

Recovery of eutrophication agents and metal ions from post treatment effluent: a study of Biochar-LDH composite in adsorption

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Abstract: Leachate generated from landfills are a side product of municipal solid waste treatment. This kind of leachate usually contains heavy metals, such as lead, and eutrophication agents, such as phosphate. In this paper, a layered double hydroxide (LDH) activated biochar composite was studied as an adsorbent towards Pb^{2+} and PO_4^{3-} removal from synthetic aqueous solutions. The biochar was synthesized from residual sawdust through pyrolysis, and posteriorly physically activated by CO_2 in a single batch process. The LDH was deposited into the biochar by coprecipitation. The precursor solution contained a molar rate of 1:1:1 of Co^{2+} , Ca^{2+} and Fe^{3+} salts. Sodium hydroxide (3M) was used as precipitation agent. Studies were carried to investigate the influence of pH, adsorbent dosage, contact time and adsorbate initial concentration. The kinetic and equilibrium data for both adsorbates were better fitted to Elovich's and Dual site Langmuir-Freundlich models, respectively. The maximum capacity of adsorption observed were 344.29 Pb^{2+}/g (0.5 g/L, 18 h, pH 5) and 26.17 mg PO_4^{3-}/g (0.88 g/L, 8h, pf 2.5), at 35 °C. The results shows that the adsorbent is efficient for phosphate and lead adsorption removal, and that it performs better for Pb^{2+} . The adsorbent was synthesized with residual sawdust, giving use to it, while the precursor solution cations can be easily found in wastes, such as electro electronic wastes. The material seems promisor for use in landfill leachate treatment.

Keywords: adsorption, lead, phosphate, landfill leachate, recycled biochar, LDH.

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1. Introduction

The generation of municipal solid wastes (MSW) is a major concern derived from modern cities growth. A common solution to this problem is landfilling [1]. Although this technique has a number of advantages, its leachate brings serious concerns. Such solution may put in danger surface water and groundwater, as it contains a myriad of organic compounds (from humic acids to pharmaceuticals), heavy metals and eutrophication agents (for instance phosphate and nitrate) [1]. To treat the leachate, some techniques are already put in use, as is the case of anaerobic treatment, aerobic treatment and anammox [2]. Those techniques are very useful, but may not reach the disposal limits proposed by local legislation. As a cheaper and easier to operate technique, adsorption is a well-known unit operation that can treat landfill leachate, both directly or after another pre-treatment.

Adsorption is a surface phenomenon, where a compound (adsorbate) migrates from the bulky solution to the surface and/or pores of a solid (adsorbent). As a well-studied field, an ever-growing number of adsorbent materials have been proposed and synthesized, such as biochar, zeolites, layered-double-hydroxides (LDH), composites, among others. LDH are a class of anionic clay, which have structure similar to brucite. A proportion of divalent and trivalent metal cations (M^{2+} and M^{3+}) are combined in a lamellar hydroxide structure, its positive charge being counter balanced by anions inside the inter-lamellar space. Its structural formulae are $[M^{2+}M^{3+}(OH)_2]^{x+}[A^{n-}]_{x/n}.yH_2O$, being A^{n-} an anion (Cl^- , NO_3^- , CO_3^{2-} , etc.), and “x” the ratio between M^{2+}/M^{3+} [3]. These materials have good capability to anionic exchange, adsorb metals on its surface, but are prone to agglomeration. LDHs are claiming attention as an adsorbent for heavy metals [4], dyes [3], phosphate [5], nitrate [6], and can also be used as photocatalysts for pharmaceuticals degradation [7]. Composites are materials synthesized as a combination of two different class of materials, and are an efficient way to diminish the agglomeration of LDH. Being deposited in a solid matrix, such as biochar, contribute to a larger reactive area for LDH, and also improves the capability of such composite to adsorb oxyanions. This class of composites have been studied as adsorbent for dyes, heavy metals and eutrophication agents [7]. The aim of this study is to produce an activated biochar/LDH composite and study its adsorption capabilities for a pre-treated landfill leachate. The preliminary studies have been carried on the adsorption of lead (Pb^{2+}), a common heavy metal pollutant, and phosphate (PO_4^{3-}), a eutrophication agent. The composite was prepared by facile coprecipitation [8]. A 1:1:1 Co:Ca:Fe chloride salt solution was used as precursor for the LDH. Then, sawdust biochar activated by CO_2 was added to the beaker, and a NaOH solution (3M) was dripped until pH 10. After a 24 hours maturation time, the composite was washed with ethanol and water, dried in an oven and macerated to obtain CoCaFe-HDL/Biochar.

