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Lead Adsorption onto Clay Soil Treated with Sugarcane Organic Waste Biochar

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Authors' contributions

This work was carried out in collaboration between both authors. Authors AAAS and AAMA designed the research work and performed the experiment, analyzed the data and wrote the first draft of the manuscript. Both authors read and approved the final manuscript.

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ABSTRACT

This work aims to maximize the utilization of sugar cane cultivation and manufacture waste in Aswan Governorate, Egypt and turn it into biochar, which can be used to clean the environment from dangerous metals. Sugarcane organic wastes (filter cake, bagasse and sphere) biochars as waste bio-adsorbent materials were obtained using the pyrolysis at 350 and 700°C and 90 min residence time under limited oxygen conditions. Two batch trails were conducted to study the effects of biochar pH and shaking time on the adsorption of Pb ion from solution in precedence of soil and biochar. Models to study the kinetics of the adsorption process as pseudo-first-order and pseudo-second-order models were used.The results showed that the absorbed or precipitated (at high suspension pH) amount of Pb decreased in the order: soil treated with biochar bagasse pyrolysis at 350°C (BB350) > soil treated with biochar sphere pyrolysis at 350°C (SB350) > soil treated with biochar filter cake pyrolysis at 350°C (FB350) > soil only. At pH 9 maximum amounts of Pb of 1.794, 1.706 and 1.688 mg/g were adsorbed or precipitated on the soil treated with BB350, SB350 and FB350 respectively. However, Pb was maximum adsorbed or precipitated (1.33 mg/g) on the soil only at pH 8. The highest removal efficiency of Pb^{2+} from the solution was85% with treated the soil with SB350 while the lowest one was 55.5% occurred with the soil that was not

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treated with biochar at a shaking time of 80 minutes. The adsorption of Pb^{2+} by the soil in presence or absence biochars different fitted the pseudo second order kinetic model for all tested treatments (R^2 ranged from 0.9901 for the soil treated with BB350 to 0.9994 for that treated with SB350).

Keywords: Adsorption kinetics; lead; pyrolysis; sugar cane wastes biochar.

1. INTRODUCTION

Water pollution caused by heavy metals as lead poses a big threat worldwide with cumulative and detrimental effects on the environment and human health [1]. Toxic elements such as lead (Pb), cadmium (Cd), chromium (Cr) and leckel (Ni) are classified as heavy metals and associated with water pollution. From these heavy metals, Pb is one of the most hazards to humans and may be found in high concentrations in industrial liquid wastes [2]. Lead enters the human body through water and food chains, leading to symptoms of the respiratory system, digestive system, nervous system, blood, urinary system, acute or chronic poisoning, and even death [3].

Heavy metal pollutions in wastewater and soils have become an urgent environmental concern and a big challenge for repair efforts [4]. Lead can be inserted to the soil body from many manufacturers ranging from ammunition industries to batteries [5]. It is considered a public health toxic when used in drinking water, even at low concentrations due to maybe bio-accumulation [6,7].

The adsorption of heavy metal ions as a Pb into solid materials has been shown to be useful in treating polluted water because of its simplicity and making it often the economical solution Cao et al., [8]. Organic matter as biochar may negatively or positively affect the availability of heavy metals such because of the formation of heavy metal complexes in soils. The adsorption is one of the most important chemical reactions that can affect the availability of heavy metals as Pb in soils.

Biochar is a carbon rich solid produced by low temperature pyrolysis (less than 700°C) from organic wastes under hypoxic or anaerobic conditions. It is a common environmentally friendly modified organic solid to enhance soil adsorption performance and it has good application prospects Zhou et al. [9]. A many functional groups of biochar are important in heavy metals adsorption as a good porous structure and surface oxygen Bian et al. [10]. The adsorption of heavy metals such as Pbincreases on the soil biochar complex because of an increase in the absorbent sites of heavy metals provided by biochar Qi et al. [11] Zhou et al. [12]. Adding biochar could ameliorate the adsorption capacity of degraded soils and reduce pollutants mobility. Biochar is an active remediation substance for polluted soils with heavy metals as Pb. It can improve the mineral retention ability in the soil due to an effective absorbent for heavy metals. Its ability for lead adsorption is mainly due to the mechanisms (cation exchange, electrostatic reactions, precipitation, and complexity) governed by the big surface area, porosity, active surface functional groups, and biochar elements contents Li et al. [13] Liang et al. [14,15]. Moreover, the ability of biochar to adsorb heavy metals as lead depends mainly on the type of the feedstock and the pyrolysis temperature Mukherjee et al. [16] and Luo et al. [17]. Biochar is a good organic matter used to increase the immobilization of heavy metals through in polluted soils and wastewater due to the electrostatic and non-electrostatic forces Xu and Zhao, [18,19]. It has adsorption capacity for heavy metals because of its increased negative surface charge and surface area Gan et al. [20] and Saleh et al. [21].

