

Article

# Adsorption Characteristics of Spent Coffee Grounds as an Alternative Adsorbent for Cadmium in Solution

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**Abstract:** The present study was conducted to ascertain the potential of spent coffee grounds (SCGs) as an alternative adsorbent for the removal of cadmium (Cd) from aqueous solutions. Therefore, Cd adsorption batch tests, using SCGs that had not undergone any chemical pretreatment, were conducted using Cd solutions with a wide concentration range (i.e., 0.1–120 mM) under various adsorption conditions, e.g., ion strength, pH, and solid/solution ratio. For comparison, zeolite, as a well-known common representative adsorbent, was included to determine the adsorption efficiency. The adsorption capacity of the SCGs increased with the decreasing ionic strength of the test solution from 200 to 0 mM of Ca(NO<sub>3</sub>)<sub>2</sub> and the increasing solid:solution ratio from 1:4 to 1:400. The most significant factor influencing the adsorption capacity of the SCGs was the pH of the test solution, with increases in the adsorption capacity as the initial solution pH was increased from 2 to 10. However, the rate for Cd removal remained constant, at 71.19%, when the initial solution pH was between 4 and 8 due to the buffer capacity of SCGs. The obtained data were fitted with the *Freundlich*, *Langmuir*, and *Dubinin-Radushkevich* isotherm models. The Langmuir isotherm provided the best correlation for Cd adsorption onto SCGs ( $R^2 = 0.96$ ) and zeolite ( $R^2 = 0.92$ ), and the maximum Cd adsorption capacity of the SCGs was 19.32 mg g<sup>-1</sup>, which was higher than that of zeolite (13.91 mg g<sup>-1</sup>). These results mean that the SCGs can be utilized as alternative low-cost biosorbents to replace conventional adsorption materials.

**Keywords:** adsorption isotherm; biosorption; coffee grounds; organic residue; zeolite

## 1. Introduction

Heavy metals, including cadmium, lead, copper, and zinc, have been widely dispersed into the environment by anthropogenic activities, such as mining operations, metal plating, and other industrial activities [1,2]. Heavy metals are not biodegradable and easily accumulate in living organisms, resulting in elevated heavy metal concentrations in the environment [3,4]. Apart from some emissions into the atmosphere in association with dust particles, heavy metals largely remain in both aquatic and soil phases.

Various types of techniques have been suggested for reducing heavy metals and their availability in aqua systems, e.g., ion-exchange, osmosis, membrane process, and electrolytic methods; however, many techniques are costly and may be accompanied by the generation of by-products [5]. Among these various techniques, the removal of heavy metals via their adsorption onto adsorbents has been considered the most versatile, as a relatively simple and cost-effective technique. With this technique, the concentrations of heavy metals in water are reduced via their adsorption onto the surfaces of adsorbent materials, with their eventual removal from the water system by removing the adsorbents. Activated carbon is one of the most widely adopted adsorbent materials due to its

high efficiency in heavy metal removal, which is attributed to abundant micro-pores and functional groups on the large surface area, onto which heavy metals could be adsorbed [6]. Despite its high efficiency, the application of activated carbon for the removal of heavy metals from water has been challenged by other method due to the high cost of generating activated carbon from source materials, such as wood, lignite, and coal. For this reason, many researches have been conducted to find inexpensive and locally available alternative adsorbent candidates for the removal of heavy metals, with competitive adsorption capacities, such as clay minerals, oyster shells, and certain waste products from industrial facilities [7,8]. In addition, Demirbas [9] tested the applicability of by-products from the agricultural industry, including tea waste, hull, barks, and fruit peel, as adsorbents of heavy metals in contaminated water.

Coffee is one of the largest agricultural products and is one of the commodities that trades very well in the international market [10,11], resulting in the generation of large amounts of coffee wastes, mainly in the form of spent coffee grounds (SCGs). SCGs are the organic residuals in powder form obtained after the extraction of coffee from the beans using hot and high-pressure steam. SCGs have been utilized for bio-energy, bio-active compounds, and materials such as subgrade materials, plastics, and composites [12]. However, examinations of the use of SCGs as an adsorbent for heavy metals are rare, even though their structural conditions indicate its applicability for this purpose. The particle size of SCGs is too small ( $\approx 20 \mu\text{m}$ ), consisting of fiber ( $>50\%$ ) and high molecular intricate lignin, and has a large surface area ( $7.5 \text{ m}^2 \text{ g}^{-1}$ ) [13–15]. Moreover, SCGs contain a tannin-embedding material, with polyhydroxy polyphenol functional groups, onto which heavy metals can be effectively adsorbed by complexation [12,16].