The composite was applied to lead (II) and phosphate adsorption from synthetic aqueous solutions, evaluating the effect of initial pH, adsorbent dosage and contact time. The pH was studied in the range of 2.1 to 6 [9] for lead adsorption, and 2.5 to 10 for phosphate [8]. Then, the adsorbent dosage was studied, varying the mass of adsorbent in a given volume of solution. A comparison between the capacity of adsorption (q_t , mg Pb^{2+} /g adsorbent) and the percentage of Pb^{2+} removal was used to fix this parameter. Kinetics studies were carried out between 0 and 1440 minutes. The best fitted kinetic model was Elovich. The isotherm studies showed that dual site Langmuir-Freundlich model was better fitted. A maximum adsorption capacity observed were 344.29 Pb^{2+} /g and 26.17 mg PO_4^{3-} /g .

The results presented shows that the adsorbent is viable for Pb^{2+} and PO_4^{3-} adsorption from aqueous solutions. The adsorbent is produced from sawdust waste, which adds value to them. Also, the metal cations used in the synthesis are common in wastes (such as electronic waste). The validation of such adsorbate may justify paths to synthesis methods using cations from those wastes.

2. Materials and methods

2.1. Preparation of biochar derived from sawdust and its activation

Biochar was prepared by pyrolysis and activated by CO_2 in a tube furnace (Sanchis/Brazil), within a 310 stainless reactor with intern volume of 0.030 m^3 , in inert atmosphere of nitrogen [10]. Sawdust was kindly donated Madeireira Haas (Venâncio Aires, Rio Grande do Sul, Brazil), residues from processed *Eucalyptus saligna*. Firstly, sawdust was submitted to pyrolysis ($550 \text{ }^\circ\text{C}$ for 120 min, heating rate of $15 \text{ }^\circ\text{C}/\text{min}$, under N_2 atmosphere), then physically activated. With the N_2 atmosphere being kept, temperature was elevated to $900 \text{ }^\circ\text{C}$ (heating hate $25 \text{ }^\circ\text{C}/\text{min}$). After the temperature being reached, a CO_2 flow was admitted into the furnace, along with N_2 atmosphere. After 180 min, with the activation process was over, and CO_2 flow was stopped. The furnace was cooled to ambient temperature under N_2 flow. The activated biochar was than washed with reverse osmose water until pH 6, dried, sieved and stored for later use.

2.2. Synthesis of CoCaFe-LDH/Activated biochar composites

The LDH/Activated biochar composite was synthesized by coprecipitation [10], [11]. For such, a precursor solution was obtained by mixing 7.5 mmol of each of the precursor salts [$1.1026 \text{ g CaCl}_2 \cdot 2\text{H}_2\text{O}$ (molecular weight, mw, = 147.01 , Dinâmica/Brazil), $1.7845 \text{ g CoCl}_2 \cdot 6\text{H}_2\text{O}$ (mw = 273.93 , Proquímicos/Brazil), and $2.0272 \text{ g FeCl}_3 \cdot 6\text{H}_2\text{O}$ (mw = 270.30 , Dinâmica/Brazil)] to 100 mL of reverse osmosis water. After complete dissolution, the liquid was poured in a triple-neck round bottom flask. Then, 5 g of the previously prepared CO_2 activated biochar was added to the flask, and the mixture was stirred for 30 minutes. Then, a pHmeter probe was set to control the solution pH, and a burette was fixed to drip the $\text{NaOH } 3\text{M}$ (mw = 39.99 , Dinâmica/Brazil) solution into the flask, under constant magnetic stirring. Once pH 10 was reached, the burette was closed, the pH probe was removed, and the three necks were closed with silicon corks. The solution was matured by 24 hours under magnetic stirring. The obtained sludge like solution was vacuum washed in a Buchner's funnel. First, with anhydro ethanol and then with reverse osmosis water. The material was dried in a drying oven overnight, kindly macerated (to separate agglomerates), sieved and stored in a glass desiccator for later.