A many of researches have described the impact of the agricultural waste organic on the biochar absorption ability, especially for heavy metals as Pb. High differences in the adsorption ability of Pb were reported between different types of biochars Xu et al. [18,19]. The pyrolysis temperature greatly influences on the pore size distribution, elementary composition, functional groups, and the pH of biochar Yuan et al. [22], and thus, its the ability to adsorb heavy metals from liquid solutions and their mobility in the soil Melo et al. [23]. Kinetic models provide direct information on the rate of reaction or diffusion. A greater diffusion or reaction rate constant indicates adsorption is faster of adsorbate as biochar Xu et al. [18,19].

The main objective of this study is to maximize the utilization of sugar cane cultivation and manufacture waste and to research into the influence of biochar produced by pyrolysis at two different temperatures (350 and 700°C), some sugarcane organic wastes biochar on the adsorption of lead in clay soil. The effect of the reaction period and solution pH using kinetic equations on lead adsorption will be also studied.

2. MATERIALS AND METHODS

A laboratory trial was conducted in the Soil & Natural Resources Department, Faculty of Agriculture, Aswan University, Aswan, Egypt in November 2019 to study the effect of a biochar produced from sugarcane organic wastes(filter cake biochar (FB), bagasse biochar (BB) and sphere biochar (SB))prolyzed at 350 and 700°C on lead (Pb) adsorption in a clay soil. A surface soil samples (0 – 20 cm depth)used in this study was obtained from El-Sabel area east of Nile river at Kom-Ombo city, Aswan governorate, Egypt. The soil samplewas air-dried, ground, mixed and sieved through a 2 mm sieve. Some chemical and physical properties of this sample are recorded in Table 1. Using the procedures ofKlute [24] and Cottenie et al. [25].

2.1 Used Biochar

Three sugarcane organic wastes (filter cake, bagasse and sphere) were used to produce the biochar in this study. These organic wastes were obtained from Kom-Ombo sugarcane factory, Aswan governorate, Egypt. Then, they washed many times and in oven dried for 5 h at 70°C. The dried mass of each organic waste was crushed in a grinder to obtain an average particle size ranging from 0.25 to 1 cm. The ground powder of each organic waste was packed in a lid-covered crucible and pyrolyzed in a furnace (Witeg, WOF-105, Germany) at two temperature degrees (350 and 700°C) for 90 min. under limited oxygen condition with a heating rate of 10°C per minute. The yield percentage of biochar was calculated. The prepared biochar was sieved to obtain amean particle size ≤ 200 μm and stored in a container prior to use. Some chemical properties of filter cake biochar (FB350 and FB700), bagasse biochar (BB350 and BB700) and sphere biochar (SB350 and SB700) pyrolyzed at 350 and 700 C, respectively, according methods of A.O.A.C. [26] are present in Table 2.

Table 1. Some selected physical and chemical properties of the used soil

Parameter	Unit	Value
Particles size distribution		
Sand	%	16.7
Silt	%	33.2
Clay	%	50.1
Texture		**Clay**
pH (1:2.5 soil: water susp.)		7.81
EC (1:5 soil: water extract)	dSm^{-1}	0.186
Organic matter	%	1.4
Cation exchange capacity (CEC)	$cmol\ kg^{-1}$	34.2
DTPA extractable Pb	$mg\ kg^{-1}$	0.256
Total Pb	$mg\ kg^{-1}$	7.55

