Wastewater in VietNam No 40/2011**

─◆─ **Column A of National Technical Regulation on Industrial Wastewater in VietNam No 40/2011**

**Fig. 6. Regeneration studies of the PG-M sorbent during 12 cycles.**
*Column A is a limited value of pollutants in industrial wastewater discharges into water resource used for domestic water supplying.*
*Column B is a limited value of pollutants in industrial wastewater discharges into water resource not used for domestic water supplying*

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**Table 2. Fe concentration in HCl solution**

| Cycle number | Fe concentration (mg/L) |
|---|---|
| 3$^{rd}$ | 6.20 |
| 5$^{th}$ | 11.19 |
| 7$^{th}$ | 13.88 |
| 9$^{th}$ | 15.72 |
| 11$^{th}$ | 22.81 |

The amount of Fe dissolved in the HCl solution increased gradually after each desorption (Table 2). From the 3$^{rd}$ to the 9$^{th}$ cycles, the Fe concentration increased 2.5 times - from 6.20 mg/L to 15.72 mg/L - and increased 4 times by the 11$^{th}$ cycle. Fe dissolved in the acid solution would reduce the available amount of the PG-M sorbent, thereby reducing the $Ni^{2+}$ removal efficiency. This was also tested by determining the $Ni^{2+}$ concentration after each re-adsorption. Thus, it was observed that the final $Ni^{2+}$ concentration after nine cycles was adequate and complied with the local standard.

## 4. CONCLUSIONS

Application of the PG-M flocculant to remove $Ni^{2+}$ ions from industrial wastewater using magnetism was a significant improvement because it is a rapid, environmentally friendly, and uncomplicated treatment process exhibiting high efficiency and low energy consumption. The optimal conditions determined to achieve the best performance (99.69 %) included a pH value equal to 10, a shaking speed of 200 rpm, and a contact time between the PG-M material and wastewater of 20 min. Regeneration was most favorable through nine adsorption-desorption cycles using 0.1 M HCl. The remarkable characteristics of the PG-M material for water treatment were demonstrated in this research.

## ACKNOWLEDGEMENT

## COMPETING INTERESTS

Authors have declared that no competing interests exist.

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