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**Development of a continuous-flow sorption
technique to assess biochar suitability for the
remediation of heavy-metal contaminated
waters.**

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Abstract

The use of sorbents for the remediation of heavy-metal contaminated waters has been widely investigated as high removal efficiencies as those of activated carbon have been reported. However, studies concerning more sustainable, low-cost materials but equally effective are necessary.

Biochar are biomass residues pyrolyzed under low oxygen conditions, resulting in a porous, low density, carbon rich material. Its large surface area and cation exchange capacity, determined by the biomass source and the pyrolysis temperatures, enables enhanced sorption of both organic and inorganic contaminants to their surfaces, reducing pollutant mobility when amending contaminated waters and soils. Hence, in this project, the sorption and desorption of copper in biochar were evaluated to assess its suitability in remediation actions addressing contaminated waters and soils.

The present project develops the setup of a continuous-flow sorption technique for the investigation of Cu(II) sorption onto a tree barks biochar. Different operating conditions were evaluated to determine the maximum sorption capacity of the biochar.

More precisely, the performance of the continuous-flow sorption technique is described through the concept of a breakthrough curve which was modeled using kinetic models such as the Thomas and Adams Bohart models. These models were fitted to experimental data to predict and determine characteristic parameters of great importance such as the maximum sorption capacity and kinetic rates. The effect of different inlet Cu(II) concentrations and flow rates on these parameters were investigated and the tree barks biochar sorption capacity was estimated. Moreover, desorption percentages were determined in order to prove the tree barks biochar's copper sorption irreversibility and were found to be lower than 0.30 % confirming its promising application for heavy-metal contaminated waters remediation.

Key words: copper, biochar, sorption, desorption, water, remediation, continuous-flow, models.

1. Introduction

The presence of heavy metals in waters and soils is of great concern as significant environmental impacts have resulted because of the increasing industrial activities and the economic development. Although this development has led to important changes in our world, they have also induced an uncontrolled exploitation of natural resources and the release of contaminants which represent a potential hazard to both the environment and human health. Accordingly, the understanding of the possible contaminant dissemination and the respective metal transformation processes, as well as, the development of mitigation strategies are crucial. When heavy metals are released, they may be transported to uncontaminated environmental compartments and tend to bioaccumulate, causing an effect to the ecosystem by introducing themselves in the trophic chain (Mohan et al., 2007). Amongst heavy metals, copper is found within the pollutants of priority interest (EPA). When found at high concentrations, toxic effects to both living organisms and the environment can be observed. Consequently, this project was focused on copper contaminated waters remediation.

Furthermore, stringent environmental regulations are resulting as a consequence of the alteration on the biogeochemical cycles, especially in waters. In order to mitigate water contamination, sorption techniques can be applied as decontamination strategies. Semipermeable barriers with sorbent can be applied for the immobilisation of metals by an irreversible sorption of metals by the solid phase of the by-product, reducing the total contaminant concentration in waters. These are very promising due to their high efficiency and the availability of a wide range of sorbents for the removal of non-biodegradable pollutants as they enable a reduction of their mobility and prevent their distribution along the trophic chain (Mulligan *et al.*, 2001).

At the moment, activated carbon and metal oxides are a few of the most used sorbents as a high sorption efficiency has been well established when applied to waters. However, their high costs prevent their global application, especially in those countries in developing areas. Thus, the development of low-cost sorbents and effective methods that reduce the impact of heavy metals are necessary. Low-cost sorbents may be obtained from industrial waste, natural material, biosolids or

even agricultural by-products for a further re-use as soil amendments as well as contaminated water treatment. In this context, the use of biochar for the treatment of contaminated waters has recently gained much attention (Mohan *et al.*, 2014; Ahmad *et al.*, 2014). Both the biomass and its respective subproducts (e.g. biochar), are generated in large quantities, resulting in a negative environmental impact because of its waste management treatment need. Thus, it is interesting to find further uses such as its application as sorbents avoiding the generation of waste and introducing them back into the economy (circular economy).

1.1 Copper in the environment

Copper is an abundant trace element and is one of the few metals that occur naturally in the Earth's crust and in surface waters (Kabata-Pendias, 2011). These natural sources include geological deposits, volcanic activity and weathering and erosion of rocks and soils. Also, it can be found as a pure metal in nature. It is ductile, malleable and has high thermal and electrical conductivity. All these properties make it a very interesting element and therefore has many different applications such as in agriculture, pesticides, metal and electrical manufacturing, between others. All these activities end up releasing copper into the environment thus, high copper concentrations are found as a consequence of anthropogenic sources.

Besides, copper is an essential nutrient at low concentrations for living organisms, as it is important for many metabolic functions to take place. Regarding plants, it even plays a further role in oxidative enzymes due to its structural and functional importance. However, when found at high concentrations and there is chronic exposure, adverse effects on survival, growth, reproduction as well as potential alterations in the brain, enzyme activity and metabolism can be observed. Even, under extreme conditions, acute effects such as mortality may result (EPA, ATSDR).

1.2 Sorption and desorption processes

As a result of the potential toxicity and the respective mobility of the different heavy metals in the environmental compartments, it is important to develop techniques which constrain this, such as sorption.

Sorption is a physical-chemical process which describes the incorporation of a contaminant in the solid phase. This process may take place by means of different mechanisms such as; absorption, adsorption, ionic exchange and coprecipitation.

Absorption is described through the process by which ions or molecules are removed from a solution and accumulate within the internal existing solid constituents while adsorption entails the accumulation of an analyte in the specific sites of the solid surface of the soil (Sparks, 2003). Physical adsorption is associated to the type of interactions, either electrostatic or Van der Waals where the cation hydration sphere is maintained, while chemical adsorption relates the formation of chemical bonds such as hydrogen bonds or specific complexation where in these cases, the hydration sphere is lost (Stumm and Morgan, 1981).

Furthermore, ionic exchange would include the substitution of an ion exchanger from the solid phase by another one present in the solution while coprecipitation, takes into account the precipitation of an element, besides not found at a saturation concentration, due to the incorporation of such element into the structure of a precipitating compound (Sposito, 2008).

On the other hand, desorption can be simply explained as the reverse of sorption. However, it remains significantly important when assessing the uses of sorbents to avoid an undesired effect. Thus, it is essential to evaluate the sorption capacity of the sorbent as well as its reversible/ irreversible rate.

Above all, sorption capacities strongly depend on the specific heavy metal found in waters or soils as well as the solid and liquid phase composition which may differ. Accordingly, the physical-chemical properties of the metal and the pH of the medium also play an important role (Sauvé *et al.*, 2000).

1.3 Biochars as sorbents

A biochar is a carbon-rich material which results from a biomass pyrolysis. This pyrolysis involves the heating of the biomass in an oven at high temperature and in the absence of oxygen. At the same time, a biofuel is produced during this pyrolysis besides the biochar itself (Lehmann *et al.*, 2006).

Various kinds of biomass can be used such as wood, leaves, manure, etc. Hence, the specific intrinsic properties of each biochar as well as its sorption capacity clearly depends on the initial biomass. Further key parameters that control the biochar's properties rely on the pyrolysis temperature, residence time and heat transfer rate (Ahmad *et al.*, 2014).