Table 2. Selected chemical properties of the used biochars

Parameter	Unit	Filter cake biochar		Bagasse biochar		Sphere biochar	
		FB350	FB700	BB350	BB700	SB350	SB700
pH (1:2.5 organic materials: water)		7.99	12.03	8.68	10.05	8.90	10.51
EC (1:5 Or.: water)		1.475	3.230	1.000	1.687	8.710	4.660
Yield	%	80.0	72.8	35.6	25.3	41.0	35.3
Total C	g /100 g	58.0	62.0	68.2	71.2	63.5	65.4
Total N	$g\ kg^{-1}$	22.0	19.0	17.0	16.0	18.0	17.0
Pb extracted by DTPA	$mg\ kg^{-1}$	0.375	0.548	0.375	0.325	4.328	3.552

2.2 Chemicals and Reagents

A stock solutionof 1000 mg L^{-1} of $Pb^{2+}$was prepared using lead nitrate (Pb $(NO_3)_2$) (sigma Aldrich Chemical Reagent Co., Ltd. Egypt). The stock solution was to prepare initial concentration (C_i) solution of 200 mg $L^{-1}Pb^{+2}$to be used in the batch experiments.

2.3 Batch Adsorption Experiments

Two batch experiments were performed in glass bottles at the room temperature (25 ± 2°C). The first experiment was to investigate the effect medium pH on Pb adsorption onto soil treated with three biochar types (FB350, BB350 and SB350). To achieve this study, 5 g soil sample were mixed with 0.4 g biochar in a 100 ml glass bottle and then 50 ml from lead solution of 200 mg L^{-1} (initial solution) were added to the bottle. Twenty four glass bottles were divided to sixmain groups representing the medium (suspension) pH (4, 5, 6, 7, 8 and 9 ±0.2). Each main group was divided to four subgroups to represent of the three biochar treatments of filter cake biochar (FB350), bagasse biochar (BB350) and sphere biochar (SB350) as well as control treatment (without biochar). Each treatment was repeated three times. The pH of the suspension in each bottle was adjusted at the required pH using 0.01 N of HCl or NaOH, that the mixture shaken on a rotary shaker (HYSC, OS-300, Korea) at 200 rpm for a 24 hour and bottles were withdrawn from the shaker and centrifuged at 1000 rpm on a centrifuge (Centurion Scientific, Pro-Analytical CR2000, United Kingdom) for 5 min to separate the adsorbent from the equilibrium solution. These solutions were filtered through filter paper (0.45 μm) and the filtrates were analyzed for lead (Pb) using Thermo Scientific, iCAP 7000 Plus Series ICP-OES.

The adsorbed amounts of Pb on each sorbent calculated as the difference between the amount of Pb present in the initial solution and that remaining in the equilibrium solution as described by Garcia-Miragaya and Page [27].

q_t (mg/g) is the adsorbed amount at time t, it was calculated using the following equation:

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (1)$$

Where:

C_0 (mgL^{-1}) is the initial concentration of the heavy metal (Pb) in added solution (200 mg/L), C_t (mgL^{-1}) is the concentration of Pb at time t. V is the volume of the solution (L) and W is the mass of Pb adsorbent (g).

The adsorbed amount of heavy metal (Pb) is q_e (mg/g) at equilibrium; it was calculated using the equation:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (2)$$

where:

C_e and C_0 (mgL^{-1}) are the equilibrium and initial liquid-phase concentrations of heavy metal (Pb), respectively.

Percentage of the Pb removal is calculated as follows:

$$\text{Percentage of Pb removal} = \frac{(C_0 - C_e)100}{C_0} \quad (3)$$

Where: C_e and C_0 (mgL^{-1}) are the equilibrium and initial concentrations of the heavy metal (Pb).

The second experiment was to study the effect of shaking periods on lead adsorption onto the studied soil treated with the investigated 6 biochar types. To conduct this study, 5 g soil sample were mixed with 0.4 g biochar in a 100 ml glass bottle then, 50 ml of lead solution having concentration of 200 mg L^{-1} (initial solution)were added giving the soil: lead solution ratio of 1:10. Thirty five glass bottles were divided to five main groups representing the shaking periods (5, 10, 20. 40 and 80 min). Each main group was divided to seven subgroups to describe the six biochar treatments of filter cake biochar (FB350 and FB700), bagasse biochar (BB350 and BB700) and sphere biochar (SB350 and SB700) as well as control treatment (without biochar). Each treatment was repeated three times. The pH of suspension in each bottle was adjusted at 7.0 using 0.01 N of HCl or NaOH and then, the bottles were shaken on a rotaryshakerat 200 rpm for thefive period times (5, 10, 20, 40 and 80 min.) and centrifuged at 1000 rpm for 5 min to separate the adsorbent from the solution. These equibrium solutions were filtered through filter papers (0.45 μm) and then the filtrates were analyzed for lead (Pb) as in the first experiment.

