Cadmium (II) removal from aqueous solution using magnetic spent coffee ground biochar: Kinetics, isotherm and thermodynamic adsorption

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Abstract

Spent coffee grounds are a waste generated in large amounts by the food industry producing instant coffee. While it is used as animal feed, mostly spent coffee grounds are burned. In this study, The spent coffee grounds were modified to be magnetic in order to remove cadmium (II) ion. The magnetic solids are easy to separate from water with a magnet. The biochar was prepared at 400 °C. Several factors that affect the adsorption were studied, such as adsorbent dosage, contact time, initial metal ion concentration and effect of solution pH. At the optimum conditions (the adsorbent dosage 0.1 g l⁻¹, pH 7, time 30 min and the initial concentration 40 mg l⁻¹), the percentage removal of Cd(II) was ~96%. The surface morphology of the adsorbent showed iron particles with a cubical shape on the adsorbent, with 3–20 μm average diameter. The adsorption data was well fit by a pseudo-second order and a Langmuir isotherm, with the maximum adsorption capacity 10.42 mg/g. The adsorption process was spontaneous and endothermic. The main goal of the study is to re-use the spent coffee grounds waste and use low-cost absorbent for cadmium (II) removal in aqueous solution. The magnetic biochar was easily manipulated by external magnetic fields after treatment. With good adsorbent performance of the magnetic biochar, spent coffee grounds could be used to treat Cd(II) contamination.

1. Introduction

Cadmium (II) (Cd(II)) is among the most toxic heavy metal ions in water bodies, hazardous to humans and with negative environmental effects from its toxicity and non-biodegradable nature [1]. Cd(II) removal from wastewater has received a lot of attention, and despite improvements it remains difficult. Several methods can be used to remove Cd(II) from an aqueous solution, e.g. complexation, chemisorption, membrane separation, microprecipitation, ion exchange, electrochemical methods, and adsorption [2]. Adsorption is well suited for removing heavy metal ions from polluted water because of low cost, high efficiency and easy operation, and low production of toxic materials [3]. Nowadays, biomass or modified biomass is a candidate adsorbent for removing Cd(II) from polluted waters [4, 5]. Several studies have reported on removal of Cd(II) from wastewater or from aqueous solutions by different biomass adsorbents, such as sugar-cane bagasse pith, chitin, sewage sludge, tea waste, dead Sargassum sp., maize corncob and Jatropha oil cake derived biochar [3, 6–9].

Biochar is a by-product from pyrolysis that currently receives significant attention due to its potential role in soil remediation, wastewater treatment, solid waste recovery, and greenhouse gas control [10–12]. Pristine
biochar or modified biochar can be a low-cost but very effective adsorbent because of its surface features, minerals content and organic structure [12]. Biochar is utilized as an adsorbent to remove heavy metal ions from wastewater or soil, because of its porous surface properties, mineral contents and chemical composition including fixed carbon and total organic carbon [13]. Biochar can be produced from various biomass feedstocks, including plant residues, agricultural wastes, and livestock manure [14, 15].

Coffee is cultivated as crops and is a globally traded commodity [16–18] so that large quantities of coffee residue, especially spent coffee grounds (SCG), are produced. SCG are the organic residues remaining after coffee is extracted from the beans with steam at high pressure. SCG has been used in fuel pellets, to make biodiesel, and in animal feeds [18]. It has small particles of about 20 μm size, containing >50% organic fibre. The lignin has a large specific surface of about 7.5 m² g⁻¹. Furthermore, SCG contains an embedded tannin materials and they contain smaller amounts of functional groups, such as polyhydroxy polyphenol, that could adsorb heavy metal ions [19–21]. Kim et al [21] reported that SCG is a good adsorbent for the removal of heavy metal ions, organic components and metalloids from aqueous solutions.

The SCG contains a large amount of organic compounds that requires large amounts of oxygen for decay when discarded into the environment. SCG can therefore pollute with its organic compounds (e.g., chlorogenic acid, quinic acid derivatives, phenol, hydroxycinnamic acid) [16, 22, 23]. In addition, some studies have reported that these organic substances may be toxic to plant growth [24]. Most studies have used SCG derived biochar as an adsorbent for the removal of heavy metal ions, such as Pb(II) and Cr(VI) from the polluted water [25, 26].

