

KINETICS, CATALYSIS, AND REACTION ENGINEERING

Removal of Nickel from Aqueous Solution Using Wine Processing Waste Sludge

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Wine processing waste sludge (WPWS) has been shown to be an effective sorbent for sorption of some heavy metals (i.e., lead and chromium), but the sorption mechanism of heavy metal by WPWS has remained obscure. The objective of this study was to explore the sorption mechanism of WPWS for heavy metals using nickel (Ni) as the sorbate. The WPWS has been characterized with wet chemistry, infrared (IR), X-ray diffraction, scanning electron microscopy (SEM), carbon-13 magic-angle nuclear magnetic resonance (¹³C NMR), and energy-dispersive spectrometry chemical analyses. The sludge contained high organic carbon (40.5%), nitrogen (23.4%), and cation-exchange capacity (1218 cmol_c kg⁻¹). SEM investigation of WPWS showed porous-like activated carbon. IR analysis of WPWS revealed that R-NH₂ and R-COOH were the major functional groups. The proportion of organic functional groups in WPWS quantified by ¹³C NMR analysis was in the following order: alkyl-C > carboxyl-C > N-alkyl-C > aromatic-C > O-alkyl-C > acetal-C > phenolic-C. The parameters affecting the sorption of Ni were the pH, initial concentration of Ni, particle size of WPWS, and reaction temperature. The WPWS sorption isotherms of Ni are only well described by the Langmuir sorption isotherm. A pseudo-second-order sorption kinetic model describes successfully the kinetics of sorption of Ni onto WPWS at different operation parameters (i.e., pH, initial Ni concentration, and particle size). Under the steady-state reaction conditions, the Gibb free energy (ΔG°) ranges from -18.969 to -23.616 kJ mol⁻¹, and ΔH° and ΔS° are 3.366 kJ mol⁻¹ and 6.056 J mol⁻¹ K⁻¹, respectively, indicating that higher temperature favors spontaneous reaction for Ni sorption by WPWS. According to the thermodynamic sorption parameters under steady-state conditions, this sorption is a spontaneous and endothermic reaction. The sorption mechanisms include physical adsorption and chemical complexation. Amino and carboxyl groups are the prominent functional groups interacting with Ni. The sorption capacity is influenced by several parameters such as the pH, initial Ni concentration, temperature, and particle size of WPWS.

Introduction

The discharge of water containing heavy metals causes critical pollution problems that involve the death of fishes and other species of biota. The origins of nickel-containing wastewater are the effluents of mining areas, Ni-plating plants, alloys, silver refineries, pigments, and battery manufacturing discharged into aquatic environments. Nickel is a cofactor of enzyme for organisms, but excess uptake is harmful to animals and plants. Long-time exposure to high Ni concentration can cause lung, nose, and bone cancers.

There are many methods for purifying wastewaters containing toxic heavy metals from aqueous systems, including biological treatment, ion exchange, chelation, reverse osmosis, coagulation-precipitation, electrochemical operation, filtration, and sorption. Unlike most

organic pollutants, heavy metals are generally refractory and cannot be degraded or readily detoxified by biological treatments.¹ A conventional alkaline neutralization precipitation (ANP) process has been employed to remove heavy metals from aqueous systems. However, the ANP process, in many cases, cannot meet the increasingly stringent effluent standard.²

The sorption process plays an important role in removing these heavy metals from waters. Several natural and synthetic hydrous solids have been employed as sorbents. For example, activated carbon has been the most extensively applied, but the high cost limits large-scale applications.^{3,4} In recent years, there have been numerous researches on the development of low-cost alternatives to activated carbon,^{5,6} such as fly ash,⁷ metal oxides,^{5,8} zeolites,⁹ peats,¹⁰ chitosans,¹¹ and activated sludges.⁶ In this research, wine processing waste sludge (WPWS) has been used as a sorbent for removal Ni.

The wine processing industry produces great quantities of waste sludge from the final clarifier and settling basin of the wastewater treatment process. The sub-

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stance causes a serious disposal problem. A significant organic carbon content makes wine processing sludge excellent sorbents of heavy metals because of its large surface area and high binding affinity. Thus, the aim of this research was to explore the removal of Ni from wastewaters using WPWS as the sorbent.

Experimental Section

Materials. (i) Sample Preparation and Characterization of WPWS. WPWS was obtained from Ilan Wine-Processing Co., Ilan, Taiwan. The WPWS taken from the coagulation settling basin and final clarifier in the activated sludge process was dried at 25 °C, ground, and sieved into four particle sizes, ranging from 50–100, 100–140, 140–200, to <200 mesh, which were represented as average diameters of 0.297, 0.149, 0.105, and <0.105 mm, respectively. The sieved WPWS was washed with double deionized water (DDW) to remove easily suspended materials. The rinsed WPWS was air-dried again and stored in a desiccator at 4 °C. A scanning electron microscope (Hitachi S-2400) equipped with an energy-dispersive spectrometer (Kevex level 4) was employed to characterize WPWS for its major constituents and morphological investigations. The samples were coated with about 20-nm-thick carbon using a Denton vacuum evaporator and analyzed by energy-dispersive spectrometry (EDS) in an automated quantitative elemental analysis mode. The pH of WPWS suspensions was measured at a 1:5 WPWS–water ratio with a pH meter. The cation-exchange capacity (CEC) of WPWS was determined by a conventional ammonium–sodium exchange method.¹² Total nitrogen analysis was carried out by the Kjeldahl method.¹³ Organic matter was determined by the combustion method at 550 °C. The P, Ca, Fe, and Al concentrations were observed from the EDS analysis. The predominant species and characteristics of functional groups of WPWS were characterized using an infrared (IR) spectrometer (Galactic Industries Corp. BIO-RAD Fis-7). Organic carbon functional groups were examined by CPMAS ¹³C NMR spectroscopy,¹⁴ using a Bruker MSL-200 NMR spectrometer. The NMR spectra were divided into the following chemical shift regions: alkyl-C (0–45 ppm), *N*-alkyl-C (46–65 ppm), *O*-alkyl-C (65–90 ppm), acetal-C (90–110 ppm), aromatic-C (110–140 ppm), phenolic-C (140–160 ppm), and carboxyl-C (160–200 ppm).¹⁵ Areas of the chemical shift regions were measured by cutting and weighing, expressed as percentages of the total area.¹⁶

