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Lawn Grass as A Sustainable Adsorbent for Nickel(II) Removal

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Lawn grass is a waste that has the potential to be converted into an adsorbent to remove nickel(II) from aqueous solution. The methodology includes preparation of the adsorbent, performance of nickel(II) adsorption, evaluation of existing models and characterization of absorbent by scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM/EDX). The results showed the optimum adsorbent amount, initial pH and time were 0.35 g, 5.62 ± 0.38 and 30 minutes, respectively. Inductively coupled plasma - optical emission spectroscopy (ICP-OES) results suggested an ion exchange mechanism through a displacement of alkaline and alkaline earth metal ions by nickel(II) ions. The results were a better fit to the Langmuir isotherm than Freundlich, with a maximum uptake of 42.02 mg/g. The calculated Langmuir maximum uptake value was comparable to other adsorbents. The adsorption performance corresponded excellently with the pseudo-second-order kinetic model compared to the pseudo-first-order kinetic model. These findings indicated that adsorption of nickel(II) using lawn grass involved a homogeneous monolayer surface, with chemisorption as the rate-limiting step. Thermodynamic evaluation revealed that the adsorption process of nickel(II) by lawn grass is non- spontaneous with weak reversible bonding and endothermic reaction. SEM results showed that the irregular and highly porous surface of lawn grass became smooth after the adsorption of nickel(II). The EDX results supported the ICP analysis which suggested an ion exchange mechanism was involved.

Key words: Adsorbent; lawn grass; nickel(II); sustainable; waste to resource

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Nickel is widely used in the production of stainless steel, alloys, electroplating and batteries. Improper effluent treatment and waste management have raised public awareness on nickel pollution, especially in fresh and marine water resources. Generally, nickel is not a cumulative poison, but acute and chronic exposure may be toxic, carcinogenic and constitute an occupational hazard. Hence, an effective treatment method is required to solve this problem and safeguard the environment.

Adsorption is a physicochemical method that is widely used to extract metals including nickel. It is one of the most commonly applied methods in industry as it is a simple and easy process. However, the use of coal-based adsorbents, mineral-based zeolite adsorbents and petrochemical-based resins have resulted in high costs and unsustainable material issues [1-3]. Therefore, a search for alternative materials is necessary. This study incorporates the option of converting local biological waste into a resource, as a sustainable approach. Plant material has a high lignocellulose component and a variety of reactive adsorption sites such as phenolic, hydroxyl, carboxyl and amine groups that are used in the adsorption of metals [4].

Recently, biobased materials such as *Pleurotus ostreatus*, spent mushroom compost, lemon peels, brewed tea waste, waste apricot, moringa bark carbon, rice bran and biobased chitosan derivatives have been investigated as possible adsorbents for nickel(II). However, these waste materials are not available in quantities sufficient for large scale adsorbent production, while chitosan derivatives are not cost-effective [4]. Lawn grass is an agricultural waste that is usually converted into fertilizer via composting. Lawn grass activated carbon is a promising adsorbent for contaminant removal, but the process of producing activated carbon has drawbacks such as chemical usage, high energy consumption and low carbon yield output [5-6]. There is a lack of research on the use of lawn grass for metal removal to date.

This study aimed to evaluate the potential of lawn grass as an adsorbent for the removal of nickel(II) ions from aqueous solution. The objectives of this study were: (i) to investigate the effects of adsorbent amount, initial pH, contact time, initial nickel(II) concentration and temperature on nickel(II) adsorption, (ii) to evaluate existing isotherm, kinetic and thermodynamic models, and (iii) SEM/EDX characterization.

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MATERIALS AND METHODS

Preparation of Adsorbent and Nickel(II) Solutions

Lawn grass was collected from UiTM Shah Alam. The sample was washed, ground and sieved to 710 µm. The sample was then dried in an oven at 80 °C to constant weight and kept in a desiccator, for use as the adsorbent. A 100 mg/L nickel(II) stock solution was prepared using nitrate(II) hexahydrate salt ($Ni(NO_3)_2{\cdot}6H_2O$) (Merck, Germany) and ultrapure water. This was used to prepare solutions at desired concentrations in the following experiments.