During the biomass pyrolysis, the organic matter is thermally decomposed, releasing gases and volatile organic compounds. Moreover, important structural changes take place, in concrete, their aromaticity increases enabling them to adopt rigid structures such that of graphite (Schmidt and Noack, 2010). Subsequently to its recalcitrant structure, biochars are very resistant to chemical and thermic oxidation processes (Skjemstad *et al.*, 1996). Besides, at relatively high temperatures between 500 °C and 700 °C biochars retain about 90 % of their carbon composition however become less polar and more aromatic as the oxygen and hydrogen contents remain very low (Chun *et al.*, 2004; Chen *et al.*, 2008). In contrast, biochars obtained at lower temperatures between 300 °C and 500 °C, are observed to have lower carbon content but higher hydrogen and oxygen percentages.

Biochars present many potential applications and advantages (Fig. 1) including soil quality improvement due to their high organic carbon content and porosity which leads to an increase in the soil water and nutrient retention (Glaser *et al.*, 2002). Moreover, the fact of converting biomass into biochar and its application to soils allows carbon sequestration, avoiding the release of CO₂ emissions into the atmosphere (Cheng *et al.*, 2008; Singh *et al.*, 2012). Thanks to the biochar's long-term stability, it has been proposed to be included as an action to mitigate climate change (Lehmann *et al.*, 2006). At the same time, the biochars large surface area and microporosity enables its effective use as sorbents (Yu *et al.*, 2009; Yang *et al.*, 2010; Lou *et al.*, 2011).

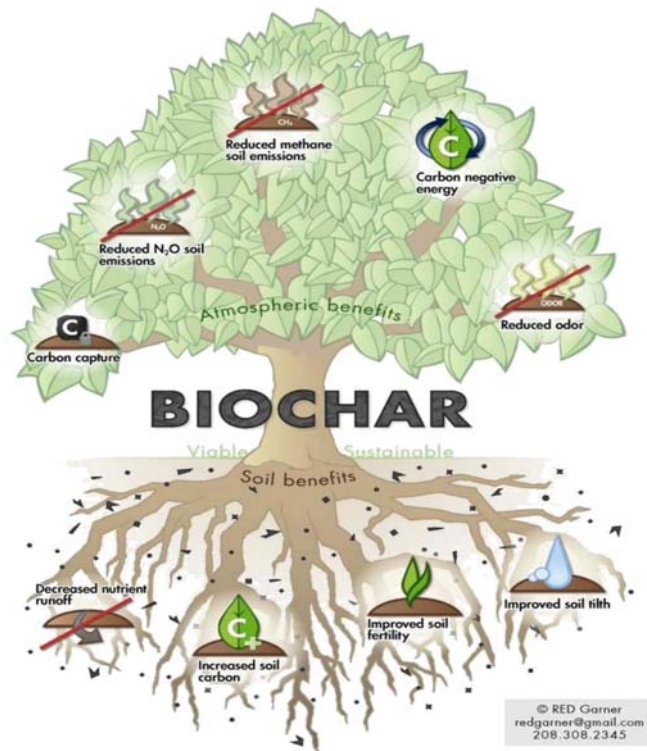


Figure 1: Biochar's advantages.

Furthermore, if biochars are compared to activated carbon, a lower surface area and porosity may be observed (Han *et al.*, 2013; Wang *et al.*, 2015). However, they result in a high content of acid functional groups in their surface which provide them an enhanced metal sorption efficiency due to its interaction capacity with different organic and inorganic compounds (Han *et al.*, 2013). On the other hand, this enhanced metal sorption strongly depends on the type of biomass applied and their specific intrinsic properties which define the biochar and closely relates it to their sorption capacities (Tan *et al.*, 2015; Wang *et al.*, 2015). Thus, biochars can be considered as low cost-biosorbents for heavy metal removal.

There are many sorption studies concerning the application of biochars as sorbents. However, assessments concerning their sorption capacity have been mainly restricted to batch experiments (Tong *et al.*, 2011; Uchimiya *et al.*, 2011; Venegas *et al.*, 2015; Doumer *et al.*, 2016). On the other hand, further interest lies on evaluating other methods such that of a continuous-flow using fixed-bed columns. Research in recent years has indicated that biomaterials may accumulate very high concentrations of inorganic contaminants and hence there are some studies concerning continuous-flow experiments with different low-cost

sorbents such as; seaweed algae (Silva *et al.*, 2002), rice husk (Vadivelan *et al.*, 2005), natural zeolite (Han *et al.*, 2007) and coconut shell (Acheampong *et al.*, 2013) between others. However, not many continuous-flow sorption studies have been done figuring biochar as an approach for environmental management and as a valuable water and soil amendment (Yu *et al.*, 2009; Yang *et al.*, 2010; Lou *et al.*, 2011).

2. Objectives

The aim of this project is to develop and optimise a continuous-flow sorption technique to evaluate the viability of the application of biochars as sorbents for water remediation. Hence, experimental analysis concerning a continuous-flow was performed for the first time in the research group instead of batch experiments, to obtain more representative results for a real case scenario.

The following specific objectives will be addressed:

- Setup of the continuous-flow sorption technique and preliminary assessments of the effect of the experimental operating conditions.
- Evaluation of the effect of the inlet copper concentration and the flow rate on the sorption rates. This allows a better understanding of the mechanisms involved and the sorption efficacy.
- Fitting of adsorption models to study the performance of the experimental breakthrough curves obtained and evaluate the resulting kinetic rates and maximum sorption capacities. Different models were applied and compared in order to detect the most accurate concerning our breakthrough curves for a future appropriate design and scale up of the sorption column.
- Study the copper desorption percentages to evaluate the reversibility/irreversibility of the sorption.

3. Materials and methods

3.1 Materials and reagents

3.1.1 Biochar

A biochar obtained from the pyrolysis of tree bark biomass from Vilafranca del Penedès (Catalunya) was investigated. This biochar was obtained by the following synthesis process where at instance the biomass was air-dried and then it was heated at 400 °C during 3 hours in a nitrogen atmosphere closed reactor, hence, without the presence of oxygen (Venegas *et al.* 2015).

The application of the tree barks biochar (TB) was decided as it is very homogenous and due to its low particle size distribution. At the same time, good sorption and desorption capacities were obtained in previous work done under batch conditions (Venegas *et al.*, 2015), therefore it seemed a potential biosorbent to start with. The characterisation of important properties of the tree barks biochar quantified previously by the research group are gathered in Table 1 (Venegas *et al.*, 2015).

Table 1: Tree barks (TB) biochar characterisation.

Parameters	TB	Major & trace elements (mg kg ⁻¹)	
pH	9	Ca	21530
Moisture content (%)	4.5	Mg	1910
TOC (%)	77	K	3380
C (%)	80	Fe	1640
DOC (%)	0.075	Al	685
EC (mS/cm)	0.37	Mn	27
N (%)	171	Cu	33
C/N	8	Zn	73

TOC: Total organic carbon; DOC: Dissolved organic carbon; EC: Electric conductivity.

3.1.2 Copper solution

A copper solution of 1000 meq L⁻¹ was prepared by dissolving 12.08 g of a copper(II) nitrate trihydrate (Cu(NO₃)₂·3H₂O) salt in 100 mL of doubled-deionised water, Mili-Q (resistivity > 18.2 MΩ). A stock solution of 50 meq L⁻¹ (1588 mg of Cu(II)) was then prepared and further copper solutions of lower concentrations

(794, 158, 64, and 32 mg L⁻¹) were then obtained by diluting this stock solution with the appropriate amount of double-deionised water.

