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Ni(II) removal from wastewater by solar energy-degreased spent coffee grounds

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ABSTRACT

Coffee is one of the most favorite drinks, and its consumption results in an enormous amount of spent coffee waste in Taiwan. In this study, the feasibility of Ni(II) removal by solar energy-degreased spent coffee grounds (SCG) was evaluated. The Taguchi experimental design was applied to determine the optimum adsorption condition. The controllable factors including the treatment procedure of SCG, initial concentration of Ni(II), SCG dose, contact time, and temperature were optimized. The results showed that the order of importance of the controllable factors was the concentration of Ni(II) > SCG dose > SCG treatment procedure. For the influence of the treatment procedure of SCG, the removal efficiency of Ni(II) in descending order was SCG degreased by solar energy > washing by boiling DI water > washing by cold DI water. Moreover, both results of Langmuir and Freundlich adsorption isotherms also showed that solar energy-degreased SCG was the most effective adsorbent for Ni(II) removal in wastewater. The maximum adsorption capacity q_m of Ni(II) by solar energy-degreased SCG was 4.29 mg/g, about twice of that by non-degreased SCG. Hence, Ni(II) could be effectively removed from wastewater by utilizing solar energy and SCG, a great reduction in energy expenditure and coffee waste.

Keywords: Adsorption; Nickel; Solar energy; Spent coffee; Taguchi method

1. Introduction

A recent tragic catastrophe of Ni pollution of rivers and lands occurred in Taiwan which was caused by an integrated circuit packaging company. The company discharged its wastewater containing Ni from its electroplating plant without meeting the Taiwan's enforced effluent standard of 1 mg/L of Ni. The company was not only fined, but also prohibited from operation until the ban was lifted by Taiwan EPA (Environmental Protection Agency) after the effluent standard was met. In other words, removing Ni from wastewater is critical for the sustainability of Taiwan's industry and environment. Hence, this study focused on removing Ni(II) from wastewater.

Traditional methods for removing heavy metal from wastewater included coagulation and flocculation, electrocoagulation, electrolysis, ion exchange, membrane filtration, and adsorption by activated carbon [1–5]. In recent years, biosorption of using agricultural waste for heavy metal removal was proposed, such as Cd(II) absorption by waste-orange peel powder [6] and bamboo charcoal [7]. For Cr(VI) absorption, chemically modified bamboo [8], anion

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exchanger derived from rice straw [9], chufa corm peels [10], chemically modified coir pith [11], and fruit peel of Leechi [12] were investigated. For Cu(II) absorption, biochars from crop straws [13] and gooseberry fruit [14] were evaluated. For Ni(II) absorption, pineapple and bamboo stem [15] were studied. In addition, for Zn(II), Pb(II), Cu(II), and Cd(II) adsorptions, coffee grounds, coffee beans, or coffee husks were investigated [16–18].

Even though coffee grounds were known to be a good absorbent, its adoption as an adsorbent required certain pretreatment processes, such as phosphoric acid activation [19–21], zinc chloride activation [16], degreased by ethanol [17] or by NaOH [22]. However, these pretreatments could also cause environmental concerns. Thus, considering the abundance of both solar energy and spent coffee grounds (SCG) in Taiwan, in this study, solar energy was used to degrease SCG instead of chemicals or solvent.

To optimize the adsorption process for Ni(II) by SCG, the Taguchi method was applied because it could significantly reduce the overall testing costs and time through a specifically designed orthogonal array [23]. The key ideas behind the Taguchi method are the orthogonal array for experimental design and signal to noise ratio (S/N) for quality assessment. The orthogonal array consists of the controllable factors and experimental combinations of equal probability. The quality characteristics are categorized into three types: larger-the-better, nominal-the-best, and smaller-the-better. This optimization method has been used in wastewater adsorption. For example, Zolfaghari et al. used modified mesoporous carbon to absorb heavy metals [24]. For textile effluents, guava seed carbon for the adsorption of acid orange 7 was conducted [25].

In this study, SCG and Taguchi method were combined to obtain the optimum operating condition of Ni(II) absorption. Moreover, the applicability of both Langmuir and Freundlich adsorption isotherms were also examined.