Therefore, the present study was conducted to assess the applicability of SCGs for the removal of heavy metals in contaminated water by determining the adsorption capacity and chemistry using Cd solutions with a wide concentration range. For comparison with the SCGs, zeolite, a known effective inorganic adsorbent, was also examined.

## 2. Materials and Methods

### 2.1. Preparation of Adsorbents and Reagents

The SCGs used in this study were obtained from a local coffee shop in Seoul, Korea. The collected SCGs were air dried for two weeks and then passed through a 0.5-mm sieve. The sieved SCGs were stored in polyethylene bottles until used and were not subjected to any physical or chemical pretreatment prior to use. Zeolite, obtained from a local horticultural market in Seoul, Korea, was included in an adsorption experiment to compare its adsorption capacity with that of SCGs. The particle size of the zeolite was  $<0.5 \text{ mm}$ , with a surface area of  $38.91 \text{ m}^2 \text{ g}^{-1}$  (ASAP 2010 Micromeritics Inc., Norcross, GA, USA). All the chemicals used in the reagent preparation were of analytical grade. Cd stock solutions (1000 mM) were prepared by dissolving  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (Junsei Chem. Co., Tokyo, Japan) in distilled water, with Cd test solutions ranging from 0.1 to 120 mM prepared by appropriated dilution. The ionic strength of the test solutions was controlled using  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (Junsei Chem. Co., Tokyo, Japan), while the solution pH was adjusted using diluted nitric acid (Kanto Chem. Co., Tokyo, Japan) and 28% ammonia solution (Junsei Chem. Co., Tokyo, Japan) [17].

### 2.2. Characterization of the Adsorbents

The selected physicochemical properties of the SCGs and zeolite were determined. The pH and electrical conductivity were measured on a 1:5 of solid:water suspension using a pH-EC meter (Thermo Orion 920A, Thermo Fisher Scientific, Waltham, MA, USA). The organic matter content was determined by loss on ignition at  $400 \text{ }^\circ\text{C}$  for 16 h. The total concentrations of trace elements in the adsorbents were determined using aqua regia (35% HCl: 60%  $\text{HNO}_3 = 3:1$ ) assisted digestion (Ethos 1, Advanced Microwave Digestion System, Milestone, Italy), followed by their determination using an inductively coupled plasma optical emission spectrometer (ICP-OES, Agilent, Santa Clara, CA, USA).

The glass cyclonic spray chamber was used as nebulizer. For the stable operation of expensive ICP equipment, basically 2% nitric acid solution is used as the base solution. ICP Multi-element standard solution XVI (Merck 109487) 21 elements diluted with nitric acid was used and 5 solutions for 0.5, 1, 2, 5, and 10 mg/L (also including 0 mg/L for blank) were made for the standard curve. In Korea, Bi, Sc, Y, In, and Tb were suggested for internal standard elements using ICP-OES. The detection limits were calculated by 3 standard deviations of the blank, and all procedures were followed by the Standard Methods for Examination of Soil Pollution by Ministry of Korea [18]. The detection limits of Cd, Cu, Pb, Ni, and Zn were 0.006, 0.001, 0.004, 0.04, 0.01, and 0.003 mg L<sup>-1</sup>, respectively. Fourier transform infrared spectroscopy (FT-IR, Agilent, Santa Clara, CA, USA) was employed to determine the chemical functional groups on the surfaces of the SCGs and zeolite in the region of 4000–400 cm<sup>-1</sup>, with a 1 cm<sup>-1</sup> resolution. Prior to the FT-IR test, the samples were dried at 105 °C for 12 h to remove moisture and were then made into KBr pellets. The prepared samples were subjected to ATR (attenuated total reflection) mode.

### 2.3. Adsorption Study

Basically, the SCGs (1 g) and zeolite (1 g) were reacted with 40 mL of Cd solutions (concentrations ranging from 0.1 to 120 mM) prepared in a 2-mM Ca(NO<sub>3</sub>)<sub>2</sub> background solution, using an end-over-end shaker for 2 h. The suspension was then filtered through a 0.45-μm filter, with the amounts of Cd remaining in the filtrate determined using ICP-OES after acidifying the filtrate with 2% (v/v) HNO<sub>3</sub>. The optimum conditions, such as reaction time, background solution concentration, pH, and the solid:solution ratio, were determined according to separate tests, as described in Section 2.4. All batch tests were conducted in triplicate at a constant temperature (25 °C), with the amounts of Cd adsorbed (C<sub>s</sub>, mg g<sup>-1</sup>) onto the SCGs and zeolite calculated using the following Equation:

$$C_s = (C_i - C_e) \times V/m/1000 \quad (1)$$

where m and V represent the weight of the adsorbents (g) and the volume of the test solutions (mL), respectively. C<sub>i</sub> is the Cd concentration in the initial solution (mg L<sup>-1</sup>) and C<sub>e</sub> is the Cd concentration in the filtrate (mg L<sup>-1</sup>) after reaction for 2 h.