Adsorption Study

Approximately 0.05 – 1.00 g of lawn grass adsorbent was weighed and added to 50 mL of 50 mg/L nickel(II) solution with an unadjusted pH of 5.62 ± 0.38, respectively. Samples were agitated in an incubator shaker (MaxQ5000, Thermo Scientific, USA) at 125 rpm for 60 min at 25 ± 1 °C. The samples were then centrifuged and the supernatants analyzed using inductively coupled plasma - optical emission spectroscopy (ICP-OES) (7300DV, Perkin Elmer, USA). All samples were prepared in duplicate and a low standard deviation of 2 was neglected. The procedures were repeated at initial pH values of 1 – 6, contact times of 1 – 120 min, initial nickel(II) concentrations of 50 – 100 mg/L and temperatures of 5 – 45 °C. The removal and uptake values of nickel(II) were calculated based on Equations 1 and 2.

$$Removal\ (\%) = \frac{(C_o - C_e)}{C_o}\ x\ 100\ \% \qquad \text{Equation 1}$$

$$Uptake\ \left(\frac{mg}{g}\right) = \frac{(C_o - C_e)\ V}{W} \qquad \text{Equation 2}$$

where *Co* is the initial concentration of nickel(II) in mg/L; *Ce* is the final concentration of nickel(II) in mg/L; *V* is the volume of solution in L; *W* is the weight of adsorbent in g.

Data Analysis for Existing Mathematical Models

For the isotherm analysis, the results from the adsorption study were fitted to linearized Langmuir and Freundlich equations (Equation 3 and 4). Pseudo-first-order kinetic and pseudo-second-order kinetic equations (Equations 5 and 6) were applied for the kinetic study. The thermodynamic parameters of Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) were calculated based on Equations 7 and 8 for the thermodynamic study.

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{b\ q_{max}} \qquad \text{Equation 3}$$

$$\ln q_e = \ln K_F + \frac{1}{\mathrm{n}\ lnC_e} \qquad \text{Equation 4}$$

where q_e represents equilibrium nickel(II) adsorption uptake (mg/g), q_{max} is maximum nickel(II) adsorption uptake (mg/g), C_e is the nickel(II) concentration at equilibrium (mg/L), b is the Langmuir constant, while K_F and n are Freundlich constants.

$$\log\ (q_e - q_t) = \log\ q_e - \frac{t\ k_1}{2.303} \qquad \text{Equation 5}$$

$$\frac{t}{q_t} = \frac{1}{2k_2\ {q_e}^2} + \frac{t}{q_e} \qquad \text{Equation 6}$$

where t is time (min), q_e and q_t are, respectively, the nickel(II) adsorption uptake at equilibrium and at time t (mg/g), and k_1 and k_2 are, respectively, the constants of pseudo-first-order and pseudo-second-order kinetics.

$$\log K_c = -\frac{\Delta H}{2.303RT} + \frac{\Delta S}{2.303R} \qquad \text{Equation 7}$$

$$\Delta G = \Delta H - T\Delta S \qquad \text{Equation 8}$$

where K_c (L/g) is the distribution coefficient, T is temperature in Kelvin and R is the gas constant. ΔG is free energy (kJ/mol). ΔH and ΔS were obtained from the slope and intercept of the plots of log K_c vs $1/T$.

Scanning Electron Microscopy (SEM)/Energy Dispersive X-ray (EDX) Characterization

Adsorbent samples before and after adsorption of nickel(II) were analyzed using scanning electron microscopy (SEM) (Hitachi Tabletop Microscope TM3030plus)/energy dispersive X-ray spectroscopy (EDX) (ZEISS SmartSEM software). SEM micrographs were recorded at 4000x magnification.