2.4 Sorption Kinetics

Two kinetic models were used in this study their pseudo first-order, pseudo second-order to describe the kinetics of lead adsorption on soil treated with biochar.

Pseudo first-order and pseudo second-order kinetic models were expressed on linear forms by using equations. (4) and (5), respectively according to Ho and McKay, [28] as follows:

$$\log (q_e - q_t) = log q_e - \frac{K_1}{2.303} t \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 \, q_e^2} + \frac{1}{q_e} t \quad (5)$$

Where; q_e equal the amount of Pb adsorbed at equilibrium per unit mass of adsorbent (mg g^{-1}) and q_t equal the amount of Pb adsorbed at time t (mg g^{-1}). K_1 (m^{-1}) is the pseudo first-order rate constant, it is calculated from the slope of the plot of log ($q_e - q_t$) related to t from equation 4, while, k_2 (g mg^{-1} min^{-1}) is the pseudo-second-order rate constant, it is calculated from the slope and intercept values of the plot of t/q_t related to t, from equation 5.

3. RESULTS AND DISCUSSION

3.1 Effect of Suspension pH

The surface charge on the absorbent (biochar) can be adjusted by changing the pH of the suspension containing the biochar. The pH is one of the most important parameters affecting metal ion adsorption processes Uyanik and Aygün [29]. Fig. 1 illustrates the effect of pH on the adsorption of Pb ions by the soil treated with and without biochars. The adsorption of lead is clearly affected by the pH of the adsorbante suspension. Lead adsorption was increased linearly from pH 4 to 6in all studied treatments. However, it was leveled from pH 6 to 7 for the soil treated with FB 350. For the soil treated with BB350 and SB350, the adsorption or precipitation of Pb highly increasing between pH 6 to 9. In addition, it continued to increase linearity for FB350 treatment after pH 7 up 9. On the other hand, the adsorbed or precipitated amount of Pb slightly decreased for the soil without biochar (control) from pH 8 to 9. The highest Pb adsorption or precipitation was recorded for the soil treated with BB350 followed by the soil treated with SB350 then the soil treated with FB350. However, the lowest amounts of Pb adsorption were adsorbed on the soil without biochar treatment. The slight increase of Pb adsorption were between pH 4 to 6in all treatments may be attributed to electrostatic repulsion forces between positively charged hydronium ions H_3O^+ and Pb^{2+}ions on adsorbents Moyo et al., [30].

The adsorption or precipitation of lead is clearly affected by biochar types the pH of soil / biochar suspension. Therefore, the absorbed or precipitated amount of Pb decreased in the order: soil + BB350 > soil + SB350 > soil + FB350 > soil only. At pH 9 maximum amounts of Pb of 1.794, 1.706 and 1.688 mg/g were adsorbed or precipitated on the soil treated with BB350, SB350 and FB350 respectively. However, Pb was maximum adsorbed or precipitated (1.310 mg/g)on the soil only at pH 8. Basically, the adsorption or precipitation capacity increased with increasing the pH for all adsorbents. Since the pH value at which Pb^{2+} ions precipitate is pH > 7 on two forms $Pb(OH)^+$ and $Pb(OH)_2$. These findings agree with those obtained by Kadirvelu et al. [31].

