ADSORPTION OF HEAVY METALS BY BIOCHAR: EXPERIMENTAL AND LITERATURE ANALYSES

by

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ABSTRACT

Biochar is a stabilized carbon with porous structure that can be used as an economical adsorbent for wastewater treatment. Since there are numerous types of biochars, it is important to understand how biochar characteristics influence adsorption performance by selecting or customizing biochars that are suitable for wastewater treatment. There is a large amount of wastewater containing low concentrations of heavy metals (e.g., cadmium and lead) produced daily all over the world. This research investigates the relationship between biochar characteristics and cadmium and lead adsorption performance in aqueous solutions both experimentally and using data collected from the literature.

A batch adsorption experiment was conducted using non-activated and steam activated biochars made from wheat (*Triticum aestivum*) straw and cattle manure pellets. Cadmium nitrate ($Cd(NO_3)_2$) solutions with 0, 50, 75, 100, 125, 150, and 200 mg Cd/L were shaken with biochars until adsorption equilibrium to generate adsorption isotherms. The adsorption isotherms had poor fitting with Langmuir, Freundlich, Sips, and Dubinin-Radushkevich models, and the possible causes were discussed.

To provide general suggestions about biochar selection for cadmium or lead removal from wastewater, data were collected from the literature on biochar adsorption in cadmium or lead solutions based on research papers published between 2011 and 2021. Biochar parameters (e.g., highest pyrolysis temperature, biochar pH, surface area, total pore volume, average pore size, ash content, atomic ratio of oxygen:carbon, atomic ratio of hydrogen:carbon), and adsorption model parameters (e.g., the maximum adsorption capacity, Qmax, of Langmuir model and the constant related to favourability of adsorption, 1/n, of Freundlich model) were collected from these research articles. Simple linear regression was used to investigate the relationship between biochar characteristics and adsorption capacity. Total pore volume, highest pyrolysis temperature, and biochar pH were identified as three potential predictors for cadmium adsorption capacity for

wastewater remediation; however, this study did not find good predictors for lead adsorption capacity, suggesting biochar selection should be adjusted based on the target contaminant.

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CHAPTER II

I. INTRODUCTION

1. Definitions And Background

Biochar is a solid product obtained from the carbonization of biomass through thermochemical conversion in an oxygen limited environment (International Biochar Initiative (IBI), 2022). Another way to define biochar is a “carbon rich product which occurs when biomass (such as wood, manure or crop residues) is heated in a closed container with little or no available air” (Lehmann & Joseph, 2015a). Both definitions indicate that the anaerobic thermal decomposition process, pyrolysis, converts waste organic material into biochar. Through pyrolysis, organic wastes can be upcycled into biochar (Kane & Ryan, 2022; Lee et al., 2022), which is mostly stabilized carbon (Pandiyan et al., 2021).

Pyrolysis produces other materials similar to biochar, such as charcoal, black carbon, hydrochar, and activated carbon. Biochar can be used as a soil amendment, mainly for carbon sequestration and environmental management; charcoal is intended to be used as an energy carrier (Lehmann & Joseph, 2015b). Black carbon usually refers to the charred organic material produced through natural or human caused fires in the environment (Atkinson et al., 2014; Lehmann & Joseph, 2015b). Hydrochar is related to biochar, but its production process and chemical composition are different from. Hydrochar is made through hydrothermal carbonization in water under pressure, while biochar is produced dry (Ahmad et al., 2014). Biochar mainly consists of aromatics while hydrochar consists mainly of alkyl moieties (Mohan et al., 2014). Activated carbon is used mainly for filtration and less for soil applications (Lehmann & Joseph, 2015b).

Production of activated carbon and activated biochar involves using steam or chemicals to increase surface area and pore properties. Activated biochar is usually produced under lower temperature and at lower price than activated carbon, while both have an excellent ability to adsorb pollutants (Tan et al., 2015). Therefore, activated biochar is a potential cost effective alternative to activated carbon (Tan et al., 2015; Tan et al., 2017).

Biochar is a recently created term (Lehmann & Joseph, 2015b), although biochar itself has a long history. Around the world, people added biochar to soil hundreds and even thousands of years ago for agricultural soil management. More recently biochar was intentionally applied as a soil amendment in activities such as land reclamation after finding benefits for soil improvement (Wuedner & Glaser, 2015; Thomas & Gale, 2015). Biochar has been used as a soil amendment to support forest restoration since the 1820s (Thomas & Gale, 2015).

2. Common Feedstocks For Biochar Production

Biochar feedstocks cover a wide range of commonly available materials, including agricultural and forestry waste (e.g., corn straw, switch grass, dairy manure, sawdust, pine wood, oak bark), industrial by-products (e.g., sewage sludge, digested residues from bioenergy facility), and other biomass (e.g., bones, algae) (Inyang et al., 2016; Duku et al., 2011). A suitable source of biochar feedstocks would be an existing long-term system (Sohi et al., 2015), and biochar feedstock sources are abundant globally.

For example, wastewater treatment plants continuously produce very large amounts of sewage sludge (or biosolids) as a by-product of their processing, and its production is increasing due to the growing global human population and development and implementation of wastewater treatment in many developing countries (Lu et al., 2012; de Souza Souza et al., 2021). Approximately 500 million tonnes/year of agricultural residues are produced around the world (Duku et al., 2011).

In Canada, biochar feedstock sources are abundant. There are 27 million tonnes of agricultural waste biomass produced every year in Canada (Dahal et al., 2018). Some available agricultural feedstocks include wheat straw, canola straw, and manure. Forestry waste is another significant feedstock source in Canada. For example, 12 million ha of sustainably managed forests in Northwest Ontario alone provide rich and sustainable woody feedstock for biochar production (Homagain et al., 2016). In Alberta, other feedstocks (e.g., sawmill wastes, pulp and paper sludge, municipal solid waste) are also available besides agricultural and forestry feedstock sources (Anyia, 2010; Kryzanowski, 2013).

3. Production And Properties Of Biochar

Biochar can be produced through both slow and fast pyrolysis processes. Slow pyrolysis uses a relatively lower temperature, lower heating rate (0.1-1 °C per second for 5-30 minutes), and longer residence time (minutes to days) than fast pyrolysis (Tipathi et al., 2016). Fast pyrolysis uses a relatively higher temperature (850-1250 ^{o}C), higher heating rate (10-200 ^{o}C per 1-10 s), and shorter residence time (a few seconds) than slow pyrolysis (Tripathi et al., 2016). Fast pyrolysis produces mainly liquid phase ($\approx$ 75% bio-oil) material and partially produces biochar; while slow pyrolysis produces mainly biochar (Tripathi et al., 2016; Mohan et al., 2006). Therefore, it is more common and economical to use slow pyrolysis than fast pyrolysis to produce biochar for wastewater treatment (Tan et al., 2015).

Biochar properties, including surface area, pore size distribution, and ion exchange capacity, are mainly influenced by pyrolysis temperature, heating rate, and feedstock type used during pyrolysis. The effect of heating rate and feedstock type on biochar properties varies with no noticeable trend, while the effect of pyrolysis temperature has a general trend.

Increasing the temperature for pyrolysis generally generates more pores, including micropores (diameter below 0.2 nm) that contribute greatly to biochar surface area (Chia et al., 2015). Therefore, biochar produced at higher temperatures usually has a greater surface area than that produced at lower temperatures (Chia et al., 2015). However, when the pyrolysis temperature is above 700 ^{o}C, pore structure may collapse, so surface area and micropore volume both may decrease due to thermal destruction (Ahmad et al., 2014; Chia et al., 2015). Generally, the abundance of oxygen and hydrogen ion functional groups are reduced when the pyrolysis temperature is above 500 ^{o}C, which decreases polarity and increases aromaticity of biochar (Ahmad et al., 2014). For example, Chen et al. (2008) reported a reduction in polarity and an increase in surface area while increasing pyrolysis temperature from 100 to 700 ^{o}C to produce biochars from pine needles, and maximum adsorption capacity (Qmax) of organic pollutants is greater with a higher surface area. Kwak et al. (2019) reported similar findings among the properties of different types of biochars. The biochars were produced at 300-700 ^{o}C and were used to adsorb an inorganic pollutant, lead, from aqueous solution.

Activation of biochar is used to maximize surface area and pore density or to generate functional groups (Chia et al., 2015; Cha et al., 2016). Examples of physical activations are steam (Kwak et al., 2019; Rajapaksha et al., 2015) and carbon dioxide (Franciski et al., 2018). The activating gas reacts with the biochar surface to remove carbon atoms so that pores are opened and enlarged (Cha et al., 2016). Some chemical activations use basic chemicals, such as zinc chloride (Park et al., 2015), potassium hydroxide (Genuino et al., 2018), and sodium hydroxide (Choudhary et al., 2020). Some use acidic chemicals, such as phosphoric acid (Cao et al., 2018), nitric acid (Kalinke et al., 2017), and hydrochloric acid (Ye et al., 2019). In chemical activation, micropores are formed through dehydration and oxidation (Cha et al., 2016).

4. Potential Biochar Uses In Soil

There are large amounts of organic waste produced every year around the world, which has become a global environmental burden. Traditional methods to manage organic wastes include landfilling, composting, and anaerobic digestion (Väisänen et al., 2016). Some of these methods involve converting the major organic wastes into biochar, which will turn the environmental burdens into value added products. Using other minor organic wastes that do not cause an environmental burden for biochar production can also have benefits. For example, converting yard waste to biochar creates value by reducing greenhouse gas emissions and increasing carbon sequestration by avoiding composting processes that generate the greenhouse gases methane and nitrous oxide (Roberts et al., 2010).

Biochar can be used as a soil amendment to improve soil quality and to promote plant growth. For example, biochar can improve water permeability, water holding capacity, and thus plant available soil water (Asai et al., 2009), which may be due to the porous structure and low density of biochar. Soil nutrients, such as phosphorous, nitrogen, and potassium, can be increased through biochar application. This is because biochar introduces these nutrients into the soil and reduces nutrient leaching by adding pores and surface area, and by increasing the soil's cation exchange capacity (Biederman et al., 2013). Therefore, plant growth can be greatly improved by biochar application. Chan et al. (2008) reported a 96 % increase in the yield of radish plants when 0 to 50 t/ha of poultry litter biochar was applied. The yield increase was attributed to the biochar's ability to increase soil available nitrogen and improve soil quality. Similarly, Asai et al. (2009) reported that wood residue biochar application increased grain yield of rice in sites with low phosphorus availability and promoted the effect of phosphorus and nitrogen and phosphorus fertilizers in such sites.