In several studies on biotechnology, analytical chemistry, bioscience and environmental technology, magnetic nano- and microparticles have been utilized [25]. Magnetic composites have been used in small-scale and industrial scale wastewater treatments. Magnetic absorbent particles enable magnetic separations after contaminant removal [26]. Many commercial magnetic composites are expensive and cannot be utilized in large-scale separations, but magnetic manipulation of cheap adsorbents and carriers could facilitate large-scale applications in biotechnology and environmental projects [26]. This is why magnetically modified biochar has been proposed as a possible low-cost adsorbent for heavy metal ions adsorption and removal [26]. Khan et al [27] reported that iron modification on biochar surface is helpful for the removal of the heavy metal ions due to high reactivity and magnetic recyclability. Thines et al [28] reported that magnetic biochar has good potential for the removal of heavy metal ions. Well-crystallined magnetic biochar was found to be more thermally stable. The magnetic biochar was also reported for the higher thermal stability as compared with the pristine biochar [27].

The aim of this study was to measure the physicochemical properties of magnetic biochar which were modified by iron composite with pyrolysis process of SCG biochar and to investigate and evaluate the adsorption potential of magnetic biochar produced in this process for removing the Cd(II) ion. During the pyrolysis process, the physical and chemical variations, change surface structure, elemental composition and oxygen containing groups. The adsorption kinetic, isotherm and thermodynamic of magnetic biochar for removing of Cd(II) ion were studied in order to understand the adsorption mechanisms.

2. Materials and methods

2.1. Materials
Sodium hydroxide (≥97%), sodium chloride (≥99%), and hydrochloric acid (≥37%) were bought from RCI Labscan. Iron (II) sulfate heptahydrate and iron (III) chloride hexahydrate were provided by Sigma-Aldrich, and potassium bromide by KBr-pubChem. Multielement standard solution for ICP was purchased from Sigma-Aldrich. SCG of Coffee arabica L. waste was collected from a coffee shop in Thailand. The samples were dried in an oven at 100 °C for 24 h. All analytical regents were prepared with distilled water.

2.2. Methods
The overview of this study was presented in figure 1. The biochar (BC) derived from SCG waste was used to remove Cd(II) from aqueous solutions. The BC was prepared by pyrolysis the raw material SCG in a muffle furnace at 400 °C, with 10 °C min⁻¹ heating rate, and the residence time was 1 h. The biochar was also modified with FeCl₃·6H₂O, FeSO₄·7H₂O and NaOH to obtain magnetic biochar (MBC). The BC and MBC were characterized by scanning electron microscopy, as well as for oxygen functional groups and elemental composition. The adsorption capacity of Cd(II) ion by MBC from aqueous solutions was investigated. In this study the optimum conditions for removal of Cd(II) by MBC surface including adsorbent dosage, pH, contact time and the initial concentration of Cd(II) ion were investigated. Adsorption kinetic, isotherm and thermodynamic experiments were also studied.
2.2.1. Preparation of BC
The SCG waste was used as raw material for preparing BC material. The obtained SCG materials were dried in oven at 100 °C for a day. The BC was produced in a muffle furnace (Model 10750126, Fisher scientific, USA) at 400 °C for 1 h, with a heating rate of 10 °C min⁻¹ under oxygen free condition.

2.2.2. Preparation of MBC
Adsorption of heavy metal ions from wastewater requires high specific surface of an adsorbent. To modify the biochar a solution was prepared by mixing 20 g of biochar and 2.09 g of FeSO₄·7H₂O and 2.03 g of FeCl₃·6H₂O into 100 ml of distilled water [29, 30]. In addition, 3 M KOH was mixed in at 100 ml of distilled water. The solution was stirred for 30 min. After that, the solution was put on the heater with a magnetic stirrer for 2 h, followed by sonication for 1 h at 25 °C. The solution was dried on the heater at 80 °C for 48 h [31]. After that the MBC was pyrolyzed in a muffle furnace at 400 °C for 1 h, with 10 °C min⁻¹ heating rate. Finally, the MBC was washed several times with distilled water and collected using a magnetic bar.