2. Materials and methods

2.1. Preparation of SCG as the adsorbent

SCG was obtained from a local coffee maker who prepared coffee by steam extraction of coffee grounds. The collected SCG was divided into three parts: one for each treatment as washed five times by cold DI water (50 mL water per g coffee grounds), washed five times by boiling DI water (50 mL boiling water per g coffee grounds), and degreased by solar energy (about 220℃, 5 d). The treated SCG was further dried at 105℃ for 24 h to remove moisture. These different treatments were designated by CDI (SCG washed by cold DI water), BDI (SCG washed by boiling DI water), and SED (SCG degreased by solar energy), respectively, as also shown in Table 1.

2.2. Experimental methods

The controllable factors considered were SCG treatment procedure, initial concentration of Ni(II), SCG dose, contact time, and temperature. They were denoted by *P*, *C*, *D*, *t*, and *T*, respectively. Each controllable factor had three testing conditions (represented by levels 1, 2, and 3) as illustrated in Table 1. A full factorial experimental design for five controllable factors with three levels each would require a total of 3^5 (243) experiments. The number of experiments could be reduced greatly by the orthogonal array. Considering the complexity and resources, the orthogonal array of L18 was chosen. Hence, the number of experiments was reduced from 243 to 18, a great reduction in time and cost.

As the goal of this study was to remove Ni(II) by SGC, the quality characteristic selected was larger-the-better of Ni(II) removal which was defined by Eq. (1). S/N for the larger-the-better quality characteristic was given by Eq. (2).

$$\text{Removal}\,(\%) = \left(\frac{C_0 - C_e}{C_0}\right) \times 100 \tag{1}$$

where C_0 and C_e were the initial and equilibrium concentrations of Ni(II) (mg/L), respectively.

$$S/N_{LB} = -10\log\frac{\sum_{i=1}^{n}\frac{1}{y_i^2}}{n} \tag{2}$$

where the subscript LB represented "larger-the-better", n was the number of repetitions under the same experimental conditions, and y_i was the measurement results.

Batch experiments were performed with the adsorbent–adsorbate suspension in a sealed conical flask of

Table 1
Controllable factors and associated levels

Factor	Description	Level 1	Level 2	Level 3
P	SCG	CDI	BDI	SED
C	Ni(II) (mg/L)	2.5	5	10
D	SCG dose (g/L)	1	2	3
t	Time (min)	60	120	180
T	Temperature (℃)	25	40	55

250 mL at 150 rpm in a temperature-controlled mechanical shaking incubator (SB-7D Model, Deng-Yng Co.). Further, pH was controlled at 5.0 ± 0.1 by either NaOH or HNO_3. This condition was chosen because pH is an important impacting parameter on the adsorption process and the dominate nickel forms are Ni(II) for $pH < 6$ [26,27]. The flask contained 200 mL of the Ni(II) solution. Each experiment was repeated three times, and the average was taken to calculate the removal (%). Prior to measuring the concentration of Ni(II), water samples were filtered through a cellulose acetate filter paper with a pore size of 0.45 μm. The stock solutions of Ni(II) was from Merck (Germany, 1,000 mg/L) and was diluted by DI water to the required concentration. It was measured by an atomic absorption spectrometry (Hitachi, Z-8200).

3. Results and discussion

3.1. Taguchi optimization

The results of the eighteen experiments are tabulated in Table 2. The average removal was the average of three repeated experiments denoted by R1, R2, and R3 in the table. The S/N ratio was calculated by Eq. (2). The results showed that the average removal of Ni (II) varied from 24.8 to 98.5%, depending on the combination of the controllable factors. The optimum removal conditions among the 18 combinations were the following: a Ni(II) concentration of 2.5 mg/L, a dose of SED of 3 g, a contact time of 120 min, and a temperature of 55˚C, which resulted in a removal efficiency of 98.5%. From these averages, the associated S/N ratio for each level of every individual controllable factor in Fig. 1. It could be observed that the variation of the S/N ratios of Ni(II) concentration is the largest, whereas that of contact time is the smallest. In other words, the most significant controllable factor was Ni(II) concentration, while the least significant one was contact time.

