Universitat de Girona
Escola Politècnica Superior

Treball Final de Grau/Carrera

Realitzat i defensat a
Czech University of Life and Sciences Prague (nom universitat) de
República Txeca (país)

Estudi: Grau en Enginyeria Química Pla 2009

Títol: Cork waste for metal removal from aqueous solution

Document:

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Convocatòria (mes/any): Juny 2015

CZECH UNIVERISTY OF LIFE SCIENCES PRAGUE

FACULTY OF ENVIRONMENTAL SCIENCES

UNIVERSITAT DE GIRONA

ESCOLA POLITÈCNICA SUPERIOR

BACHELOR THESIS

‘‘CORK WASTE FOR METAL REMOVAL FROM AQUEOUS SOLUTION’’

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PRAGUE 2015

Content

CZECH UNIVERSITY OF LIFE SCIENCES PRAGUE

Department of Environmental Geosciences

Faculty of Environmental Sciences

FINAL THESIS ASSIGNMENT

Daniel Cava Barrocal

Exchange programs

Thesis title

Cork waste for metal removal from aqueous solution

Objectives of thesis

The main objective of the thesis is to evaluate the potential of cork waste to adsorb toxic metals (Cr and Cu) from aqueous solution.
Particular objectives are:
1) to prepare BIOCHAR from the cork
2) to perform the sorption batch kinetic experiments with the cork and the biochar, evaluate the effect of time on Cr and Cu adsorption and fit the experimental data to the commonly applied pseudo-first-order and and pseudo-second-order equations
3) to perform the sorption batch equilibrium experiments, construct Langmuir and Freundlich equilibrium isotherms and compare the sorption capacity of the cork and the prepared biochar

Methodology

1)Prepare a review on the biosorption of metals; why we need to remove Cr and Cu from water, what are the important properties of this metals, and the sources of contamination, which biomaterials can be used, what kind of experiments can be done, how to study the biosorption?

2)Perform the batch laboratory experiments according to methodology described in Sillerova et al. (2013). Kinetic sorption experiments should be done up to 48 hours with following intervals: 1, 2, 3, 4, 24, 48 hours. Concentration of Cr and Cu should be between 10-50 mg/l, two different pH should be tested for each metal. Equilibrium sorption experiments should be performed using at least 5 different initial concentrations of Cr and Cu (10-100 mg/l) and to initial pH values. Use 0.4 g of cork and 40 ml of aqueous solution (containing Cr or Cu) for one sample. Always prepare 2 replicates of each sample. Before analysis always filter the sample using 0.45 um filter and then dilute the sample for ICP-OES.

3) Apply the obtained experimental data to the commonly used models (kinetic data – pseudo-first-order and and pseudo-second-order equations; equilibrium data – Langmuir and Freundlich equilibrium isotherms) and evaluate the important parameters such as maximum sorption capacity or rate constants)

4) Compare the waste cork and the biochar, define the best conditions for the biosorption of each metal onto these materials

The proposed extent of the thesis
30 pages

Keywords
biosorption, cork, biochar, chromium, copper

Recommended information sources

H. Šillerová, M. Komárek, V. Chrastný, M. Novák, A. Vaněk, O. Drábek, J. Colloid Interface Sci. 396 (2013) 227-233.
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V.M. Nurchi, I. Villaescusa, Coord. Chem. Rev. 252 (2008) 1178–1188.

Expected date of thesis defence
2015/06 (červen)

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Electronic approval: 14. 4. 2015
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Prague on 21. 05. 2015

DECLARATION

I hereby declare that the present Bachelor Thesis entitled “Cork waste for metal removal from aqueous solution” is my own work and the literature and other sources, which I used, are stated list of references which are attached to this work

In Prague, 21th of May 2015

………………..………………

Daniel Cava Barrocal

ABSTRACT:

In this work the potencial of cork waste to remove Cu (II) and Cr (VI) from aqueous solutions has been studied. Raw cork and biochar prepared by pyrolysis of the cork, were used. Kinetic and equilibrium batch sorption experiments were performed in order to compare the sorption efficiency of each material. Adsorption isotherms were expressed by Langmuir and Freundlich equilibrium models. Moreover the batch kinetic experiments were fitted to the commonly pseudo-first-order and pseudo-second-order equations.

The results showed that the metal removal using raw cork as the sorbent is pH-dependent with the uptake of 61.5% for chromium at pH 3 and 55.6% for copper at pH 6. Two types of cork size (0.5mm and 2 mm particle size) showed the same adsorption potential.

Biochar with high specific surface area (300 m^2 g^{-1}) can be easily prepared from the raw cork.

The raw cork results show that pseudo-second-order describe better kinetic data for both metals. According to kinetic data the adsorption of chromium using biochar is the best option for removing this metal from water.

Biochar is able to sorb copper and chromium. The Langmuir model is not able to fit the experimental values for Cr, nevertheless is able to fit Cu, where the maximum adsorption was 13.4 mg kg^{-1}. Freundlich model can fit the experimental values for both metals. Where Cu maximum adsorption was 14.8 mg kg^{-1} and Cr maximum adsorption was 4.6 mg kg^{-1}.