3.2 Continuous-flow sorption technique

3.2.1 Experimental setup

The process consisted on an automatic system where a contaminated copper solution was continuously injected and different fractions were collected as it passed through a column of biochar. The following operating parameters were set based on a study concerning volcanic ashes (Cabr  *et al* 2016). First of all, the material, TB, was packed into a vertical column of 8 cm long and 2.25 cm² of cross-sectional area (Teledyne ISCO Ref. 69-3873-140). Moreover, the column was filled with a known amount of TB and the material was compacted and its height was recorded. A silica filter of average pore size diameter of 60   was attached at the column inlet and outlet. A peristaltic pump (Miniplus3, Gilson) was set at the head of the column to ensure a constant and stable flux rate from top to bottom of the column. At the column outlet, a fraction collector (FC 204, Gilson) was connected directing the samples to polypropylene test tubes (Fig. 2).

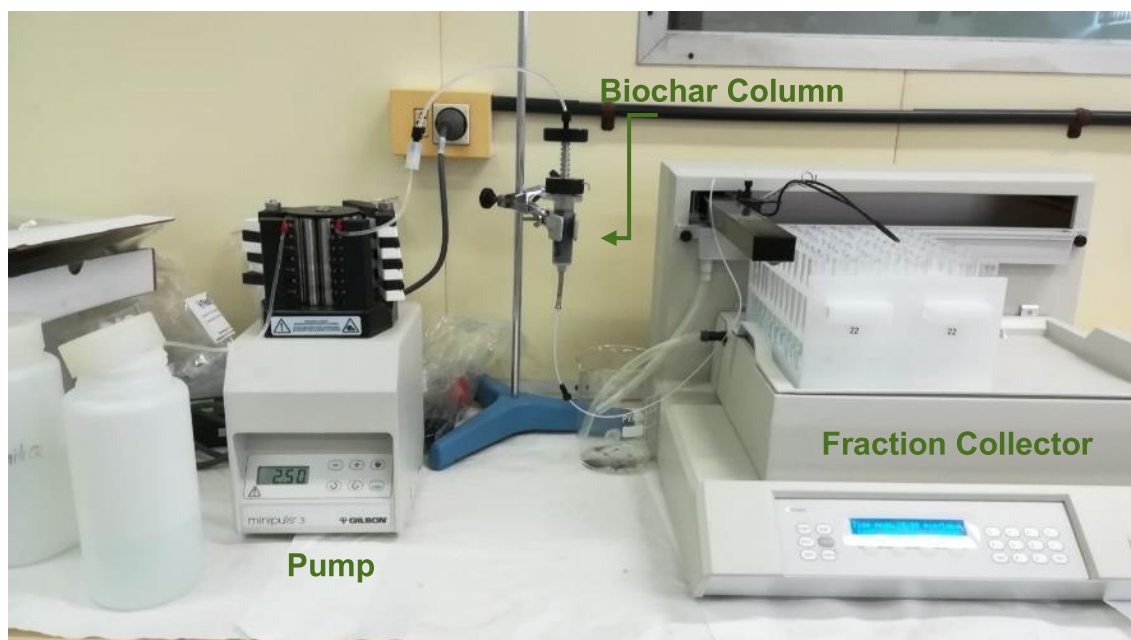


Figure 2: Continuous-flow sorption technique.

Then, a pre-equilibrium stage was performed where a contaminant free solution (double deionised water) was injected at a constant flow rate (Q) of 0.28 mLmin⁻¹ or 1 mL min⁻¹ to humidify the biochar and promote a pre-equilibrium between the

solid and the matrix until a constant flow rate was established. Following a known contaminant concentration (C_0) was injected at the same flow rate and the outlet concentration at a given time t was analysed (C_t). This time t was set according to the fraction collector time mode established. This step would be considered as the sorption stage where the sorbent will gradually be sorbing the contaminant until a saturation point is reached. Finally, a desorption stage was carried out where the contaminant solution stopped being injected and instead a contaminant free solution (double deionised water) was injected. Again, the outlet concentrations (C_t) were measured and the copper concentration is expected to drop to 0. This step enables to prove the irreversibility of the processes implied and a copper desorption percentage can be obtained.

3.3 Quantification of copper concentration

Copper determinations in the inlet solution and collected samples were carried out with an atomic absorption spectrometer (AAS, Perkin Elmer, model 1100 B) with an air-acetylene flame (see figure 3). This is a routine analytical technique used frequently at the laboratory thanks to its low cost and high robustness. The linear range of the AAS for Cu(II) is from 0.5 to 5 mg L⁻¹. A 6-point calibration curve was applied with a blank solution and copper solutions of 0.5, 1, 2, 3.5 and 5 mg L⁻¹. A resulting linear calibration line ($R^2 > 0.999$) was required as bases to continue with the sample measurements. Before measuring, all samples were prepared in a 1 % HNO₃ medium.

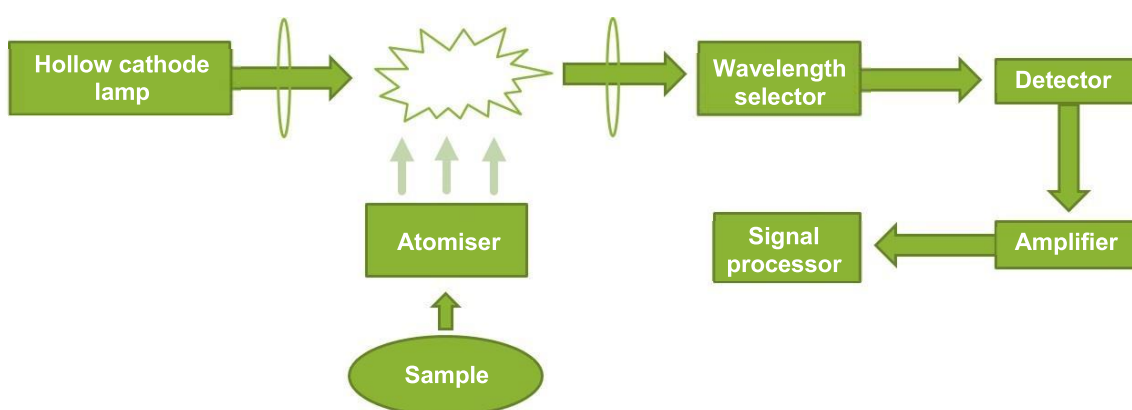


Figure 3: Flame atomic absorption spectroscopy.

3.4 Data treatment

As explained above, the continuous-flow sorption technique involves the use of a column which is traversed by a constant flow with the target analyte solution, in this case copper. As a result, an S-shaped breakthrough curve (Fig.4) is obtained which demonstrates how the solid sorbent is gradually getting saturated.