The optimum condition could be obtained from the range of S/N ratio given in Fig. 1 and Table 3. A larger range implied a more significant factor and should be utilized first. The range in descending order was $C > D > P > T > t$. Moreover, no significant difference was observed in the S/N ratios for *T*1 and *T*2. Hence, the optimum operating condition deduced was *C*1, *D*3, *P*3, *t*3, and *T*1. The removal efficiency increased by decreasing initial Ni(II) concentration; this was due to more efficient interactions between the adsorbate and the adsorbent, and the fixed available adsorption sites of the latter. The increase in the SCG dose resulted in an increase in removal as more active sites were available for the adsorbate. Moreover, the enhanced adsorption efficiency with the increased

Table 2
Removal of Ni(II) and S/N ratio

	Factor						
Test	*P*	*C*	*D*	*t*	*T*	Average removal ± std (%)	S/N ratio
1	CDI	2.5	1	60	25	71.6 ± 0.34	37.10
2	CDI	5	2	90	40	57.9 ± 0.25	35.25
3	CDI	10	3	180	55	46.8 ± 0.21	33.40
4	BDI	2.5	1	90	40	78.6 ± 0.34	37.91
5	BDI	5	2	120	55	57.9 ± 0.33	35.26
6	BDI	10	3	60	25	51.5 ± 0.25	34.23
7	SED	2.5	2	60	55	93.0 ± 0.39	39.37
8	SED	5	3	120	25	83.2 ± 0.45	38.40
9	SED	10	1	180	40	44.1 ± 0.24	32.89
10	CDI	2.5	3	180	40	84.3 ± 0.16	38.52
11	CDI	5	1	60	55	27.8 ± 0.25	28.89
12	CDI	10	2	120	25	40.6 ± 0.33	32.16
13	BDI	2.5	2	180	25	88.5 ± 0.34	38.94
14	BDI	5	3	60	40	70.0 ± 0.29	36.90
15	BDI	10	1	120	55	24.8 ± 0.34	27.87
16	SED	2.5	3	120	55	98.5 ± 0.21	39.87
17	SED	5	1	180	25	49.4 ± 0.50	33.87
18	SED	10	2	60	40	46.9 ± 0.17	33.42

Note: std: Standard deviation.

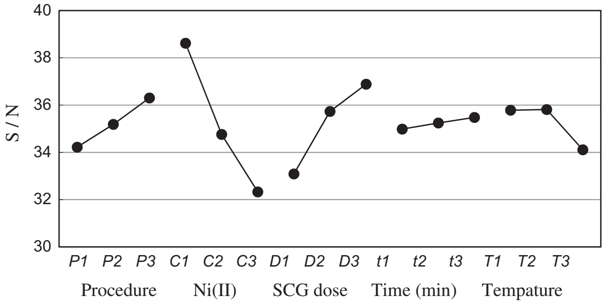


Fig. 1. Response distributions of S/N ratios.

Table 3
Response table of S/N ratios

	P	*C*	*D*	*t*	*T*
Level 1	34.22	38.62	33.09	34.98	35.78
Level 2	35.19	34.76	35.73	35.24	35.81
Level 3	36.30	32.33	36.88	35.48	34.11
Range	2.08	6.29	3.80	0.49	1.70
Rank	3	1	2	5	4
Significance	Yes	Yes	Yes	No	Yes

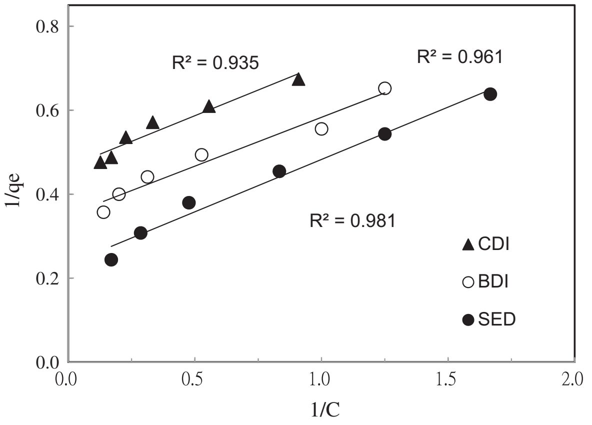


Fig. 2. Langmuir adsorption isotherms.

contact time was because of the adsorbate being transported from the exterior to the interior sites of the adsorbent particles as time proceeded. Lastly, the reduced removal due to the increased temperature was caused by desorption of the adsorbate from the adsorbent. Thus, The optimum controllable factors were Ni(II) concentration of 2.5 mg/L, SCG dose of 3 g, solar energy-degreased SCG, contact time of 180 min, and temperature of 25˚C. For practical applications, the controllable contact time could be 60 min as the results from 60 to 180 min had no significant difference.