KEYWORDS:

Raw cork, biochar, biosortion, biosorbent, copper, chromium, metal removal

1. INTRODUCTION

To prevent damage to the environment, metals and metalloids have to be removed from polluted water. They must be recycled for industrial use or disposed of in a place that presents no threat to environment and life. Chemical contaminants at low concentrations are difficult to remove from aqueous solutions, in fact at trace concentrations (1-100 mg/L), the commercial methods such as: chemical precipitation, reverse osmosis, chemical oxidation or reduction and many others methods, are expensive and inefficient in some cases (Valeria et al., 2008)[1]. The process of biosorption is a good alternative available for such situations. Adsorptive removal of metals and metalloids from wastewaters is usually carried out by activated carbon, activated alumina or polymer resins, which are expensive materials. Therefore, the need exists for low cost, effective and regenerable adsorbent materials which are able to remove metal ions from wastewater. A low cost sorbent should be abundant in nature, by-product or waste material from another industry and requires little processing even though when an improvement in sorption capacity compensates for the cost of additional processing. (Valeria et al., 2008; Villaescusa et al., 2000)[1-2]

Many plant residues like sugar beet pulp, black husk, red pumpkin waste, rice bran, olives stones, brewers draff, sunflowers stalks, mushrooms, hazelnut shells and cork, which are abundantly available, they have been proven via physical adsorption, chemical activation and pyrolysis for instance biochar. In the last decades the removal of metals and metalloids from wastewater by these products have been reported. (Villaescusa et al., 2000; Sillerová et al., 2013)[2-3]

2. REVIEW

2.1. Biosorption

Precipitation, evaporation, electroplating, ion exchange, membrane process are some example of commercial methods of metals and metalloids removal from contaminated water and soils. However these methods have several disadvantages such as unpredictable metal ion removal, high reagent requirement, generation of toxic sludge, etc. Therefore it is essential to find an alternative to remove metals and metalloids from soils and water. Biosorption is a process, which represents a biotechnological innovation as well as a cost effective tool. (Das et al., 2008) [4]

The biosorption process involves a solid phase (sorbent, e.g. biochar) and a liquid phase (solvent) where there are dissolved species to be sorbed (i.e. metal ions). After a specific contact time, the process reaches an equilibrium between the amount of solid-bound sorbate species and its portion remaining in the solution. (Das et al., 2008) [4]

The mechanism of metal biosorption is a complicated process. There are many parameters to take into account, e.g. type of biomaterial, pH of the aqueous solution, surface area, functional groups, porous structure and mineral components. For metals and metalloids the possible adsorption mechanisms are: electrostatic attraction, ion-exchange, physical adsorption, surface complexation and precipitation. The possible mechanisms are summarized in figure 1.