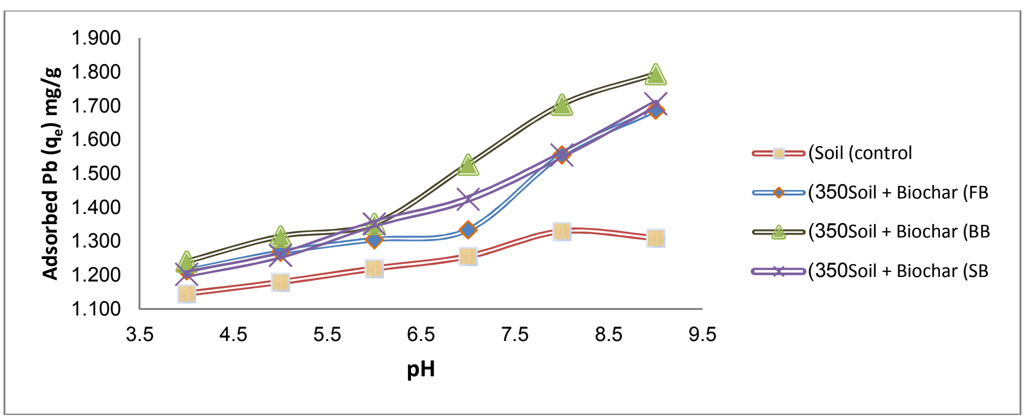

Fig. 1. Effect of soil / biochar suspension pH on Pb adsorption (mg/g) on soil treated with different biochars

3.2 Effect of Shaking Time

A rapid adsorption that occurred initially at first shaking time for $Pb^{2+}$was observed during the first 25 minutes due to the availability of the exposed surface area of adsorbents (Fig. 2). It was followed by a slower Pb adsorption during the residual shaking time mainly from 25 to 80 minutes. These findings agree with those obtained by Qadeer and Akhtar, [32]. The equilibrium adsorption capacity was reached in about 30 minutes, but unimportant changes in Pb^{2+} adsorption capabilities were observed after about 40 minutes(Fig. 2).The lowest Pb adsorption values were for the soil that was not treated with biochar. However, biochar treatments had biggest impacts on lead adsorption with increasing the shaking time. Therefore, the addition of biochar showed a clear effect on the absorbed amount of lead compared to the soil untreated biochar. This indicates that the biochar is important in removing Pb contaminants through the adsorption process.

The effects removal efficiency of Pb^{2+} from the solution is shown in Fig. 3. A highest amount of Pb^{2+} (85%) removed with treated the soil with sphere biochar pyrolyzed at 350°C(SB350)while the lowest one(55.5%) occurred with the soil that was not treated with biochar at a shaking time of 80 minutes. Moreover, all other treatments which contained the biochar had higher efficiencies in removing Pb^{2+}comparedto the soil without biochar treatment. The removed amount of Pb^{2+} ions increased acceleratory in the beginning of the shaking upto 25 minutes, and then it slightly increased upto 80 minutes (Fig. 3). The results also displayed that the pyrolysis temperature had no any apparent effect on the amount removed of Pb^{2+} ions during the adsorption process.

3.3 Adsorption Reaction Kinetics

An initial concentration of $Pb^{2+}$of 200 mg $L^{-1}$was selected to determine the adsorption rate constant. Both pseudo-first-order and pseudo-second-order kinetic models for the Pb^{+2} adsorption reaction were applied at five different periods of shaking time mainly, 5, 10, 20, 40 and 80 minutes.

Adsorption kinetics are used to provide information about the adsorption reaction mechanism. The kinetics of adsorption models are classified into two classes which are adsorption reaction modelspseudo first-order model (Lagergren, 1898) andpseudo second-order model Debnath and Ghosh [33] and Kongsuwan et al. [34].