2.2.3. Characterizations of biochar and modified biochar
The C, H, N, S and O contents of SCG and MBC were measured using Elemental analysis (Flash 200, Thermo Scientific, Italy). The morphologies of BC and MBC were assessed via Scanning Electron Microscopy (SEM) (SEM Quanta 400, FEI, Czech Republic) and x-ray diffraction (XRD, Empyrean, PANalytical, Netherland, Cu-Kα radiation (λ = 0.154 nm) at 40 kV, scan range (2θ) = 5°–90° and step rate = 0.026 ° s⁻¹). Chemical composition of MBC was analyzed by using an x-ray fluorescence (XRF) spectrometer (Zetium, PANalytical, Netherlands). The specific surface and pore volume of MBC was analyzed by Brunauer—Emmett—Teller (BET) theory utilizing a surface area and porosity analyzer (BET) ASAP2460, Micromeritics, USA, at 77.300 K and by the BET equation for pore size calculation. The oxygen functional groups of SCG, BC and MBC were determined utilizing FTIR with the KBr pellet method over wavenumber range 400–4000 cm⁻¹ with Spectrum GX Fourier transform infrared (FTIR) spectroscopy system (Perkin Elmer, Foster City, CA, USA). The samples were also analyzed by ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometer, Optima 2100 DV, PerkinElmer).

2.3. Batch adsorption experiment
In batch adsorption experiments with MBC the effects of adsorbent dosage (0.01, 0.03, 0.05, 0.08, 0.1 or 0.2 g l⁻¹), the initial metal ion concentration (5, 10, 20, 40, 60, 80 or 100 mg l⁻¹), solution pH (3–9), and the contact time (2–300 min) were tested.
The adsorption capacity $Q_e$ (mg g$^{-1}$) and % removal were estimated as follows:

$$Q_e = \frac{C_0 - C_e}{m} \times V$$

(1)

$$\%\text{removal} = \frac{C_0 - C_e}{C_0} \times 100$$

(2)

where $C_e$ (mg l$^{-1}$) is the initial concentration of the heavy metal ions and $C_e$ is the equilibrium concentration, $V$ (L) is the volume of the solution, and $m$ (g) is the mass of the adsorbent [32].

2.3.1. Adsorption kinetics experiment

For kinetics experiments, batch adsorption had initial Cd(II) concentration of 40 mg l$^{-1}$ with 0.1 g of MBC and solution at pH 7. Samples were taken at various times (2, 6, 10, 20, 40, 60, 120, 180 and 300 min) to determine the extent of adsorption. The adsorption kinetics were fitted with equation (3) for pseudo-first order model and equation (4) for pseudo-second order model.

$$Q_t = Q_e[1 - \exp(-k_1t)]$$

(3)

$$\frac{t}{Q_t} = \frac{1}{(k_2Q_e)} + \frac{t}{Q_e}$$

(4)

Here $t$ is the time of adsorption, $Q_t$ is the equilibrium adsorption capacity (mg g$^{-1}$), $Q$ is the adsorption at time $t$, and the $k_1$ (1 min$^{-1}$) and $k_2$ (g mg$^{-1}$·min) are coefficients for (i.e., model parameters that enable fitting the data) [33].

2.3.2. Adsorption isotherm experiment

Adsorption isotherms of Cd(II) were determined by using 0.1 g l$^{-1}$ MBC, for 30 min at solution pH 7 in a 20 ml centrifuge tube at various initial concentrations (5, 10, 20, 40, 60, 80 and 100 mg l$^{-1}$). The test solutions were prepared from the stock solution to Plug Seal Centrifuge Tubes [34].

Adsorption isotherms of Cd(II) ion were fitted with the following equations.

$$\frac{Q_e}{Q_m} = \frac{1}{Q_m b} + \frac{C_e}{Q_m}$$

(5)

$$Q_e = k_f C_e^n$$

(6)

Here $C_e$ (mg l$^{-1}$) is the equilibrium concentration the solution, $Q_e$ (mg g$^{-1}$) is the adsorption capacity at equilibrium, $Q_m$ is the maximum adsorption capacity (mg g$^{-1}$), n is the Langmuir adsorption constant and $k_f$ (mg g$^{-1}$) is the Freundlich constant [33].