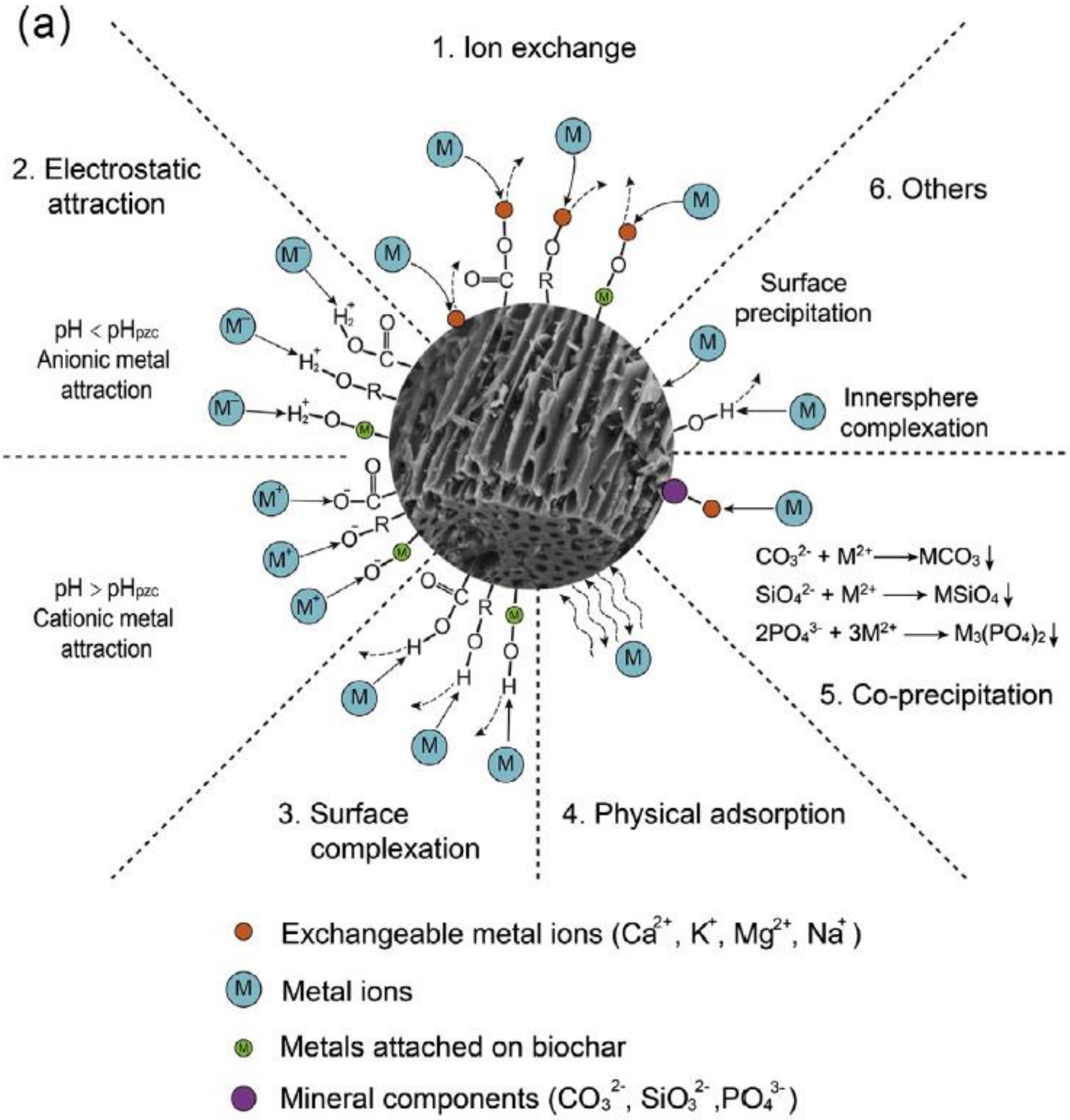

Figure 1. Adsorption mechanisms of metals and metalloids in biochar (Tan et al. 2015)[24]

2.2. Biosorbent, cork and biochar

Biosorbent is defined as: natural product able to remove pollutants from contaminated ecosystems. Its structure is rich in carbon and functional groups (hydroxyl, carboxylate and carbonyl) that make possible the adsorption in his surface, for instance: grape stalks, olive stones, shells, cork, etc. are common biosorbent examples.

Cork is extracted from the bark of the oak tree. It is usually used as a bottle stopper, however it is one of the cost-effective organic materials that has been used to remove metals (Olivella et al., 2011)[6], PAH's and others pollutants from water, thanks to his structure composed mainly by lignin, suberin (hydrophobic biopolymer) and hydrophilic polysaccharides (cellulose and hemicellulose). This structure provides cork a wide range of possibilities to bond to pollutants. (Olivella et al., 2011)[6]

Biochar is carbon-rich structure material, porous with oxygen functional groups and wide contact surface. It is produced by pyrolysis of biomass under conditions of minimal oxygen presence improving the metal sorption efficiency. (Trakal et al., 2014; Tan et al., 2015)[9,24]

Biochar is normally prepared from a waste materials such as woody biomass, animal waste, sludge or variety of agriculture residues. However not all types of biochar has the same sorption potential, it depends on: source and composition of the original waste material, pyrolysis process (mainly the temperature), biochar post activation or modification, minerals components in the biochar, different sorption mechanisms and finally the conditions during metal sorption (Trakal et al., 2014; Tan et al., 2015) [22, 24].The dosage of biochar has an important effect on the sorption capacity. According to Tan an increase of the concentration of biochar decrease the adsorption efficiency. (Tan et al., 2015) [24]

There is a sorption enhancement when using biochar instead of raw material, due to increase of surface area of the sorbent because at high temperatures the organic matters of materials are completely carbonized. Moreover more nano-pores are developed. (Tan et al., 2015)[24]

Surface chemical composition plays an important role in the adsorption capacity of biochar. The chemical characteristics of the biochar surface are strongly connected to its chemical composition. The hydrogen to carbon (H/C) and oxygen to carbon (O/C) ratios are used to indicate surface characteristics of biochar's surface. An increase of H/C ratio indicates that the surface of biochar are more aromatic and aliphatic, however an increase of O/C ratio indicates that there are more functional groups such as: hydroxyl, carboxylate and carbonyl that may contribute to higher cation exchange capacity. (Tan et al., 2015)[24]

Physical characteristics of sorbent are important for adsorption as well. Specific surface area (SSA) is usually expressed in square meters per gram of sorbent. The most common method used for its determination is the BET (Branauer-Emmett-Teller) method using a specialized instrument, which calculates the adsorption of N_2 molecules onto a degassed sorbent. After that the concentration of the sorbed N_2 is recalculated to the SSA. [28] Typically activate carbons may get specific surface areas until 1500 m^2/g. (McDougall, 1991)[31] This huge area is possible thanks to pores.

The most common methods of the biochar activation are mainly two: chemical activation and physical activation. The first one uses chemicals such as: phosphoric acid, sulphuric acid and dehydrating agents such as: calcium, potassium, sodium hydroxide, sodium carbonated or metals salts. (McDougall, 1991)[31] All these chemicals are used for improving adsorption onto activated carbon surface. According to Atanes using potassium hydroxide (KOH) increases area and the total pore volume. (Atanes et al. 2012)[32]

Finally a regeneration can be used for metal removal from the surface of the activated carbons. Physical activation is the first, it is the formation of biochar from the raw material by thermal in an inert atmosphere such as: N_2 for removing water and volatilization of volatile organic compounds from carbon surface. This step is normally carried out high temperatures, but it depends on raw material. (McDougall, 1991)[31]

Table 1 summarized different values of specific surface area, pore volume from different researchers.

Reference	**S_{BET} ($m^2 \cdot g^{-1}$)**	**V_p ($cm^3 \cdot g^{-1}$)**
Atanes et al. 2012 [32]	584	0.53
Chubar et al 2004 [33]	201	-
Neng et al 2011 [34]	1060	0.57
Carrot et al 2005 [35]	554	0.22
Carvalho et al 2003 [36]	728	0.32
Carvalho et al 2003 [37]	507	0.21
Mestre et al 2009 [38]	891	0.42
Cansado et al 2012 [39]	986	0.60
Mestre et al 2011 [40]	556	0.25

Table 1. Specific surface area (S_{BET}) and pore volume values (V_p)

2.3. Chromium

Chromium (Cr) has several oxidation states but the most stable are: trivalent and hexavalent. Trivalent chromium is the dominant state from chromium. Other forms will tend to be converted to the trivalent oxide in contact with natural environment. Even in the environment which is not thermodynamically stable, trivalent form is very slow to react. Cr (VI) is known for his mobility in soil and water systems and it can run long distance, whereas Cr (III) is not transported over great distance because his low solubility and tendency to be adsorbed in the pH range typical for natural soil and water.