All chemicals used in this study were analytical grade, and solutions were prepared with DDW. A stock of the Ni solution (90 mg L⁻¹) was prepared from Ni(NO₃)₂ using DDW and diluted to desired concentrations. For sorption isotherms and kinetic experiments, all Ni solutions were adjusted initially at pH 5.5 because of the best sorption behavior, and a 1 × 10⁻² M KNO₃ solution was employed to control the ionic strength. A mechanical shaker with adjustable vibrational speed was employed to achieve perfect mixing with a constant speed of 110 rpm.

Methods. (i) Sorption Isotherms. For the sorption isotherms, 0.85 g of WPWS (<0.105 mm) was equilibrated separately with 100-mL solutions containing different Ni concentrations (i.e., 15, 25, 40, 55, and 70 mg L⁻¹). The temperatures examined were 10, 20, 30, 40, and 50 °C. After adjustment of the initial pH with either a 0.1 M HNO₃ or 0.1 M NaOH solution, the

suspensions were shaken by the shaker with a constant speed of 110 rpm for 2 h. Then, the suspensions were filtered with a 0.45-μm Millipore filter. The filtrates were analyzed for Ni concentrations using an atomic absorption spectrophotometer (AAS; Hitachi Z-6100 Polarized Zeeman). All experiments were conducted in triplicate.

(ii) Kinetic Experiments. To conduct kinetic experiments, 1.2 g of WPWS was separately added to a series of 100-mL Ni solutions with different particle sizes of WPWS (0.297, 0.149, 0.105, and <0.105 mm), Ni concentrations (30, 45, 60, 75, and 90 mg L⁻¹), and temperatures (10, 30, and 50 °C). The suspensions were agitated vigorously by the shaker from 3 min to 2 h. At the end of desired time intervals, proper volume of mixing solutions were immediately taken to filter through the 0.45-μm Millipore filter. The Ni concentrations in the filtrates were determined by AAS.

(iii) Sorption Isotherms. To determine the sorption capacity of WPWS, a sorption isotherm was conducted by analyzing sorption data to fit the models of Freundlich and Langmuir sorption isotherm equations. The relative coefficients of these models were calculated using linear least-squares fitting. The Freundlich isotherm equation $x/m = k_F C_e^{1/n}$ after linearization becomes

$$\log \frac{x}{m} = \log X = \log k_F + \frac{1}{n} \log C_e \quad (1)$$

where X is the mass of sorbed Ni ions per mass of WPWS, mg g⁻¹; C_e is the equilibrium concentration of Ni, mg L⁻¹; and k_F and n are constants of the Freundlich equation that are related to the sorption capacity and intensity, respectively.¹⁷ k_F and n can be calculated from the slope and intercept of the linear plot, with $\log X$ vs $\log C_e$.

The Langmuir sorption isotherm equation of $x/m = Q_m k_L C_e / (1 + k_L C_e)$ after linearization is

$$\frac{m}{x} = \frac{1}{X} = \frac{1}{Q_m} + \frac{1}{Q_m k_L C_e} \quad (2)$$

Langmuir constants k_L and Q_m are related to the energy of sorption and sorption capacity, respectively. Both of them can be determined from the slope and intercept of the linear plot, with $1/X$ vs $1/C_e$.

(iv) Kinetic Models. The sorption kinetics of Ni by WPWS relative to the WPWS particle size, WPWS dosage, and initial Ni concentration were studied using the pseudo-first-order and pseudo-second-order sorption equations.¹¹ The pseudo-first-order equation is shown as follows:

$$dq_t/dt = k_1(q_e - q_t) \quad (3)$$

where k_1 (min⁻¹) is the rate constant of the pseudo-first-order adsorption, q_t (mg g⁻¹) denotes the amount of sorption at time t (min), and q_e (mg g⁻¹) is the amount of sorption at equilibrium. After definite integration by application of the conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, eq 3 becomes

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (4)$$

The sorption rate constant, k_1 , can be determined by plotting $\log(q_e - q_t)$ vs t .

The pseudo-second-order equation can be written as

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (5)$$

where k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the rate constant. Integration of eq 5 and application of the conditions give

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \quad (6)$$

Equation 6 can be rearranged into a linear form.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

k_2 and q_e can be obtained from the intercept and slope of plotting t/q_t vs t .

(v) Desorption Studies. The nickel-loaded WPWS was collected from the suspension in an isotherm experiment at 30 °C, and these samples were found to contain 3.17 mg g^{-1} of Ni. After air-dried treatment, 1 g of the samples was mixed vigorously for 7 days with 100 mL of DDW and 100 mL each of 0.1 M HNO_3 and 0.5 M HNO_3 solutions. The Ni content in the filtrate solutions was determined by AAS, and the desorption ratio of Ni from WPWS was then calculated.