Biochar application to soil can reduce greenhouse gas emissions from that soil (Lehmann, 2007). For example, carbon dioxide emission from soil can be reduced since biochar application induces lower enzymatic activities, higher carbon use efficiency, and higher carbon dioxide adsorption (Zhang, et al., 2019). Wang et al. (2017) found that enhanced soil aggregation in a silty loam textured soil, which helped with soil carbon stabilization, and hence also helped with carbon sequestration. Biochar application can also sequester carbon in a stabilized form, resulting in a net removal of carbon dioxide from the atmosphere. This positive result and/or effect takes into consideration the combination of biochar production and the application to soil (Lehmann, 2007). Therefore, in general biochar application in soil may be a potential method to mitigate global climate change (Woolf et al., 2010).

Biochar can be used as an economical adsorbent for wastewater treatment due to its porous structure. It can adsorb both organic contaminants (e.g., color or dye, phenols, pesticides, antibiotics) and inorganic contaminants (e.g., metal ions, anions such as chloride) (Mohan et al., 2014). More details will be discussed in Section 1.5.

Biochar can be used for in-situ soil and sediment remediation (Ahmad et al., 2014; Yang et al., 2020). Adding basic biochar would increase soil pH, hence increasing the electrostatic force between soil and cations (Sposito, 1989), and possibly inducing precipitation of pollutants such as heavy metals. The surface area and functional groups added through biochar application would improve the adsorption capacity of the soil. In a sorption experiment by Uchimiya et al. (2011), copper adsorption was enhanced by a basic broiler litter biochar (pyrolyzed at 700 ^{o}C) in a clay rich, alkaline soil with high heavy metal adsorption capacity and an eroded, acidic sandy loam soil with low heavy metal adsorption capacity. In a 60 day incubation experiment, rice straw biochar significantly immobilized zinc in a zinc contaminated soil (Liu et al., 2021). Biochar application can also enhance adsorption and microbial degradation of organic pollutants (e.g., trifluralin, pendimethalin) in contaminated sediment (Gong et al., 2016).

5. Adsorption Of Potential Toxic Elements In Aqueous Solutions

There is significant interest in using biochar to adsorb potentially toxic elements from aqueous solutions, and removal of heavy metals from aqueous solutions by biochar has become one of the most researched topics on water treatment (Tan et al., 2015; Wu et al., 2020). Some popular empirical models that are used to explain the equilibrium data or adsorption isotherms of biochar adsorption are Langmuir, Freundlich, Langmuir–Freundlich, Redlich–Paterson, and Temkin equations (Tan et al., 2015; Febrianto et al., 2009; Aksu, 2002).

Langmuir and Freundlich models are most commonly used (Han et al., 2020; Febrianto et al., 2009; Tan et al., 2015), and equilibrium data generally fit them better than other models (Tan et al., 2015). The Langmuir model assumes “monolayer sorption onto a surface with a finite number of identical sites” (Aksu, 2002), so the theoretical Qmax can be calculated based on the Langmuir model. The Freundlich model assumes sorption onto a heterogenous surface and is not restricted to the formation of a monolayer (Tan et al., 2015), so there is no Qmax that can be calculated using the Freundlich model.

For different biochars (with different properties) and potentially toxic elements, the best fit adsorption model can vary. For example, the copper adsorption isotherm of a cow manure biochar produced at 600 ˚C fit the Langmuir model (R^2 = 0.98) better than the Freundlich model (R^2 = 0.91), but the adsorption isotherm for cadmium fit the Freundlich model (R^2 = 0.99) better than the Langmuir model (R^2 = 0.97) (Kołodyńska et al., 2012). However, in the same experiment, the cadmium adsorption isotherm of a cow manure biochar produced at 400 ˚C fit the Langmuir model (R^2 = 0.99) better than the Freundlich model (R^2 = 0.83) (Kołodyńska et al., 2012).

Competitive adsorption occurs when there are more than one potentially toxic element in the solution (Park et al., 2016). The Qmax of individual potentially toxic elements generally becomes lower with the co-occurrence of other potentially toxic elements. For example, Park et al. (2016) reported the Qmax of heavy metals (lead, cadmium, chromium, copper, zinc) onto sesame (*Sesamum indicum* L.) straw biochar under mono or multi metal conditions. Cadmium adsorption had the greatest difference in Qmax between mono (86 mg/g) and multi metal (5 mg/g) conditions. While comparing the Qmax of organic pollutants between mono and multi metal conditions, Ahmed et al (2017) also reported reductions in the Qmax of three widely used sulfonamides antibiotics: sulfamethazine, sulfamethoxazole, and sulfathiazole.

6. Summary

Biochar is a stabilized form of carbon, which typically has porous structures. Biochar can be converted from organic wastes through pyrolysis. The conditions during biochar production and feedstock types determine biochar properties such as pH, surface area, and functional groups. Depending on biochar properties, biochar has multiple potential uses, such as amending soil, treating wastewater, remediating soil, and sequestrating carbon. Adsorption of potentially toxic elements (e.g., heavy metals) from aqueous solutions has become a research hotspot, which is related to the potential use of biochar in wastewater treatment.

7. Thesis Structure

The thesis is organized into four chapters.

Chapter I provides background information about biochar definition, production, properties, and potential application.

Chapter II focuses on the cadmium adsorption experiment by non-activated and/or steam activated biochars and some potential causes of its unexpected results.

Chapter III is a critical analysis that collected and reanalyzed data from research articles about biochar adsorption in cadmium or lead aqueous solutions. This chapter provides suggestions about biochar selection for treating wastewater with low cadmium or lead contamination.

Chapter IV summarizes the research and discusses the research limitations, research application, and future research.

II. BIOCHAR ADSORPTION OF CADMIUM

1. Introduction

Cadmium (Cd) is a non-essential trace metal that is toxic to plants and animals. Since Cd has a high transference rate from soil to plant, it enters the food chain and can adversely affect the health of animals (Satarug et al., 2003). Cadmium can also accumulate in the human body and cause diseases, such as erythrocyte destruction, skeletal deformity, renal degradation, and cancer (Mohan & Singh, 2002).

Industrial wastewater such as oil sands process water (OSPW) contains Cd. Comparing the standards of heavy metals for the protection of aquatic life in the Environmental Quality Guidelines for Alberta Surface Waters (Government of Alberta, 2018) and the average concentrations in OSPW in research published from 2009-2019 (average hardness of OSWP ≈ 90 mg/L calcium carbonate), the average concentration of Cd (0.81 μg/L) in OSPW was 5.4 times the standard concentration (0.15 μg/L). However, the average concentrations of lead, cobalt, and zinc in OSPW were 3.44, 1.94, and 0.503 times the standard concentrations, respectively (Bauer et al., 2019; Hendrikse et al., 2018; Loganathan et al., 2015; Syncrude Canada Ltd., 2019; Siwik et al., 2000; Lari et al., 2016; Huang et al., 2016; Qin et al., 2019; Anderson et al., 2011; Abolfazlzadehdoshanbehbazari et al., 2013). If the data used included numbers that were below the detection limit, the number was taken as half of the detection limit when calculating the average. Therefore, Cd is considered to be one of the most concerning heavy metals in wastewaters such as OSPW.

Methods such as chemical precipitation, membrane filtration, and adsorption are commonly used to remove Cd from wastewater (Cheng et al., 2022). Precipitation is a widely used technique to remove heavy metals, such as Cd, in remediating wastewater since it is inexpensive and simple (Carolin et al., 2017). However, it requires large chemical inputs and produces large amounts of hazardous waste. It is difficult to remove heavy metals with low concentrations (Carolin et al., 2017; Vikrant et al., 2019). Membrane filtration is efficient in heavy metal removal and requires small space, but it is a very costly method (Ahmed et al., 2016). Adsorption is a cost effective, renewable, and efficient method to remove heavy metals such as Cd, however choosing a suitable adsorbent can be challenging (Kwikima et al., 2021).

Biochar can be used as an absorbent to remove Cd from aqueous solutions. For example, a *Canna indica* (Indian shot) derived biochar that was pyrolyzed at 500 °C had a high maximum adsorption capacity (Qmax) of 188.79 mg Cd/g biochar (Cui et al., 2016). The Qmax values of the 300-700 °C pig manure biochars that were studied by Wang et al. (2018) were even higher at 212.51–240.23 mg Cd/g biochar in 5 mM sodium nitrate ($NaNO_3$) solutions at pH 5. That high pore volume and ash content in the biochar greatly contributed to Cd removal.

Steam activation is a partial gasification process that induces steam to biochar after pyrolysis to generate biochars with higher surface area and better structures (Wang & Wang, 2019; Rajapaksha et al., 2016). Steam helps remove volatiles and trapped products of incomplete combustion and enhances carbon formation (Alaya et al., 2000; Wang & Wang, 2019). Therefore, the improved biochar properties can increase adsorption capacity. For example, 800 °C steam activation increases the Qmax of a bagasse (dry pulp remaining after crushing sugarcane or sorghum) biochar produced at 650 °C from 7.09 to 47.6 mg Cd/g biochar by increasing surface area (Hass et al., 2018).

Commonly researched biochar feedstock types include straw, manure, sludge, wood, and bone. Biochar properties vary greatly when derived from different feedstock types. For example, straw derived biochar usually has a high volatile content that can be easily removed during biochar production, which may lead to a low yield and high porosity (Wang & Wang, 2019; Strunecký et al., 2021). Straw and manure derived biochars usually have higher pH and nutrient concentrations than wood derived biochars (Gul et al., 2015). Different physicochemical properties due to different feedstocks can greatly impact adsorption performance.

Kwak et al. (2019) studied four feedstock types; wheat (*Triticum aestivum*) straw, canola (*Brassica napus*) straw, cattle manure pellets, wood saw dust, and biochar production methods (non-activation, steam activation; at 300, 500, 700 °C pyrolysis temperature). The biochars with the highest lead adsorption capacities were all produced at 700 °C with steam activation, and the feedstocks were canola straw, wheat straw, and manure pellet. Among the eight 700 °C steam activated and non-activated biochars produced from the four feedstocks studied by Kwak et al. (2019), canola straw biochars and wheat straw biochars had similar properties. However, properties of the manure pellet biochars were different from that of wheat straw and canola straw biochars (e.g., pH, ash content, elemental composition, adsorption capacity). In its response to steam activation, wheat straw had a much higher increase in surface area than manure pellets, although manure pellets had a greater increase in lead adsorption capacity than wheat straw. The investigation into Cd adsorption characteristics of the biochars had high lead Qmax and their disparate properties were expected to be helpful in selecting biochar to be used for heavy metal removal from the OSPW.

Therefore, the objective of this experiment was to investigate the Cd adsorption characteristics and Qmax of four biochars (non-activated wheat straw biochar, steam activated wheat straw biochar, non-activated manure pellet biochar, steam activated manure pellet biochar). Since lead and Cd are both heavy metals, based on Kwak et al. (2019), the hypotheses are that steam activation will increase Qmax of biochars, and wheat straw biochars will have higher Qmax than manure pellet biochars. However, the results from the inductively couple plasma analyses were abnormal, so the results were not able to address the hypotheses. The possible reasons of the abnormality are explained in this chapter.