2.3. Adsorption experiments

The adsorption experiments were conducted with two different adsorbates: lead (Pb^{2+}) and phosphate (PO_4^{3-}). For the lead experiments, $\text{Pb}(\text{NO}_3)_2$ (mw = 331.2 Vetec/Brazil) was used as Pb^{2+} source. $500 \text{ Pb}^{2+} \text{ ppm}$ stock aqueous solutions were prepared, dissolving lead nitrate in reverse osmosis water. All the other Pb^{2+} solutions

were diluted from this stock solution. Similarly, KH_2PO_4 (mw = 136.06, NEON/Brazil) was used as PO_4 source. 100 ppm P- PO_4 (306,655 ppm PO_4) stock aqueous solutions were prepared, and other PO_4 solution were diluted from this stock. The as prepared composites were the adsorbent studied. The experiments were conducted in 125 mL Erlenmeyer's flasks, which were shaken in a shaker incubator (TE 4200 Tecnal/Brazil), at 150 rpm at atmospheric temperature (unless in the equilibrium experiments, were the temperature was set to 35 °C). Lead experiments were conducted with 50 mL solutions, at 50 ppm Pb^{2+} , at an adsorbent dosage of 0.5 g/L for 4 hours. The phosphate experiments were conducted with 25 mL solutions, at 25 ppm PO_4^{3-} , at an adsorbent dosage of 1 g/L for 18 hours. After the contact time, the solution was filtered through filter paper and prepared for analysis. The experiments were conducted in triplicates. For each essay, a "blank test" was used for each desired concentration. These flasks were treated as the others but did not receive adsorbent. The Pb^{2+} experiments were sampled in dilute nitric acid media and analyzed with flame atomic absorption spectroscopy (model 240 FS AA, Agilent/USA). The phosphate experiments were sampled by diluting to 50 mL with osmose reverse water. Then, the pH was corrected to a range between 6.5 to 7.5 with dilute HCl and NaOH. After that, the solution was complexed (via ascorbic acid – molybdite methodology [12]) and analyzed in quartz cuvettes via UV-visible spectrophotometer (model UV mini, Shimadzu/Japan). In each step of the experiments, one of the fixed parameters was studied and updated. The collected concentration data were used to calculate the adsorption capacity at any time [q_t (mg/g)] or at equilibrium [q_e , (mg/g)] and the removal efficiency [RE (%)] with equations 1 to 3.

$$q_t = (C_o - C_t) * V/W \quad (1)$$

$$q_e = (C_o - C_e) * V/W \quad (2)$$

$$RE = (C_o - C_t) * C_o \quad (3)$$

Where C_o , C_t and C_e stand for initial, given time "t" and equilibrium concentrations (mg/L, ppm), respectively. V is solution volume (L) and W is the mass of adsorbent (g)

2.3.1. pH influence

For these set of experiments, the solutions had its initial pH altered to a desired value with dilute solutions of either. NaOH or HCl (HCl 37%, mw = 34.46, Dinâmica/Brazil), in concentrations of 1, 0.1 and 0.01 M. After the experiments, the final pHs were noted, so a pH_{pzc} could be calculated. For the lead experiments, the pH were set to 2.1, 3, 4, 5 and 6. No pH higher than 6 were used in lead adsorption, as lead is known to precipitate in more alkali media [9]. For the phosphate experiments, the pH studied were 2.5, 4, 6, 8 and 10. The minor value (2.5) was chosen after a dissolution test in lesser pH values. The adsorbent was contacted with solutions containing 25 ppm PO_4^{3-} at pH 2, 2.1, 2.3 and 2.5 (other parameters were the same conditions previously related). The final solutions in pH 2 to 2.3 were all slightly yellowish, which were interpreted as a sign of LDH dissolution.