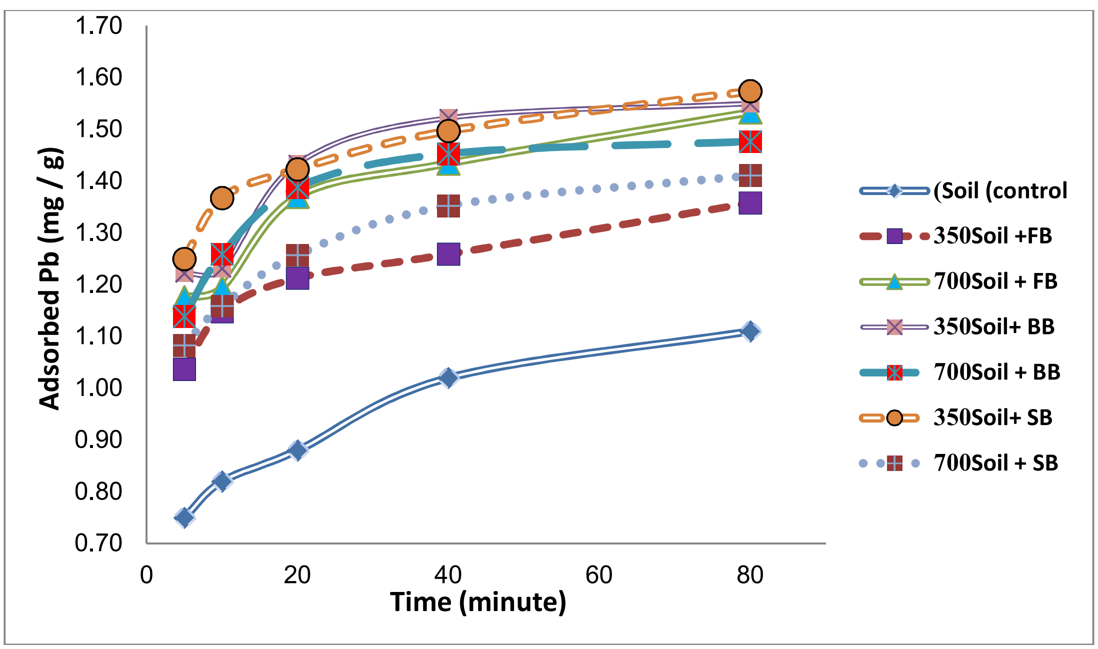

Fig. 2. Effect of shaking time on the adsorption of Pb^{2+}on the soil treated with different biochar types

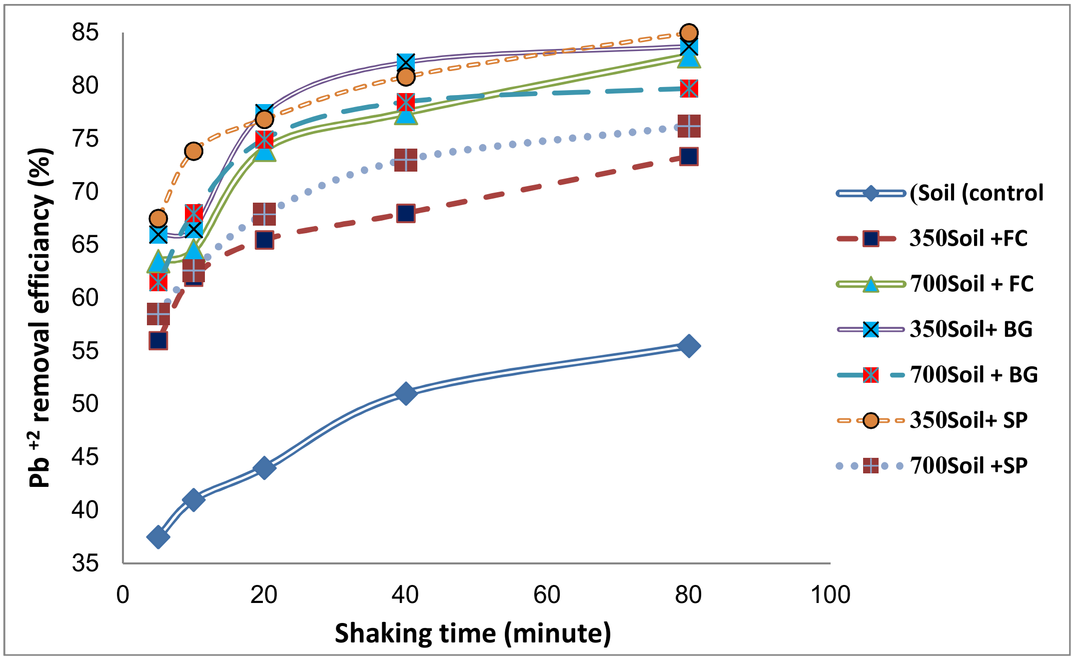

Fig. 3. Effect of shaking time on the removal efficiency of Pb^{2+} by the soil treated with different biochar types

3.4 Pseudo First Order Model

The first-order Lagergren equation was widely used to describe the adsorption of an adsorbate from an aqueous solution. It is considered that the direct rate of adsorption sites is proportional to the number of unoccupied sites. The pseudo first-order plots of adsorption kinetics of Pb^{2+} onto the soil treated with or without the investigated biochars with using Pb^{2+}initial concentration of 200 mg/l are present in Table 3 and Fig. 4. It is obvious that the results of all treatments including the untreated soil did not correspond with the linear pseudo first order equation (Table 3 and Fig. 4). The coefficient of determination (R^2) of Pb adsorption reactions for all the treatments are low and ranges from 0.4290 for the untreated soil to 0.7660for BB700 treated soil.This confirms that Pb adsorption on the soil treated without and with the investigated biochars is not a pseudo first order reaction. Similar results were obtained by El-Damaraw et al. [35].