### 2.4. Optimization of the Operating Parameters for the Cd Adsorption Study

The influences of ionic strength, solution pH, and solid:solution ratio on the adsorption of Cd onto the SCGs were examined in order to optimize the conditions for the maximum adsorption of Cd onto the SCGs. Initially, a preliminary test was carried out to determine the optimum reaction time. In the preliminary test, the equilibrium of the suspension was reached within half an hour; hence, for the rest of the experiment, a 2-h reaction time was adopted to ensure complete reaction between the SCGs and Cd in solution. Four different background concentrations (0, 2, 20, and 200 mM), adjusted with Ca(NO<sub>3</sub>)<sub>2</sub>, were examined in conjunction with Cd concentrations ranging from 0.1 to 100 mM, with the solution pH fixed at 6.0. SCGs (1 g) were reacted with each of the Cd concentration solutions (40 mL) prepared in different background solutions during 2 h. To study the influence of the solution pH on the Cd adsorption capacity, nine Cd solutions (1 mM) were prepared in 2 mM of background solution, with the pH of each solution then adjusted to 2, 3, 4, 5, 6, 7, 8, 9, and 10. Each pH-adjusted Cd solution (40 mL) was reacted with SCGs (1 g) for 2 h. For the solid:solution ratio test, the amount of SCGs (1 g) was fixed, with different volumes of Cd solutions (1 mM of Cd in 2 mM of background solution), from 4 to 400 mL, reacted with 1 g of SCG for 2 h. All the suspensions, after shaking for 2 h, were filtered using a 0.45-μm filter and then acidified with 2% (v/v) HNO<sub>3</sub>, followed by the determination of the amounts of Cd remaining in the filtrates using ICP-OES. Each batch test experiment was conducted in triplicate.

## 2.5. Sorption Models

The equilibrium adsorption data from the batch experiments were modeled using the *Freundlich*, *Langmuir* and *Dubinin-Radushkevich* (D-R) adsorption isotherms. The empirical *Freundlich* adsorption isotherm, based on Henry's Law, describes the adsorption of adsorbates onto an energetically heterogeneous and multi-layered surface [19]. The *Freundlich* isotherm is given below:

$$C_s = K_f \times (C_e)^{1/n} \quad (2)$$

where  $K_f$  and  $n$  are *Freundlich* constants, which are determined from the intercept and slope of a plot of  $\ln C_s$  against  $\ln C_e$ .  $C_e$  is the Cd concentration ( $\text{mg L}^{-1}$ ) in the solution, and  $C_s$  is the amount of Cd ( $\text{mg g}^{-1}$ ) adsorbed onto the adsorbents after equilibrium.  $K_f$  is related to the binding energy between the adsorbate and adsorbent, and influences the adsorption capacity, while  $n$  represents the adsorption intensity. A value of  $1/n$  between 0.1 and 0.5 indicates that the examined material is efficient for metal adsorption [5]. Therefore, the *Freundlich* isotherm was introduced to evaluate the efficiency of SCGs as an adsorbent of Cd via comparison of the  $n$  values.

In contrast to the *Freundlich* isotherm, the *Langmuir* model represents mono-layer adsorption occurring on an energetically uniform surface of an adsorbent, which has been adopted in many monolayer biosorption processes and successfully applied [20]. Many studies have adopted this model because it makes it easy to calculate the maximum amount adsorbed and allows comparison between adsorbents as well as with other studies. The Cd concentrations ( $C_e$ ) and amounts of Cd adsorbed onto the adsorbents ( $C_s$ ) were used to calculate the maximum Cd adsorption capacity ( $q_m$ ) of the adsorbent using the *Langmuir* isotherm, as follows:

$$C_s = q_m \times k \times C_e / (1 + k \times C_e) \quad (3)$$

where  $k$  is the *Langmuir* constant, which denotes the affinity of the binding sites for Cd. The constants ( $q_m$  and  $k$ ) can be determined from the linear regression between  $C_e/C_s$  and  $C_e$ .