About 80% (Barnhart, 1997)[7] of the chromium mined goes to metallurgical applications. The major part to make stainless steel. About 15% is used in chromium chemicals manufacture and the 5% is used in refractory applications, for instance to protect reactors of high temperatures and chemical agents. The properties of chromium such as: corrosion resistance, capacity to make alloys, for example to make stainless steel, as a catalyst and magnets manufacture are the main reasons to use this metal.

As mentioned above, chromium can exist in many oxidation forms: -2 to +6 but only the trivalent, iron chromite (mineral) and hexavalent can be found in the natural environment. The zero and hexavalent forms are used in significant volumes in commercial products and consequently it is important to concern environmental and human health effects resulting from industrial activity. (Barnhart, 1997)[7, 26]

Cr (VI) has toxic effects on humans. Inhalation and retention of Cr (VI) can cause perforation of the nasal septum, asthma, bronchitis, pneumonitis, inflammation of the larynx and liver and increased incidence of bronchogenic carcinoma. Skin contact of Cr (VI) compounds can induce skin allergies, dermatitis, dermal necrosis and dermal corrosion. The toxicity of Cr (VI) is originated from itself as an oxidizing agent. In addition from the formation of free radicals during its reduction from Cr (VI) to Cr (III), where is occurred inside the human cells. Cr (III) formed in a significant concentration can cause a further effect to health because of high capacity to coordinate various organic compounds resulting the inhibition of some metallic-enzyme systems. (Kotas et al., 2000)[8, 25] Epidemiological studies from EPA have reported that inhaled chromium is a human carcinogen, resulting in an increase of lung cancer. EPA has calculated a probability of a person developing cancer from a continuously breathing air, it has estimated of $1.2.10^{-2}$ $(\mu g/m^3)^{-1}$.[25]

The atmosphere has turned into the main pathway for transferring chromium to different ecosystems. The Cr particles travel throughout the air by wind before they fall down or are washed by the rain onto the terrestrial surfaces and water surfaces. The distance run by the metal depends on meteorological factors, topography and vegetation. Cr wet precipitation and dry fallout from atmosphere are generally affected by particle size. The transport of the metal onto water and terrestrial systems is affected by chemical speciation: chemical forms of Cr and their affinity to chemical and photochemical redox transformations, precipitation/dissolution and adsorption/desorption process occurring in the environment. There are two main ways that Cr moves from terrestrial to water systems: surface run-off and transport through the soil to groundwater. In addition soluble Cr (III) complexed forms by organic bonds can be transported to groundwater. Despite Cr (III) is not as toxic as Cr (VI), it is important control it into the environment because it can be oxidized to Cr (VI). Under anoxic conditions, trivalent chromium should be the only form. In oxygenated aqueous solutions Cr (III) has a strong dependents at pH<6. At intermediate pH values the Cr (III)/Cr (VI) ratio is dependent on O_2 concentration. In oxygenated surface waters, not only the pH and O_2 concentration have an important role, the concentration of reducers, oxidation mediators and complexing agents have an important role. Chromium in water systems can be produced from natural sources such as: weathering of rock constituents, wet precipitation and dry fallout from atmosphere and run-off from the terrestrial systems. (Kotas et al., 2000)[8]

In addition can be produced from industries, which discharge wastewater into the river. In this last case, the mainly form is Cr (VI). Also the chromium can get into the soil throughout industry activities. An increase in local Cr concentration in soils is originated from fallout and washout of atmospheric Cr-containing particles as well as from the sludge and refuse from industry activity. (Kotas et al., 2000)[8]

There are many conventional methods for removing chromium (VI) from soil and water such as:

1. Oxidation/reduction-Precipitation- Adsorption: The most common, the main goal is converting Cr (VI) to Cr (III) using for example Fe (II) as oxidising agent, because is less toxic. After that Cr (III) can precipitate depending on pH and/or be adsorb depending on the sorbed. (Hawley et al., 2004)[27]
2. Natural attenuation relies on natural processes to clean up or attenuate pollution in soil and groundwater.[28]
3. Biological transformations: Microorganisms can carry out enzymatic redox reductions in their metabolic process. Therefore, Cr (VI) can be reduced non-metabolically by reactions in microorganism's surfaces. In addition

phytoremediation is used to remove Cr (VI) from contaminated soils. The plant *Leptospermum scoparium* was reported as very usful plant to uptake Cr (VI) from soils. (Hawley et al., 2004)[27,28]

Many others were reported such as: ion exchange, membrane filtration etc. (Hawley et al., 2004)[27]

2.4. Copper

Copper (Cu) has three common oxidation states: Cu (0) (solid metal) Cu (I) and Cu (II). Moreover there are Cu (III) and Cu (IV) not as common. Copper is known from over 150 different minerals such as: chalcocite, chalcopyrite, bornite, cuprite, malachite and azurite, but also in its pure form in the crust, for this reason was the first metal utilised by humans.[14]