2.3.2. Dosage of adsorbent

To study the effect of adsorbent, the mass of adsorbent was altered in each flask. The pH used was fixed in the latter step as 5 to lead and 2.5 for phosphate. The studied dosages were for Pb^{2+} 0.2, 0.3, 0.5, 0.75, 1, 1.25

and 1.5 g/L, in 50 ppm Pb²⁺, 50 mL solutions. The studied dosages for PO₄³⁻ were 0.5, 0.75, 1, 1.25, 1.5 g/L, in 25 ppm PO₄³⁻, 25 mL.

2.3.3. Kinetic studies

To study the adsorption kinetic, the adsorbent was contacted in different times with the adsorbate. The adsorbent dosage was fixed to 1 g/L for lead adsorption and 0.88 g/L for PO₄³⁻ adsorption. Studied times in the experiments were: 3, 5, 10, 15, 30, 60, 120, 240, 480, 1080 and 1440 min. The collected data were analyzed through Pseudo-first order (PPO), Pseudo-second order (PSO) and Elovich's model [13]. The models are depicted in equations 4 to 6, respectively.

$$q_t = q_1(1 - e^{-k_1*t}) \quad (4)$$

$$q_t = \frac{k_2*q_2^2*t}{1 + k_2*q_2} \quad (5)$$

$$q_t = \frac{1}{\beta} \ln(\alpha * \beta) + \frac{1}{\beta} \ln(t) \quad (6)$$

where: k_1 is the rate constant of the pseudo first order kinetics (1/min), k_2 is the rate constant of the pseudo second order kinetics [g/(mg.min)]. q_1 and q_2 are theoretical values for adsorption capacity (mg/g). α is the initial adsorption rate constant (mg/g.min) and β is related to the extent of surface coverage and activation energy for chemisorption (g/mg). The best fitted model criteria were higher adjusted R² (R²_{adj}) and lower reduced chi square (χ^2) [14]. Also, Average relative error (ARE) was used to qualify adjustment [10].

2.3.4. Equilibrium studies

The equilibrium curves were constructed at a temperature of 35 °C. The equilibrium time was considered as 18 hours for Pb²⁺ adsorption and 8 hours for phosphate experiments. The collected data was fitted with Langmuir, Freundlich [13] and dual site Langmuir-Freundlich models [15], which are depicted in equations 7 to 9, respectively.

$$q_e = k_f * C e^{nf} \quad (7)$$

$$q_e = \frac{q_m * k_L * C e}{(1 + k_L * C e)} \quad (8)$$

$$q_e = \frac{q_{m1} * k_{L1} * C e}{(1 + k_{L1} * C e)} + k_{f2} * C e^{nf2} \quad (9)$$

Where: k_F is the Freundlich constant (mg/g) (mg/L)^{nF} and nF is Freundlich intensity parameter; q_m is the maximum adsorption capacity (mg/g), and k_L is the Langmuir constant (L/mg). The constants q_{m1} and k_{L1} are the Langmuir constants for portion 1 of the composite and k_{f2} and n_{f2} for the Freundlich second portion. R²_{adj}, adjusted, reduced χ^2 and ARE were used as parameter to the choice of the best fitted model [14].

3. Results and discussion

3.1.1. Effect of pH on adsorption

The pH is a crucial parameter for adsorption studies. A change in this parameter tend to influence how the adsorbent and adsorbate interacts, especially due to adsorbent pH_{pzc} and to the adsorbate's pKa and speciation. Figure 1 a and b depict the results of the influence of pH on the adsorption of Pb^{2+} and PO_4^{3-} . The insets of these figures show the pH_{pzc} in each system.