The SCGs used in the current study constituted an organic-based material and hence the batch data were fitted using the *Dubinin-Radushkevich* (D-R) isotherm, which also derives the maximum adsorption capacity for comparison with other adsorbents. This model is more general than the *Langmuir* isotherm in the case of biosorption due to the different assumptions relating to the adsorption sites and the mechanism. Biosorbents are comprised of weakly acidic and basic functional groups; carboxyl groups ( $-\text{COOH}$ ) exhibit high affinity for trace metals and are the notable acidic group on the surface of biosorbents. Given that the model was developed regarding biosorbents, it does not assume a homogenous surface, a constant sorption potential, or the absence of a steric barrier between the adsorbent and approaching particles [19]. The D-R equation is as follows:

$$C_s = q_m \times \exp(-B \epsilon^2) \quad (4)$$

$$\epsilon = RT \ln(1 + 1/C_e) \quad (5)$$

where  $B$  ( $\text{mol}^2 \text{kJ}^{-2}$ ) represents a constant related to the adsorption energy, while  $R$  and  $T$  indicate the gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ) and absolute temperature in  $K$ , respectively.  $\epsilon$  is the Polanyi sorption potential from which the mean adsorption free energy  $E$  ( $\text{kJ mol}^{-1}$ ) per molecule of the adsorbate is determined.  $E$  represents the energy required when Cd is transferred from infinity in the solution to the surface of the adsorbent, which can be computed using the following equation:

$$E = 1/(-2B)^{-0.5} \quad (6)$$

The value of  $B$  and  $q_m$  can be calculated from the slope and intercept of a linear regression between  $\epsilon^2$  and  $\ln C_s$ .  $E$  values between  $8$  and  $16 \text{ kJ mol}^{-1}$  indicated the biosorption process occurred based on

chemical ion-exchange, while  $E < 8 \text{ kJ mol}^{-1}$  denotes the biosorption process occurred on a physical nature basis [21].

## 2.6. Data Analysis

Any significant variation between the adsorption experiments was determined using a one-way analysis of variance (ANOVA) test at the 99% confidence level, with probability ( $p < 0.01$ ) using a statistical analysis system program (SAS 9.4, SAS Institute Inc., Cary, NC, USA). Before performing the ANOVA test, all data passed the normality test. Then, the Tukey test was used to compare individual means. Average values from the triplicate experiments were used in the graphs and fitted curves using SigmaPlot (10.0, Systat software Inc., San Jose, CA, USA).

## 3. Results and Discussion

### 3.1. Characterization of Adsorbents

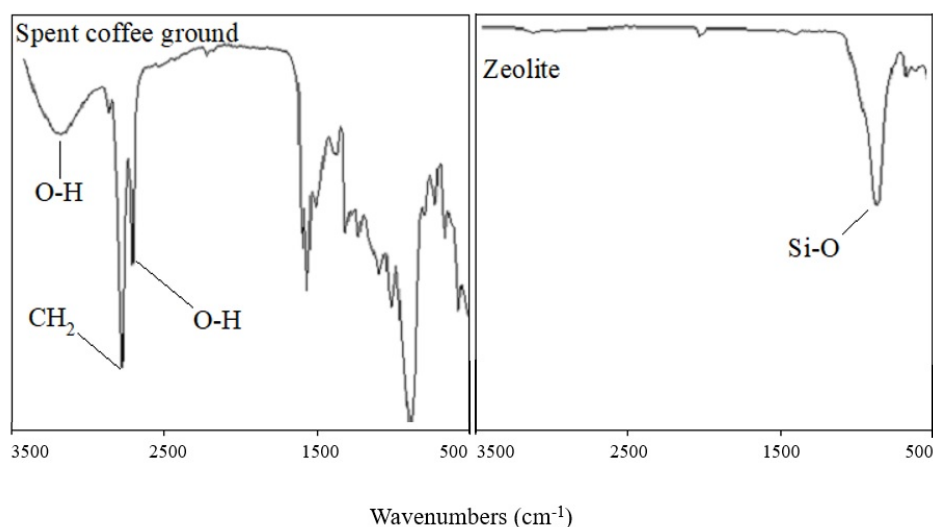
The physicochemical properties of the SCGs and zeolite are given in Table 1. The pH of the zeolite (7.26) was higher than that of the SCGs (5.18), while the electrical conductivity (EC) of the SCGs was higher than that for the zeolite. The SCGs were rich in organic matter, accounting for 94.65% of the total mass, while zeolite contained only 1.31%. The SCGs contained trace metals; however, the amounts were negligible compared with those in the zeolite and. Hence, the influence of these metals on the adsorption experiments was assumed to be negligible.

**Table 1.** Selected physicochemical properties of spent coffee ground (SCGs) and zeolite.

Adsorbent	pH	EC <sup>a</sup> (mS m <sup>-1</sup> )	LOI <sup>b</sup> (%)	Trace Elements (mg kg <sup>-1</sup> )					
				As	Cd	Cu	Ni	Pb	Zn
SCGs	5.2 ± 0.1	185 ± 11	94.7 ± 0.5	ND <sup>c</sup>	0.01 ± 0.00	12.6 ± 0.3	0.4 ± 0.05	1.1 ± 0.1	6.2 ± 0.2
zeolite	7.3 ± 0.1	74 ± 8	1.3 ± 0.2	4.3 ± 0.1	0.39 ± 0.02	19.9 ± 0.4	17.3 ± 0.7	15.6 ± 1.8	43.0 ± 2.3

<sup>a</sup> Electrical conductivity; <sup>b</sup> Loss-on-ignition; <sup>c</sup> Not detected.