3.5 Pseudo Second Order Model

Regard to the adsorption system following by pseudo second-order kinetic model, the adsorbate was purposed to adsorbed onto two surface type sites of the adsorbent (biochar). Also, this model considers that the rate of lead adsorption is based on the square of the number of vacant sites on the adsorbent Namasivayam and Kadirvelu, [36].

The parameters of the pseudo second-order plot for the adsorption kinetic of Pb^{2+} onto the soil treated with and without different biochars adsorbent are present in Table 3. The coefficient of determination of the second-order model for Pb^{2+} adsorption is clearly higher than those of the first-order model, which they range between 0.9901 for the soil treated with BB350 to 0.9994 for that treated with SB350.

This indicates that, the pseudo second-order model is suitable to describe the Pb^{2+} adsorption process on the soil treated with or without these investigated biochars. The highest adsorbed amount of Pb^{2+} derived from the pseudo second-order model of the soil treated with or without biochars is given in Table 3. These values are very much consisted with the equilibrium maximum adsorption capacities. Previous studies on heavy metals adsorption kinetic on some types of biochars gave the same results Yahaya et al. [37] and Nwabanne and Igbokwe, [38]. It is clear that, the pseudo second order model provides better fit for the experimental Pb^{2+} adsorption kinetic data. The change in the adsorption capacity with time was found to fit the pseudo second order equation that depended on the adsorption capacity of the absorbed phase. Because this equation mainly depends on the adsorption capacity, the description of the adsorption phenomenon indicates that the chemical reaction is rate controlling. It is clear that, these chemical sorption systems involve vacancy forces by sharing or exchanging electrons between the adsorbents and the solute. This fully affirms the hypothesis based on two types of sites Sparks and Suarez, [39], highly active sites, which react at the start time and are present at low concentrations on soil and biochar, and least active sites, which react when the first sites are saturated and are largely present on the surface of the soil and biochar.