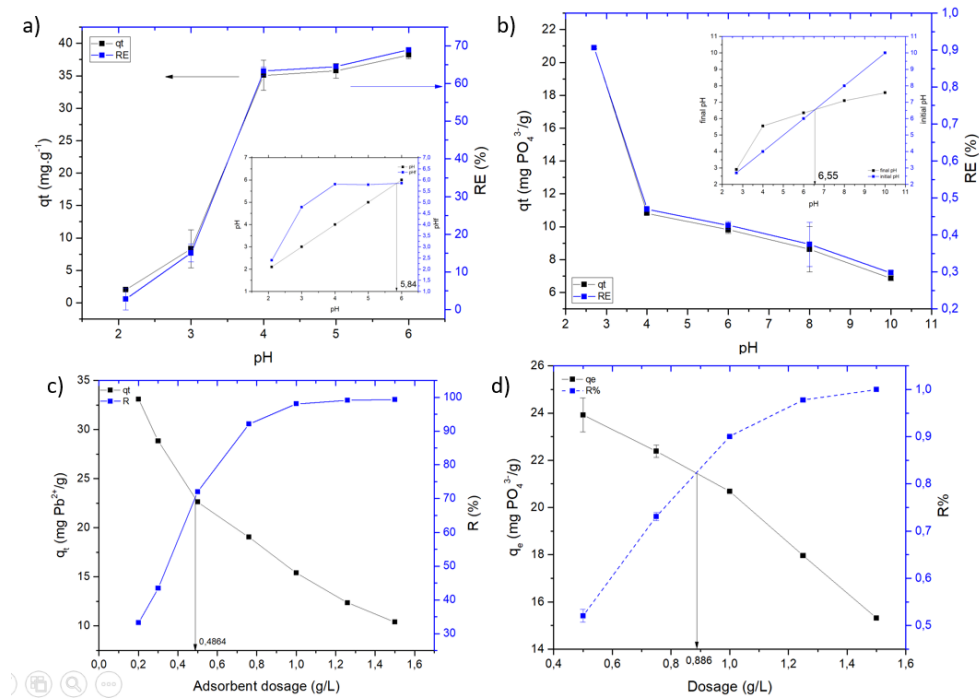


Figure 1: pH influence on the capacity of adsorption and efficiency removal of a) lead (experimental conditions: $T = 25 \text{ }^\circ\text{C}$, adsorbent dosage = 0.5 g/L, contact time: 4 h, $C_0 = 50 \text{ mg/L}$, $V = 50 \text{ mL}$) and b) phosphate (experimental conditions: $T = 25 \text{ }^\circ\text{C}$, adsorbent dosage = 1 g/L, contact time: 18 h, $C_0 = 25 \text{ mg/L}$, $V = 25 \text{ mL}$). Dosage studies for c) lead (experimental conditions: $T = 25 \text{ }^\circ\text{C}$, pH 5, contact time: 4h, $C_0 = 50 \text{ mg/L}$, $V = 50 \text{ mL}$) and d) phosphate (experimental conditions: $T = 25 \text{ }^\circ\text{C}$, pH = 2.5, contact time: 18 h, $C_0 = 25 \text{ mg/L}$, $V = 25 \text{ mL}$)

Figure 1a inset indicates that the composite has a pH_{pzc} of around 5.94 in Pb^{2+} solutions. The low adsorption capacity under lower pHs (2.1 and 3) may happen due to the competition of H^+ and Pb^{2+} for the active sites. The highest capacity of adsorption (38.19 mg/g, 68,92 %) occurred around pH 6, where the adsorbent has a negative induced charge, while the Pb^{2+} is still the dominant species. pH 5 was chosen, as the capacity and removal under this condition (q_t 37.76) were close to pH 6. This was done in order to avoid the solution precipitation while correcting the pH on the next steps and avoid precipitation.

The inset of figure 1 b shows that the pH_{pzc} in phosphate solution was around 6.55. The lowest capacity happened in pH 8 and 10. In this area, most of the adsorbate is speciated in HPO_4^{2-} form [16], the adsorbent has a negative induced charge, and there probably are site competition with OH^- . As the pH becomes less alkali, the speciation changes from HPO_4^{2-} to $H_2PO_4^-$, while the capacity slowly increases until pH 4 (q_t 10.81 mg/g). The highest capacity was at pH 2.5 (20.89 mg/g), where the major species is H_3PO_4 , but $H_2PO_4^-$ coexist. The pH 2.5 was maintained for the next steps.