Results and Discussion

Characterization of WPWS. The pH and CEC of WPWS were 7.8 and 1218 $\text{cmol}_c \text{kg}^{-1}$, respectively. The chemical composition of WPWS is organic matter (40.5%), nitrogen (23.4%), phosphorus (6.9%), calcium (5.6%), iron (7.9%), and aluminum (1.3%). High CEC and organic matter contents of WPWS show tremendous sorption sites on the complicated conformation. A high nitrogen content revealed that nitrogen is the most prominent chemical in the activated sludge pool in a wastewater treatment plant. Phosphorus and calcium from flocculating agents of WPWS are also the main elements. After 50 \times magnifications of SEM micrographs, WPWS particles (100–140 mesh) appear mostly spherical in shape (Figure 1a). After 12000 \times magnifications, WPWS shows a morphology of rough surface texture and porous structure, which is similar to that of activated carbon (Figure 1b). In fact, according to its origin, WPWS can be regarded as a biosorbent. The overall sorption is located in the cell wall of microorganisms and included sorption, complexation, or precipitation processes.¹⁸ Chitin and chitosan are prominent polysaccharides of the cell walls of microorganisms including bacteria and fungi. Chitin consists only of *N*-acetylglucosamine residues joined by $\beta(1\rightarrow4)$ -glycosidic links. In chitosan, the hydroxyl at the second carbon in D-glucose is replaced by an amino group. The IR spectrum (Figure 2) revealed a broad IR band at 3280–3400 cm^{-1} , representing $-\text{OH}$ stretching of water molecules and $-\text{OH}$ groups of glucose and $-\text{NH}$ stretching of the protein and acetamido ($-\text{NHCOCH}_3$) groups of chitin.¹⁹ An intense band at 1032 cm^{-1} can be attributed to the $-\text{CN}$ stretch vibration of the chitin–chitosan as well as protein fractions. A moderate band at 1535 cm^{-1} could also be assigned to $-\text{NH}$ bending, and another one at 1649 cm^{-1} could be attributed to the $-\text{COO}$ asymmetric vibration. Therefore, we suggest that $\text{R}-\text{NH}_2$ and $\text{R}-\text{COOH}$ are the main functional groups in WPWS. The carboxyl and unprotonated amino groups

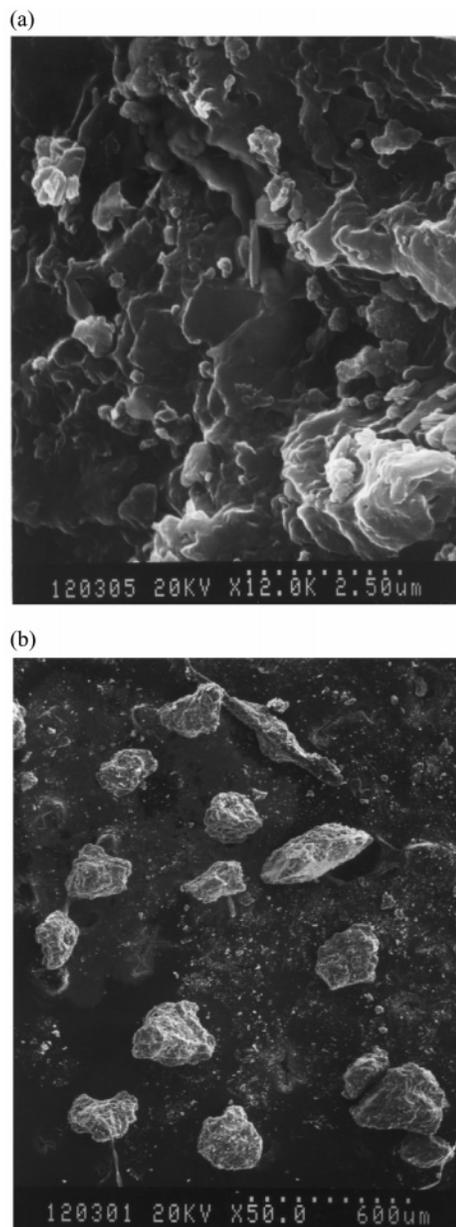
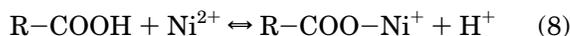


Figure 1. SEM micrographs of WPWS (100–140 mesh) at different magnifications: (a) 50 \times ; (b) 12000 \times .

can serve as coordination and electrostatic interaction sites for sorbing transition metals.¹¹ The sorption mechanism can be expressed as



The transition-metal ion (i.e., Ni^{2+}) can be caught by one $-\text{NH}_2$ group as well as two $-\text{OH}$ groups of the glucose residue, and the fourth ligand site is probably occupied by a water molecule.²⁰ The concentrations of these organic functional groups in WPWS follow the trend of alkyl-C (39.9%) > carboxyl-C (15.1%) > *N*-alkyl-C (14.1%) > aromatic-C (10.5%) > *O*-alkyl-C (9.5%) > acetal-C (8.2%) > phenolic-C (3.7%). In the functional groups of WPWS, carboxyl-C and *N*-alkyl-C are the principal functional groups participating in the reaction chelating with heavy metals, and they also show high correlation with CEC. The sum of carboxyl-C