Various functional groups on the SCGs and zeolite were determined to estimate the potential substitution and/or binding sites using FT-IR absorption spectrometry (Figure 1). The adsorption bands at approximately 3400, 2950, and 2850 cm<sup>-1</sup> for the SCGs were assigned to the O–H, –CH<sub>2</sub>–, and O–H stretching vibrations, respectively. A distinctive double-peak appeared at 2920–2880 cm<sup>-1</sup>, which was assigned to the C–H stretching vibration in methylamine (N–CH<sub>3</sub>), which has often been found in by-products of coffee [5]. The sharp peaks at 1745–1740 cm<sup>-1</sup> and 1058–1033 cm<sup>-1</sup> were due to the carboxyl groups of carboxylic acid or its ester. The bands in the range of 1200–900 cm<sup>-1</sup> were assigned to sulfonate S=O bands, indicating the existence of sulfur and a carboxyl linkage bond derived from xanthine derivatives, such as caffeine [17]. With zeolite, the band near 1010–1110 cm<sup>-1</sup> (e.g., 1016 cm<sup>-1</sup>) was assigned to the stretching vibration of complex Si–O in the tetrahedral sheets, a constituent element of zeolites [22]. The greater amount of organic functional groups on the SCGs than zeolite implied there would be more chances for Cd to be adsorbed onto the SCGs.

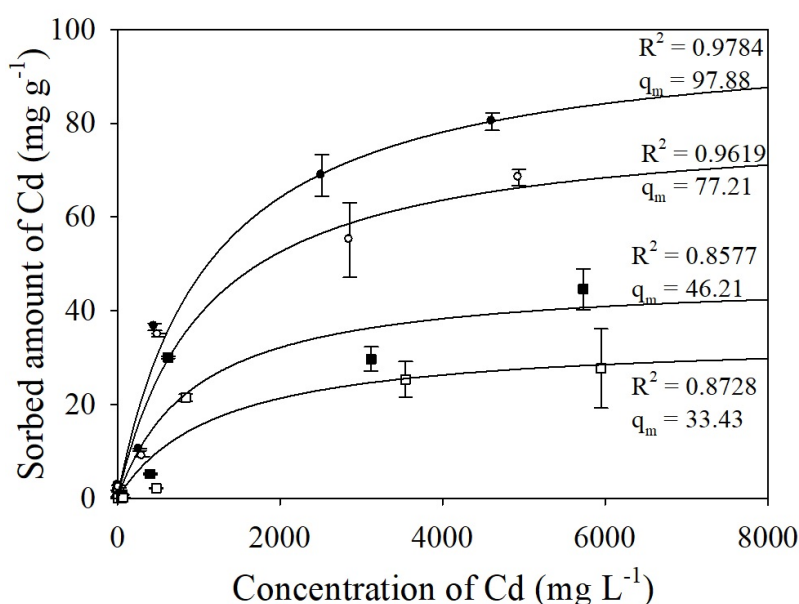


**Figure 1.** Fourier transform infrared spectroscopy (FT-IR) spectrum of spent coffee grounds and zeolite measure by attenuated total reflectance method.