3.2. Adsorption isotherms

The relationship between the amount of substance adsorbed per unit mass of adsorbent at constant temperature and its concentration in equilibrium is called the adsorption isotherm. Generally, adsorption isotherms provide vital information in optimizing the use of adsorbents. Langmuir and Freundlich models are commonly used to describe the adsorption isotherms and provide significant parameters for predicting adsorption capacities [28,29]. In this study, for evaluating the adsorption isotherms of various SCG treatments, the combined condition with Ni(II) concentration of 10 mg/L, contact time of 60 min, and temperature at 25˚C was adopted while the SCG dose was varied from 1 to 6 g.

3.2.1. Langmuir isotherm

The theoretical Langmuir adsorption isotherm is based on three well-known assumptions, namely adsorption cannot proceed beyond monolayer coverage, all surface sites are equivalent, and at most one adsorbed atom can be accommodated, while the ability of a molecule to adsorb at a given site is independent of the occupied neighboring sites. The Langmuir equation, represented as Eq. (3), is probably the best known and most widely applied isotherm.

Table 4
Langmuir and Freundlich isotherm parameters for Ni(II) adsorption

	Langmuir isotherm				Freundlich isotherm		
SCG type	q_m (mg/g)	K_L (L/mg)	R_L	R^2	K_F [mg/g (L/mg)$^{1/n}$]	n	R^2
CDI	2.15	1.90	0.05	0.935	1.46	5.62	0.986
BDI	2.85	1.51	0.06	0.961	1.71	4.03	0.975
SED	4.29	0.94	0.10	0.981	1.98	2.46	0.996

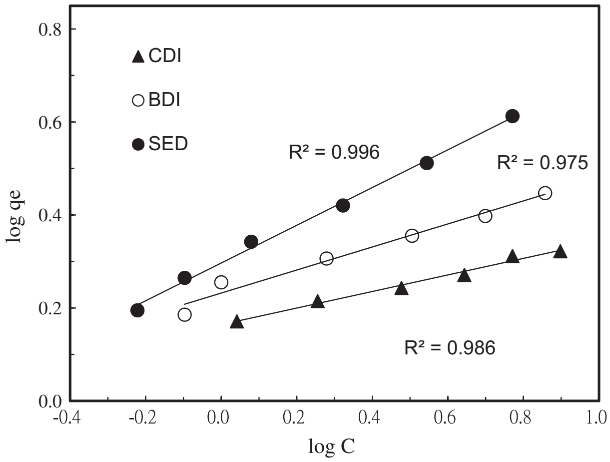


Fig. 3. Freundlich adsorption isotherms.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{3}$$

Its linear form can be expressed as Eq. as below (4):

$$\frac{1}{q_e} = \frac{1}{q_m K_L}\frac{1}{C_e} + \frac{1}{q_m} \tag{4}$$

In these equations, q_e is the solid phase equilibrium amount of Ni(II) adsorbed per unit mass of SCG (mg/g), C_e is the equilibrium concentration of Ni(II) in the solution (mg/L), q_m is a constant related to the area occupied by the monolayer of the adsorbate and is the maximum adsorption capacity of Ni(II) (mg/g), and K_L (Langmuir constant) is a direct measure of the adsorption intensity (L/mg). From the plot of $1/q_e$ vs. $1/C_e$ given in Fig. 2, K_L and q_m could be determined from the slope and intercept of the linear curve. The values of q_m thus obtained were 2.15, 2.85, and 4.29 mg/g for CDI, BDI, and SED of SCG, respectively, as in Table 4. The order of q_m was SED > BDI > CDI, indicating that solar energy-degreased SCG had a better adsorption capacity of Ni(II).