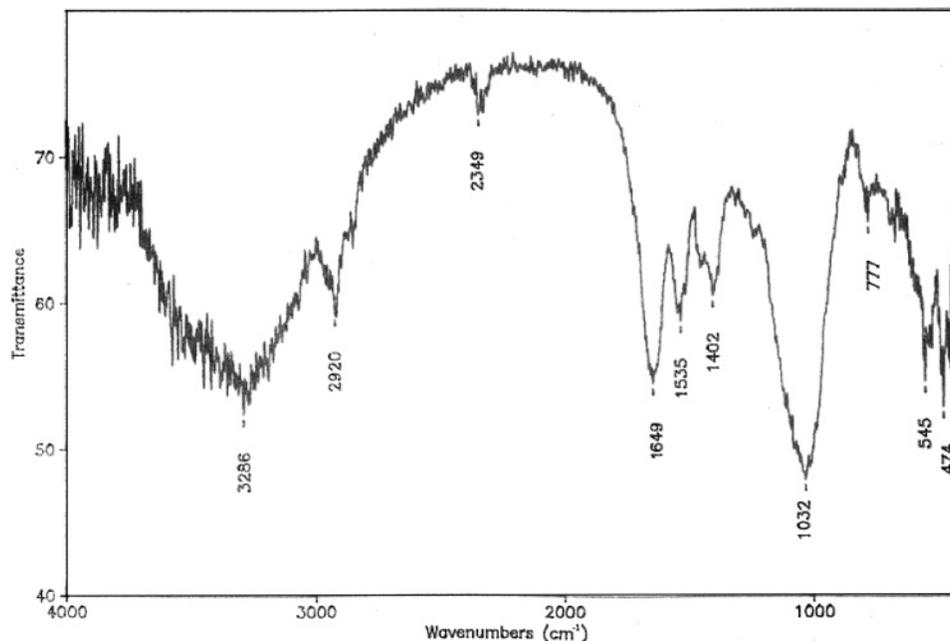


Figure 2. IR spectrum of WPWS (100–140 mesh).

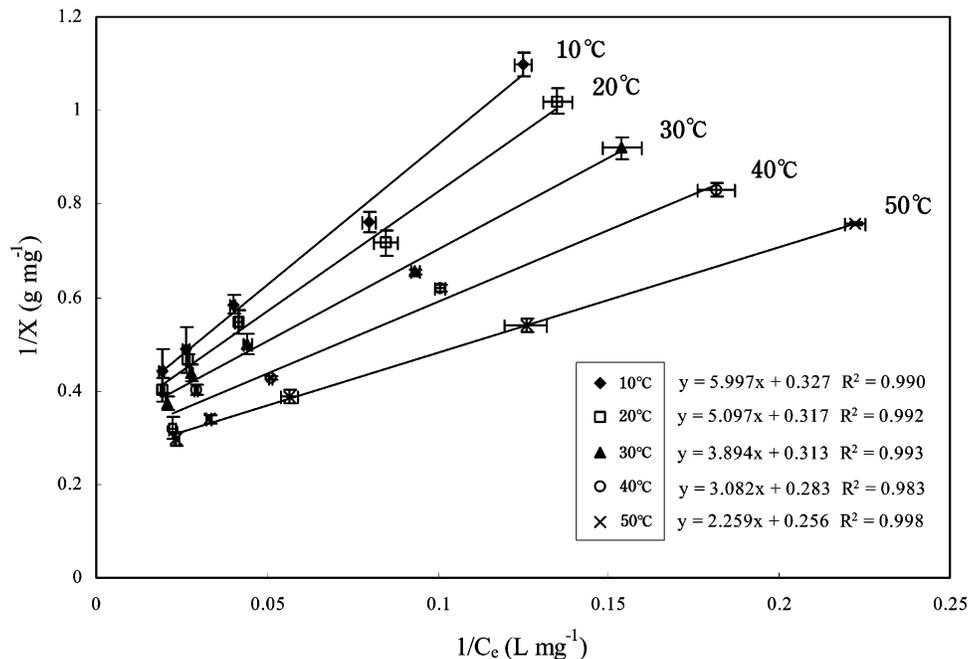


Figure 3. Langmuir isotherm of Ni sorption by WPWS at 10–50 °C ($C_0 = 15, 25, 40, 55,$ and 70 mg L^{-1} , <200 mesh, dosage = 8.5 g L^{-1} , pH 5.5). Error bars represent ± 1 standard error.

and *N*-alkyl-C was over 29%; therefore, we conclude that WPWS significantly interacts or forms complexes with Ni in solution. The carboxyl functional groups complexed with Ni were related to its pK values. For example, the dissociation constant (pK) of acetic acid is 4.75; the pK_1 and pK_2 values of oxalic acid are 1.23 and 4.19, respectively; the pK_1 , pK_2 , and pK_3 values of citric acid are 3.08, 4.74, and 5.40, respectively.²¹ On the other hand, *N*-alkyl-C and acetal-C are the main components of hemicellulose, and O-alkyl-C is an important component of cellulose. Lignin is composed of aromatic-C and phenolic-C. Hence, cellulose and lignin might be derived from the residues of rinsed cereal grains in wine processing. Alkyl-C, aromatic-C, and carboxyl-C are the main components of WPWS involving microbial resynthesis products in an activated sludge aeration tank.

Thus, we consider that WPWS was produced in microbial activity. There were abundant *N*-alkyl-C groups and amino acids like groups in WPWS present in the IR spectrum (Figure 2). Therefore, *N*-alkyl-C groups are relevant to amino acid compounds in WPWS.

pH Effect on Ni Sorption by WPWS. The maximum removal efficiency of Ni sorption by WPWS is near pH 5.5 (data not shown). The protonated effect on the carboxyl group increased with a decrease in the pH, and therefore the sites of negative charge of the WPWS surface are deficient in low pH. This led to a low amount of Ni sorbed by WPWS under these conditions because of the electrostatic repulsion effect.