### 3.2. Sorption Dynamics

#### 3.2.1. Effects of Ionic Strength on Cd Adsorption

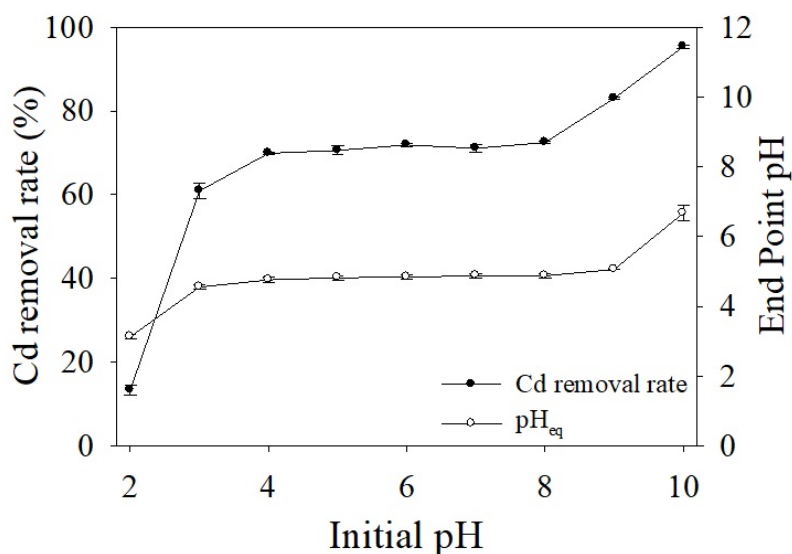
Wastewater usually contains electrolytes, with various ionic species being present. The presence of salt and co-existing ions could negatively affect the sorption kinetics of metal ions due to competition for the adsorption sites [23]. The effect of the ionic strength on the Cd adsorption onto the SCGs was examined in background electrolyte concentrations of 0, 2, 20, and 200 mM  $\text{Ca}(\text{NO}_3)_2$  at pH 6. The amount of Cd adsorbed and its affinity significantly decreased with increasing ionic strength ( $p < 0.01$ ) (Figure 2). The maximum adsorption capacities of SCGs ( $q_m$ ) obtained by the Langmuir isotherm were 97.88, 77.21, 46.21, and 33.43  $\text{mg g}^{-1}$ ; with 0, 2, 20, and 200 mM background concentrations, respectively. Increasing the ionic strength can decrease the thickness of the electric double layer [23], which consequently decreases the adsorption of the target ions. Moreover, the co-existing ion (e.g.,  $\text{Ca}^{2+}$ ) competes with Cd for the adsorbent surfaces, as indicated in the previous report [24].



**Figure 2.** Equilibrium isotherms of cadmium adsorption by spent coffee grounds under different background electrolyte concentrations of 0 (●), 2 (○), 20 (■), and 200 (□) mM.

### 3.2.2. Effects of Solution pH on Cd Adsorption

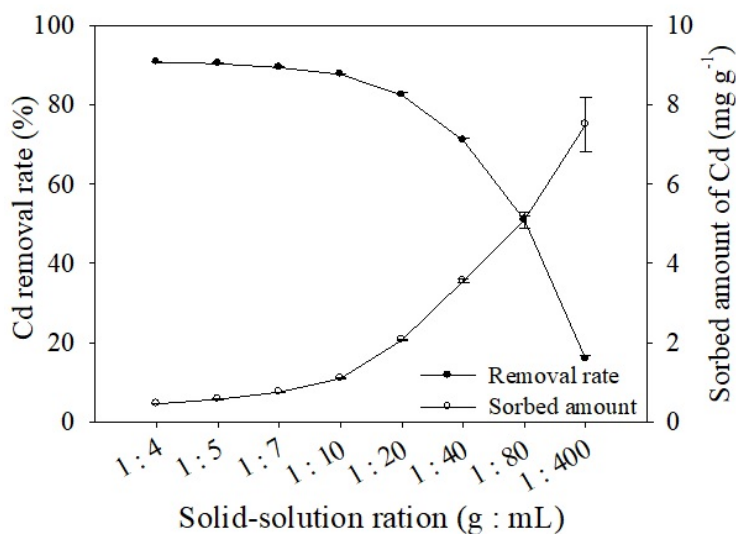
The pH of solution affects the extent of metal adsorption because it strongly influences metal species and their precipitation [25]. The effect of pH on Cd adsorption was conducted by adjusting the initial solution pH from 2 to 10 (Figure 3). The amount of Cd removed through adsorption onto the SCGs appeared to generally increase on increasing the initial pH in three steps. A sharp increase in the pH from 2 to 3, a relative constant Cd removal with pH from 3 to 8, and a further increase in Cd removal at pH 8 were also observed. This changing pattern in the rate of Cd removal was in good agreement with the end point pH of the solution after equilibrium between the SCGs and Cd in solution, implying that the rate of Cd removal was governed by the end point solution pH. The initial lower rate of Cd removal at pH 2 was attributed to the positively charged surface of the SCGs, which was derived by the high concentration and mobility of hydronium ions at the lower pH than the point of zero charge of the SCGs [1,25]. The point of zero charge of SCGs was experimentally determined to be pH 5.5, using the solid addition method [26]. Another possibility could be due to the decreased binding opportunities as the metal binding ligands on the SCGs are broken down under strongly acidic conditions, i.e., at pH < 2 [27]. To sum up, at low pH, the binding sites are saturated with protons on the one hand, and the carboxylate, amino, and phenolic groups are no longer dissociated on the other. Despite increasing the initial pH from 4 to 8, the constant rate of Cd removal ( $71.19 \pm 1.03\%$ ) within this range was attributed to the constant end point pH of  $4.79 \pm 0.05$ . This constant end point pH was induced by the buffering capacity of the SCGs, because SCGs contain a diverse range of surface functional groups, e.g., polyphenol functional groups [16,28], which can render a change in the pH of the solution. As well as this constant Cd removal in association with the increases in the initial pH, a further increase in the rate of Cd removal was observed with increases in pH beyond 8, where the end point pH also increased, but never reached 100% because of chemical precipitation under the experiment conditions [29]. This was attributed to an increase in the density of the negative surface charge on the SCGs via deprotonation derived by an elevated  $\text{OH}^-$  concentration [21]. In addition, the abundant carboxyl groups in the SCGs favor the adsorption of metal ions when hydrolysis by dissociation occurs with an increase in pH, allowing more Cd to be adsorbed [2,30,31]. In contrast to this result, Boonamnuyvitaya et al. [16] showed no further increase in Cd removal by SCGs at pH > 8. They suggested that the adsorption of Cd at solution pH > 8 was related with the formation of hydroxyl Cd species, such as  $\text{CdOH}^+$ ,  $\text{Cd}(\text{OH})_2(\text{aq})$ , having lower polarity than the Cd free ion. In addition, the formations of  $\text{Cd}(\text{OH})_3^-$  and  $\text{Cd}(\text{OH})_4^{2-}$  facilitated the adsorption through stable complexes' formation with the various ligands in the aqueous phase [5,16,17]. The inconsistent pH dependent Cd removal in a previous study was assumed to have been due to the lack of pretreatment of the SCGs and the different properties of the SCGs used in the present study. Despite the inconsistent rate of Cd removal at high pH, the increasing trend with increasing the solution pH from pH 2 to pH 7 has been commonly observed in most previous studies [17,21,32]. Taking this into account, and considering the general pH range of environmental samples [33], further Cd sorption studies were carried out at pH 6, which showed a maximum rate of Cd adsorption (71.90%) onto the SCGs.