2. Materials And Methods

2.1. Biochar production

Two feedstocks, wheat straw and cattle manure pellets were used to produce the biochars with and without steam activation. The feedstock sources and biochar production method were the same as that described in Kwak et al. (2019). Wheat straw was from a local farm in Alberta and was chopped to fragments of less than 10 mm long. Manure pellets were obtained from Paragon Soil and Environmental Consulting Inc. in Edmonton, Alberta and were not chopped but left in a cylindrical shape (diameter = 3 mm, length = 3-7 mm). Both feedstocks were dried at 60 ^{o}C for 24 hours before pyrolysis.

The biochars were produced under 2 hour pyrolysis at 700 ^{o}C with and without an additional 1 hour steam activation. A muffle furnace (Lindberg Blue M, Moldatherm, Thermo Scientific) was set with a heating/cooling rate at 10 ^{o}C/min and constant heating at 700 ^{o}C for 2 hours for non-activated biochars and 3 hours for steam activated biochars.

Inside the muffle furnace, feedstocks were pyrolyzed in a stainless steel reactor (15 cm diameter, 17 cm height) with an inlet tube and an outlet tube. The inlet tube was connected to nitrogen gas at a rate of 150 mL/min to constantly flush oxygen out from the reactor. Nitrogen gas was turned on approximately 30 min before heating and turned off after the reactor cooled to room temperature (approximately 20 ^{o}C). When 1 hour steam activation was started following the 2 hour pyrolysis, nitrogen gas was replaced with deionized water at 5 mL/min to generate steam in the reactor. The deionized water was then switched back to nitrogen gas when the 1 hour steam activation ended, and nitrogen gas was kept running until the reactor cooled to room temperature (approximately 20 ^{o}C). Before the batch adsorption experiment was conducted using the produced biochars, each biochar was mixed thoroughly and then passed through a 2 mm sieve.

The resulting biochars are non-activated wheat straw biochar (WS-N), steam activated wheat straw biochar (WS-S), non-activated manure pellet biochar (MP-N), and steam activated manure pellet biochar.

2.2. Batch adsorption experiment

This experiment used a modified method described in Kwak et al. (2019). All glassware was acid washed in 4 % nitric acid (HNO_3) before use. Cd solutions with 0, 50, 75, 100, 125, 150, and 200 mg Cd/L were prepared using cadmium nitrate ($Cd(NO_3)_2$). A specific amount of biochar (0.02 g) was weighed and added into each 50 mL Falcon tube. There were five replicates for each treatment, which means that all procedures after biochar weighing were repeated five times. A 30 mL Cd solution (50-200 mg Cd/L) was added into each Falcon tube with or without biochar and the Falcon tubes were shaken for 24 hours on a reciprocating shaker. After shaking, 10 mL of each mixture or Cd solution without biochar was filtered through a 45 μm syringe filter. The filtrate was then immediately acidified to below pH 2 by adding analytical grade 70 % HNO_3 and the sample was then sent for inductively coupled plasma (ICP) analysis on a Thermo ICAP-6300 Inductively Coupled Argon Plasma - Optical Emission Spectrometer (ICP-OES) at a laboratory, which will be referred to as the ICP lab in this study.

The ICP analysis was conducted three times since the data from the first analysis (referred below as the original data) seemed abnormal, and the ICP lab explained that there was a dilution error causing the abnormality of the original data. Therefore, the ICP lab conducted the second analysis without dilution claiming that the second analysis had more accurate results, and the resulting data set is referred to as the updated data. Since the results from the second analysis were also abnormal as described in Section 3.1., to test if the updated data were accurate, 20 of the samples were randomly selected from all the tested samples (with and without biochar) for an additional analysis without dilution. The resulting data are referred to as the 20 sample data.

The following equation was used to calculate the equilibrium Cd concentration on biochar.

$$q_{e1} = \frac{(C_0 - C_{e1}) * V}{W}$$

Where:

q_{e1} (mg/g) = Cd concentration adsorbed on biochar at equilibrium in a sample.

C_0 (mg/mL) = initial concentration of Cd in solution (average tested Cd concentration in replicates without biochar for the original and updated data, or 50, 75, 100, 125, 150, and 200 mg Cd/L for the original without tested C_0).

C_{e1} (mg/mL) = concentration of Cd at equilibrium in a sample with biochar and Cd solution.

V (mL) = volume of the solution (30 mL).

W (g) = weight of biochar (0.02 g).

After calculating the average of the equilibrium Cd concentration on biochar among replicates (q_e) based on q_{e1} values calculated using the equation above, the original data had several negative q_e values likely due to the lower tested initial Cd concentration than expected. Therefore, the third data set (referred to as original without tested C_0) used in this research uses 50, 75, 100, 125, 150, and 200 mg Cd/L as C_0 for q_e calculations instead of using the tested C_0.

2.3. Adsorption isotherm models

The adsorption isotherm data were fitted by four commonly used models, which are Langmuir, Freundlich, Sips, and Dubinin-Radushkevich (D-R) models (Chen et al., 2019; Kwak et al., 2019; Li et al., 2021). The model fitting was conducted using the OriginPro 2021 software (OriginLab Corporation, Northampton, MA, USA).

The equation of the Langmuir model is as follows.

$$q_e = \frac{Qmax * b * C_e}{1 + b * C_e}$$

Where:
q_e (mg/g) = Cd concentration adsorbed on biochar at equilibrium (average among replicates).
Qmax (mg/g) = maximum adsorption capacity.
C_e (mg/L) = Cd concentration in the solution at equilibrium (average among replicates).
b = the constant related to adsorbing energy (L/mg).

The equation of the Freundlich model is as follows.

$$q_e = K_f * C_e^{1/n}$$

Where:
K_f [(mg/g)/(mg/L)^n] = an indicator of adsorption capacity.
1/n = the constant related to the favourability of the adsorption.

The equation of the Sips model is as follows.

$$q_e = \frac{K_s * C_e^{n_s}}{1 + a_s * C_e^{n_s}}$$

Where:
K_s (L/mg) = Sips model constant.
a_s (L/mg) = Sips model constant.
n_s = Sips model constant related to adsorption intensity.

The equation of the D-R model is as follows.

$$\ln(q_e) = \ln(Qmax) - \beta * \varepsilon^2$$

$$\varepsilon = R * T * \ln(1 + \frac{1}{C_e})$$

Where:
β (mol^2/kJ^2) = the adsorption mean free energy constant.
ε = the Polanyi sorption potential.
R = 8.314 kJ/mol
T = 298.15 K

3. Results And Discussion

3.1. Results of batch adsorption experiment and model fitting

The original data showed signs of possible errors before any of the isotherm graphing or model fitting. The ICP lab stated that there were dilution errors.

In the original data, the tested C_0 values (43.52, 63.35, 87.24,105.01, 127.92, 174.74 mg Cd/L) were much lower than the expected C_0 values (50, 75, 100, 125, 150, and 200 mg Cd/L), so negative q_{e1} values were calculated for MP-N samples with 200 mg/L initial concentration level, and MP-S samples with 75, 150, and 200 mg/L initial concentration levels. Negative q_{e1} values do not occur in a normal adsorption experiment, and this cannot be theoretically explained unless the negative q_{e1} values are caused by errors. The five replicates without biochar at each concentration level did not have consistent initial Cd concentrations (C_{01}). The standard deviation among the five replicates of each concentration level ranged from 2.19 to 32.19 mg/L. The largest standard deviation was 150 mg/L, and there was an increasing trend in the standard deviation when concentration level increased. The variation of the C_{e1} values among replicates was also high, especially among 100-200 mg Cd/L levels. The standard deviation of the C_{e1} values among replicates of same treatments ranged from 0.35 to 56.7 mg/L, and MP-N at 200 mg/L level had the largest standard deviation. The resulting q_{e1} values were also not consistent among replicates. Normally, there may be some fluctuations among C_{e1} values of replicates due to the heterogeneity of biochars, but it is not normal to have similar inconsistencies in both C_{e1} and C_{01} results of the replicates from the original data.

Therefore, the heterogeneity of biochars is not the main cause of the inconsistency among the replicates. It is difficult to determine which values are true due to such high variation among replicates. For example, for WS-N in 150 mg/L of Cd, two similar C_{e1} values were 114.58 and 114.68 mg/L, and two other similar values were 92.54 and 92.86 mg/L. The two pairs of values were very different from each other. The fifth value was 105.68 mg/L, which was in between. Therefore, the problem is not caused by single data points since there are no obvious outliners.

The original without tested C_0 used the same set of C_{e1} values as the original data. While changing the C_0 values to 50, 75, 100, 125, 150, and 200 mg Cd/L eliminates the negative q_{e1} values, the q_{e1} values still vary among replicates due to fluctuating C_{e1} values among replicates, especially for the 100-200 mg Cd/L concentration levels.

The updated data were produced from an ICP analysis without any dilution, which seems normal without isotherm graphing or model fitting. The tested C_0 values were 52.9, 78.5, 103.8, 128.0, 151.1, 193.9 mg Cd/L, which were closer to the expected values (50, 75, 100, 125, 150, 200 mg Cd/L) than those in the original data set. The variation of C_{01} or C_{e1} values among replicates was much smaller than in the original data, and thus resulting q_{e1} values were more consistent among all of the replicates.

The original, original without tested C_0 and updated data sets generally do not fit the four models (Langmuir, Freundlich, Sips, and D-R models) well based on the R^2 values listed in Table 1. Although some R^2 values were relatively high, there were abnormal signs in other model parameters. For example, some Qmax and/or K_s values from Langmuir and/or Sips models were unreasonably high (e.g., WS-N and MP-N). While fitting the Freundlich model, R^2 values of WS-N, WS-S, and MP-N from the original data and the original without tested C_0 were relatively high, and the other two model parameters seemed normal. However, due to the low quality of the data caused by dilution errors, the Freundlich model may not truly describe the Cd adsorption characteristics of the biochars. If the Freundlich model describes the Cd adsorption characteristics based on the original or original without tested C_0 by chance, the adsorption of Cd onto biochars would be multilayer adsorption on heterogenous surface (Freundlich, 1906). The isotherms from the updated data set did not fit Langmuir, Sips, and D-R models ($R^2 = 0$) (Table 1) and had low R^2 for the Freundlich model (Table 1).