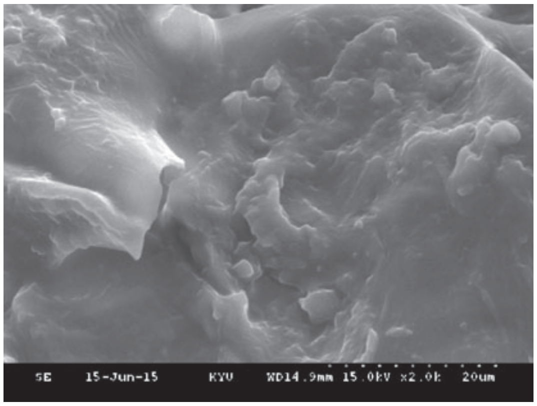
Moreover, the characteristic parameter referred to as the separation factor "R_L" given by Eq. (5) [22,30] could be used to predict the affinity between the adsorbate and adsorbent.

$$R_L = \frac{1}{1 + K_L C_0} \tag{5}$$

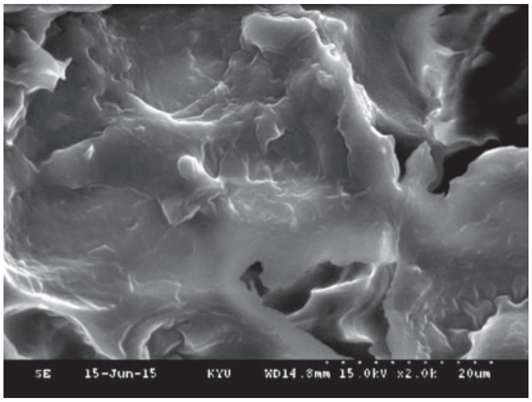
where C_0 is the initial concentration of Ni(II). The separation parameter R_L provides important information about the nature of adsorption: irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$). The values of R_L obtained were 0.05, 0.06, and 0.10 for CDI, BDI, and SED of SCG, respectively. They were all in the range of 0–1, indicating

Table 5
Comparison of adsorption various matter from coffee

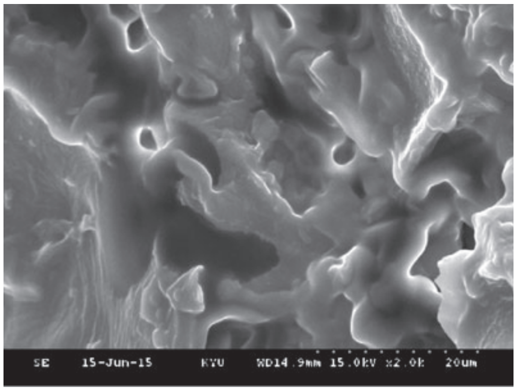
Coffee type	Coffee preparation	Adsorbate	q_m (mg/g)	Refs.
Coffee ground	Activated by H_3PO_4 (450°C)	Methylene blue Nylosan Red	Methylene blue = 370.4 Nylosan Red = 367	Reffas et al. [19]
Activated coffee residues	Activated by $ZnCl_2$ in N_2 (600°C, 4 h)	Formaldehyde	245	Boonamnuayvitaya et al. [16]
Activated coffee husk	Carbonization at 673 K in N_2 (2 h)	Dye(RBO3R)	66.76	Ahmad and Rahman [32]
Degreased coffee bean	Degreased by NaOH	Malachite Green	55.3	Baek et al. [22]
Untreated coffee husks	DI water washing	Methylene	111	Oliveira et al. [33]
Degreased coffee beans	Extracted by ethanol	Cd(II)	6.72	Kaikake et al. [17]
Spent coffee ground	Degreased by solar energy	Ni(II)	4.29	Present study
Exhausted coffee ground	Leached by NaOH solution	Heavy metals	Cu(II): 3.1 Pb(II): 15.8 Zn(II): 6.1 Cd(II): 3.2	Utomo and Hunter [18]
Activated spent coffee ground	Chemical activation agents such as H_3PO_4 and $ZnCl_2$	Pesticide (malathion)	1.168	Bouchenafa-Saïb et al. [21]



(a) SEM image of CDI



(b) SEM image of BDI



(c) SEM image of SED

Fig. 4. SEM images of SCG (2000×).

favorable adsorption of the three SCGs, and the order of affinity between SCG and Ni(II) was SED > BDI > CDI.