RESULTS AND DISCUSSION

Adsorption Study

Figure 1 shows contrasting trends for the removal and uptake of nickel(II) by lawn grass. An increase in the adsorbent amount from 0.05 – 0.35 g caused an increase in removal from 16 – 50 %, which was then followed by a saturation phase at 50 % removal with 0.35 – 1.00 g adsorbent. This trend for removal may be attributed to the increase of adsorption sites on the adsorbent, which caused an aggregation of adsorbent, and finally, adsorption sites became fully occupied with the nickel(II) ions. On the other hand, the nickel(II) uptake decreased from 8.09 to 1.28 mg/g when the adsorbent amount increased from 0.05 to 1.00 g. An increase in the ratio of adsorption sites to nickel(II) ions resulted in a decrease in uptake. The adsorbent amount of 0.35 g was selected for further study as it was the optimum amount that saved time and materials in the adsorption process. This study's result was consistent with Tay et al. (2016) [3] in terms of the removal and uptake trends for nickel(II).

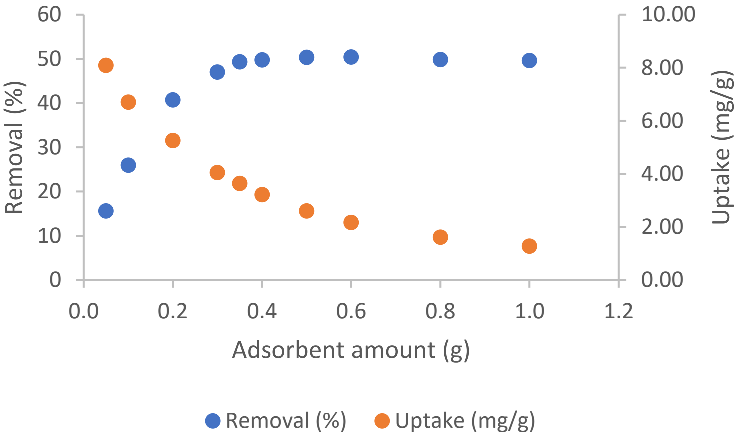

Figure 1. Effect of adsorbent amount on adsorption performance (initial pH 5.62 ± 0.38, 60 min contact time, 50 mg/L initial nickel(II) concentration and 25 ± 1 °C temperature)

The effects of initial pH on nickel(II) adsorption removal and uptake are illustrated in Figure 2. Both had a similar trend where initially the performance was low at pH 1 - 2, but then increased rapidly at pH 2 – 3, and was then followed by a constant performance at pH 3 - 6. At pH 1 – 2, approximately 10 % removal and 3.28 mg/g uptake were recorded. There was a rapid increase from pH 2 – 3 and then saturation from pH 3 – 7 where 50 % removal and 15.56 mg/g uptake were recorded. At low pH conditions, the nickel(II) ions compete with hydrogen ions for the adsorption sites. As the pH increased from 2 – 3, adsorption sites were deprotonated and the attraction between adsorption sites and nickel(II) ions increased, thus improving the adsorption performance. Finally, the observed constant results were due to adsorption sites being occupied and precipitation occurring due to excessive hydroxide ions. The unadjusted pH conditions at pH 5 to 6 were selected as the optimum pH that involved minimum usage of chemicals and human resources for operation. Ghasemi et al. (2013) [7] and Khaskheli et al. (2017) [8] also recorded a similar optimum at pH 5 and 6, as well as a similar trend for nickel(II) adsorption.