Freundlich and Langmuir Isotherms versus Temperature Effect. As shown in Figure 3, only the Langmuir sorption isotherm equations applied to the

Table 1. Calculated Langmuir Sorption Isotherm Parameters (Q_m and K_L), Determination Constants (R^2), and Thermodynamic Data

T (°C)	Q_m (mg g ⁻¹)	K_L (L mol ⁻¹)	K_L (L mg ⁻¹)	R^2	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)
10	3.061	3197.389	0.054	0.990	-18.969		
20	3.157	3647.912	0.062	0.992	-19.960		
30	3.196	4716.545	0.080	0.993	-21.288	3.366	6.056
40	3.534	5389.893	0.092	0.983	-22.337		
50	3.907	6653.293	0.113	0.998	-23.616		

experimental data gave a good correlation (R^2 ranged from 0.983 to 0.998). The constants K_L and maximum sorption capacity Q_m are listed in Table 1. Both K_L and Q_m increase with an increase in the temperature from 10 to 50 °C, and it can be concluded that WPWS shows better sorptive capacities for Ni at higher temperature. The maximum sorption capacity is 3.907 mg g⁻¹ at 50 °C. On the other hand, the sorption data cannot fit in the Freundlich isotherm. The Langmuir isotherm equation can be written as

$$x/m = \frac{3.907 \times 0.113C_e}{1 + 0.113C_e} \quad (10)$$

where the maximum value of x/m is 3.469 mg of Ni g⁻¹ of WPWS when $C_e = C_0 = 70$ mg L⁻¹ of Ni solution at 50 °C. In this manner, we can estimate the maximum sorption capacity of WPWS previously in diverse operation conditions, and it is useful to evaluate the Ni elimination system.

Sorption Kinetics

Effects of the Particle Sizes. Figure 4 shows the time profiles of the Ni concentration at different particle sizes of WPWS. C_0 denotes the initial Ni concentration in the aqueous phase (mg L⁻¹), and C_t denotes the Ni concentration in the aqueous phase at time t . The value of C_t/C_0 can be considered as the symbol of Ni removal, and C_t/C_0 decreased with an increase in Ni removal. Generally, increasing the particle size of the sorbent resulted in a lower sorption rate, but the WPWS particle size has little influence on the sorption rate in this case except the 50–100 mesh one. It is supposed that the aggregations of WPWS collapsed into small sizes when

vigorously mixed in a suspension. It reach sorption equilibrium within 20 min for all particle sizes. The pseudo-second-order equations show a good correlation of the experimental results with the linearized form (R^2 ranged from 0.991 to 0.999). The results elucidate that the kinetic behavior of Ni sorption by different particle sizes of WPWS has been satisfactorily explain with the pseudo-second-order sorption equation. Compared with the former, the pseudo-first-order equation shows a poor correlation relationship with the experimental data (R^2 ranged from 0.734 to 0.912). Thus, only the pseudo-second-order equation can be useful for the kinetic study. The calculated sorption rate constants, k_2 , for the pseudo-second-order equation at WPWS of 50–100, 100–140, 140–200, and <200 mesh sizes are 0.069, 0.094, 0.135, and 0.139, respectively (pH 5.5, dosage = 12 g L⁻¹, $C_0 = 0.05$ g L⁻¹).

Effects of the Initial Ni Concentrations. As shown in Figure 5a, solutions with higher initial concentrations of Ni show poor removal ratios. On the other hand, all of the different concentration treatments reach sorption equilibrium within 50 min. Only the pseudo-second-order sorption equation fitted the experimental data well, showing high correlations and interpreting sorption phenomena (Figure 5b). The calculated sorption rate constants, k_2 , for 30, 45, 60, 75, and 90 mg L⁻¹ Ni solutions were 0.276, 0.162, 0.109, 0.073, and 0.068, respectively (pH 5.5, 100–140 mesh, dosage = 12 g L⁻¹). A lower initial concentration would have a high k_2 value, owing to numerous Ni²⁺ ions competing against and interacting with limited sorbed sites on WPWS. In addition, increasing the Ni concentration in the solution seems to reduce the diffusion of Ni in the boundary layer of a WPWS solid.

Effects of the Temperature. Time profiles of the

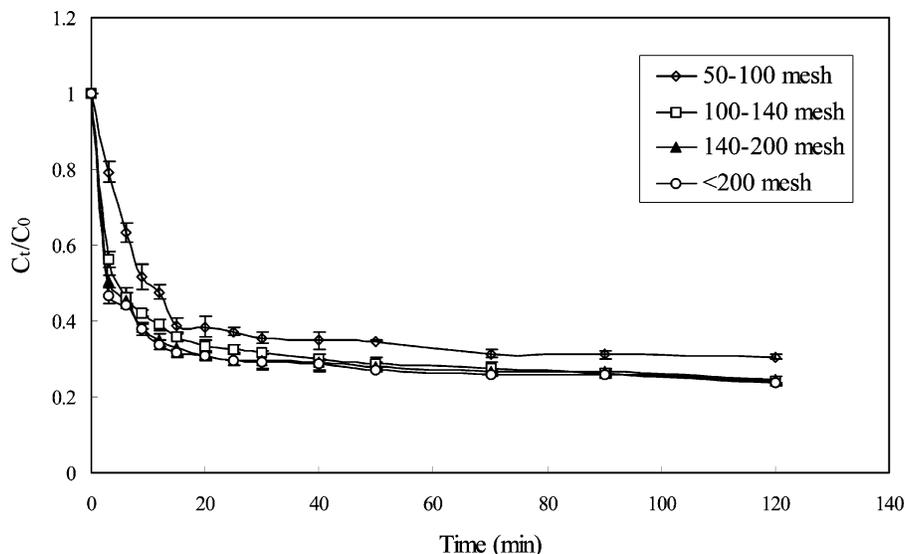


Figure 4. Time profiles of Ni sorption by WPWS with different particle sizes ($C_0 = 0.05$ g L⁻¹, dosage = 12 g L⁻¹, pH 5.5, $T = 30$ °C). Error bars represent ± 1 standard error.