3.2.2. Freundlich isotherm

The Freundlich isotherm described in Eq. (6) is also well known as it is the earliest established relationship for the adsorption process. This model can be applied for adsorption on heterogeneous surfaces with the interaction between adsorbed molecules. The application of Freundlich equation also suggests that the adsorption energy decreases exponentially upon completion of the adsorption centers of an adsorbent.

$$q_e = K_F C_e^{1/n} \tag{6}$$

The equation can be linearized as:

$$\log q_e = \frac{1}{n}\log C_e + \log K_F \tag{7}$$

In both equations, the constants of n and K_F are calculated from the slope and intercept of the plot of log q_e vs. log C_e. The Freundlich constant K_F indicates the adsorption capacity of the adsorbent, and n is a measure of the deviation of the model from linearity of the adsorption. The adsorption is chemical, physical, and linear for n being less than, greater than, and equal to 1, respectively [31]. From the results illustrated in Fig. 3 and Table 4, the n values of the three SCGs were all larger than 1, indicating that they were physical adsorption. The above results revealed that Ni(II) adsorption by various SCGs followed both Langmuir and Freundlich isotherms, similar to those reported for the adsorption of Pb(Π) and Hg(Π) on modified carbon [24].

3.2.3. Comparison of maximum adsorption capacity q_m

The studies of using coffee as the adsorbent are summarized in Table 5 for further illustration. The results showed that coffee as an adsorbent could be used in many ways, such as degreased coffee bean, activated SCG, and activated coffee husk, while the adsorbate could be dyes, pesticide, methylene, Cu(II), Pb(II), Zn(II), and Cd(II). However, no study focused on Ni(II) adsorption. Our result of Ni(II) adsorption was similar to those of Utomo and Hunter [18]. They used NaOH solution to leach coffee ground, and the values of q_m for Cu(II) and Cd(II) were 3.1 and 3.2 mg/g, respectively. In addition, q_m of Cd(II) adsorption of Kaikake et al., using the degreased coffee beans by ethanol, was 6.72 mg/g [17], also comparable to our finding for Ni(II). Overall observation revealed that coffee ground was an effective adsorbent. It could adsorb not only organics (pesticide, methylene and dyes), but also inorganics (heavy metals).

3.3. SEM observations

In order to reveal the surface structure of SCG, morphological analysis was performed by SEM. The obtained 2000× surface micrographs of CDI, BDI, and SED are shown in Fig. 4(a)–(c), respectively. As illustrated in Fig. 4(a), the surface of CDI consisted of fragments without any porosity, indicating that metal adsorption was limited to only a thin surface layer. For BDI, some surface protrusions and a few cavities were created. Thus, the adsorption surface increased slightly as shown in Fig. 4(b). In contrast, a large number of protrusions and cavities were produced for SED as shown in Fig. 4(c). These structures significantly increased the surface area for adsorption. Therefore, metal adsorption increased dramatically by about 1.5–2 times as compared with those of CDI and BDI.

4. Conclusion

This study evaluated the feasibility of employing SCG as an adsorbent for Ni(II) removal. The Taguchi experimental design was applied to determine the optimum condition for adsorption. The average removal of the eighteen experimental results varied from 24.8 to 98.5%, depending on the combination of the controllable factors. The optimum removal conditions were the following a Ni(II) concentration of 2.5 mg/L, a dose of SED of 3 g, a contact time of 120 min, and a temperature of 55˚C with the removal efficiency of 98.5%. For the influence of treatment procedure of SCG, the removal efficiency of Ni(II) in descending order was SED > BDI > CDI. That is, solar energy-degreased SCG was more effective in adsorbing Ni(II) than the other two. Further, both Langmuir and Freundlich adsorption isotherms showed that the solar energy-degreased SCG was an effective adsorbent for Ni(II) removal. The maximum adsorption capacity q_m (4.29 mg/g) of Ni(II) by solar energy-degreased SCG was about twice that of non-degreased SCG.

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