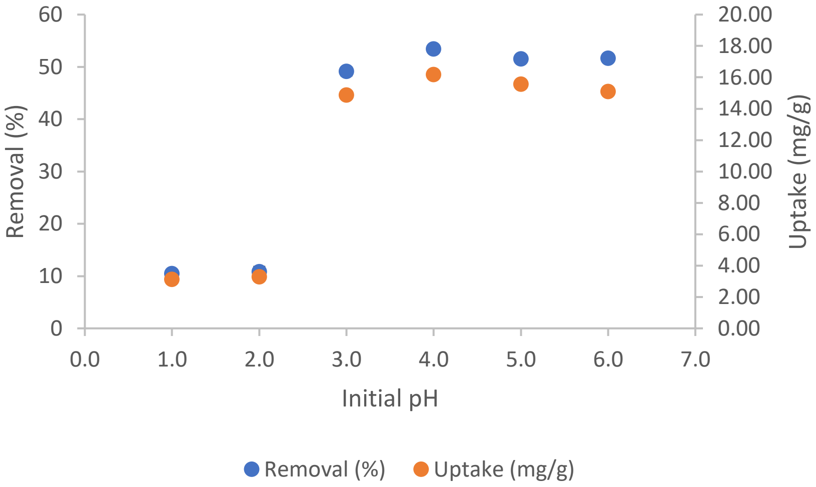

Figure 2. Effect of initial pH on adsorption performance (0.35 g adsorbent, 60 min contact time, 50 mg/L initial nickel(II) concentration and 25 ± 1 °C temperature)

Figure 3(a) depicts the effect of contact time on the removal and uptake of nickel(II). A similar trend with a rapid increase, then a gradual increase and saturation phase was observed for the removal and uptake of nickel(II). For the rapid increase from 1 – 5 min, removal and uptake were 25 % and 14.91 mg/g. Then, removal and uptake increased gradually from 5 – 30 min and achieved saturation from 30 – 120 min at 54 % and 15.62 mg/g. The available vacant adsorption sites caused a rapid increase initially, but then the nickel(II) ions had to travel further into the micropores to find available adsorption sites, which resulted in the gradual increase phase. When the adsorption sites at the macropores and micropores were fully occupied, the adsorption of nickel(II) achieved saturation. A similar trend for the nickel(II) adsorption performance with contact time was also reported by Khaskheli et al. (2017) [8].

From ICP analysis, potassium (K), calcium (Ca), magnesium (Mg) and sodium (Na) concentrations were found to increase with time (Figure 3(b)). Such trends corresponded with a decrease in nickel(II) ions and an increase in the removal and uptake trends of nickel(II). This phenomenon suggests that an ion exchange mechanism had occurred through a displacement of alkaline and alkaline earth metal ions by nickel(II) ions. A contact time of 30 min was selected for the kinetics study.