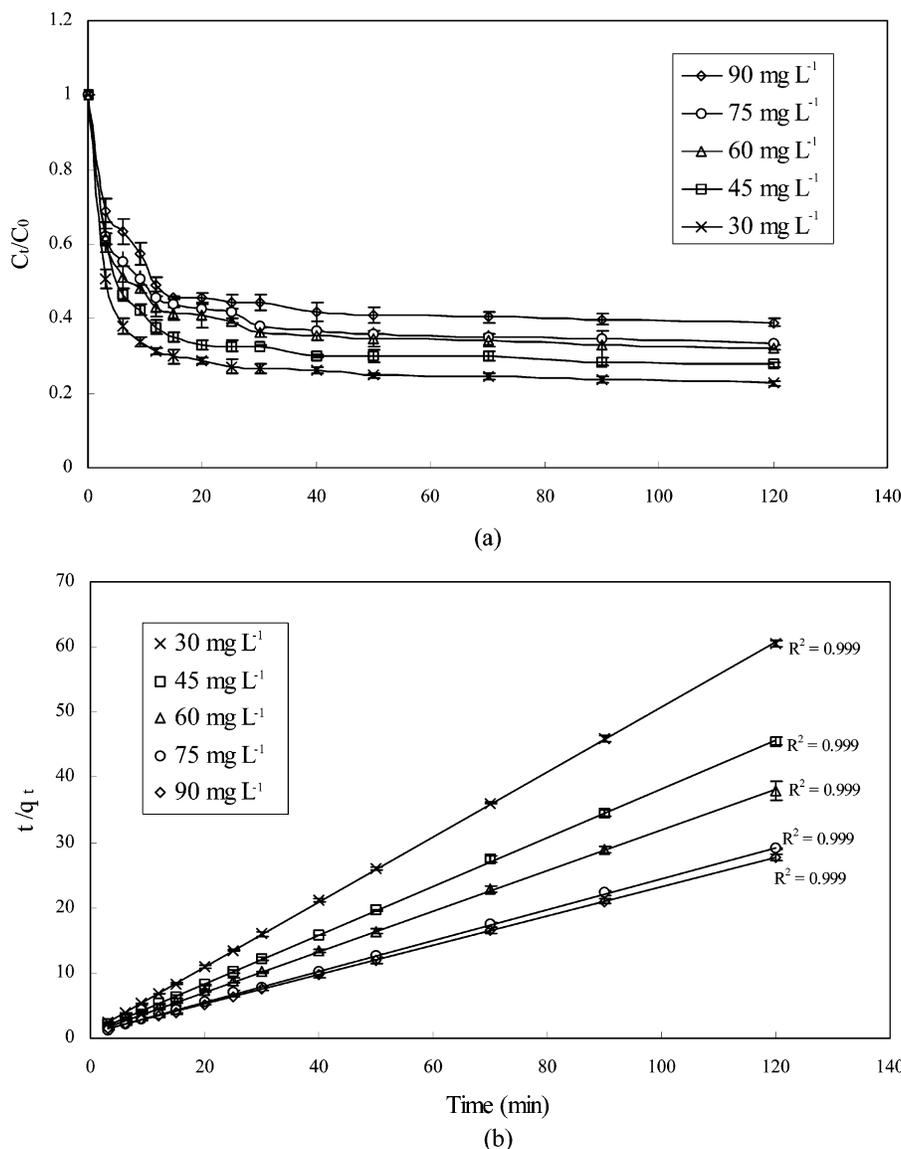


Figure 5. Time profiles (a) and pseudo-second-order kinetic model (b) of Ni sorption by WPWS with different initial Ni concentrations (dosage = 12 g L⁻¹, 100–140 mesh, pH 5.5, $T = 30$ °C). Error bars represent ± 1 standard error.

Ni concentration at different temperatures of WPWS are shown in Figure 6a. A higher temperature treatment for WPWS possesses a higher sorption rate as well as removal efficiency. According to the kinetic model for different temperature treatments, only the pseudo-second-order equation shows a high correlation coefficient (Figure 6b).

Thermodynamic Studies. The Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) are calculated using the following thermodynamic equations:

$$\Delta G^\circ = -RT \ln(K_L) \quad (11)$$

$$\ln(K_L) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (12)$$

where T is the absolute temperature in Kelvin (K) and R is the universal gas constant (8.314 J mol⁻¹ K⁻¹). The Langmuir sorption constant K_L is derived from isotherm experiments at 10, 20, 30, 40, and 50 °C. Thus, ΔH° and entropy ΔS° can be obtained from the slope and intercept of a $\ln K_L$ vs $1/T$ plot, respectively, assuming the sorption kinetics to be under steady-state conditions.

The calculated thermodynamic constants are listed in Table 1. The ranges of ΔG° values (from -18.969 to -23.616 kJ mol⁻¹) decrease with an increase in the temperature from 10 to 50 °C, and the negative sign of ΔG° indicates that the sorption processes of Ni for WPWS are spontaneous reactions under experimental conditions. The term *chemisorption* means a chemical bond formed between the adsorbed molecule and the solid surface, and physical sorption denotes a van der Waals type force formed between the interfaces. Jaycock and Parfitt²² reported that physical sorption energies are in the range of 0 to -20 kJ mol⁻¹ and chemisorption energies in the range of -80 to -400 kJ mol⁻¹. Therefore, the interaction between Ni and WPWS can be regarded as physical sorption rather than chemisorption. The values of enthalpy (ΔH°) and entropy (ΔS°) were calculated to be 3.366 kJ mol⁻¹ and 6.056 J mol⁻¹ K⁻¹, respectively. The positive sign of ΔH° shows that the sorption of Ni by WPWS was endothermic, and the positive value of ΔS° indicates a higher disorder tendency at the interface between WPWS and Ni solutions. According to these results, the Ni–WPWS suspension