The poor fitting is due to the abnormal adsorption isotherms of the three data sets shown in Figures 1-4. The original and original without tested C_0 generally had increasing trends in q_e with higher C_e except for the isotherm of MP-S from the original data set. Such increasing trend in q_e is normally seen in adsorption isotherms corresponding to the adsorption models. The isotherm of MP-S from the original data set did not fit any of the models ($R^2 = 0$) (Table 1) since it did not have a clear trend, and the q_e values at 100 and 125 mg Cd/L levels were much higher than those at 150 and 200 mg Cd/L. Although the general trend in q_e of the original data set was increasing, the q_e of each biochar for the concentration level of 75 mg Cd/L was always lower than the values obtained for the 50 mg Cd/L concentration level. Additionally, q_e of each biochar at 150 mg Cd/L level was always lower than the values obtained when using 125 mg Cd/L, except for WS-N, which is abnormal.

After eliminating the negative q_e values in the original without tested C_0, q_e of 75 mg Cd/L concentration level was greater than 50 mg Cd/L concentration level, and R^2 values generally increased for all models. However, q_e at 150 mg Cd/L concentration level of each biochar remained lower than 125 mg Cd/L concentration level except for WS-N, so eliminating the negative q_e values did not eliminate all the abnormality in the isotherms from the original data set.

The updated data set had a lower model fit than both of the original and the original without tested C_0, as seen by the R^2 values provided in Table 1. However, the updated data seemed to have better quality than the other two data sets before isotherm graphing and model fitting. The main reason is that all the isotherms from the updated data set had a decreasing trend in q_e with increasing C_e (Figures 1-3). This decreasing trend cannot be theoretically explained and is likely caused by errors.

Table 1. Model parameters of Cd adsorbed by biochars from Langmuir, Freundlich, Sips, and Dubinin-Radushkevich (D-R) models.

Biochar Type	Data Set	Langmuir			Freundlich			Sips				D-R		
		Qmax mg/g	b L/mg	R^2	K_f (mg/g)/(mg/L)^n	1/n	R^2	K_s L/mg	a_s L/mg	n_s	R^2	Qmax mg/g	β mol^2/kJ^2	R^2
WS-N	Original	77489	5.15E-06	0.74	0.31	1.05	0.74	0.31	5.10E-06	1.05	0.66	35.32	8.78E-05	0.10
	Original2	24787	2.85E-05	0.92	0.87	0.96	0.92	6.17E+05	12.57	0.96	0.90	67.45	1.23E-04	0.45
	Updated	26	NA	0.00	53.77	-0.12	0.36	NA	NA	0.97	0.00	30.84	-1.98E-05	0.00
WS-S	Original	37	-1.48E+15	0.00	9.97	0.31	0.30	9.93	2.04E-03	0.32	0.07	39.76	3.20E-05	0.04
	Original2	122	0.02	0.69	8.10	0.48	0.73	8.05	9.65E-04	0.48	0.65	70.68	6.07E-05	0.47
	Updated	36	NA	0.00	54.17	-0.06	0.11	NA	NA	0.77	0.00	41.07	-4.65E-06	0.00
MP-N	Original	234519	1.34E-06	0.74	0.02	1.61	0.87	0.02	1.37E-06	1.61	0.82	37.64	4.69E-04	0.52
	Original2	215922	2.81E-06	0.90	0.18	1.26	0.94	0.05	1.98E-04	1.58	0.92	76.11	4.07E-04	0.77
	Updated	12	NA	0.00	31.42	-0.13	0.02	NA	NA	0.41	0.00	16.76	-2.95E-05	0.00
MP-S	Original	11	NA	0.00	5.33	0.18	0.00	NA	NA	NA	0.00	12.96	3.11E-04	0.00
	Original2	37	-9.93E+24	0.00	2.97	0.56	0.37	-1.13E+10	-3.09E+08	84.97	0.00	54.20	3.85E-04	0.74
	Updated	10	NA	0.00	25.16	-0.15	0.20	NA	NA	0.42	0.00	12.25	-4.81E-05	0.00

Abbreviations: WS-N: non-activated wheat straw biochar; WS-S: steam activated wheat straw biochar; MP-N: non-activated manure pellet biochar; MP-S: steam activated manure pellet biochar; Original2: Original without tested C_0

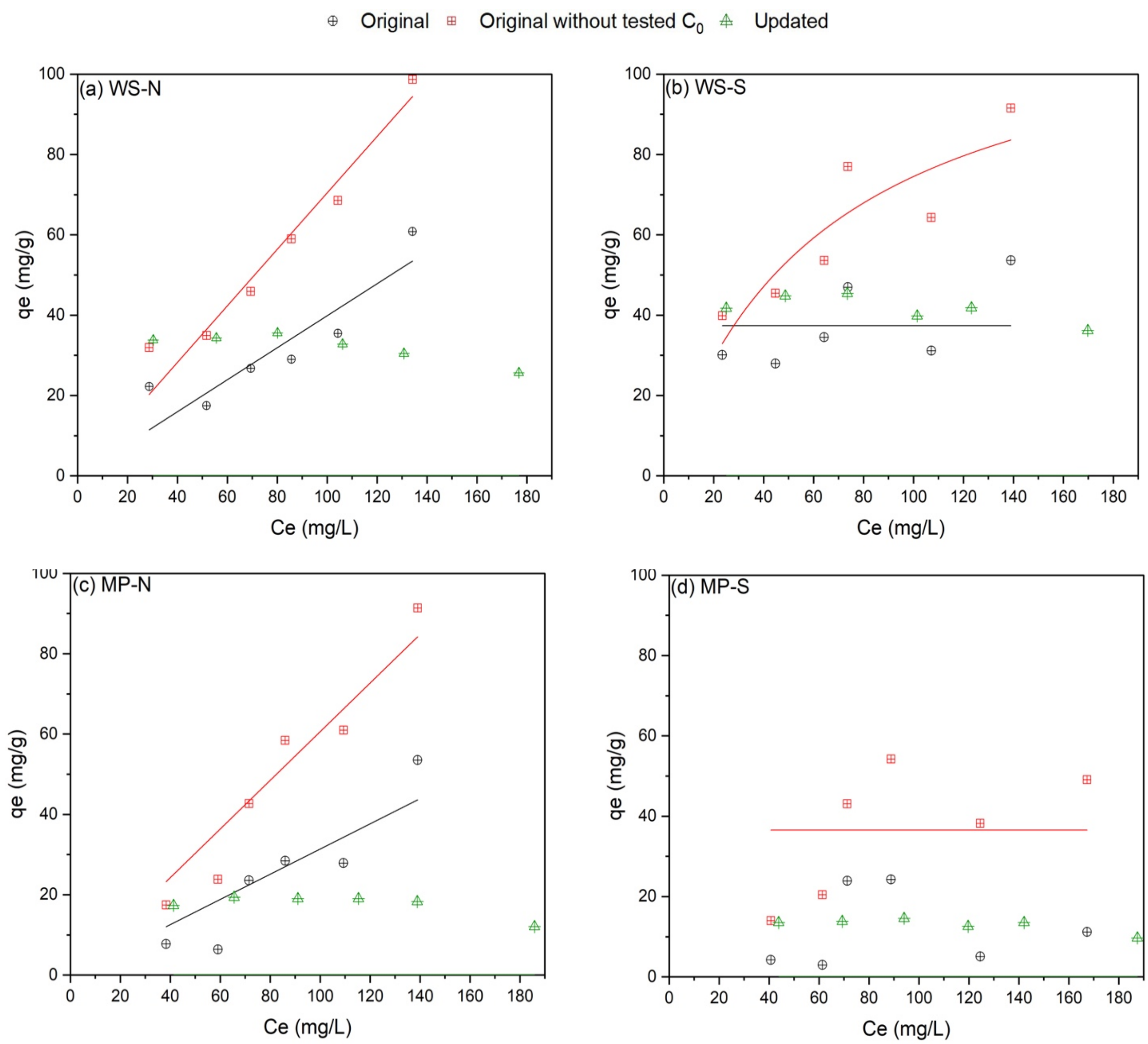

Figure 1. Adsorption isotherm of Cd on (a) non-activated wheat straw biochar (WS-N), (b) steam activated wheat straw biochar (WS-S), (c) non-activated manure pellet biochar (MP-N), and (d) steam activated manure pellet biochar (MP-S) fitted by the Langmuir model.

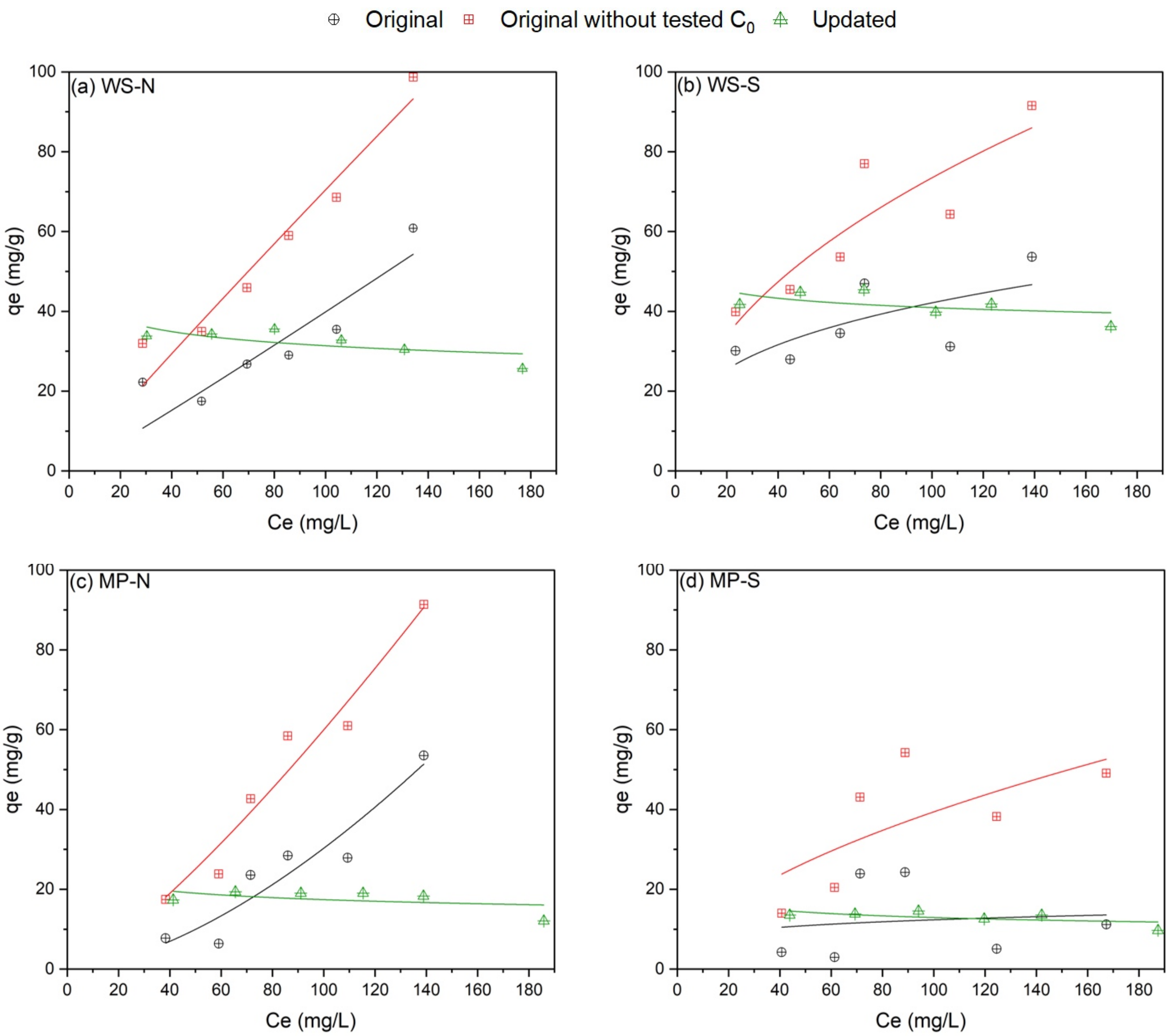

Figure 2. Adsorption isotherm of Cd on (a) non-activated wheat straw biochar (WS-N), (b) steam activated wheat straw biochar (WS-S), (c) non-activated manure pellet biochar (MP-N), and (d) steam activated manure pellet biochar (MP-S) fitted by the Freundlich model.