3.1.2. Dosage studies

The influence of dosage results is depicted in figure 1 c and d, for Pb^{2+} and PO_4^{3-} adsorption respectively. A common trend is observed, as the dosage increases, the removal efficiency raises and capacity decreases. The results showed that a smaller dosage is needed to adsorb Pb^{2+} than to PO_4^{3-} , as the further reached 100 % RE earlier. The ideal dosage was considered the point where adsorption capacity and removal trends intercept. The intercept was at 0.48 g/L for Pb^{2+} and 0.886 g/L for PO_4^{3-} . The dosage where fixed at 0.5 g/L for lead adsorption and 0.88 g/L for phosphate adsorption.

3.1.3. Kinetic studies on Pb^{2+} adsorption

The kinetic data are depicted in figure 2 a and b, and the parameter of the fitted models are shown in table 1, for lead and phosphate adsorption respectively. According to the data shown, the best fitted kinetic model was Elovich in both scenarios. This suggests a heterogeneously distributed adsorption energy through the systems [17], and that chemisorption occurs in both systems, with multilayers being formed as the adsorption occurs [18]. The values of α indicates how fast initial adsorption occurs [19], and denote a faster initial rate for phosphate adsorption than for lead (7.30 mg Pb^{2+} /g.min and 271.10 mg PO_4^{3-} /g.min). As the system did not find a complete equilibrium through the range of time tested, the contact times of 18 hours for Pb^{2+} and 8 h for PO_4^{3-} were chosen due to the small change in capacity after those times.

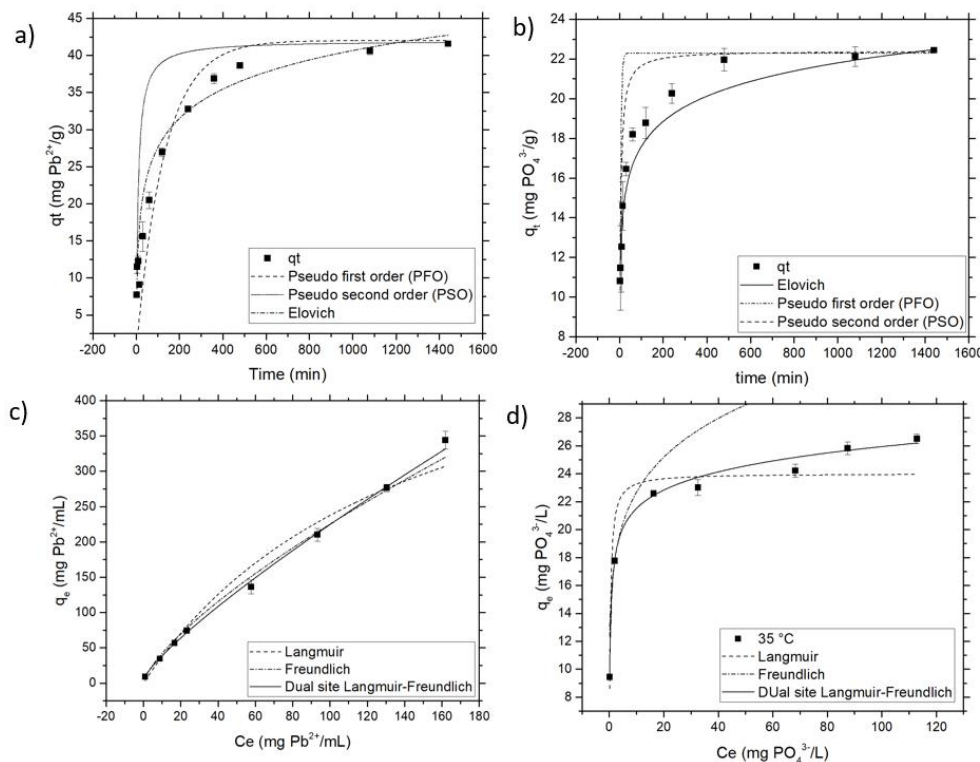


Figure 2: kinetic curves for the adsorption of a) lead (experimental conditions: $T = 25\text{ }^{\circ}\text{C}$, adsorbent dosage = 0.5 g/L, pH 5, $C_0 = 50\text{ mg/L}$, $V = 50\text{ mL}$) and b) phosphate (experimental conditions: $T = 25\text{ }^{\circ}\text{C}$, adsorbent dosage = 0.88 g/L, $C_0 = 25\text{ mg/L}$, $V = 50\text{ mL}$), and equilibrium isotherms for c) lead (experimental conditions: $T = 35\text{ }^{\circ}\text{C}$, adsorbent dosage = 0.5 g/L,