**Figure 3.** Cd removal rate (●) by spent coffee grounds and the end point pH after equilibrium (○) with the increase in initial solution pH.

### 3.2.3. Effects of Solid/Solution Ratio on Cd Adsorption

The effects of the solid:solution ratio (weight of the SCGs:volume of the Cd solution, SSR) on the amount of Cd adsorbed per unit (g) of SCGs and on the rate of removal are shown in Figure 4. As expected, the rate of Cd removal decreased from 91.04% to 15.14% on increasing the SSR from 1:4 to 1:400 while the Cd concentration in SSR was held. Initially, no significant decrease in the rate of Cd removal was observed until the SSR was increased to 1:10; after this point, a significant decline occurred ( $p < 0.01$ ). In contrast, the net amount of Cd adsorbed per SCGs weight (g) increased with the increasing volume of Cd solution, from 0.46 mg at 1:4 to 7.50 mg at 1:400. These results may be attributed to: (1) the superiority of the exchangeable binding sites with excess SCGs compared to the insufficient availability of metal ions in solution for adsorption onto these binding sites, resulting in a lower metal uptake per unit; and (2) the interference among binding sites due to lack of adsorbent. These results are in good agreement with many previous studies [6,34,35]. Therefore, a solid:solution ratio of 1:10, where a minimum amount of SCGs was required to obtain a maximum rate of Cd removal, was used for further adsorption studies.



**Figure 4.** Cd removal rate (●) and the amount of Cd adsorbed per a unit (g) of spent coffee grounds (○) with an increase in the solid:solution ratio.



### 3.3. Adsorption Capacity of the Adsorbents

Zeolites are alkaline minerals known to have great adsorption capacities and have been used to remove heavy metals or other contaminants in wastewater treatment [28]. The data for the adsorption of Cd onto the SCGs and zeolite were fitted to the *Freundlich*, *Langmuir* and *Dubinini-Radushkevich* (D-R) isotherms, with the diagrams converted to linear forms to obtain adaptable parameters via linear regression analyses, as presented in Table 2.

**Table 2.** Adsorption parameters of spent coffee grounds (SCGs) and zeolite for cadmium, fitted with the *Freundlich*, *Langmuir*, and *Dubinini-Radushkevich* equation.