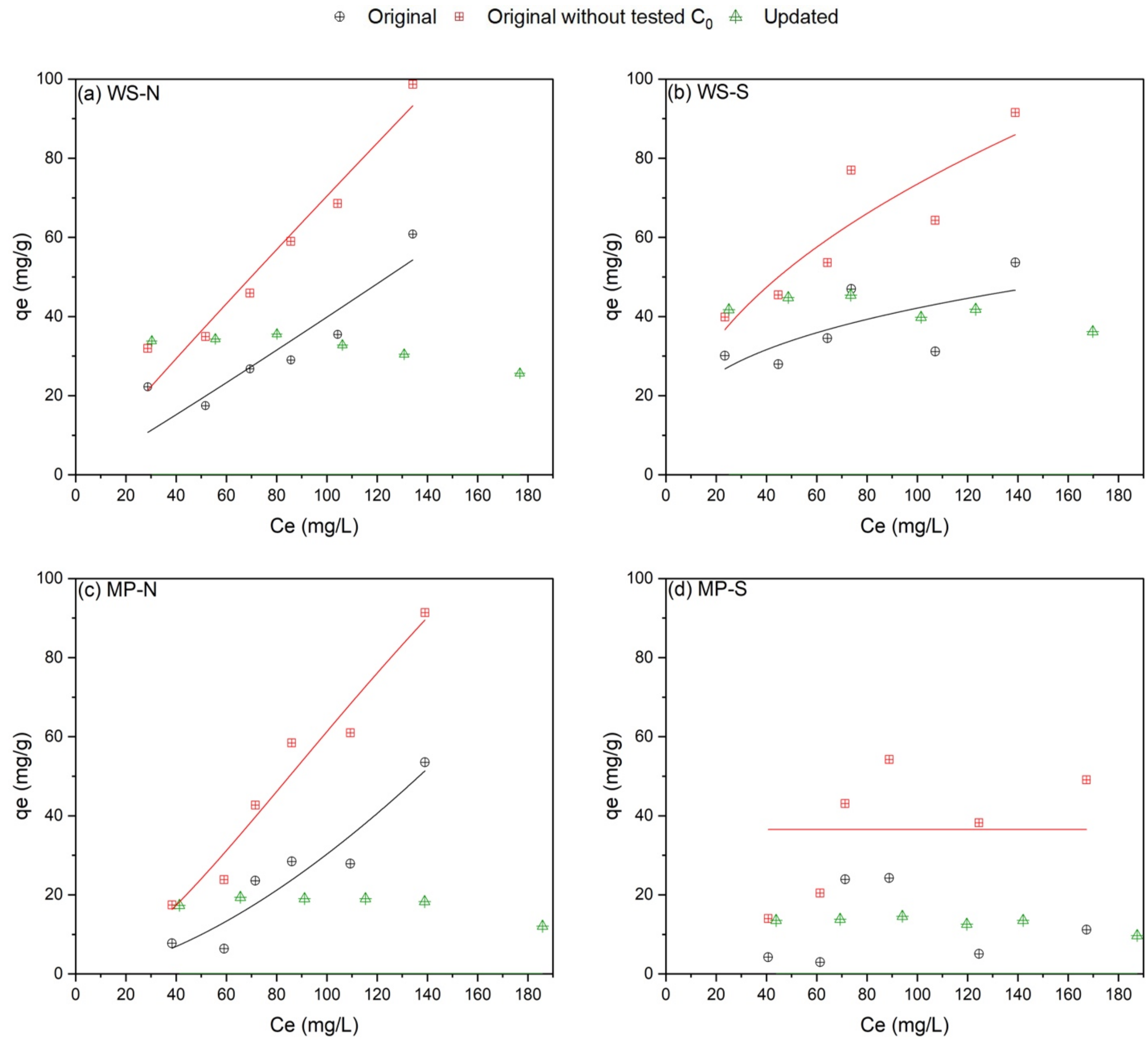

Figure 3. Adsorption isotherm of Cd on (a) non-activated wheat straw biochar (WS-N), (b) steam activated wheat straw biochar (WS-S), (c) non-activated manure pellet biochar (MP-N), and (d) steam activated manure pellet biochar (MP-S) fitted by the Sips model.

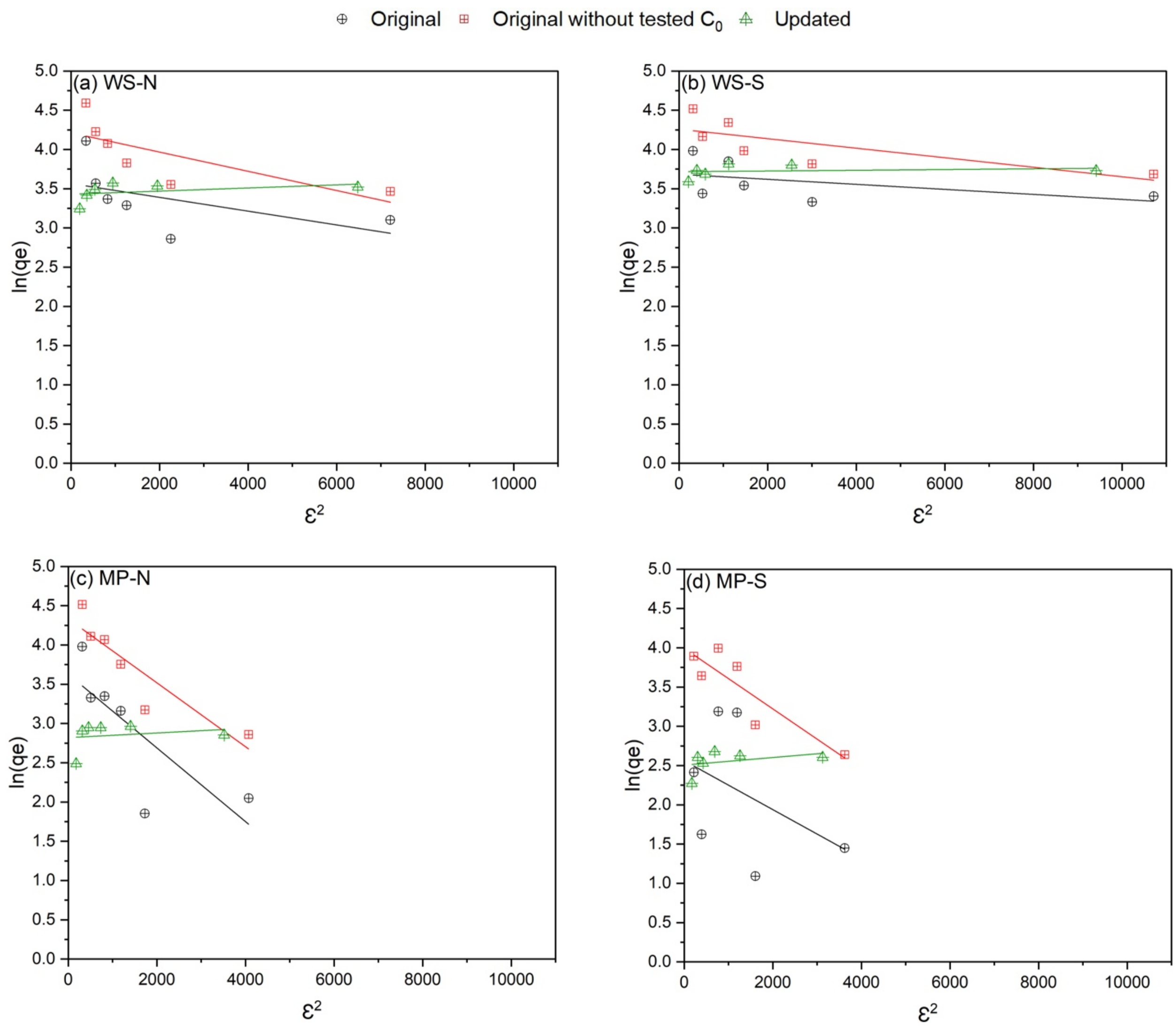

Figure 4. Adsorption isotherm of Cd on (a) non-activated wheat straw biochar (WS-N), (b) steam activated wheat straw biochar (WS-S), (c) non-activated manure pellet biochar (MP-N), and (d) steam activated manure pellet biochar (MP-S) fitted by the Dubinin-Radushkevich (D-R) model.

3.2. Possible reasons for abnormal data

The main problems of the original data are inconsistent C_{01} and C_{e1} values among replicates and generally lower C_0 values than expected. The poor model fitting also reflects the abnormality of the original data. These problems are consistent with the dilution error stated by the ICP lab. The adsorption experiment was replicated five times, but the replicates of the same concentration levels were analyzed followed by each other. Since there were no patterns in the Cd concentrations regarding replicates while having less precision at high concentration levels, the major source of error would be the ICP analysis rather than the adsorption experiment. Since the initial concentrations were approximately known, C_{01} values can help identify possible sources of error. The generally lower C_0 values than expected may indicate lower C_e values than the actual value since the samples with and without biochar were analyzed together. One possible cause of the generally lower results is that the chosen dilution factor was too high. Higher dilution factor would introduce more sources of error.

The ICP analysis for the updated data did not use dilution, so Cd concentrations were more consistent among the replicates without dilution errors, which further explains that the fluctuation of Cd concentration among the replicates in the original data were mainly caused by dilution errors. The main problem of the updated data was the abnormal trend in the adsorption isotherms and not being able to fit the adsorption models. The precision of the updated data may be better than the original data, but accuracy of the updated data may not be high. Based on a standard test method of ICP analysis, Method 200.7 released by United States Environmental Protection Agency (USEPA, 1994, p. 7), linear dynamic range is “the concentration range over which the instrument response to an analyte is linear.” Any analyte that has a concentration greater than 90 % of the linear range must be diluted and reanalyzed (USEPA, 1994). The ICP lab stated that they established a linear range up to 200 mg/L, but some samples at high concentration levels may have exceeded 90 % of 200 mg/L. Therefore, the upper limit of the established linear range may not be high enough for the samples, which may be a possible source of error.