2.3.3. Adsorption thermodynamic experiment

The thermodynamics of Cd(II) ion adsorption on MBC were investigated. The temperatures 15, 25 and 35 °C were used in an incubator shaker. When the quantity of adsorbate in the aqueous solution was constant or in an equilibrium state, the change in standard adsorption energy could be obtained as follows.

$$\Delta G^0 = -RT \ln k_c$$

(7)

The relationship of $\Delta G^0$ to $\Delta S^0$ and $\Delta H^0$ is

$$\Delta G^0 = \Delta H^0 - T \Delta S^0$$

(8)

By substituting (7) into equation (8), the familiar van’t Hoff equation is obtained

$$\ln k_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$

(9)

Here, $k_c$ (l g$^{-1}$) is an equilibrium constant for two phases. The values of $\Delta H^0$ and $\Delta S^0$ will be estimated from slope and intercept of a linear fit to $\ln k_c$ versus $1/T$ [32].

3. Results and discussion

3.1. Characterization of BC and MBC

The chemical compositions of raw biomass before pyrolysis and of MBC were investigated. The results in table 1 show the chemical compositions of SCG, BC and MBC. The carbon content in the SCG was 50.06 and after pyrolysis the carbon content had increased, while the oxygen contents before and after pyrolysis were 35.588 and 10.53 showing decrease. From a previous study it is observed that the carbon content and oxygen content were lesser than in this study [35]. In the SCG the major elements were determined by x-ray fluorescence (XRF) spectroscopy. The elements in SCG are listed in table 2. The results showed that C, H, N and O contributed
51.24% with other inorganic elements, while 48.76% were the main organic contents in SCG. For the magnetic composite material MBC, the Fe3O4 content is the main component of inorganic chemistry with the percentage of 44.8. In MBC component, the inorganic components Si, Ca, P, S, Fe were in the forms SiO2, CaO, P2O5, SO3, Fe3O4, and Na+Mg2+K+Ca2+ can occur in aqueous phase as the prior literature which indicating that these minerals can be utilized in soil remediation and fertilizer [36–39]. The elements N, K and P are also necessary in soil fertilization for plant growth. Biochars from chicken manure and coffee husk have been demonstrated as fertilizers [40]. The chemical compositions suggest that this biochar is good for plant growth. Dong et al [41] reported that Mg, Ca, P and K can increase nutrient uptake and rice plant growth. Also the high amount of K (1.85) in the biochar is positive for use as fertilizer.

Figure 2 shows the XRD pattern for MBC, showing Fe3O4 peak. Several peaks of iron oxide were observed in the 2θ range covered, showing that the iron oxide was in form of Fe3O4. Fe3O4 peaks include 30.18, 35.61, 43.35, 53.72, 57.32 and 62.93° [42–44]. By adding NaOH dropwise, the pH of the solution was increased.
Therefore, on the surface of biochar $\text{Fe(OH)}_3$ and then $\text{Fe(OH)}_2$ were precipitated and then $\text{Fe(OH)}_2$ can oxidized to $\text{Fe(OH)}_3$ by dissolved oxygen. However, the iron oxide is converted to magnetite ($\text{Fe}_3\text{O}_4$) during pyrolysis [3, 36, 45, 46]. The $\text{Fe}_3\text{O}_4$ was observed after modification with iron components, and also previous studies have reported $\text{Fe}_3\text{O}_4$ composites [47]. The XRD results confirm that MBC has $\text{Fe}_3\text{O}_4$ composites on BC surface with the high crystalline structure of cubic spinel $\text{Fe}_3\text{O}_4$ [48].

BET analysis can determine the specific surface area of biochar from nitrogen adsorption isotherm. The surface area is the key characteristic of a porous material considered for absorbent [49]. The results of BET for MBC show that the specific surface area and pore volume were 3.60 m$^2$ g$^{-1}$ and 0.015 cm$^3$ g$^{-1}$ as shown in table 3. However, The results from the current study indicate that the surface area and pore volume values of the modified biochar MBC is quite identical to the reported values of SCG biochar [50] and the values are quite low comparing with the reported values of other adsorbents [31, 51].