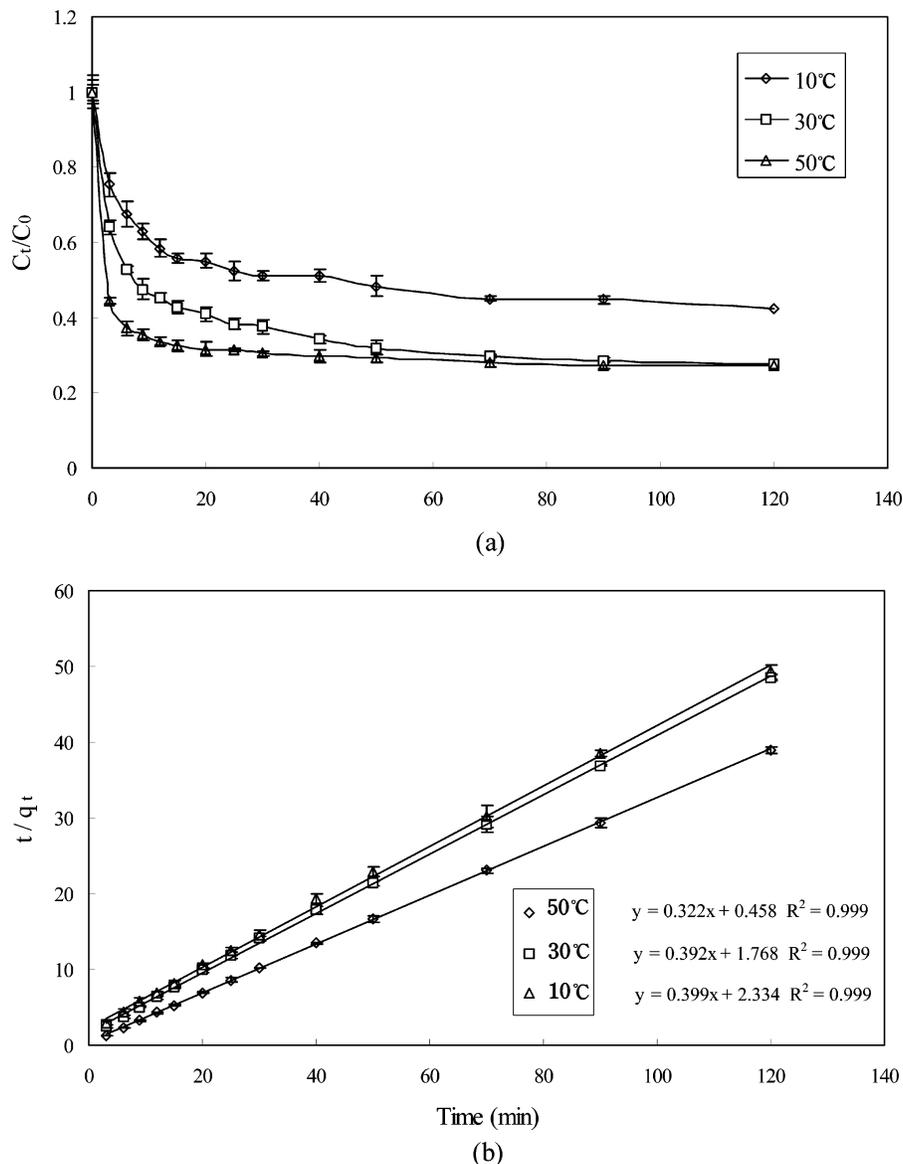


Figure 6. Time profiles (a) and pseudo-second-order kinetic model (b) of Ni sorption by WPWS at different operation temperatures ($C_0 = 0.05 \text{ g L}^{-1}$, dosage = 12 g L^{-1} , 100–140 mesh, pH 5.5). Error bars represent ± 1 standard error.

system was spontaneous and at higher temperatures favors Ni sorption by WPWS.²³

Desorption Studies. Desorption studies can further clear up the mechanism of sorption. If the sorbed Ni on the WPWS surface can be detached by water, then Ni conjunction on WPWS occurs between weak bonds. An acid solution can desorb Ni easily; the sorption is then competing with H^+ .²⁴ The experimental data reveal that the Ni desorption values of samples treated with DDW, 0.1 M HNO_3 , and 0.5 M HNO_3 were 0.9%, 27.6%, and 28.4%, respectively. These results show that complexation is also important to the interaction between Ni and WPWS.

Conclusions

The WPWS, in fact, is an effective biosorbent of Ni in solutions because of its characteristics of rough surface texture, high CEC, high organic matter contents, and abundant amino and carboxyl functional groups. The sorption mechanisms include physical adsorption and chemical complexation. Amino and carboxyl groups are the prominent functional groups interacting with Ni.

The sorption capacity is influenced by parameters such as the pH, initial Ni concentration, temperature, and particle size of WPWS. In the sorption isotherm, sorption of Ni on WPWS is well described by the Langmuir isotherm equation, and the maximum sorption capacity is $66.55 \mu\text{mol g}^{-1}$ at 50°C . In the sorption kinetics, only the pseudo-second-order sorption equation fits the experimental results well. A higher initial concentration of Ni results in a decrease in the sorption rate of external diffusion. According to the thermodynamic sorption parameters under steady-state conditions, this sorption is a spontaneous and endothermic reaction. In addition, high temperature favors Ni sorption. The interaction between Ni and hydroxyl, aromatic, acetic, and phenolic functional groups of WPWS remains unclear, which merits further exploration.