However, establishing a higher linear dynamic range may not solve the problem. Although the linear working range of ICP-OES may be wide, the concentration of 200 mg Cd/L is too high for the instrument to obtain an accurate result. In Method 200.7 (USEPA, 1994), the dilution test is recommended for quality control for samples with high analyte concentrations, which are ≥50 times higher than the detection limit of the ICP instrument while <90 % of the upper detection limit determined by the established linear range. Approximately ±10 % of the determined concentration is the acceptable range after dilution with a factor of 5, or the results may be inaccurate due to chemical or physical interference effect (USEPA, 1994). This indicates that accuracy was negatively impacted when the concentrations in the analytes were too high from the detection limit and may fail the dilution test while the dilution test might not be properly conducted to determine if the high sample concentrations had influence on the results.

Normally, the linear dynamic range would be built up to three to five orders of magnitude above the detection limit to get accurate results (Boumans, 1979, p. 352). The detection limit of the ICP-OES instrument at the ICP lab is 0.3 µg/L, so the upper limit of the linear dynamic range needs to be lower than 30 mg/L for accuracy, which is much lower than 200 mg/L. Therefore, building a lower linear dynamic range and dilution were recommended for the analysis. Although the ICP lab stated that the R^2 from the linear dynamic range up to 200 mg/L was high, the high R^2 for a wide linear dynamic range may not indicate precise or accurate measurements across the whole linear range (PerkimElmer, n.d.).

Quality control may also affect results. The concentrations from the 20 sample data were 4-12 % (average = 8 %) lower than the corresponding sample concentrations of the updated data. Method 200.7 states that the difference between the mean concentrations of three analyses for a quality control sample and its stated concentration need to be less than ±5 % (USEPA, 1994). This indicates that multiple analyses for the same sample need to provide consistent results. There were only two analyses (updated and 20 sample) for the same samples using the same method, and their differences were greater than ±5 %, which still shows possible poor results for the ICP analyses. If not, other possible reasons of the inconsistent results would be that the ICP instrument does not have stable performance.

3.3. Things to consider before and after sending samples to an ICP laboratory

Since different ICP instruments may be suitable for testing samples with different concentration levels, it would be important to ask the ICP laboratory what the concentration range of the samples that they usually test for is, the lower detection limit, and the linear working range of the ICP instrument. At the same time, the ICP laboratory should be told the concentration range of the samples and asked what the procedure of quality control and analysis of the samples with this concentration range will be. If dilution is needed, and the dilution factor needed will be very high, dilution may be a big source of error. The laboratory should be asked what the linear range that they will build for the concentration range of the samples will be. It will be helpful if the ICP laboratory can provide the graph of the linear range that they built for the samples, which helps determine the accuracy of the results. There are some parameters in the raw data from the ICP instrument like relative standard deviation can help determine if the results are reliable, so ask the ICP laboratory if they are willing to provide the raw data.

4. Conclusions

Both the original and updated data were abnormal and generally could not fit adsorption isotherm models. The original data was not accurate or precise possibly due to dilution errors with high dilution factors. The updated data were precise but not accurate probably due to the much higher analyte concentrations of the samples than the detection limit, so dilution was recommended. Dilution is recommended when the analyte concentrations are much higher than the detection limit. Sending high concentration samples to an ICP laboratory that has an ICP instrument with higher detection limit would be more suitable so that the laboratory could use a lower dilution factor to limit the sources of error.

III: BIOCHAR SELECTION FOR WASTEWATER TREATMENT BASED ON BIOCHAR CADMIUM OR LEAD ADSORPTION IN AQUEOUS SOLUTIONS: A CRITICAL ANALYSIS

1. Introduction

1.1. Wastewater definitions

Wastewater refers to used water, and its various terms differ within and among jurisdictions. Wastewater is a general term, defined as “spent or used water from a home, community, farm, or industry that contains dissolved or suspended matter” by the United States Environmental Protection Agency (USEPA, 1997). Effluent is a general term for any treated and untreated wastewater “that flows out of a treatment plant, sewer, or industrial outfall; generally “wastes discharged into surface water” (USEPA, 1997). Bow River Basin Council (2002) includes municipalities, industries, or agricultural operations” as sources of effluent. Therefore, effluent basically can refer to released treated and untreated wastewater from any operation. Discharge is a type of effluent that is released into the environment (Office of Legislative Counsel, Ministry of Attorney General, Victoria, BC, 2012). USEPA (1997) defines sewage as the “waste and wastewater produced by residential and commercial sources and discharged to sewers”, while North American Lake Management Society (n.d.) includes industrial establishments as another source of sewage. Alberta Municipal Affairs (2000) defines sewage as human excreta, or water carried wastes from drinking, bathing, laundering, or food processing, which is closer to the definition of domestic wastewater, blackwater, and greywater in Quebec, Canada (Gouvernement du Québec, 2021). In California, United States, domestic wastewater is similar to municipal water, although domestic wastewater does not include industrial wastewater (California Department of Water Resources, 2021). Sewage is usually a part of municipal wastewater which includes wastewater from households, commercial establishments, and industries (USEPA, 1997).

Industrial wastewater (e.g., coal mining, diary, textile wastewaters) may be a part of municipal wastewater and can sometimes be similar to commercial wastewater (e.g., restaurant, hair salon, commercial kennels wastewaters) (Florida Department of Environmental Protection, 2021). For example, wastewater from a commercial laundry with more than four washing machines is considered industrial wastewater in Florida, United States (Florida Department of Environmental Protection, 2021). Process wastewater (or process water) is usually produced during the production or treatment of some product or material, and is mostly related to industrial wastewater. It is defined as “any water that comes into contact with any raw material, product, byproduct, or waste” (USEPA, 1997). Process affected water is mostly used in the phrase oil sands process-affected water, which is interchangeable with oil sands process water, referring to contaminated water produced during bitumen extraction (McQueen et al., 2017).

1.2. Concerning pollutants

Industrial effluent guidelines exist for a wide range of industries (59 in total), including battery manufacturing, seafood processing, coal mining, landfills, paint formulating, petroleum refining, and textile mills. (USEPA, 2020). The constituents in industrial wastewater vary greatly by sources, and the main pollutants are usually heavy metals and organic pollutants (Xiang et al., 2020). Some heavy metals of concern are cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), arsenic (As), lead (Pb), and zinc (Zn) (Barakat, 2011). For example, ore mining industries usually produce wastewaters with high heavy metal content. Organic pollutants such as dyes (e.g., methylene blue) from industries such as textile, leather, plastic, and paper are also of commonly concern (Han et al., 2009; Rafatullah et al., 2010).

In textile wastewater, there are many other pollutants besides organic and inorganic dyes. Some examples are inorganic pollutants (e.g., chlorin, sulfate, phosphate), pesticides, organochlorines, organophosphates, cotton waxes, and dirtiness in raw wool (e.g., wax or grease, urine, feces, vegetable material) (Correia et al., 1994). Pulp and paper mill wastewater contains various toxic contaminants such as fatty acids, resin, organochlorine compounds, volatile organic compounds, and inorganic dyes (Pokhrel and Viraraghavan, 2004). Food processing, leather, petroleum refining, and textile industries usually have both high salinity and organic pollutants (Lefebvre et al., 2006; Holkar et al., 2016). The organic pollutants such as oil in oil spills and oil contaminated industrial water also need to be removed from wastewater (Wang et al., 2015). In pharmaceutical wastewater, analgesics drugs, antidepressants, antiepileptics, and antibiotics are pollutants of concern (Rivera-Utrilla et al., 2013). Industrial wastewaters cover a huge variety of organic and inorganic pollutants, and the constituents depend on the type of industries.

In Canada, municipal wastewater effluents are the largest single effluent discharges by volume (Government of Canada, 2014), and municipal wastewater is one of the largest sources of pollution to surface water in Canada (Government of Canada, 2020a). Municipal wastewater includes industrial water, sanitary sewage, and other used waters from the community with and without surface runoff and stormwater (Government of Canada, 2020a). Some pollutants in stormwater runoff in urban areas are heavy metals (e.g., Zn, Cu, Pb, Cd), nutrients (e.g., phosphate, ammonium), and hydrocarbons (e.g., polycyclic aromatic hydrocarbons, mineral oil hydrocarbons) (Göbel et al., 2007). There are various contaminants in municipal wastewater, including human and other organic waste, nutrients, pathogens, microorganisms, suspended solids, and household and industrial chemicals (Government of Canada, 2020a). Municipal wastewater can contain high heavy metal contents. One sample in China contained 160±100 μg Pb/L and 170±64 μg Cr/L (Du et al., 2020), and one in India contained 130.1 mg lead/L and 861 mg zinc/L (Rekhate et al., 2021). Besides contaminants such as suspended solids and organic matter and nutrients that are normally targeted to be removed from municipal wastewater, some emerging contaminants such as antibiotics, pharmaceuticals, personal care products, hormones, and artificial sweeteners are gaining more attention (Tran et al., 2018). These emerging contaminants widely exist in water bodies in the environment mainly caused by municipal discharge that still contains them after treatment (Petrie et al., 2015).

Typical pollutants in agricultural wastewater are organic load, nitrogen, phosphate, total solid, fats, oil, grease, and pathogens (Kataki et al., 2021). For example, fertilizers, decomposed crop residues, and diaries are sources of nutrients in agricultural runoff and wastewater (Government of Canada, 2020b). Pesticides, herbicides, and veterinary drugs are concerning sources of contaminants in agricultural wastewater since they contain toxic organic pollutants and/or heavy metals (Dias et al., 2015).

1.3. Heavy metal removal treatments

Chemical precipitation is the most widely used technique to remove heavy metals from industrial wastewater because it is a relatively simple and inexpensive method (Ku & Jung, 2001; Fu & Wang, 2011). Hydroxide precipitation is the most widely used method in chemical precipitation (Huisman et al., 2006). Sulfide precipitation is also effective, forming metal sulfide precipitates that are much less soluble than metal hydroxide precipitates (Fu & Wang, 2011). For wastewaters with a heavy metal concentration above 1000 mg/L, limestone can be used as an economic, simple, and effective treatment to precipitate the contaminants (Barakat, 2011). Filtration or sedimentation following chemical precipitation is used to separate the precipitates from wastewaters (Fu & Wang, 2011). Chelating precipitation is an alternative especially for treating wastewater with “coordinate agents” (Fu & Wang, 2011). Ion exchange is a widely used and highly efficient treatment for heavy metal contaminated wastewater, using ion exchange resin that can exchange its cations with the metal ions in wastewater (Fu & Wang, 2011).