	<i>Freundlich</i>			<i>Langmuir</i>			<i>Dubinini-Radushkevich</i>		
	1/n	Kf	R <sup>2</sup>	q <sub>m</sub> (mg g <sup>-1</sup> )	k (L mg <sup>-1</sup> )	R <sup>2</sup>	q <sub>m</sub> (mg g <sup>-1</sup> )	E (kJ mol <sup>-1</sup> )	R <sup>2</sup>
SCGs	0.32	0.85	0.95	19.32	<0.01	0.96	19.79	14.08	0.96
Zeolite	0.39	0.10	0.87	13.91	<0.01	0.92	14.48	16.44	0.81

The Langmuir model gave a better fit of the data than the other models for both adsorbents, with a higher coefficient of determination for the Langmuir model ( $R^2 = 0.96$  for SCGs and  $0.92$  for zeolite) than those of the Freundlich ( $R^2 = 0.95$  for SCGs and  $0.87$  for zeolite) and D-R models ( $R^2 = 0.96$  for SCGs and  $0.81$  for zeolite). This means that the monolayer-based adsorption of Cd onto the surface of the SCGs was more likely than a multilayer-based adsorption [21]. The value of  $1/n$  ( $0.32$ ) of the SCGs calculated using the Freundlich equation implied that the SCGs employed in this study had a high adsorptive potential, as values of  $1/n$  between  $0.1$  and  $0.5$  are recognized as indicating that this material could be an efficient adsorbent [5]. The maximum adsorption capacities of the SCGs and zeolite were  $19.32$  and  $13.91$  mg g<sup>-1</sup>, respectively, based on the Langmuir model, which were slightly increased to  $19.79$  and  $14.48$  mg g<sup>-1</sup>, respectively, with the D-R model. The sorption mean free energy (E) calculated by the D-R model was  $14.08$  for the SCGs; therefore, the Cd adsorption of  $16$  kJ mol<sup>-1</sup> indicates that a metal adsorption process had occurred based on chemical ion-exchange [19]. The adsorption capacity of the SCGs for Cd was not only higher than that for the zeolite, but also those of many other agro-waste materials, including coffee residues, reported in the literature (Table 3). In previous studies, some of the coffee residues had undergone a pretreatment (Soxhlet extraction by ethanol, dissolution with water-methanol (1:3), treatment with 2% formaldehyde, and leaching with NaOH) and a common washing procedure with distilled water [5,17,25,32]. Saeed and Iqbal [36] reported the high maximum adsorption capacity of black gram husk as  $38.76$  mg g<sup>-1</sup> for Cd, but they washed and boiled adsorbents at a high temperature. Ammari et al. [37] also reported the maximum Cd adsorption capacity of alga (*Hydrodictyon reticulatum*) in natural state but its capacity is as low as  $7.40$  mg g<sup>-1</sup>. Despite the alkaline treatment of alga, it only increased to  $12.74$  mg g<sup>-1</sup>. Schiewer and Patil [38] used the peels of orange, grapefruit, and lemon for Cd removal, but the maximum Cd adsorption capacities were  $0.67$ ,  $0.49$ , and  $0.93$  meq g<sup>-1</sup>, respectively. Massimi et al. [39] compared the removal efficiency of multi element in solutions using 12 types of food waste materials, including coffee waste and decaf coffee waste. They showed that coffee waste and decaf coffee waste could remove not only Cd but also Mo, Sb, Sn, Th, Ti, and W in solutions with high removal percentages. Compared with many studies, the current study showed that the SCGs without any pretreatment exhibited a higher Cd adsorption capacity and hence appeared to be a better candidate adsorbent than any other raw agro-waste material for the removal of Cd from solution.

**Table 3.** Maximum Cd adsorption capacities ( $q_m$ , mg g<sup>-1</sup>) of spent coffee grounds calculated based on Langmuir isotherm and those of other agro-waste materials reported in literature.

Type	Biosorbents	Maximum Adsorption Capacity	References
Coffee residues	Spent coffee grounds	19.32	- <sup>a</sup>
	Untreated coffee grounds	15.65	[21]
	Exhausted coffee ground	11.60	[32]
	Coffee husks	6.85	[25]
	Degreased coffee beans	6.72	[17]
	Coffee	6.47	[5]
	Spent coffee grounds	4.34	[40]
Agro-waste	Rice husk	14.40	[15]
	Grape stalk waste	13.93	[3]
	Physic seed hull	11.89	[19]
	Corn starch	8.88	[29]
	Peanut hull	5.96	[20]

<sup>a</sup> Present study.

#### 4. Conclusions

The present study illustrates that SCGs exhibit a higher Cd adsorption capacity (19.32 mg g<sup>-1</sup>) than conventional adsorbents, such as zeolite (13.91 mg g<sup>-1</sup>) and other agro-waste materials. Additionally, unlike the previous study using coffee residues, the SCGs used in this study has not undergone any physico-chemical pretreatment. This implies that SCGs with no pretreatment can be utilized as an alternative low-cost adsorbent to replace conventional materials. In addition, the utilization of SCGs as a valuable material is an example of how to reduce waste. However, the current study only tested for the removal of Cd in pure solutions; therefore, further studies will be required to examine their adsorption capacity under complex conditions, such as the existence of multi-metals in solution.

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