Copper is a ductile, malleable and soft metal. This means it can be turned into thin sheets, wires and pipes. Copper is produced mainly by smelting or leaching from ore after several steps of crushing, roasted, smelting, refining and finally followed by electrodeposition from sulphate solutions. The major part of copper produced is used in the electrical industries; the remaining is combined with other metals to form alloy. The most important alloys for the copper are: brasses (Cu and Zn), bronze (Cu and Sn) and nickel silvers (Cu, Zn and Ni).[15]

Smelting, mining, domestic waste emission and industrial such as: metal plating, steelworks and refineries, make Cu enter to the soil. In addition, fertilizers applications, algicides, fungicides, molluscicides can enter in the soil and water throughout groundwater streams. (Flemming et al., 1989)[10]

Copper can be either immobile or mobile in the soil. Immobile copper is non-bioavailable and can be adsorbed or precipitated into the soil. Copper is present in solution in cationic form and is attracted to negatively charged minerals, anionic species, hydroxides, phosphorous and sulfate, thus can make complexes and remain in the soils. In high pH, high organic matter (OM) and high cation exchange capacity (CEC) copper remains immobile and presents difficult sorption for plants and animals. When pH, CEC and OM are low, copper become mobile and potentially bioavailable, especially for groundwater and plant roots. Bioavailability is defined as the portion of a pollutant in the environment that is available for uptake by organisms and/or plants. (Mackie et al., 2012)[42]

Chronic Cu^{2+} toxicity primarily affects the liver, because it is the first site of Cu deposition after it gets into the blood. Cu toxicity is typically manifested by liver cirrhosis and damage to renal tubules, the brain and other organs. Symptoms can progress to coma, hepatic necrosis, vascular collapse and death. Consuming Cu-contaminated water or food is associated with development of acute gastrointestinal symptoms. (Gaetke et al., 2003)[11]

For removing copper (II) from wastewaters and contaminated soils there are many conventional methods and new trends:

1. Precipitation is the most widely used for metals and metalloids. Setting pH to basic conditions (9-11) to favour precipitation of the insoluble metal hydroxide. (Fu et al., 2011; Barakat, 2010)[29, 30]

$$Cu^{2+} + 2OH^{-} \leftrightarrow Cu(OH)_2$$

2. Electrokinetics remediation is a physical-chemical technique based on applying a current or a voltage across two electrodes located in the end of a cell. The current makes a physical and chemical change into the soil, including the transport of contaminants according to the charged of the ion, towards the anode or cathode. (Hansen et al, 2013)[41]

New trends are developed for removing metals and metalloids from wastewaters:

1. Adsorption using modified natural materials, for instance: zeolites, who has a very good selectivity for Cu^{2+}. (Barakat, 2010) [30]
2. Adsorption using industrial by-products such as: ashes, waste iron, waste titanium oxide, iron slags. (Barakat, 2010)[30]

3. MATERIALS AND METHODS

3.1. Materials and reagents

Cork wastes generated in the wine stoppers production was supplied by a cork stopper company in Costa Brava (Girona, Spain). Cork waste was crushed into small particles size and sieved in two types of particles size: 2 - 0.5 mm and 0.5 - 0.25 mm. The cork used in this project is *Quercus suber*. Characterization of this cork was reported by Olivella (Olivella et al., 2011)[6], where chemical composition, elemental analysis atomic ratios of cork and distribution of acidic functional groups was determined. The results are summarized in table 2.

		Quercus suber
Extractives		
	Aliphatic, %	5.6
	Phenolic, %	10.8
Suberin, %		44.1
Total lignin, %		25.7
Holocellulose, %		5.0
Elemental analysis		
	C, %	61.7
	H, %	8.7
Atomic ratios		
	H/C	1.70
	O/C	0.37
surface acid concentration (mmol/g)		
	Total acid groups	1.8805
	Strong acids	0.7330
	Phenolic OH groups	0.9155
	Weak acid groups	0.2320

Table 2. Chemical composition, elemental analysis, atomic ratios and distribution of acidic functional groups (Olivella et al., 2011)[6]

The initial solutions of Cr (VI) and Cu (II) were prepared by dissolving an analytical grade $K_2Cr_2O_7$ and $CuNO_3\cdot 3H_2O$ (analytical grade) respectively in a previously prepared solution of background electrolyte 0,01M $NaNO_3$. All the solution were prepared using ultrapure water. The pH of the solutions was set by HNO_3 or NaOH.

The biochar was prepared by pyrolysis of the cork waste (2 mm fraction) at approximately 600ºC in a muffle furnace under 16.7 ml min^{-1} nitrogen flow rate at atmospheric pressure and retention time of 2 hours. Additionally, the raw cork and the prepared biochar were analysed for moisture and ash content, bulk density, fixed carbon content and combustible content according to the Czech standard methods ČSN EN 14775, ČSN EN 15148, ČSN 44 1377. The yield of the pyrolysis (in %) was calculated as the quotient between the weight of biochar and weight of initial cork.

The surface area was measured by N_2 adsorption isotherms at 25ºC using ASAP 2050 (Micrometrics Instrument Corporation, USA) surface area analyser.