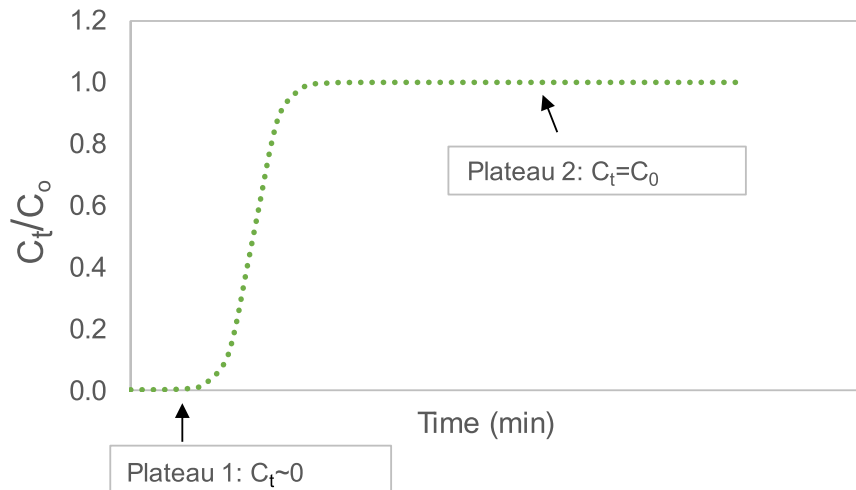


Figure 4: Continuous-flow sorption breakthrough curve.

Two objectives are expected to be observed; at instance, the presence of a *plateau 1* which explains the initial contaminant sorption where we expect to observe values of $C_t \approx 0$ as the contaminant is being sorbed onto the biochar. At a certain point, the *plateau 1* breaks as the sorption rate decreases and hence a slight contaminant concentration starts to appear at the outlet. This concentration keeps on increasing until a further *plateau 2* is observed where $C_t/C_0 \approx 1$ meaning that the outlet concentration is the same as the injected concentration thus, the biochar has reached its saturation point in terms of analyte sorption.

3.4.1 Parameters derived from mass balance equation

The biochar's sorption capacity for a given inlet concentration and flow rate can be calculated through a mass balance resumed by equation (1):

$$q_{\text{exp}} = \frac{C_0 Q t - C_t V_t}{m} \quad (1)$$

where C_0 would be the inlet concentration, Q the flow rate, C_t the outlet concentration collected at time t , V_t the volume collected at time t , and m the

biochar mass. Thus, q_{exp} is expressed as the amount (mg) of contaminant, copper, per mass (g) of sorbent in this case TB. The q_{exp} values were obtained for every different operating condition.

3.4.2 Sorption models and derived parameters from fitting

The time for the breakthrough appearance and its shape are important concerns in order to understand the effect of the operating conditions and the dynamic response of the sorbent column. Hence, the breakthrough data obtained was fitted to adsorption models, where kinetic parameters and sorption capacities of the column were determined.

The Thomas model and the Adams Bohart model are commonly adopted to predict breakthrough curves. By applying these models, the kinetics of the breakthrough curves as well as the maximum sorption capacities can be evaluated enabling a better understanding of the interaction processes that take place between the solid and liquid phases and a validation of the sorbent efficiency when trying to remediate contaminated waters.

Thomas Model

The Thomas model is a theoretical model widely used to describe adsorption in a continuous-flow sorption process and to predict breakthrough curves. This model assumes a Langmuir isotherm and that sorption can be described by a pseudo second-order reaction rate expression shown in equation 2.

$$\frac{C_t}{C_0} = \frac{1}{1 + \exp(k_{Th} q_0 m / Q - k_{Th} C_0 t)} \quad (2)$$

From the operational parameters established; the initial concentration (C_0), flow rate (Q), sorbent mass (m), effluent time, and the measured outlet concentration collected at time t (C_t), the respective Thomas adsorption parameters are deduced. Hence, a velocity constant (k_{Th}) and a maximum adsorption capacity (q_0) are estimated. This maximum adsorption capacity is given in milligrams of contaminant (copper) per grams of sorbent (TB biochar) thus can be compared to the sorption capacity (q_{exp}) deduced from Eq. 1.

Furthermore, the Thomas model considers that both the axial and radial dispersion in the fixed-bed column are negligible (Thomas 1944).

Adams Bohart Model

Adams Bohart model is based on the surface reaction theory which assumes that equilibrium is not instantaneous. Thus, the adsorption rate is proportional to the adsorption capacity which still remains on the sorbent. This model is used for the description of the initial part of the breakthrough curve (Bohart and Adams, 1920).

$$\frac{C_t}{C_0} = \exp \left(k_{AB} C_0 t - k_{AB} N_0 \frac{Z}{F} \right) \quad (3)$$

Equation (3), shows how the model takes into account the operating parameters concerning in this case the bed height (Z) and linear velocity rate (F), as well as the inlet concentration (C_t) and the time t , to predict a kinetic constant (K_{AB}) and a maximum adsorption capacity (N_0) in terms of milligrams of copper per volume of biochar.

The corresponding errors associated to each parameter were obtained for both the Thomas and Adams Bohart models using a SOLVSTAT excel macro or regression analysis where in this second case the associated error was multiplied by the different parameters involved.

4. Results and discussion

4.1 Repeatability of experiments

4.1.1 Tree barks biochar packing conditions

Six experiments of copper(II) sorption in biochar were performed in a fixed-bed column. The copper(II) inlet concentration, the flow rate, the mass of biochar introduced and the column height were recorded and are shown in Table 2. An average constant flow rate of 0.28 mL min^{-1} was achieved for five of the experiments and in another case 1.0 mL min^{-1} , while an average mass of 3.53 g of biochar was packed into the columns obtaining a height of 4.08 cm . From the amount of mass and the respective volume occupied, the biochar's bulk density for each experiment was calculated giving an average of 0.43 g cm^{-3} . The relative standard deviation (RSD) associated to each packing parameter was around 3 % in all cases hence a packing procedure repeatability was proved.

Table 2: Operating conditions and fixed-bed properties.

Experiment	Cu concentration (mg L ⁻¹)	Flow rate (mL min ⁻¹)	Biochar mass (g)	Column height (cm)	Bulk density (g cm ⁻³)
1	794	0.27	3.51	4.0	0.44
2	171	0.27	3.33	3.9	0.44
3	158	0.29	3.60	4.1	0.44
4	64	0.28	3.58	4.3	0.41
5	32	0.28	3.60	4.1	0.44
6	32	1.0	3.55	4.1	0.43

4.1.2 Breakthrough curves

The repeatability of the breakthrough curves was also studied for copper concentrations around 5 meq L⁻¹ concretely measured to 171 mg L⁻¹ and 158 mg L⁻¹. As we can observe in Figure 5 the respective breakthrough curves obtained were very similar hence experimental repeatability was demonstrated. Concerning the breakthrough curve's slope and the time that was needed to reach the breakthrough point also remained consistent for both experiments.