pH 5, contact time: 18 h, $C_0 = 20\text{-}500$ mg/L, $V = 50$ mL) and d) phosphate (experimental conditions: $T = 35$ °C, adsorbent dosage = 0.88 g/L, contact time: 8h, $C_0 = 5\text{-}150$ mg/L, $V = 25$ mL).

Table 1: Kinetic parameter data calculated for the adsorption of Pb^{2+} and PO_4^{3-} on to the composite. The adjusted models were pseudo first order (PFO), pseudo second order (PSO) and Elovich's.

Kinetic model	Adsorbate	
PFO	Pb^{2+}	PO_4^{3-}
q_1 (mg g⁻¹)	42±10,0701	22.29153±0.2843
k_1 (min⁻¹)	0.00774 ± 0.0058	0.2180 ± 0.0335
Reduced χ^2	4752.6082	60.0712
R²	0.7429	0.91155
R²_{adj}	0.7172	0.9017
ARE (%)	35.4186	20.3607
PSO		
q_2 (g mg⁻¹ min⁻¹)	42 ± 3.1004	22.4101 ± 0.1954
k_2 (min⁻¹)	2.66 10 ⁻³ ± 0.7785 10 ⁻³	0.0128 ± 0.0018
χ^2	2979.8046	27.6159
R²	0.8388	0.95934
R²_{adj}	0.8227	0.9548
ARE (%)	35.3411	12.9368
Elovich		
α (mg.g⁻¹.min⁻¹)	7.307 ± 0.3335	271.1002 ± 91.0260
β (g.mg⁻¹)	0.17611 ± 0.0031	0.54611 ± 0.0168
χ^2	56.8006	5.6981
R²	0.9969	0.9916
R²_{adj}	0.9966	0.9907
ARE (%)	12.8323	4.6868

3.1.4. Equilibrium studies

Equilibrium data are depicted in figure 2 c) for lead adsorption, and d) phosphate adsorption. The fitted model parameters are in table 2 and 3, for lead and phosphate respectively. Both systems were better fitted with Dual site Langmuir-Freundlich (DSLFF) isotherms. This model suggests that two different kind of active sites play different roles simultaneously in the adsorption [15]. The composite studied here is made of a CoCaFe-LDH part and a CO₂ activated biochar, making it possible for different materials to interact with both adsorbates. The values of q_{m1} in both cases suggests that the monolayer is readily saturated. Since the values of n_F indicates the magnitude

of the adsorption driving force [13], the values of n_{F2} in both adsorption systems (when compared to the common n_F) suggests different trends. For lead adsorption, $n_{F2} > n_F$ suggesting that the heterogeneous driving force is greater than it would be for a pure Freundlich system. In the phosphate system, $n_{F2} < n_F$ in all temperatures, suggesting that the heterogenous adsorption energy does not interfere much in the system. This may explain the reason why the isotherm shapes are more related to Freundlich for lead adsorption, while more similar to Langmuir for phosphate adsorption. The maximum capacity experimentally observed was 344.29 Pb^{2+}/g (35 °C, 0.5 g/L, 18 h, pH 5) and 26.17 $mg PO_4^{3-}/g$ (35 °C, 0.88 g/L, 8h, pf 2.5). The maximum capacities predicted by DSLF (q_m) model were 399.80 Pb^{2+}/g and 26.1882 $mg PO_4^{3-}/g$, at the same conditions as the observed ones.

Table 2: Isotherms parameters for lead and phosphate adsorption on CoCaFe-LDH/Activated biochar. Adjust made to Langmuir, Freundlich and Dual site Langmuir-Freundlich models.