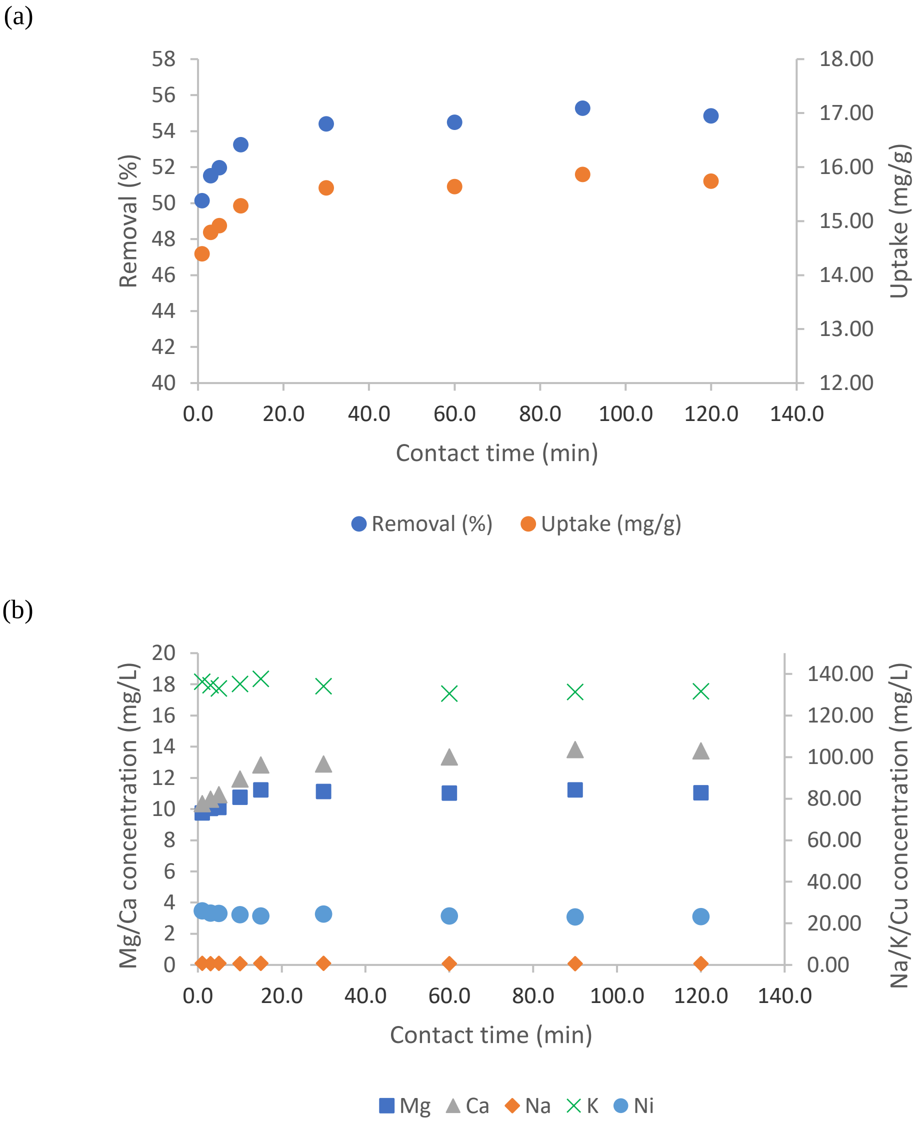

Figure 3. (a) Effect of contact time on adsorption performance (b) ICP analysis of potassium, calcium, magnesium, sodium and nickel(II) ion concentrations (0.35 g adsorbent, initial pH 5.62 ± 0.38, 50 mg/L initial nickel(II) concentration and 25 ± 1 °C temperature)

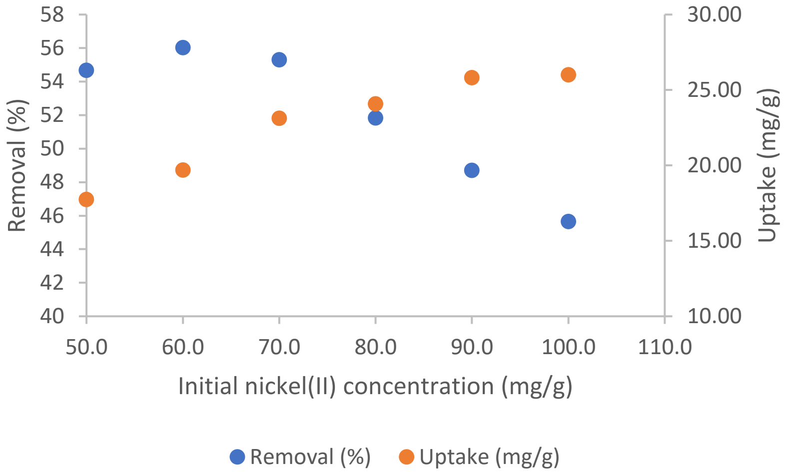

Figure 4. Effect of initial nickel(II) concentration on adsorption performance (0.35 g adsorbent, initial pH 5.62 ± 0.38, 60 min contact time and 25 ± 1 °C temperature)

The effect of the initial nickel(II) concentration on the removal and uptake of nickel(II) are shown in Figure 4. Removal showed a decreasing trend from 55 – 46 % but uptake increased from 17.73 – 26.01 mg/g when the initial concentration was increased from 50 – 100 mg/L. A decrease in the ratio of adsorption sites to nickel(II) ions resulted in a decrease in nickel(II) removal. As the initial concentration of nickel(II) increased, an increase in driving forces to overcome resistance occurred, thus an increase in the adsorption uptake was recorded. Tay et al. (2016) [3] also observed a similar trend for initial nickel(II) concentrations in their study.