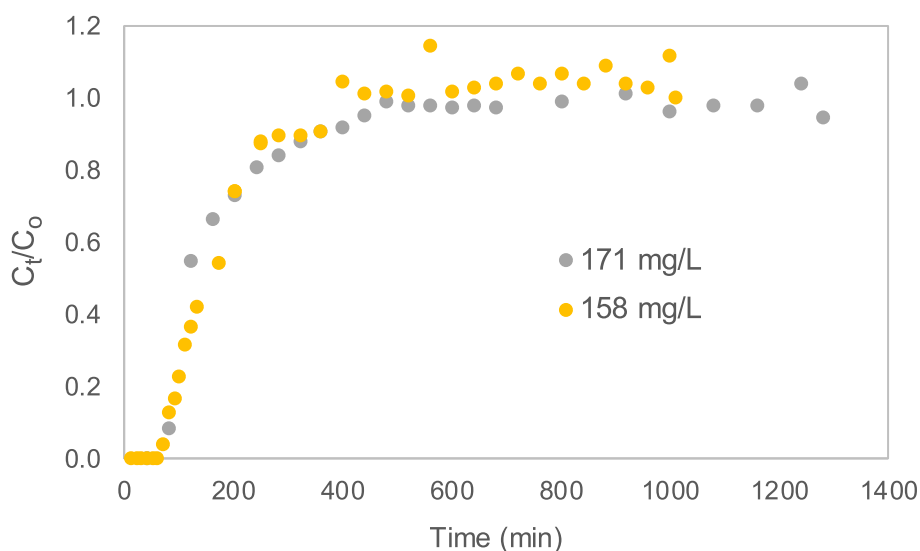


Figure 5: Experimental breakthrough curves repeatability.

4.2 Effect of the initial copper concentration

Figure 6 presents the sorption breakthrough curves for the different concentrations analysed at the same flow rate. We observed that as the initial concentration increased a steeper breakthrough curve resulted and the earlier the *plateau 2* was reached.

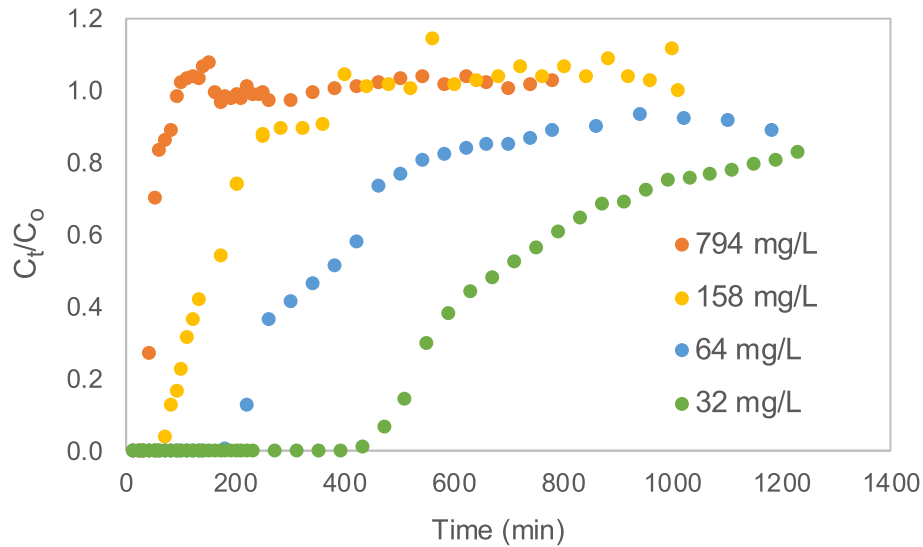


Figure 6: Varying inlet concentration breakthrough curves .

Accordingly, higher values of copper sorption capacity (q_{exp}) were obtained for the highest concentration as we can see in Table 3. This phenomena could possibly be attributed to the influence of a higher gradient concentration between the liquid and the solid phases at increasing initial concentrations, that is to say, as a consequence of a greater driving force. A high concentration could therefore, provide a large driving force for the biosorption process. However, the saturation of the sorbent requires much more time but due to the high gradient concentration, breakthrough is reached before all the active sites of the TB are occupied by Cu(II), leading to a shorter *plateau 1* (Acheampong *et al.*, 2013).

Table 3: Tree barks biochar sorption capacity.

Cu concentration (mg L ⁻¹)	Flow rate (mL min ⁻¹)	q_{exp} (mg g ⁻¹)
794	0.27	3.96
158	0.29	1.66
64	0.28	2.03
32	0.28	2.20
32	1	1.50

Concerning the concentrations of 64 and 32 mg L⁻¹ we observe a delay in the breakthrough point proceeded by a decrease in the curves steepness. At the same time, a C_t/C₀ relationship of 1 is never reached eventhough the solutions were left during more time. We assume that the reason for this is that at lower concentrations, the more specific sites are involved hence there are other sorption mechanisms that could be taking place.

4.3 Effect of the flow rate

The effect of the flow rate on the copper sorption onto the TB biochar was examined at two different flow rates; 0.28 mL min⁻¹ and 1.0 mL min⁻¹ at a constant bed height of 4.1 cm and at an initial copper concentration of 32 mg L⁻¹. The results are presented in Fig. 7 where we can observe that at a higher flow rate, the breakthrough curve occurred faster and hence the *plateau 1* resulted shorter. Subsequently, as we can observe in Table 3, the copper sorption capacity (q_{exp}) decreased at an increasing flow rate. This phenomenon could attributed to an insufficient residence time of the solute to provide contact between the copper and the available binding sites at the internal and external surfaces of the biochars at the highest flow rates (Chu, 2010; Salman *et al.*, 2011). This idea appeared to be consistent with the decreased value of q_{exp} from 2.20 to 1.50 mg g⁻¹ when the flow rate was increased from 0.28 mL min⁻¹ to 1 mL min⁻¹ respectively.

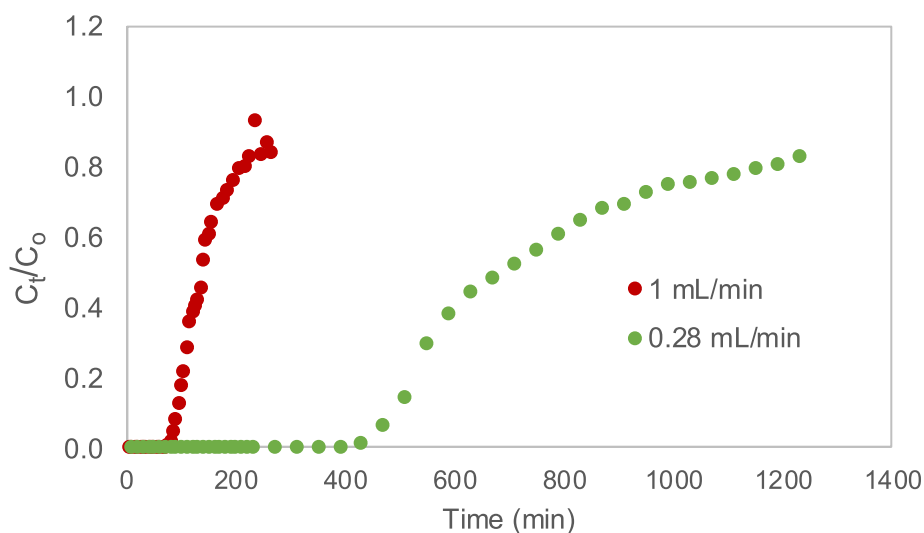


Figure 7: Different flow rate breakthrough curves.

However when we zoom into the 1 mL min⁻¹ breakthrough curve (Figure 8) we observe that eventhough the time to reach breakthrough is largely reduced, the sorption pattern remains very similar to that of 0.28 mL min⁻¹ and that eventhough

the flow rate was increased, for a concentration of 32 mg L^{-1} a C_i/C_0 relation of 1 was still not reached emphasising again a possible explanation due to sorption mechanisms involving the more specific sites of the sorbent.