Isotherm model	Adsorbate	
	Pb^{2+}	PO_4^{3-}
Langmuir		
q_m ($mg g^{-1}$)	833.3275 ± 228.382	$19.6813 \pm 0,47$
k_L ($L mg^{-1}$)	0.0039 ± 0.0015	$4.6905 \pm 1,170$
R_L	0,4342	$1.546 \cdot 10^{-3}$
Reduced Chi-square	1.7499	197,7483
R^2	0.9869	0.9336
R^2_{adj}	0.9847	0.9203
ARE (%)	16.1024	24.1658
Freundlich		
k_F ($mg g^{-1})(mg L^{-1})^{-1/n_F}$	6.2664 ± 0.7112	16.0233 ± 0.3362
n_F	0.7788 ± 0.0248	0.1509 ± 0.0343
Reduced Chi-square	0.4644	479.8689
R^2	0.9965	0.8389
R^2_{adj}	0.9959	0.8389
ARE (%)	6.1491	18.1614
Dual site Langmuir-Freundlich		
q_{m1} ($mg g^{-1}$)	20.4622 ± 9.6113	11.1038 ± 0.4151
k_{L1} ($L mg^{-1}$)	0.4917 ± 0.3059	2.1673 ± 1.0285
k_{F2} ($mg g^{-1})(mg L^{-1})^{-1/n_{F2}}$	2.5794 ± 1.0251	7.9896 ± 1.0798
n_{F2}	0.9474 ± 0.0741	0.1351 ± 0.0277
Reduced Chi-square	0.1726	2.3246
R^2	0.9991	0.9995
R^2_{adj}	0.9989	0.9999
ARE (%)	2.8838	1.3573

A comparison between lead and phosphate adsorption capacities with other materials and studies is depicted at table 3. The material has good adsorption performance for both adsorbates but is clearly more efficient for lead removal.

Table 3: Comparative table of maximum capacity calculated to other materials/authors.

Adsorbate	Model	qm (mg/g)	pH/Temperature	Reference
Pb²⁺				
CoCaFe-HDL/Biochar	DSLFF	399.80 mg/g	pH 5, 35 °C	This work
Sludge biochar/LDH	Langmuir	285.2 mg/g	pH, 45°C	[20]
HNTs-DMSA	Langmuir	863.66 mg/g	45 °C	[21]
PO₃⁴⁻				
CoCaFe-HDL/Biochar	DSLFF	26.37 mg/g	pH 2.5, 35 °C	This work
Cerium oxide decorated CoAl-LDH	Freundlich	16.03 mg/g	25 °C	[22]
Portland cement/slag powder/coal ash-hydrate	Langmuir	8.84 mg/g	pH 7, 25 °C	[23]
CaFe-HDL/Biochar	Freundlich	99.55 mg/g	pH 2.15, 55 °C	[8]

4. Conclusion

Composite CoCaFe-LDH/activated biochar was easily synthesized through coprecipitation technique. The precursor sawdust biochar was pyrolyzed and activated in the same batch. The adsorption studies were carried out separately, with synthetic solutions of either lead (Pb²⁺) or phosphate (PO₃⁴⁻). The influence of pH and adsorbent dosage were studied. The pH was fixed in 2.5 and 5 for phosphate and lead adsorption, respectively. Dosage study shows that lead system needs a smaller adsorbent dosage than phosphate system. Adsorbent dosages were fixed to 0.5 g/L for lead and 0.88 g/L for phosphate. Kinetic and equilibrium data had a better fit for Elovich and dual site Langmuir-Freundlich models, respectively for both systems. Equilibrium time was set as 18 h for lead adsorption and 8 h for phosphate. The maximum capacity experimentally observed was 344.29 Pb²⁺/g (0.5 g/L, 18 h, pH 5) and 26.17 mg PO₄³⁻/g (0.88 g/L, 8h, pf 2.5). The maximum capacities predicted by DSLFF model was 399.80 Pb²⁺/g and 26.1882 mg PO₄³⁻/g, at the same conditions as the observed ones. The results show that the adsorbent has good capacity for lead and phosphate and may be a promisor option for landfill leachate treatment.

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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