Figure 5 indicates that adsorption performance slightly decreased with increasing temperature. When the temperature was increased from 5 – 45 °C, a slight decrease in removal and uptake was observed, from 56 to 52 % and 18.60 to 15.38 mg/g, respectively. An increase in temperature leads to an increase in heat absorption and effective collision. However, this condition also alters the binding sites and cause weak binding affinity, thus slightly decreasing adsorption performance. These factors are suggestive of an endothermic reaction.

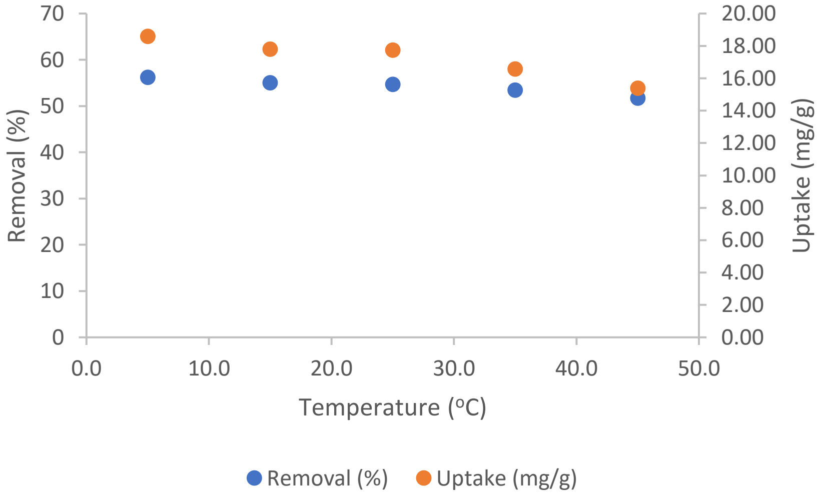

Figure 5. Effect of temperature on adsorption performance (0.35 g adsorbent, initial pH 5.62 ± 0.38, 60 min contact time and 50 mg/L initial nickel(II) concentration)

Table 1. Comparison of Langmuir and Freundlich isotherm models for nickel(II) adsorption

Langmuir		***Freundlich***	
q_{max} (mg/g)	42.02	K_F	1.62
b (L/mg)	0.03	n	2.08
r^2	0.9336	r^2	0.8778

Table 2. Comparison of the Langmuir maximum uptake for nickel(II) for adsorbents

Adsorbent	q_{max} **(mg/g)**	***Reference***
Modified zeolite	25.41	[1]
Lignocellulose montmorillonite nanocomposite	94.86	[4]
Grape shell ash	23.52	[7]
Okra leaves	1.0	[8]
Glutaraldehyde crosslinked magnetic chitosan bead	0.076	[9]
Bioclastic granules	54.9	[10]
Lawn grass	**42.02**	**This study**

Data Analysis for Existing Mathematical Models

Table 1 compares the nickel(II) linearized Langmuir and Freundlich isotherm models. The obtained result was a better fit to the Langmuir model which had a regression coefficient (r^2) of 0.9336, compared to the Freundlich model which had an r^2 value of 0.8778. The calculated Langmuir maximum uptake was 42.02 mg/g. Table 2 shows that the Langmuir maximum uptake in this study was comparable with other adsorbents. The low b value of 0.03 L/mg implied that lawn grass adsorbent showed low selectivity towards nickel(II) ions. The results also revealed the monolayer characteristics of nickel(II) adsorption on the lawn grass. The low constant value of 1.62 K_F and 2.08 n in the Freundlich isotherm model represented slow adsorption of nickel(II). A similar observation on the better fit to Langmuir than Freundlich was documented by Rani et al. (2020) [9] and Tay et al. (2016) [4].