The FTIR spectra of SCG and biochar BC are shown in figure 3, and for MBC in figure 4. The peaks at 2925 cm$^{-1}$ and 2855 cm$^{-1}$ for C–H stretching were related to aliphatic functional groups, which showed up in SCG and MBC after adsorption but not in BC and MBC before adsorption, therefore demonstrating reducing reactions in the non-polar aliphatic fraction. The peaks in 1590–1596 cm$^{-1}$ were attributed to aromatic C=C and C=O [35]. The peak at 1430 cm$^{-1}$ is for –OH and –CH bending (acid, hydrocarbon, olefin, phenol and alcohol) [52]. The C=O bond is a key factor in the heavy metal ion’s coordination [53]. The shift of the Fe–O stretching peak from 584 to 582 cm$^{-1}$ was also observed for MBC after adsorption of Cd(II) ion. In the BC and MBC, the functional groups CH, OH, C=O, and CO, play an important role in the Cd(II) adsorption by surface complexation, by ion exchange, and by cation attraction [3, 32, 54].

SEM imaging of the samples shows changes in the surface morphology of the biochar due to the pyrolysis. Figure 5 indicates relative changes in the surface morphologies of BC and MBC. In (figures 5(A) and (B)) we have BC which has a rough, rigid and cracked surface morphology. The MBC in (figures 5(C) and (D)) shows several particles with cubical shapes on the surface, with diameters of about 3–20 μm.

Yu et al [44, 49] reported that $\text{Fe}_3\text{O}_4$ crystals are cubic. The results in figure 5(C) indicate that hydrolysis and dehydration during pyrolysis at 400 °C moderately changed the nature of the biomass. These results confirm

\[ \text{Specific surface area and pore volume of SCG, biochar and modified biochar according to the literature.} \]

| Feedstock      | Specific surface area m$^2$ g$^{-1}$ | Pore volume (cm$^3$ g$^{-1}$) | References |
|----------------|-------------------------------------|-------------------------------|------------|
| Raw SCG        | <0.1                                | N.D.                          | [50]       |
| SCG biochar$^*$| 1.53                                | 0.008                         | [50]       |
| MBC            | 3.60                                | 0.015                         | Current study |

$^*$ SCG biochar were prepared at heat rate $6 \, ^\circ\text{C} \cdot \text{min}^{-1}$ up to the desired temperature ($550 \, ^\circ\text{C}$) and held for 1.5 h. N.D. (not detected).
that temperature and residence time in pyrolysis of biomass affect surface morphology of candidate adsorbents [55–57].

### 3.2. Effect of pyrolysis temperature on adsorption

The adsorption efficiency by MBC is greater than that of BC due to crystallinity and the % removal of MBC (~97%) is greater than that of BC (~62%) at pyrolysis temperature of 400 °C, as indicated in the figure 6, in which the experiment conditions including the adsorbent dosage 0.1 g l\(^{-1}\), pH 7, time 30 min and the initial concentration of Cd(II) 40 mg l\(^{-1}\) were used [58, 59]. The results in figure 6 show that increasing the pyrolysis temperature of BC and MBC affected adsorption % of Cd(II) ion. The % removal of Cd(II) by MBC decreased with increasing pyrolysis temperature from ~97 to ~76% which related with the functional groups on surfaces interacted with the heavy metal ions [60, 61]. Hence, the MBC prepared at 400 °C pyrolysis temperature is appropriated for Cd(II) removal.
3.3. Batch adsorption experiments

From the preliminary work as shown in figure 6, the result showed that the % removal of Cd(II) of MBC is better than BC. According to that results further in batch adsorption study MBC was selected for the removal of Cd(II).

3.3.1. Effect of adsorbent dosage

Dosage is the key factor in adsorption, because of the adsorbent-adsorbate equilibration [62]. The results in figure 7 show that when the dosage of biochar increased, the removal of Cd(II) also improved. However, 0.1 is the optimum amount of this biochar adsorbent. The removal % was ~96%. At this amount, several stages of adsorption can be utilized to reach a higher removal. Higher dosage of adsorbent provides more active sites; therefore, the removal will be greater; but after a specific adsorbent amount, the removal does not improve appropriately because the covering and accumulation for binding or exchanging on the adsorption sites are not present [62].