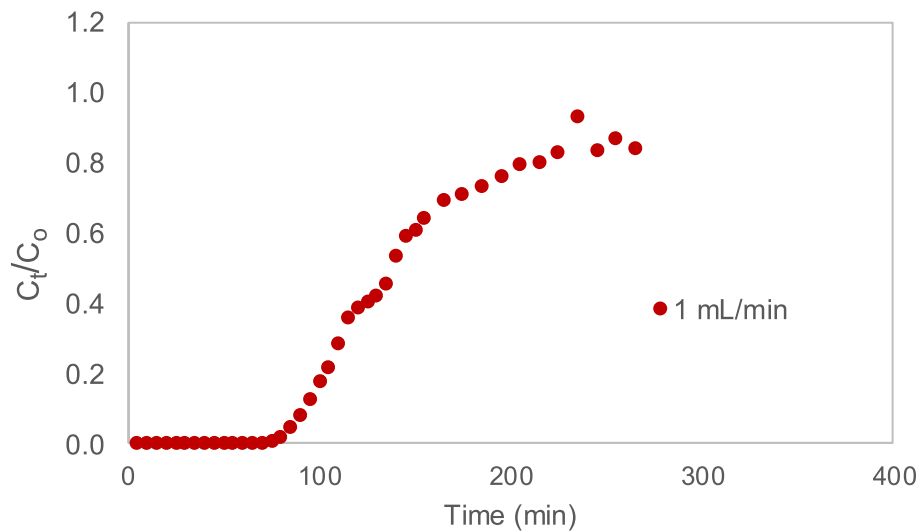


Figure 8: Higher flow rate breakthrough curve .

4.4 Fitting of breakthrough curves

Adsorption modelling of the breakthrough curves is essential to determine important continuous-flow sorption parameters. Hence, both nonlinear and linear analysis were used to obtain Thomas adsorption model parameters as well as the Adams Bohart model to describe the initial part of the breakthrough curve.

4.4.1 Nonlinear Thomas fitting

The breakthrough curves and the respective nonlinear Thomas fitting for the different concentrations are shown in Figure 9 where, qualitatively, it seems that at high concentrations (794 and 158 mg L^{-1}) a better fitting is achieved. However, when the lower concentrations were fitted, the model appears to deviate from the *plateau 1* and *plateau 2* experimental points. If we take into account the fact that the C_i/C_0 relationship for these concentrations did not reach 1 and the slight fitting deviation, we could possibly attribute this to the fact that at lower concentrations, where the more specific sites are enrolled, the model requirements may not be met as other processes rather than adsorption could be taking place.

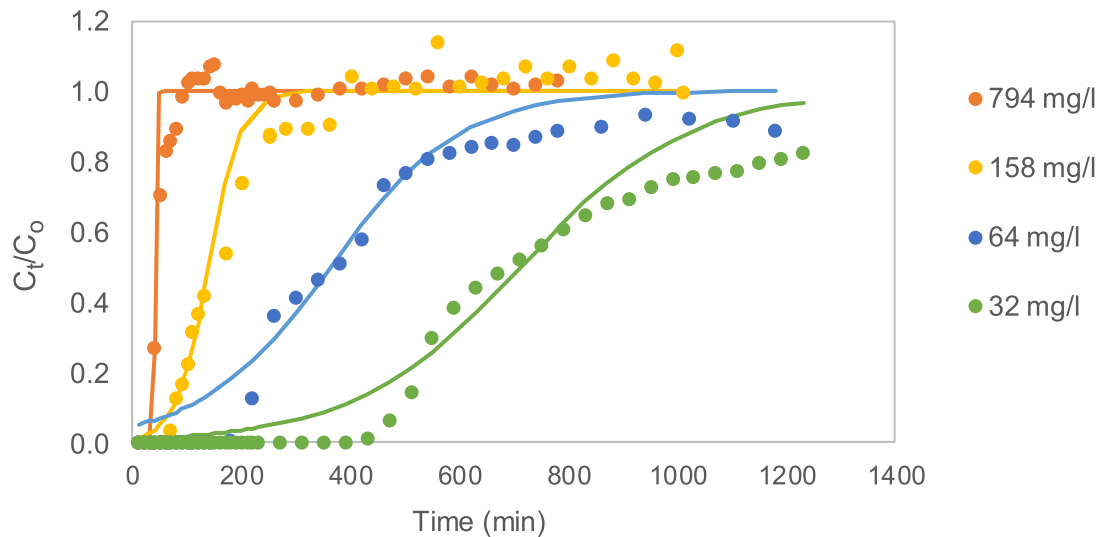


Figure 9: Nonlinear Thomas fitting for varying concentrations. The discontinuous lines are the experimental points and the continuous lines correspond to the model fitting.

However, when the Thomas constant rates (k_{Th}) and the maximum sorption capacities (q_0) as well as their respective associated error were evaluated (Table 3), for the highest concentration of 794 mg L^{-1} , a very large error was associated to the the derived K_{Th} parameter, hence the q_0 value could not be derived. This error could be related to the fact that in this case, sorption takes place really quickly, hence, further experimental points concerning lower time intervals would be necessary for a better approach.

From the other preliminary experiments, it appears that the q_0 value for the TB biochar remains around 1.80 mg g^{-1} regardless the inlet concentration. The p-values obtained were of 0.075 which enables us to say that the fitting parameters derived are significant for a significance level of 0.1.

Table 4: Thomas model parameters using nonlinear regression analysis. In brackets the respective parameter associated error.

Inlet concentration (mg L^{-1})	Flow rate (mL min^{-1})	Non linear Thomas		
		K_{Th} ($\text{mL mg}^{-1} \text{ min}^{-1}$)	q_0 (mg g^{-1})	p-value
794	0.27	0.86 (3)	-	-
158	0.29	0.22 (0.03)	1.74 (0.06)	0.08
64	0.28	0.13 (0.01)	1.79 (0.07)	0.08
32	0.28	0.19 (0.01)	1.96 (0.04)	0.07

Figure 10 shows the nonlinear Thomas fittings for the two different flow rates. When the flow rate was increased to 1.0 mL min⁻¹, we observed that the K_{Th} consequently increased from 0.19 to 0.94 (0.07) while the q_0 slightly decreased from 1.96 to 1.30 (0.02), possibly related to the fact that increased flow rates difficulties the maximum sorption capacity to be reached.