3.2. Kinetic batch sorption experiments

The effect of time on the adsorption of Cr (VI) and Cu (II) was investigated. The experiment was carried out in stoppered plastic tubes by shaking a fixed mass of 0.4 g of raw cork or 0.1 g of biochar with 40 ml of metal solution at 300 rpm (GFL Shaker 3006). Two types of cork size were compared: 2 mm and 0.5 mm. The contact time between metal solution and cork in the shaker were: 1, 2, 3, 4, 12 and 48 hours. Furthermore, in case of Cu (II) sorption onto raw cork, extra times were sampled (10 min, 20 min and 30 min) because Cu (II) kinetic got the equilibrium in four hours. After agitation, samples were filtered through a (0.45 µm) filter. The concentration of Cr and Cu was determined by ICP-OES (inductively coupled plasma optical emission spectroscopy, Agilent Technologies 700 series, USA). The sorbed metal concentration was calculated as a difference between initial and final metal concentration in solution. Each sample was prepared in duplicate.

3.2.1. pH effect on Cr (VI) and Cu (II) sorption

The effect of pH of the initial solutions on the sorption process was evaluated. It is well known that pH is one of the most important parameter affecting the sorption process due to the different chemical speciation of metal ions and different protonation of sorbent's surface. (Villaescusa et al., 2004)[13] Metal uptake is pH-dependent. Fiol et al., 2003[20] found that the optimal pH for Cr (VI) is pH 3. However for Cu (II), the maximum capacity was obtained at pH 6 (Nurchi et al., 2007)[2].

For setting the pH, HNO_3 and NaOH in different concentrations (1M, 0.1M and 0.01) were used.

3.3. Point of zero charge determination (pH_{pzc})

Point of zero charge is defined as the pH at which the sorbent surface charge is equal to zero. At this pH, the charge of the positive surface sites is equal to those of negative one. (Fiol et al., 2008)[21] When the solution pH is higher than pH_{pzc}, sorbent solid surface is negatively charged and can interact with positive metal species. By another hand, when the solution pH is lower than pH_{pzc}, solid surface is positively charged and can interact with negative metal species.

Suspensions of 40 mg of cork were put in contact in 40 ml of 0.03 M KNO_3 solutions at different pH values (3, 3.5, 4, 4.5, 5, 5.5 and 6). The suspensions were agitated for 24 hours in a shaker at 300 rpm (GFL Shaker 3006). The experiment was subsequently repeated in order to evaluate pH_{pzc} values more precisely using pH values (3.8, 3.9, 4.1, 4.2 and 4.3). Suspensions of 10 mg of biochar were put in contact in 40 ml of 0.03 M KNO_3 solutions at different pH values (8, 8.25, 8.5, 8.75 and 9). The suspensions were agitated for 24 hours in a shaker at 300 rpm (GFL Shaker 3006).

The samples were measured using pH-meter until constant pH value.

The change of pH (ΔpH) during equilibrium was calculated and the pH_{pzc} was identified as the initial pH with minimum ΔpH.

3.4. Equilibrium batch sorption experiments

In order to obtain the adsorption isotherm, the experiment was performed at different initial concentration of Cu (II) and Cr (VI) (10, 50, 100, 150, 200, 250, 300 mg/L) and setting pH values at 3 for Cr (VI) and 6 for Cu (II). Chromium samples were prepared by mixing 0.1 g of biochar with 40 ml of $K_2Cr_2O_7$ solution and copper samples were prepared by mixing 0.1 g of biochar with 40 ml of $Cu(NO_3)_2{\cdot}3H_2O$ solution. Then samples were agitated for 24 hours on a shaker at 300 rpm (GFL Shaker 3006). Samples were filtered (0.45 µm) and total concentrations of chromium and copper were determinated using ICP-OES Agilent Technologies 700 series, USA.

For description of the adsorption process, adsorption isotherms are commonly used. Langmuir and Freundlich isotherm models are used due to their simplicity. The model are simple, well established and easily interpretable. It should be pointed out that these models are just mathematical expressions of the sorption and they hardly reflect sorption mechanisms. Langmuir and Freundlich equilibrium isotherms were constructed from the obtained data using nonlinear least square regression. Nevertheless these methods are empirical and the fitted values do not provide information about exact sorption mechanisms but they are useful for compering with other studies. (Sillerová et al., 2013) [3]

4. RESULTS AND DISCUSION

4.1. Characterization of raw cork and biochar

The characterization of raw cork and biochar with their respective standard deviation are presented in table 3.

Samples	W (wt. %)	A (hm. %)	h (hm. %)	A^d (hm. %)	h^d (hm. %)	V^d (hm. %)	FC^d (hm. %)
Cork	4.43	1.08	94.49	1.13	98.87	82.65	16.22
SD	0.24	0.08	0.32	0.09	0.09	0.57	0.57
Biochar	2.64	3.63	93.72	3.73	96.27	18.02	78.25
SD	0.06	0.35	0.39	0.36	0.36	1.65	1.65

Table 3. Characterization of raw cork and biochar. Values are given with standard deviation. W= water, A= ash original sample, h= combustible original sample, A^d= ash dry sample, h^d= combustible dry sample, V^d= volatile combustible, FC^d= fixed carbon

Where W is water content in the original sample, A is ash content in the original sample and h is the combustible in the original sample. Ashes content in biochar is higher than in raw cork because water and the combustible were volatilitzed by the process of pyrolysis.

A^d is ashes content in the dry sample and h^d is combustible content in the dry sample

V^d (Volatile combustible of the dry sample) and FC^d (Fixed carbon in the dry sample). Most of the volatile combustible was removed from cork during pyrolysis of it, however there is an important gain of fixed carbon in biochar.

The mass of cork was reduced by approximately 87% by the pyrolysis. Biochar's specific surface area was 308 ($m^2 \cdot g^{-1}$) determinated by BET.