Adsorption is also considered to be an effective and economic method for treating heavy metal contaminated wastewater, and activated carbon adsorbents are the most commonly used although they are relatively expensive method (Fu & Wang, 2011). Flotation, including ion flotation and precipitation flotation, are also used for heavy metal removal from wastewater through bubble attachment and those methods have high metal selectivity (Fu & Wang, 2011). Some other widely studied adsorbents are nano sized metal oxides, biochar, chitosan and chitosan composites, zeolite, xanthate, dead biomass, and several others (Bailey et al., 1999; Ngah et al., 2011; Mohan et al., 2014). Membrane filtration can remove inorganic pollutants such as heavy metals, suspended solids, and organic compounds (Barakat, 2011). For heavy metal removal, different types of membrane filtration such as ultrafiltration, nanofiltration, reverse osmosis, and electrodialysis can be used (Fu & Wang, 2011; Barakat, 2011). Electrochemical technologies (e.g., electrodeposition, electrocoagulation, electroflotation) use electricity to treat wastewater (Chen, 2004). For example, electrocoagulation has been used to treat wastewater containing suspended solids, oil and grease, and even organic or inorganic pollutants that can be flocculated, and electroflotation is majorly used in the mining industry for mineral recovery with increasing application in treating wastewater (Chen, 2004).

1.4. Organic pollutants removal treatments

Biological wastewater treatment (or conventional method) is a simple and inexpensive treatment with aerobic and anaerobic biodegradation by microorganisms (Roy & Saha, 2021). Chemical treatments, such as oxidation and ozonation, can also be used for treating organic pollutants (Roy & Saha, 2021). There are organic pollutants that are persistent and/or nondegradable in conventional wastewater treatment systems (Martínez-Huitle & Brillas, 2009; Aksu, 2005), which need other types of treatments. Some current physical and chemical treatments for organic pollutant removal are adsorption, coagulation flocculation, ion exchange, and membrane filtration, but one potential problem is dealing with the solid wastes that contain pollutants from the wastewater since the organic toxics are not destroyed (Padmanabhan et al., 2006; Roy & Saha, 2021). Research shows that electrochemical methods using iron or aluminum electrodes can be used to degrade dyes and phenols (Martínez-Huitle & Brillas, 2009; Busca et al., 2008). Photocatalytic wastewater treatment is another advanced oxidation technology that has been widely studied for degrading organic pollutants and microorganism into simple molecules (e.g., carbon dioxide & water) (Chong et al., 2010; Padmanabhan et al., 2006).

1.5. Limitations of existing wastewater treatments

Chemical precipitation does not work effectively for all heavy metals at all pH, especially when the wastewater has high acid content (Zhao et al., 2016; Shrestha et al., 2021). The change in pH during the treatment may increase the dissolved concentration of another metal, and heavy metal precipitation may be reduced with the presence of complexing agents (e.g., EDTA) (Lin et al., 1998; Zhao et al., 2016). There are also difficulties in separating small precipitate particles from water, especially in sulfide precipitation that produces colloidal precipitates (Lewis et al., 2010; Zhao et al., 2016). Therefore, chemical precipitation is not suitable for treating large volumes of wastewater with low heavy metal concentrations and complex constituents (Zhao et al., 2016; Shrestha et al., 2021; Dąbrowski et al., 2004). Although chemical precipitation is an inexpensive treatment, the disposal of the wet sludge at the end of the treatment can be expensive (Shrestha et al., 2021).

It is expensive to apply ion exchange on a large scale because ion exchange resin requires chemical regeneration that may simultaneously generate secondary pollution (Fu & Wang, 2011). Electrochemical technologies are sometimes necessary for treating persistent pollutants and are relatively effective and environmentally friendly, but their expensiveness prevents them from being widely used (Azimi et al., 2017). Flotation is also effective but costly to operate and maintain (Fu & Wang, 2011).

Wastewater needs to be treated by removing potential membrane foulants (e.g., suspended solids) before entering a direct membrane filtration system (Hube et al., 2020), and membrane fouling is a potential problem that prevents membrane filtration from being widely used (Fu & Wang, 2011). The low permeate flux and costly and complex process also has its limitations (Fu & Wang, 2011).

Coagulation-flocculation is mainly used to remove suspended solids and hydrophobic colloids in wastewater treatment and does not work for all types of pollutants (e.g., heavy metals and highly water-soluble dyes) (Fu & Wang, 2011; Hao et al., 2000). It can produce large volume of sludge that is difficult to dispose (Fu & Wang, 2011).

Adsorption may not be the appropriate treatment for removal of organic pollutants since the toxic organic pollutants are not degraded and/or destroyed. Potentially, adsorption can be used as a low cost treatment for removing the low concentration heavy metals in wastewaters to fill the gap left by chemical precipitation that is only suitable for wastewaters with high heavy metal concentrations. The effectiveness of adsorption depends on adsorbents (Fu & Wang, 2011), and biochar has been considered a low cost and efficient adsorbent for heavy metal removal. Cadmium (Cd) and lead (Pb) are concerning pollutants with high toxicity and bioaccumulation (Liu et al., 2020; Sud et al., 2008), and their adsorption is the most widely studied among the bivalent heavy metal pollutants (Li et al., 2017). Therefore, this study is intended to provide suggestions about biochar selection for wastewater treatment of wastewaters with low heavy metal contamination based on the literature about Cd or Pb adsorption by biochar.

2. Materials And Methods

2.1. Data collection and selection

Articles about biochar adsorption in Cd or Pb solutions up to September 21, 2021 (data analysis started on September 22, 2021) were sourced using the Scopus database. The search terms used for data collection included: (TITLE-ABS-KEY (biochar) AND TITLE-ABS-KEY (adsorption OR sorption OR wastewater OR "waste water" OR effluent OR "process water") AND TITLE-ABS-KEY (cadmium OR lead OR cd OR pb) AND NOT TITLE-ABS-KEY (review OR soil))

This study focused on biochar selection for wastewater with low heavy metal concentrations. Therefore, the following concentration range for data collection aimed to include lower concentrations and exclude higher concentrations while still having adequate data points for data analysis. The selected concentration ranges kept the numbers of the selected Cd and Pb articles almost equivalent. Studies with batch adsorption experiments using Cd concentration ranges with lower limits of <50 mg/L and higher limits of 75-999.99 mg/L were included. Studies with batch adsorption experiments using Pb concentration ranges with lower limits of ≤50 mg/L and higher limits of 100-999.99 mg/L were included. Articles were selected that used Langmuir and/or Freundlich models, which are the most commonly used models in such studies, to construct the biochar adsorption isotherms. The equations of the two models were listed in Section 2. This study excluded composites (e.g., magnetic biochar, metal oxides modified and/or loaded biochar), organic modified (amino modified, chitosan coated, alginate modified, thiolated), and nitrogen doped biochars. As a result, this study covers 72 articles about Cd adsorption by biochar and 74 articles about Pb adsorption by biochar.

Adsorption model parameters (e.g., maximum capacity (Qmax) of Langmuir model and 1/n of Freundlich model), biochar production conditions (e.g., highest pyrolysis temperature), and biochar properties (e.g., surface area, total pore volume, average pore size, biochar pH, elemental composition) were collected from the articles.

2.2. Data analyses

Simple linear regression was used to analyze data since simple linear regression mainly shows the general trend of how one parameter would affect another, which aligns with the objective of this study. lm() was used to fit simple linear regression model using the collected parameters through RStudio 2021.09.0 (RStudio, PBC, Boston, MA, USA).

3. Results And Discussion

The Cd articles used 0.05-30 mg/L as the lower limit and 75-400 mg/L as the higher limit for adsorption isotherm experiments; the Pb articles used 0.005-50 mg/L as the lower limit and 100-800 mg/L as the higher limit for adsorption isotherm experiments. The range of Cd Qmax was 0-175.44 mg/g, and the range of Pb Qmax was 0.7-558.88 mg/g.

By comparing the correlation coefficients of Langmuir and Freundlich model fitting, 128 of the Cd treatments fit the Langmuir model better than the Freundlich model, and 37 of the Cd treatments fit the Freundlich model better than the Langmuir model. Of the Pb treatments, 117 fit the Langmuir model better than the Freundlich model, and 49 fit the Freundlich model better than the Langmuir model. This result indicates that most of the Cd and Pb adsorption by biochar studies were better described as monolayer adsorption onto a homogenous surface, and the adsorbed molecules do not interact with each other (Jin et al., 2014). Among Cd treatment, only 2 of the 1/n values were greater than 1, which means Cd adsorption onto the biochars were mostly favourable. Among Pb treatments, 128 of the 1/n values were smaller than 1, and 43 of the 1/n values were greater than 1. More unfavourable adsorptions occurred among Pb adsorption than Cd adsorption.

By analyzing the data from the Cd articles using simple linear regression, the p-values of the linear regression between three of the biochar parameters and Qmax are significant, respectively (Table 1). Biochars with higher total pore volume, pyrolysis temperature, and pH would tend to have higher Cd Qmax based on their significant linear regression. Since multiple factors would affect Cd Qmax simultaneously, the results are giving general suggestions about biochar selections for treating Cd containing wastewaters.

The relationship of total pore volume and Qmax for Cd has the most significant p-value of 0.001 with a positive slope. This result suggests that higher total pore volume would support a higher Cd Qmax. Higher total pore volume provides more binding sites and channels for pollutants to interact with biochar (Chen et al., 2018; Tan et al., 2021). Therefore, a high total pore volume is the most straightforward way to predict a high Cd adsorption capacity while selecting biochar.

High surface area is usually considered a key factor of high adsorption capacity while it does not have significant linear regression with Cd Qmax. Sun et al. (2014) also found that surface area does not have a strong relationship with Cd adsorption, indicating factors other than surface area are affecting Cd adsorption. One possible reason is that surface area does not directly reflect pore size/volume. If the high surface area is mostly given by pores that are too small to trap Cd molecules, a higher surface area would not lead to a higher Qmax for Cd.

Table 1. Simple linear regression between biochar parameters and Qmax for Cd.