A comparison of pseudo-first-order kinetic and pseudo-second-order kinetic models is shown in Table 3. The regression coefficient (r^2) of the pseudo-second-order kinetic model was excellent (r^2=1.0000) compared to the pseudo-first-order kinetic model (r^2= 0.9902). The high adsorption constants for K_1 and K_2 were similar at 0.03 and indicated rapid adsorption. The calculated maximum uptake for the pseudo-second-order kinetic model at 15.80 mg/L better corresponded to the experimental maximum uptake (q_{exp}) at 15.62 mg/g when compared to the pseudo-first-order kinetic model at 1.15 mg/g. The pseudo-second-order kinetic model indicated that chemisorption was the rate-limiting step. Studies by Liakos et al. (2021) [2] and Rani et al. (2020) [9] were in agreement with the pseudo-second-order kinetic model and supported chemisorption rather than mass transport physisorption as the rate-limiting step.

The values for enthalpy change (ΔH), entropy change (ΔS) and Gibbs free energy (ΔG) were 3127 kJ/mol, -14 kJ/mol and 7021-7581 kJ/mol, respectively. The positive value of ΔH indicated that the adsorption of nickel(II) using lawn grass adsorbent was endothermic. The ΔS value indicated a low degree of derangement at the solid-solution interface thus confirming that weak and reversible bonding had occurred which showed good potential for metal recovery and reuse of the adsorbent. The positive ΔG value suggested that adsorption of nickel(II) is a non-spontaneous reaction.

Table 3. Comparison of pseudo-first-order and pseudo-second-order kinetic models for nickel(II) adsorption

Pseudo-first-order		***Pseudo-second-order***	
q_e (mg/g)	1.15	q_e (mg/g)	15.80
K_1	0.03	K_2	0.03
r^2	0.9902	r^2	1.000