4.2. pH_{pzc} cork and biochar

The raw cork pH_{pzc} was 4.1 because it had the lowest ΔpH, 0.005. According to Fiol and Villescusa (Fiol et al. 2008)[21], at higher pH than pH_{pzc} cork surface is negatively charged and at lower pH than pH_{pzc} cork surface is positive charged. Thus, in both solution, electrostatic attraction between Cu^{2+} - cork surface negatively charged and $HCrO4^{-}$ - cork surface positive charged are the main sorption mechanism.

The biochar pH_{pzc} was 8.1 because it had the lowest ΔpH, 0.035.

4.3. Kinetics batch experiments

The effect of time on Cr (VI) and Cu (II) sorption onto raw cork of 2 mm and 0.5 mm was investigated. The initial pH in both solutions were 5.6 of Cu (II) and 5.4 of Cr (VI). Results of raw cork kinetics are plotted in figures 2 and 3.

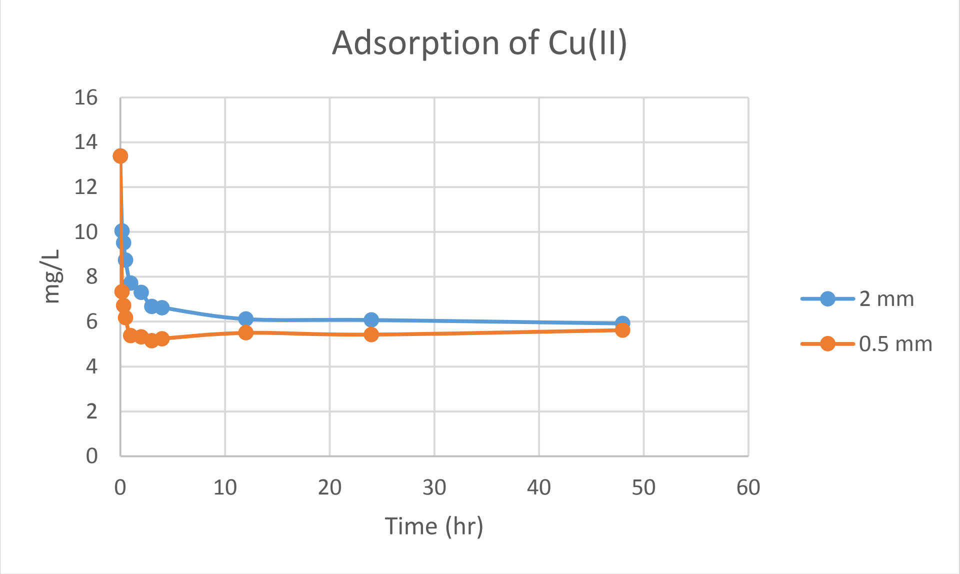

Figure 2. Adsorption of Cu (II) using raw cork

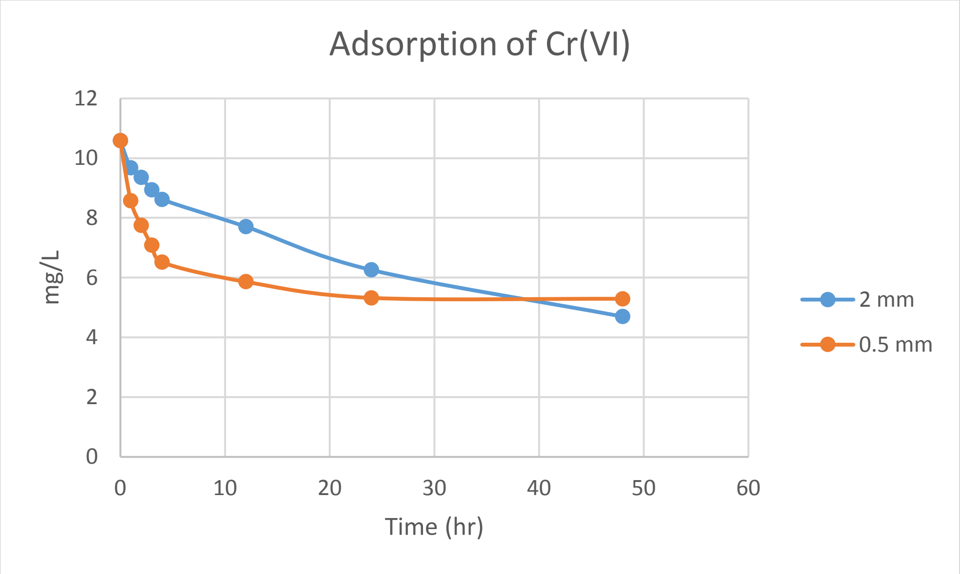

Figure 3. Adsorption of Cr (VI) using raw cork

Adsorption equilibrium of Cu (II) in both particle size of cork was achieved approximately after 4 hours. However adsorption equilibrium of Cr (VI) in both particle size of cork was significantly slower, they achieved equilibrium after 24 hours and in case of 2 mm particle size after 48 hours. Using 0.5 mm particle size achieve equilibrium faster than 2 mm one, probably due to a bigger specific surface area and the ions may be attract easier. However both size fractions of the cork adsorb approximately the same amount of metal once at equilibrium.