Biochar Parameters	Range	p-Value	Slope
Highest pyrolysis temperature	300-1000 ^oC	0.010	Positive
Biochar pH	2.42-12.36	0.040	Positive
Surface area	0.004-1467 m^2/g	0.260	Negative
	0.004-471.67 m^2/g [a]	0.464	Negative
Total pore volume	0.001-1.312 cm^3/g	0.001	Positive
Average pore size	1.37-270 nm	0.360	Positive
	1.37-38.34 nm [b]	0.950	Negative
Ash content	2.4-85.1%	0.082	Positive
Atomic ratio of oxygen:carbon	0.0-8.3	0.001	Positive
	0.0-1.5 [c]	0.781	Positive
Atomic ratio of hydrogen:carbon	0-4.6	0.007	Positive
	0-1.7 [d]	0.605	Positive

[a] Range excludes three points with extremely high surface areas (745, 1120, and 1467 m^2/g).
[b] Range excludes one point with an extremely high average pore size value (270 nm).
[c] Range excludes three points with extremely high atomic ratios of the oxygen:carbon (3.0, 4.7, and 8.3).
[d] Range excludes two points with extremely high atomic ratios of hydrogen:carbon (3.1 and 4.6).

The relationship between the highest pyrolysis temperature and Qmax for Cd has the second significant p-value of 0.010, and the slope is positive. The result indicates that a greater highest pyrolysis temperature generally leads to a higher Qmax for Cd. A possible reason is related to the increased surface area and pore volume by a higher pyrolysis temperature. Among all the Cd and Pb articles covered by this study, the highest pyrolysis temperature has a significant relationship with both surface area (p-value = 1.69E-05) and total pore volume (p-value = 0.032) with positive slopes. Generally, a higher pyrolysis temperature would result in a higher surface area and total pore volume, which may lead to a higher adsorption capacity (Ahmad et al., 2014). It should also be noted that a high pyrolysis temperature can cause pore structure collapse or blockage (Li et al., 2017), which may negatively impact adsorption capacity. Higher pyrolysis temperatures usually lead to a lower yield and a higher energy cost, which may increase the production cost of biochar.

Biochars with a higher pH tend to have a higher Cd Qmax based on the significant linear regression. Among the articles covered within this study, the highest pyrolysis temperature had a significant linear regression with biochar pH (p-value = 7.60E-05) with a positive slope. Higher pyrolysis temperature may produce higher ash content, which would then contribute to a high biochar pH (Li et al., 2017). Ash content may increase pH buffer capacity of biochar and therefore support local surface precipitation of Cd (e.g., cadmium hydroxide) (Chen, et al., 2015). Higher biochar pH would induce deprotonation of surface charges, forming negative charges on the biochar surfaces, so electrostatic attraction of Cd is enhanced (Yuan et al., 2020).

By analyzing the Pb data using simple linear regression, the p-value of the linear regression between ash content of and Qmax for Pb is significant (Table 2). Ash content is highly influenced by pyrolysis temperature, pyrolysis atmosphere, and feedstock type (Ahmed et al., 2016; Xiang et al., 2022; Mukome et al., 2013). High ash content would lead to a low surface area (p-value = 0.012), which is in agreement with Li et al. (2022) and Xiao et al. (2022). Many of the Pb articles reported overly high ash contents (37 % of the reported ash content values are over 50 %), which may not be desirable in actual application due to low yield of the carbonized structure. Therefore, the significant linear regression between ash content and Qmax for Pb in this study may not provide very good suggestions for biochar selection for a wastewater treatment application.

Table 2. Simple linear regression between biochar parameters and Qmax for Pb.

Biochar parameters	Range	p-value	Slope
Highest pyrolysis temperature	250-1000 ^{o}C	0.742	Negative
Biochar pH	2.12-12.88	0.545	Positive
Surface area	0.21-1099 m^2/g	0.645	Positive
Total pore volume	0.00016-2.28 cm^3/g [a]	0.125	Positive
Average pore size	1.22-65.01 nm	0.337	Negative
Ash content	0.8-97.7%	0.048	Negative
Atomic ratio of oxygen:carbon	0.0-1.3	1.41E-05	Positive
	0.0-0.1 [b]	0.052	Positive
Atomic ratio of hydrogen:carbon	0.0-0.1	0.130	Positive

[a] This range excludes two points with extremely high total pore volumes (63 cm^3/g and 54,000 cm^3/g).
[b] This range excludes two points with extremely high atomic ratios of oxygen:carbon (0.7 and 1.3).

The linear relationship between atomic ratio of the ratio of oxygen:carbon and the Qmax for Pb is close to significant with a positive slope. A higher atomic ratio of oxygen:carbon indicates higher surface polarity and higher abundance of oxygen containing functional groups (Li et al., 2020; Chen et al., 2018). Complexation with oxygen containing functional groups, such as carboxyl (–COOH) and hydroxyl (–OH) groups, significantly contribute to Pb adsorption onto the biochar (Liu et al., 2020). The non-significant p-values indicate that multiple factors contribute to Pb adsorption, while this study did not find obvious patterns of the relationship between biochar characteristics and Qmax for Pb.

4. Conclusions

This study reviewed research articles about biochar adsorption in Cd or Pb contaminated solutions and explored relationships between biochar characteristics and adsorption capacity among the covered articles. The reviewed articles had various biochar characteristics, levels of pollutant concentration, and operation conditions. Although this study did not find good predictors for Pb adsorption capacity, total pore volume, the highest pyrolysis temperature, and biochar pH would be three potential predictors for Cd adsorption capacity for wastewater remediation. In wastewater remediation, pyrolysis condition, feedstock type, yield, operation condition, and adsorption efficiency should all be considered to evaluate the cost-effectiveness. Since the operation condition in wastewater remediation would be greatly different form laboratory condition, biochar adsorption under industrial conditions needs to be further researched.

IV: RESEARCH SYNTHESIS

1. Research Summary

The objective of the adsorption experiment was to investigate cadmium (Cd) adsorption characteristics by non-activated and steam activated biochars which had good lead (Pb) adsorption performance in a previous study (Kwak et al., 2019) of the same laboratory. The Cd adsorption isotherms of non-activated manure pellets and wheat straw biochars were investigated through a batch adsorption experiment in solutions of different Cd levels. The adsorption isotherms did not fit the adsorption models (Langmuir model, Freundlich model, Sips model, Dubinin-Radushkevich model), which was unexpected. Some possible reasons of the unexpected fitting were dilution errors, improper linear dynamic range, improper quality control, and unstable performance of the ICP instrument.

The objective of the critical analysis was to provide suggestions about biochar selection for Cd or Pb removal from wastewater through analyzing data from the literature. Data from the literature about biochar adsorption in Cd or Pb solutions between 2011 and 2021 were collected and reanalyzed. Biochar parameters (e.g., highest pyrolysis temperature, biochar pH, surface area, total pore volume, average pore size, ash content, atomic ratio of oxygen:carbon, atomic ratio of hydrogen:carbon) and adsorption model parameters (e.g., Qmax of Langmuir model and 1/n of Freundlich model) were collected from the research articles. The significant simple linear regressions between biochar parameters and Qmax were used to make suggestions about biochar selection for wastewater treatment. Total pore volume, highest pyrolysis temperature, and biochar pH showed significant linear regression with Cd Qmax with positive slopes, which suggests that biochars with higher values of these three parameters tends to have higher Cd adsorption capacity and to be better for Cd removal from wastewater. Although ash content showed significant linear regression with Pb Qmax, the overly high ash content reported in many of the Pb articles would not be desired in wastewater treatment application. Therefore, the significant linear regression between ash content and Pb Qmax would not make good suggestion about Pb removal from wastewater. Therefore, no good predictor for Pb adsorption capacity was discovered in this study.

2. Research Limitations

Understanding of the results from the adsorption experiment was limited since this study mainly focused on model fitting of the adsorption isotherms. Many analyses conducted before and/or after adsorption would help to further investigate the adsorption process. For example, the change in surface functional groups can be tested by Fourier-transform infrared spectroscopy (FTIR) (Kwak et al., 2019); precipitates can be identified by X-ray diffraction (XRD) (Lee et al., 2022); pore and/or precipitate size distribution can be discovered through Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS) (Hao et al., 2021); surface complexation and precipitation can be explored by X-ray photoelectron spectroscopy (XPS) (Lee et al., 2022); solution pH measurements can be used to describe the adsorption condition. Lack of such analyses would restrict understanding of the adsorption mechanism and potential factors influencing the results.

The critical analysis that was done for this research is limited by the type of parameters that were available to collect from the published research articles. Most articles only reported a few biochar characteristics, depending on their research purposes or funding and/or time availability. The biochar characteristics reported within some of the articles may not overlap with what other articles reported. For example, a few of the articles reported micropore volume, and these articles might not report elemental composition such as phosphorous content, which were reported in a few of other articles. Therefore, there were not enough data points of such parameters (e.g., micropore volume and phosphorus content) in the covered research articles to draw a meaningful conclusion in this study.

Many of the research articles that were reviewed did not describe operation conditions in detail, and different operation conditions among the research articles were not studied in this research. For example, biochar dosage, initial solution pH, and solution temperature would influence adsorption performance (Navarathna et al., 2019; You et al., 2019). The operation conditions of biochar adsorption on a laboratory scale can be greatly different from the operation conditions on an industrial scale. Research about biochar adsorption on an industrial scale is still quite limited, so this study did not account for the effect of the operation conditions while analyzing data or making suggestions.

The methods that are used for biochar production are developing quite rapidly, and thus engineered biochars are viable emerging options for different environmental remediation purposes. This study did not cover composite biochars (e.g., magnetic biochar, metal oxides modified, loaded biochar), organic modified biochars (amino modified, chitosan coated, alginate modified, thiolated), or nitrogen doped biochars. There are only a few of published articles about Cd and/or Pb adsorption by each type of engineered biochars, so this study excluded these biochars as well.

3. Research Applications

Biochar is considered as a potential material for treating wastewater with low Cd and/or Pb contamination. There is huge amount of wastewater with low Cd and/or Pb contamination, such as oil sands process affected water, municipal wastewater, pulp and paper wastewater, and textile wastewater (Aprianti et al., 2019; Halimoon et al., 2010). Since there are numerous types of biochars, those that are more efficient at remediating wastewater with low Cd or Pb contamination need to be selected from the various options.

The predictors of high Cd adsorption capacity identified in the study can help in the quick selection of appropriate biochar for Cd removal from wastewater. After narrowing down the biochar choices based on the predictors, further tests can be conducted to evaluate the adsorption performance and decide on the final biochar selection. The predictors may guide the production of customized biochar for environmental remediation purposes. Although this study did not identify good predictors for Pb removal by biochar, it implied that the biochar characteristics suitable for one contaminant may not be effective for other contaminants. Biochar selection should be adjusted based on target contaminant.

4. Future Research

Future research about biochar adsorption needs to report as many biochar characteristics as possible so that biochar selection for wastewater treatment would be easier. In wastewater treatment application, operation conditions such as biochar dosage, solution pH, temperature, co-existence of contaminants, and how wastewater flows through biochar would significantly influence adsorption isotherm and kinetics. Future research needs to consider these parameters in experimental design and have experiments on both laboratory scale and industrial scales to better investigate the biochar adsorption performance in wastewater treatment application. Future research can also explore more engineering biochars that aim at certain contaminants or certain environmental remediation scenario.

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