q_{exp} (mg/g) = 15.62

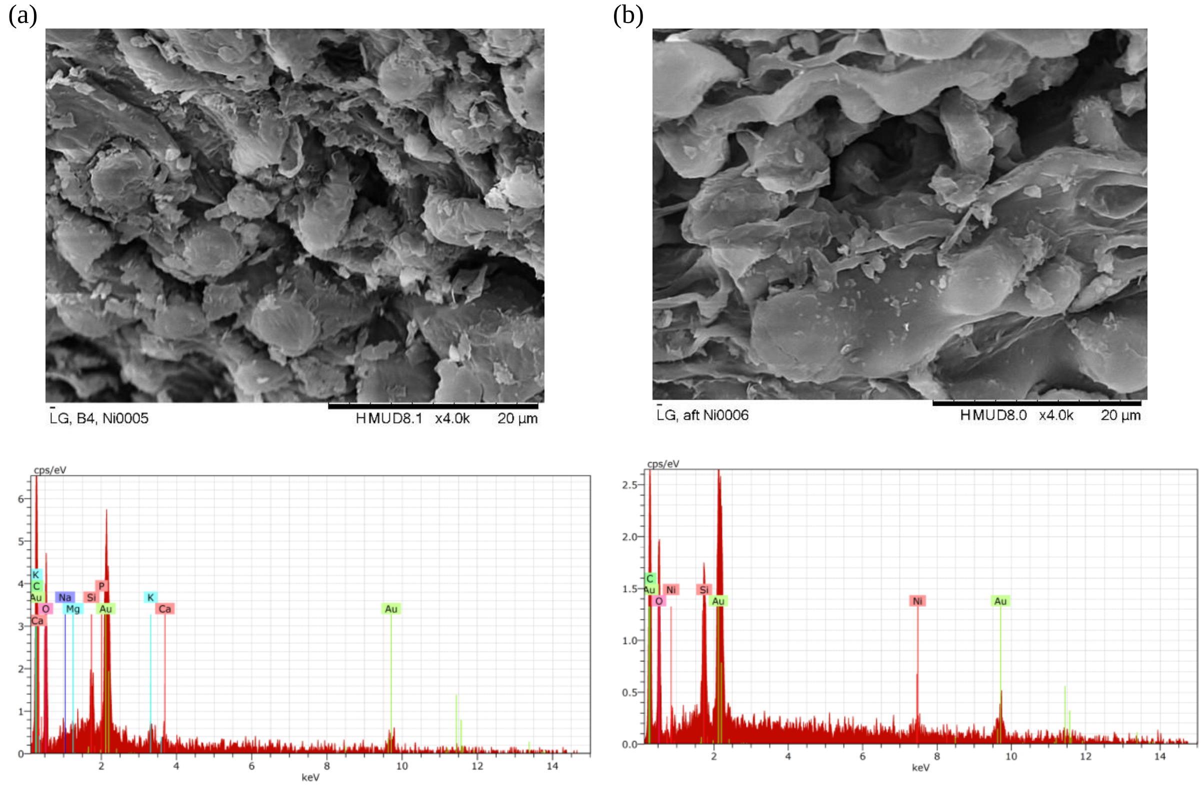

Figure 6. SEM micrographs and EDX spectra (a) before and (b) after nickel(II) adsorption by lawn grass

Scanning Electron Microscopy (SEM)/Energy Dispersive X-ray Analysis (EDX) Characterization

The SEM micrographs and EDX spectra are given in Figure 6. Before adsorption, the surface of lawn grass was rough and highly porous (Figure 6(a)). However, it became smooth after nickel(II) ions deposited a monolayer and closed the surface pores (Figure 6(b)). The EDX before adsorption in Figure 6(a) exhibited the presence of carbon, oxygen, silicon, potassium, calcium, magnesium, sodium and phosphorus. Nickel peaks appeared after adsorption, as can be observed in Figure 6(b). The EDX results indicated nickel(II) ions were bound to the surface of the lawn grass adsorbent. After adsorption, the EDX spectrum also showed that potassium, calcium, magnesium, sodium and phosphorus were not present. These elements were involved in adsorption and support the ICP analysis results implying ion exchange. These observations are consistent with those of Aslam et al. (2020) [5] and Venue et al. (2019) [10].

CONCLUSION

This study investigated the potential of lawn grass as an adsorbent for nickel(II) adsorption. The optimum adsorption performance was found with 0.35 g of adsorbent, pH 5.62 ± 0.38 and 30 min contact time. The result was a better fit to Langmuir than Freundlich, indicating monolayer adsorption had occurred. The calculated Langmuir maximum uptake at 42.02 mg/g was comparable to other nickel(II) removal adsorbents. The pseudo-second-order kinetic model exhibited a higher correlation coefficient than the pseudo-first-order kinetic model, and revealed that chemisorption was the rate-limiting step. Evaluation of thermodynamic parameters such as Gibbs free energy, enthalpy change and entropy change implied the adsorption of nickel(II) using lawn grass was a non-spontaneous endothermic reaction which formed weak, reversible bonds. ICP results suggested ion exchange had occurred during nickel(II) adsorption. SEM results showed the morphology of the adsorbent surface became more smooth and less porous after adsorption. The EDX results, which showed nickel(II) peaks after adsorption, confirmed that adsorption of nickel(II) had occurred on the surface of lawn grass. The displacement of potassium, calcium, magnesium, sodium and phosphorus peaks with nickel peaks further supported the ICP results of the ion exchange mechanism. The results of this study provide important data for large scale pilot studies and industrial applications. Further work should be done on functional groups, mechanisms and modelling of nickel(II) adsorption processes.

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The authors declare that they have no conflict of interest.

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