3.3.2. Effects of pH

The effect of pH was studied by utilizing the MBC. The results show that pH affected removal of Cd(II). It is very important in the removal of heavy metal ions because it modifies adsorbent surface charge and ionization.
Figure 8 shows that when pH increased from 3 to 7, the adsorption efficiency of Cd(II) gradually increased and the aqueous solution reached a steady value at pH 4 until pH 9. At pH 4 to 8 the removal efficiency of Cd(II) was around 96%. However, the adsorption of Cd(II) rapidly decreased at pH 9. Li et al. [56] reported that increased pH is useful to hydrolysis due to the electronic structure of Cd(II) ion. Furthermore, the adsorption behavior of biochar formed by the hydrolysis of metal hydroxides is more prominent than those produced by free hydroxides. In this experiment, increased pH of the solution showed further hydrolysis of Cd(II), which were continuously adsorbed to inner active sites of carbon. The other study also shows that by increasing the pH also increased the adsorption capacity of the Cd(II). Li et al. [58] reported that the adsorption of Cd(II) increased by increasing the pH 3–4, at the pH 5–7 the adsorption were steady state. The present study also shows the same result at the adsorption study at pH 5–8. At pH 7 the adsorption sites of carbon are saturated. By increasing the solution pH, the competitiveness of Cd(II) decreases compared to protons for binding sites, and the precipitation or creation of hydroxide complexes of Cd(II) might improve removal efficiency [54]. Thus, the highest adsorption capacities were observed in solutions of pH 7.0 and the other adsorption experiments were controlled at this neutral pH for the optimum condition.

### 3.3.3. Effects of initial metal ion concentration

The initial metal ion concentration is the key factor to the adsorption of Cd(II). The removal of Cd(II) was determined for initial metals concentrations 5, 10, 20, 40, 60, 80 and 100 mg l\(^{-1}\) at 30 min contact time and pH 7. Figure 9 shows the removal percentage of Cd(II) by MBC. The highest removal of Cd(II) was 96.7% at 30 min, pH 7, and adsorbent dosage 0.1 g/20 ml. On increasing the initial metal ion concentration, the removal efficiency decreased because the initial metal ion concentration is the mass transfer driving force in the aqueous to solid phase and Cd(II) removal decreased when the initial Cd(II) concentration increased due to the limited adsorption sites [25]. Thus, the optimization for an initial metals concentration of 40 mg l\(^{-1}\) was used for further experiments.

### 3.3.4. Effects of time

Time is an important parameter for the adsorption of heavy metal ions, affecting via adsorption kinetics. In this study experiments were performed from 2 to 300 min. Figure 10. (A) and (B) illustrate the removal efficiency and adsorption capacity of Cd(II) on MBC. The removal efficiency slowly increased over 2–60 min and the adsorption capacity also increased. The equilibrium adsorption was practically reached at 30 min from start. Thus, particle adsorption diminishes fundamentally with expanding contact time because the active sites on the surface are exhausted [63, 64].

### 3.3.5. Batch adsorption kinetics

Kinetic models reveal the rate of adsorption that can be restricted by diffusion or by chemical reactions, and this is important to the design and adsorption system and for determining a suitable contact time. In this study, pseudo-first and pseudo-second order kinetic models were tested.
Table 4 shows the fitted kinetic models and the coefficients of determination ($R^2$), and the pseudo-second order kinetic model gave a good correlation ($R^2 = 0.99$). The results indicate that the adsorption maybe chemisorption or diffusion limited. The Cd(II) showed the adsorption completely occurred with pseudo second-order reaction and the adsorption were occurred to be controlled by the chemical adsorption process [31]. The adsorption capacity $Q_e$ was estimated from the fitted pseudo-second order model as 7.96 mg g$^{-1}$. $k_1$ is the best fit model of pseudo-first order was observed 0.068 (1 min$^{-1}$), which showed that Cd(II) filled at the adsorption site of adsorbent [59]. The $k_2$ is low at 0.014 g mg$^{-1}$ min$^{-1}$, which indicates that the adsorption process occurred due to the number of unoccupied sites. The results show that the rate of adsorption decreased with contact time. Figure 9 shows the maximal 87% adsorption at about 30 min.