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Literature Cited

- (1) Weng, C. H.; Huang, C. P. Treatment of Metal Industrial Wastewater by Fly Ash and Cement Fixation. *J. Environ. Eng.* **1994**, *120*, 1471.
- (2) Luo, B.; Patterson, J. W.; Anderson, P. R. Kinetics of Cadmium Hydroxide Precipitation. *Water Res.* **1992**, *26*, 745.
- (3) Reed, B. E.; Jamil, M.; Thomas, B. Effects of pH, Empty Bed Contact Time and Hydraulic Loading Rate on Lead Removal by Granular Activated Carbon Columns. *Water Environ. Res.* **1996**, *68*, 877.
- (4) Seco, A.; Marzal, P.; Gabaldon, C. Adsorption of Heavy Metals from Aqueous Solutions onto Activated Carbon in Single Cu and Ni Systems and in Binary Cu–Ni, Cu–Cd and Cu–Zn Systems. *J. Chem. Technol. Biotechnol.* **1997**, *68*, 23.
- (5) Srivastava, S. K.; Gupta, V. K.; Mohan, D. Removal of Lead and Chromium by Activated Slag- a blast furnace. *Waste. J. Environ. Eng.* **1997**, *123*, 461.
- (6) Lee, S. M.; Davis, P. A. Removal of Cu(II) and Cd(II) from Aqueous Solution by Seafood Processing Waste Sludge. *Water Res.* **2001**, *35*, 534.
- (7) Gupta, G. S.; Prasad, G.; Singh, V. N. Removal of Chrome Dye from Aqueous Solutions by Mixed Adsorbents: Fly Ash and Coal. *Water Res.* **1990**, *24*, 45.
- (8) Smith, E. H.; Amini, A. Lead Removal in Fixed Beds by Recycled Iron Material. *J. Environ. Eng.* **2000**, *126*, 58.
- (9) Panayotova, M. Use of Zeolite for Cadmium Removal from Wastewater. *J. Environ. Sci. Health., A* **2000**, *35*, 1591.
- (10) Ho, Y. S.; McKay, G. The Kinetics of Sorption of Divalent Metal Ions onto Sphagnum Moss Peat. *Water Res.* **2000**, *34*, 735.
- (11) Wu, F. C.; Tseng, R. L.; Juang, R. S. Kinetic Modeling of Liquid-phase Adsorption of Reactive Dyes and Metal Ions on Chitosan. *Water Res.* **2001**, *35*, 613.
- (12) Rhoades, J. D. Cation Exchange Capacity. In *Methods of Soil Analysis, Part 2, Chemical and Microbiological Properties*, 2nd ed.; Page, A. L., Ed.; American Society of Agronomy: Madison, WI, 1982.
- (13) Bremner, J. M.; Mulvaney, C. S. Nitrogen Total. In *Methods of Soil Analysis, Part 2, Chemical and Microbiological Properties*, 2nd ed.; Page, A. L., Ed.; American Society of Agronomy: Madison, WI, 1982.
- (14) Oades, J. M. Recent Advances in Organomineral Interactions: Implication for Carbon Cycling and Soil Structure. In *Environmental Impact of Soil Component Interactions, vol. 1. Natural and Anthropogenic Organics*; Huang, P. M., Berthelin, J., Bollag, J. M., McGill, W. B., Page, A. L., Eds.; CRC Press: Boca Raton, FL, 1995.
- (15) Preston, C. M.; Sollins, P.; Sayer, B. G. Changes in Organic Components for Fallen Logs in Old-growth Douglas-fir Forests Monitored by ¹³C Nuclear Magnetic Resonance Spectroscopy. *Can. J. For. Res.* **1990**, *20*, 1382.
- (16) Chen, M. C.; Wang, M. K.; Chiu, C. Y.; Huang, P. M.; King, H. B. Determination of Low Molecular Weight Dicarboxylic Acids and Organic Functional Groups in Rhizosphere and Bulk Soils of *Tsuga* and *Yushania* in a Temperate Rain Forest. *Plant Soil* **2001**, *231*, 37.
- (17) Prasad, M.; Amritphale, S. S.; Chandra, N. Kinetics and Isotherms for Aqueous Lead Adsorption by Natural Minerals. *Ind. Eng. Chem. Res.* **2000**, *39*, 3034.
- (18) Jansson-Charrier, M.; Guibal, E.; Roussy, J.; Delanghe, B.; Le Cloirec, P. Vanadium(IV) Sorption by Chitosan: Kinetics and Equilibrium. *Water Res.* **1996**, *30*, 465.
- (19) Bai, R. S.; Abraham, T. E. Studies on Enhancement of Cr(VI) Biosorption by Chemically Modified Biomass of *Rhizopus nigricans*. *Water Res.* **2002**, *36*, 1224.
- (20) Monteiro, O. A. C., Jr.; Airoldi, C. Some Thermodynamic Data on Copper–chitin and Copper–chitosan Biopolymer Interactions. *J. Colloid Interface Sci.* **1999**, *212*, 212.
- (21) Sillen, G. L.; Martell, A. E. Organic Ligands. In *Stability Constants of Metal–ion Complexes*; Bjerrum, J., Schwarzenbach, G., Sillen, L. G., Eds.; American Chemical Society: London, 1964; section 2.
- (22) Jaycock, M. J.; Parfitt, G. D. Introduction to Interfaces and the Forces Involved in Their Formation. In *Chemistry of Interfaces*; Bamford, C. H., Burgess, J., Eds.; Ellis Horwood: West Sussex, England, 1981.
- (23) Petrucci, R. H. Spontaneous Change: Entropy and Free Energy. In *General Chemistry*, 5th ed.; Macmillan: New York, 1989.
- (24) Netpradit, S.; Thiravetyan, P.; Towprayoon, S. Application of Waste Metal Hydroxide Sludge for Adsorption of Azo Reactive Dyes. *Water Res.* **2003**, *37*, 763.

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