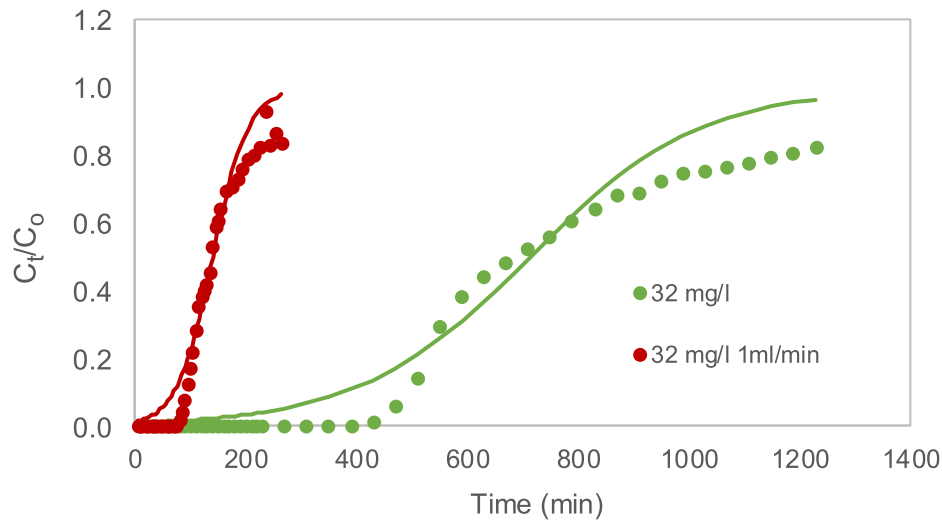


Figure 10: Nonlinear Thomas fitting for the two flow rate conditions. Where the discontinuous lines are the experimental points and the continuous lines correspond to the model fitting.

4.4.2 Linear Thomas fitting

As the fitting of the nonlinear Thomas model deviated from the experimental points at low concentrations, the linear thomas fitting was applied for a better modelling of the breaking of the *plateau 1* of the breakthrough curves. Hence, Eq. 4 was applied (Achaempong *et al.*, 2013):

$$\ln\left(\frac{C_0}{C_t} - 1\right) = \frac{k_{Th} q_0 m}{Q} - k_{Th} C_0 t \quad (4)$$

where the K_{Th} is obtained from the slope of the graph while the q_0 from the y-intercept. The linear fitting was performed concerning only the first experimental points from the curve.

Figure 11 shows the respective linear fitting for each concentration where a better agreement with the experimental points was observed. As we can observe from Table 5 the q_0 for the highest concentrations 794 mg L⁻¹ and 158 mg L⁻¹ did not seem to vary from that obtained by the nonlinear Thomas fitting. However, major differences concerning the kinetic parameter were observed as not all the experimental points were taken into account hence they can be negligible.

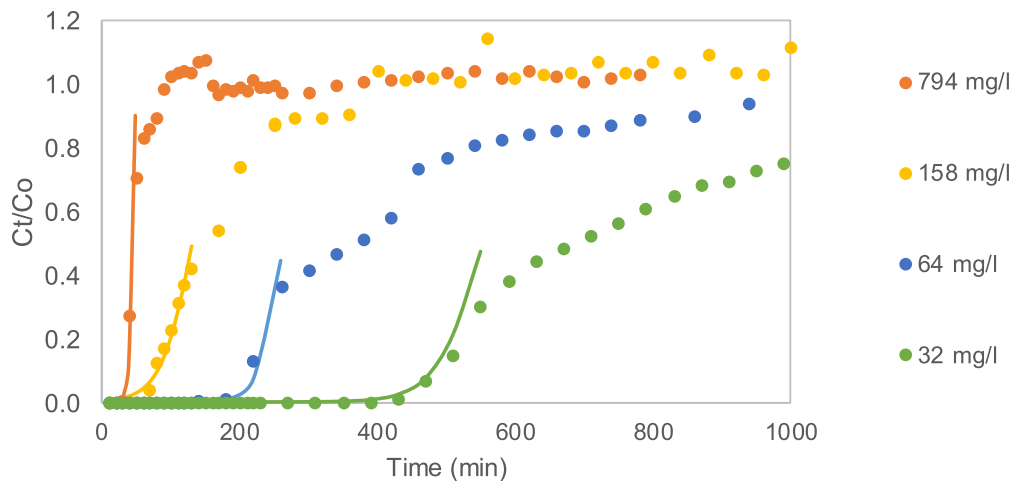


Figure 11: Linear Thomas fitting for the different concentrations. Where the discontinuous lines are the experimental points and continuous lines correspond to the model fitting.

From Table 5 we can observe the q_0 values determined for each varying concentration. In the case of the 794 mg L⁻¹ concentration, we obtained an insignificant q_0 value as the p-value was very high. This fact, could possibly be attributed to the fact that our column height / geometry was not appropriate for such elevated concentrations and seems that other processes regarding axial and radial dispersion could be taking place, thus the Thomas model requirements would not be met.

Table 5: Thomas model parameters using linear regression analysis. In brackets the respective parameter associated error.

Inlet concentration (mg L ⁻¹)	Flow rate (mL min ⁻¹)	Linear Thomas		
		K_{Th} (mL mg ⁻¹ min ⁻¹)	q_0 (mg g ⁻¹)	p-value
794	0.27	-	2.76 (-)	0.18
158	0.29	-	1.63 (0.18)	0.0003
64	0.28	-	1.30 (0.10)	0.006
32	0.28	-	1.52 (0.17)	0.01
32	1.0	-	0.94 (0.09)	0.01

Regarding the other concentrations, a much better fitting was achieved as the p-values obtained were significant for a significance level of 0.05 and we observed that as a consequence, the q_0 values slightly decreased from that obtained from the nonlinear fitting.

Concerning the lower concentrations of 64 and 32 mg L⁻¹ where, as explained before a C_t/C_0 relation of 1 was not reached due to the involvement of specific sites, even lower q_0 than those obtained from the nonlinear Thomas were obtained implying an even stronger sorption interaction possibly related to intra-porous absorption mechanisms.

In the case of the increased flux rate the same effect was observed where the q_0 decreased from a nonlinear Thomas value of 1.30 to 0.94.

Kinetic parameters were not determined as only a part of the curve is fitted, hence the value obtained would not represent the kinetics of the whole breakthrough curve.

4.4.3 Adams Bohart fitting

According to the literature, the Adams Bohart model is useful for the description of the initial region of the breakthrough curve ($C_t/C_0 < 0.15$). Thus, predictions were proceeded using this criteria and are shown in Figure 12.

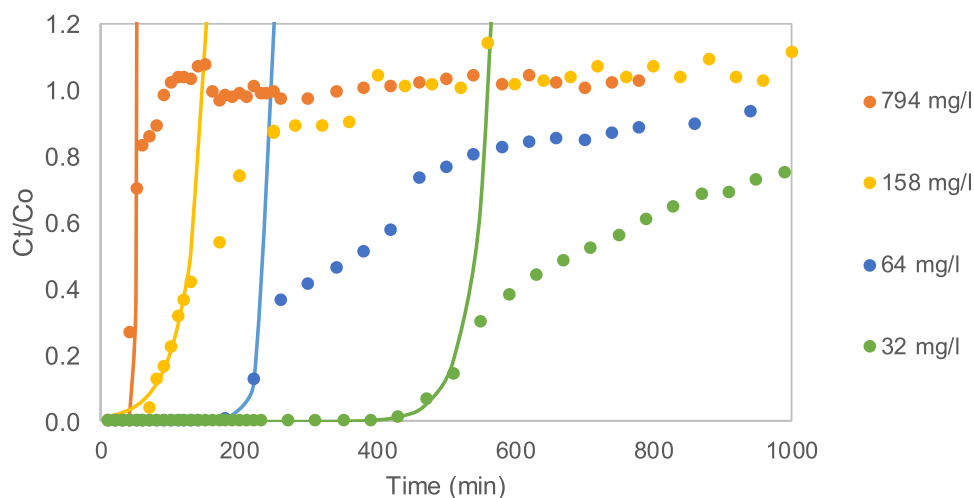


Figure 12: Adams Bohart fitting for the different concentrations. Where the discontinuous lines are the experimental points and continuous lines correspond to the model fitting.