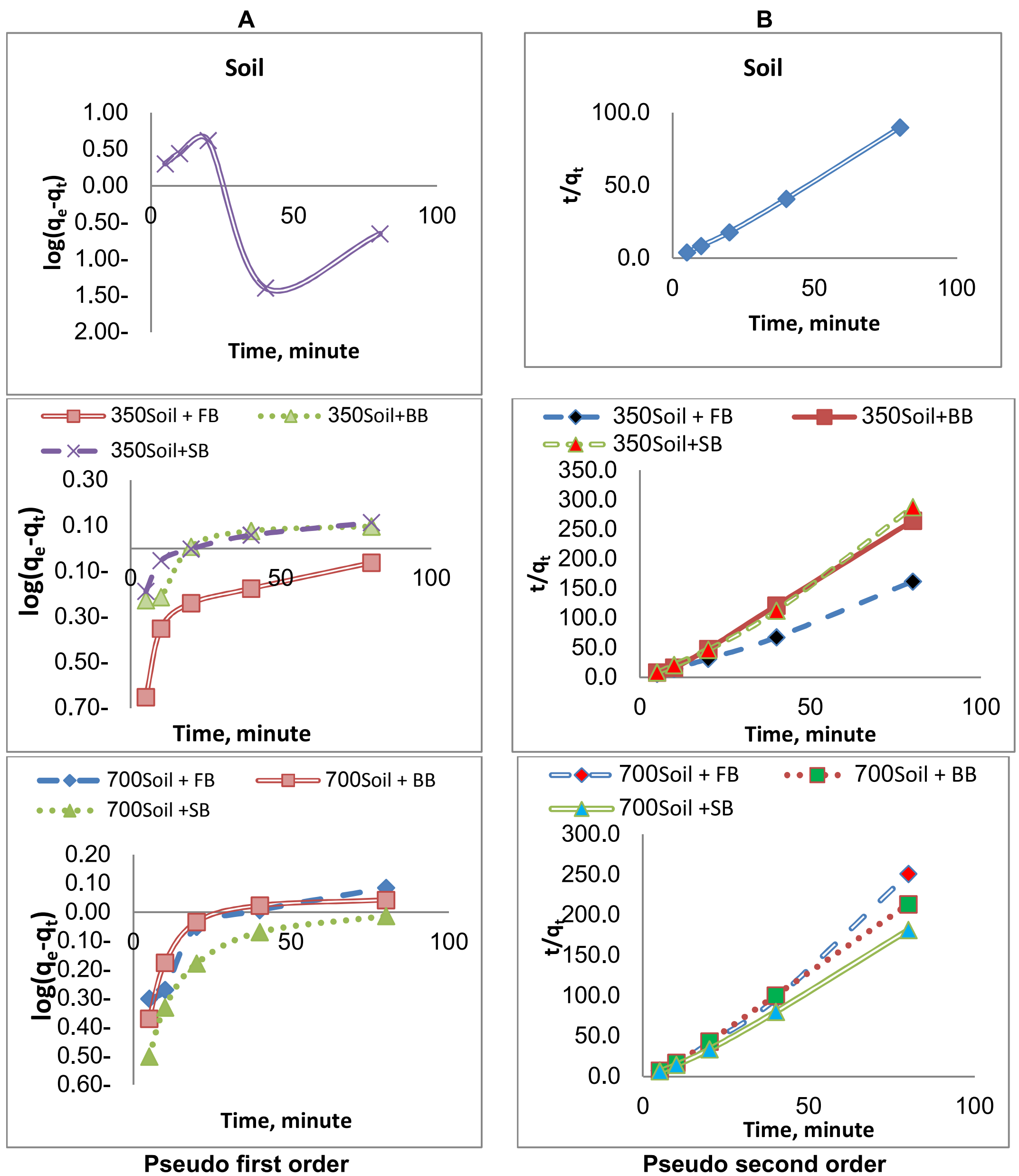

Fig. 4. Pseudo first order (A) and pseudo second order (B) kinetic plots for the Pb^{2+}adsorption by the soil treated with or without different types of biochar

Table 3. Parameters of Pseudo-first-order and Pseudo-second-order for Pb^{2+} adsorption (q_e: amount of Pb^{2+} adsorbed at equilibrium $K_1$and K_2: pseudo first and second-order rate constant respectively)

Treatment	Pseudo first order			Pseudo second order		
	q_e (mgg^{-1})	K_1 (m^{-1})	R^2	q_e (mgg^{-1})	K_2 (g mg^{-1} min^{-1})	R^2
Soil (control)	2.77	0.04	0.4290	0.87	4.76	0.9979
Soil + FB 350	0.48	0.33	0.6637	0.55	27.15	0.9942
Soil + FB 700	1.26	1.59	0.6726	0.63	48.43	0.9980
Soil+ BB 350	1.11	2.10	0.7377	0.95	18.72	0.9901
Soil + BB 700	0.89	2.34	0.7660	1.26	6.36	0.9888
Soil+ SB 350	1.13	1.51	0.5783	0.74	38.52	0.9994
Soil +SB 700	0.64	3.94	0.7240	1.60	3.86	0.9970

4. CONCLUSION

In this study, effect of suspension pH and kinetic equations were applied for Pb adsorption on the soil treated with or without biochars prepared from three feedstocks (sugarcane organic wastes) at two pyrolysis temperatures350 and 700°C. The removed amount from the solution of lead was increased with increasing suspension pH at all treatments. The highest adsorbed or precipitated amounts of Pb were between 1.794 to 1.688 mg/g on the soil treated with different biochars, while, it was 1.310 mg/gwith the soil without biochar. The adsorption of Pb^{2+} by the soil in presence or absence biochars different fitted the pseudo second order kinetic model. Therefore, Sugarcane Organic Waste Biochars are effective adsorbents for the removal of Pb^{2+} from contaminated soils and wastewater, because it is a low cost and locally available.

DISCLAIMER

The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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