| $C_e$ (mg g$^{-1}$) | $Q_e \text{exp}$ | $Q_e \text{cal}$ | $k_1$ | $R^2$ | $k_2$ | $R^2$ |
|------------------|-----------------|-----------------|-------|-------|-------|-------|
| 40               | 7.47            | 5.10            | 0.068 | 0.84  | 0.014 | 0.99  |

Figure 9. Effects of initial metal ion concentration (pH 7, contact time = 30 min, $V = 20$ ml and adsorbent dosage 0.1 g l$^{-1}$).

Figure 10. Effects of contact time on adsorption of Cd(II) ($C_e = 40$ mg l$^{-1}$, pH 7, adsorbent dosage 0.1 g l$^{-1}$, $V = 20$ ml).
3.3.6. Adsorption isotherm
For the adsorption isotherm of Cd(II) by MBC, the experiment was performed with various initial concentrations (5, 10, 20, 40, 60, 80 and 100 mg l\(^{-1}\)) and the equilibrium isotherm data were fit with two candidate models, the Langmuir model [65] and the Freundlich model [66].

The results from model fitting are summarized in table 5, showing that the Langmuir isotherm gave a better fit for the adsorption of Cd(II) with \(R^2 = 0.98\), indicating monolayer adsorption on a homogenous surface.

The \(n\) in Freundlich isotherm model when between 0 and 10 [67] indicates a comparatively strong adsorption, here of Cd(II) on the adsorbent surfaces. However, the low \(R^2\) makes this isotherm model overall not appropriate for our data. The adsorption capacity of Cd(II) by MBC is considerable compared to the other reported adsorbents [29, 68–71].

3.3.7. Adsorption thermodynamics
From thermodynamics we can assess whether the adsorption process is spontaneous or not. The Gibbs free energy change is important because it shows the spontaneity of a chemical reaction. The Gibbs free energy combines energy and entropy [28]. Table 6 shows negative values of \(\Delta G°\) so the process is thermodynamically viable, spontaneous and conforming to a chemical reaction in Cd(II) adsorption. Additionally, when the temperature increased the \(\Delta G°\) decreased (−2.55 to −6.35 kJ mol\(^{-1}\)), indicating feasibility increase with temperature [31]. The \(\Delta H°\) is positive so that the process is endothermic and increasing temperature should be more adsorption. It is also observed absorbent capacity should increase with temperature. \(\Delta S°\) is positive indicating increased randomness at the solid-solution interface in the adsorption process [31].

4. Conclusion
This study related on the reuse of waste as a low-cost adsorbent. The obtained magnetic biochar was easily manipulated after treatment by external magnetic fields. The magnetic biochar produced by pyrolysis of biochar derived from spent coffee grounds waste at 400 °C. Modifications had affected specific surface area, surface morphology and surface functional group of magnetic biochar on their physical and chemical characters and accessibility to cadmium (II) ion adsorption. On the surface of magnetic biochar, Fe\(_3\)O\(_4\) crystallites were observed. At the optimum adsorption conditions, the magnetic biochar has high adsorption efficiency for removal of cadmium (II) ion at percentage removal around 96%. The high adsorption efficiency of cadmium (II) by Fe\(_3\)O\(_4\)-composited biochar was due to the various functional groups including oxygen containing in Fe-O functional group. Second-order kinetic fit well the Cd(II) adsorption by Fe\(_3\)O\(_4\)-composited biochar, while the Langmuir isotherm model fit equilibrium adsorption well. The thermodynamics of adsorption were endothermic with spontaneous chemical reaction, and adsorption capacity was 10.42 mg g\(^{-1}\). From these studies, Fe\(_3\)O\(_4\)-composited biochar derived from spent coffee grounds waste can be a viable alternative for a low-cost adsorbent in wastewater treatment.

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