From Figure 12, it seems that good agreements were obtained concerning the experimental points and the fitting. In Table 6, the derived kinetic parameters and maximum sorption capacities are shown. We observe that a TB sorption capacity of approximately 40 mg L⁻¹ could be established as it remained consistent regarding the concentrations of 158, 64, 32 mg L⁻¹ at a flow rate of 0.28 mL min⁻¹ and at significant p-values of significance level of 0.05.

Regarding the 794 mg L⁻¹ concentration, although the p-value gave significant, the error associated to the value of N_0 could be possibly related to the fact that for the plotting of ($C_t/C_0 < 0.15$) very few points were taken into account as the sorption took place very quickly and further reading resolution would be necessary for a better fitting agreement.

Table 6: Adams Bohart model parameters. In brackets the respective parameter associated error.

Inlet concentration (mg L ⁻¹)	Flow rate (mL min ⁻¹)	Adams Bohart		
		K_{AB} (mL mg ⁻¹ min ⁻¹)	N_0 (mg L ⁻¹)	p-value
794	0.27	2.16 (0.0006)	20 (2.60)	0.00001
158	0.29	0.77 (0.00006)	44.23 (0.74)	0.004
64	0.28	1.03 (0.0001)	39.23 (0.67)	0.003
32	0.28	0.92 (0.0004)	47.52 (0.5)	0.008
32	1.0	4.13 (0.0004)	9.32 (0.09)	0.008

4.5 Desorption assays

As mentioned before, desorption is the final, but essential, step when evaluating the sorption capacity of a sorbent to explore its sorption reversibility. Thus, desorption assays on three biochar of different previous sorption inlet concentrations were performed (Fig. 13).

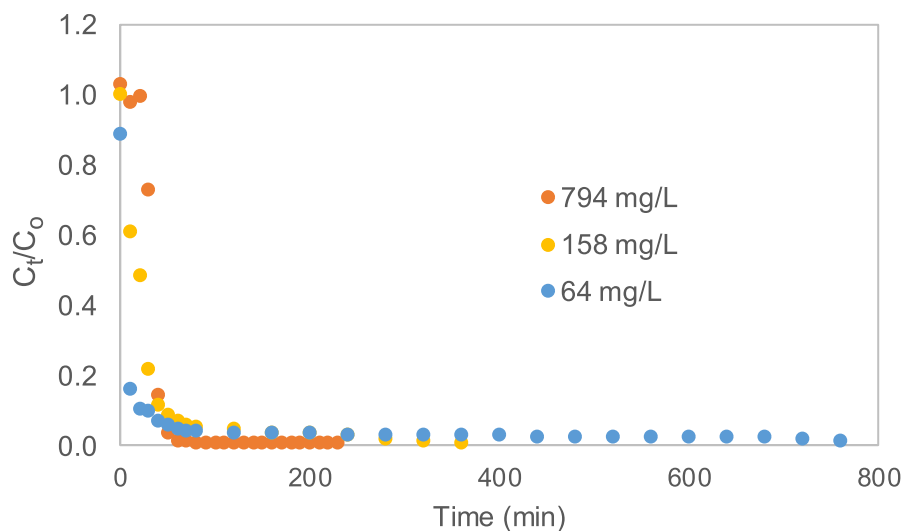


Figure 13: Desorption experimental curves.

As we can observe from Figure 13 each concentration appear to follow similar trends where the C_t/C_0 relationship dropped from the inlet concentration of the previous sorption step to approximately 0 in a short time. The first part would be described by the discharge of the previous sorption step contaminant concentration from the system. Furthermore, we observe that no matter the time it was left to desorb, the C_t/C_0 remained close to 0 without variations.

Moreover, desorption copper percentages were calculated considering Eq. 5 where C_t would be the concentration found after the discharge time and V_t the volume of the fraction. The desorption percentages are recorded in Table 7.

$$\text{Desorption \%} = \frac{C_t V_t}{q_0 m} \times 100 \quad (5)$$

Table 7: Copper desorption percentages parameters.

Previous sorption inlet concentration (mg L ⁻¹)	Flow rate (mL min ⁻¹)	Desorption time (min)	Desorption (%)
794	0.28	230	0.17
158	0.28	360	0.28
64	0.28	760	0.22

Desorption percentages determined were less than 0.3 % in all cases and it seems that there was not much influence concerning the previous sorption step inlet concentration.

5. Conclusions and future perspectives

The development of a continuous-flow sorption technique to assess the application of tree barks-based biochar for copper removal from waters was investigated in this project. The main following conclusions can be drawn.

Regarding the setting up of the continuous-flow sorption technique, a high dependency of the operation conditions on the type of breakthrough curve obtained, the derived parameters and the processes taking place was proved. Through the bibliographical research and the experiments carried out the

important role of the height and column geometry, the biochar packing, the flow rate and the analyte concentration was proved and thus must be taken into consideration when performing such experiments. Moreover, the resolution of the readings, that is to say, the number of points per hour measured is important in order to ensure more precise sorption breakthrough curves.

Through the evaluation of the effect of the inlet copper concentration and the flow rate on the sorption, it was proved that they largely affect the shape of the breakthrough curves and the biochar saturation point. At the same time, the continuous-flow sorption technique proved to be very promising as it enables to study the kinetics involved and to estimate maximum sorption capacities concerning the tree barks biochar and other material to be tested in the future.

The Thomas and Adams Bohart modelling, helped to derive very useful parameters concerning the sorption kinetics and the maximum sorption capacity. However, some limitations were observed specially concerning the highest concentration where badly fitting and very large errors associated to the parameters were obtained. Nevertheless, although the different models were applied and compared in order to detect the most accurate, we believe that all three are necessary to proceed, as they were complementary to each other. All parameters derived provided important information that should be taken into account in a future for appropriate design and scale up of the sorption column for the biochar application as semipermeable barriers for in-situ remediation.

From the preliminary results we can conclude that at lower concentrations other mechanisms from that of sorption only based on surface adsorption seem to be taking place, possibly intraporal absorption, hence full TB saturation was not reached. For the higher concentration of 794 mg L^{-1} , the column was possibly too small for such concentration and hence axial and radial dispersion seem to be taking place thus no good fitting agreement was derived. The results obtained from 158 mg L^{-1} proved good fitting agreements and C_t/C_0 relations of 1. Moreover, similar maximum sorption capacities were obtained from two approaches such as the mass balance (q_{exp}) and the Thomas model (q_0), thus indicating that the maximum sorption capacity was well derived for a range of various initial Cu concentrations tested.

With respect to the evaluation of the reversibility/irreversibility of the sorption, desorption yields lower than 0.30 % were obtained thus we can say that TB has a low sorption reversibility and confirms its suitability for Cu removal from waters.

Further experiments addressed to better examine the role/effect of the flow rate as well as the evaluation of the effect of the column's height remain interesting to be explored and necessary to ensure a better robustness of the technique to assess the suitability of other candidate materials for water remediation. Likewise, the related effect of the particle size of the sorbent material could be studied and the continuous-flow sorption studies could be related to previous batch work performed by the research group.

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