It is important to note that there are parameters such as cork surface ionization and the most important parameter, the pH. The pH in both solutions are around 6, according to Nurchi (Nurchi et al., 2007)[2] is the optimal pH for copper. In addition pH_{pzc} for raw cork was 4.1, therefore, cork surface is negatively charged favouring electro-attraction to Cu^{2+} instead of $HCrO_4^-$ and CrO_4^{2-}.

The % metal removal was calculated using the following expression:

$$\%\,metal\ removal = \frac{C_i - C_{teq}}{C_i} \times 100$$

Where C_i (mg/L) is initial metal concentration and C_t (mg/L) metal concentration at equilibrium time t. Results are summarized in table 4.

Particle size (mm)	% metal removal Cu (II)	% metal removal Cr (VI)
0.5	61.5	50.0
2	55.8	55.6

Table 4: Comparative % metal removal between Cu (II) and Cr (VI) using different particle sizes.

The results shown in table 4 that both fractions of cork can adsorb approximately the same in both metal. Therefore, in the following experiments was used 0.5mm fraction for studying pH effect and pH_{pzc} and 2mm was used as biochar.

4.3.1. pH effect

As said previously, pH is the most important variable governing metal sorption. For copper the optimal pH value is 6 according to Nurchi and Villaescusa (Nurchi et al., 2007)[2]. However for Cr (VI) the optimal pH value is 3 according to Fiol. (Fiol, et al. 2003)[20]

To study pH effect, pH of Cu (II) solution was set to approximately 7 to see differences between the previous experiments, where the pH was 5.6. pH of Cr (VI) was set at 3.1, the initial solution was 5.4. Results are plotted in figures 4 and 5.

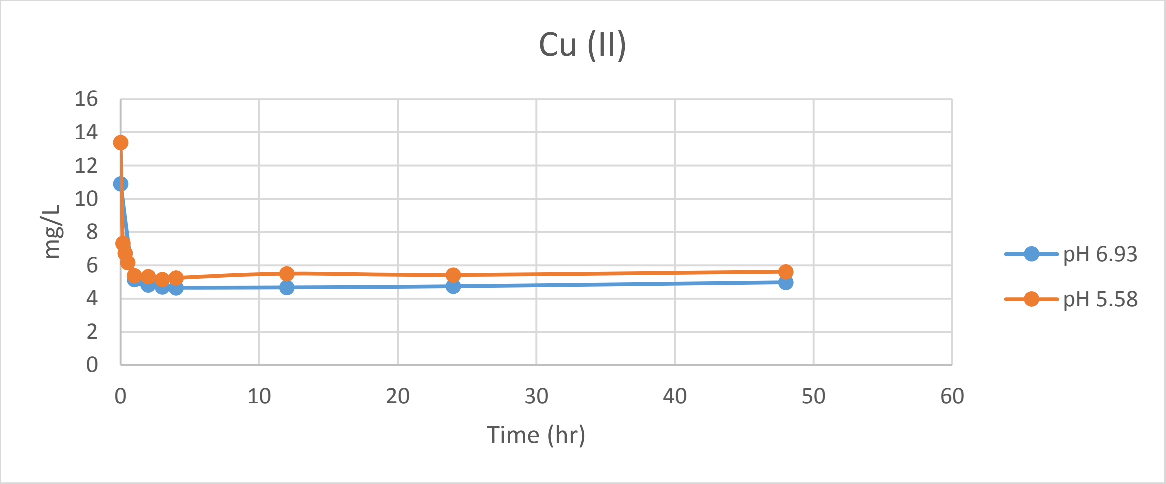

Figure 4. Comparative Cu (II) adsorption in two different pH

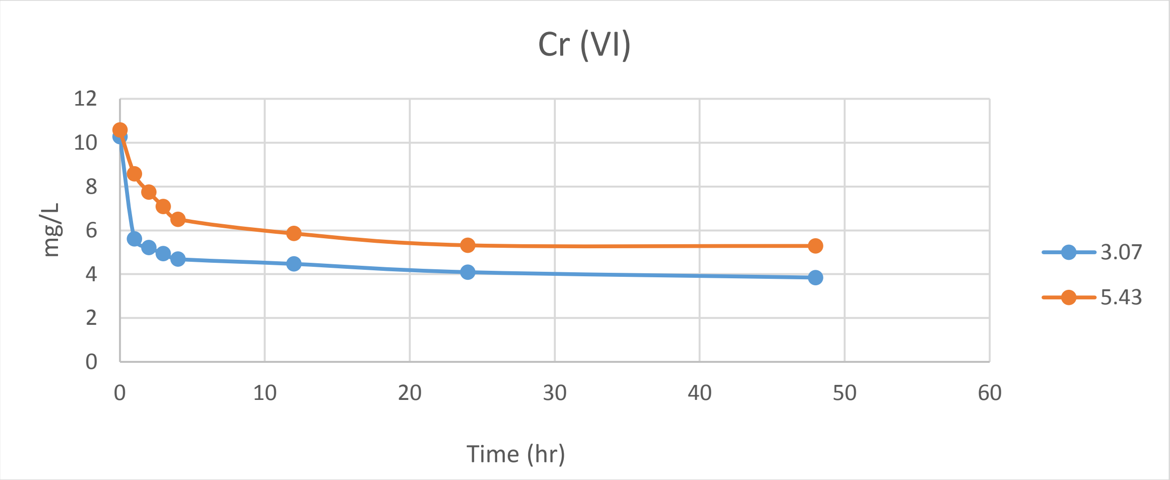

Figure 5. Comparative Cr (VI) adsorption in two different pH

Results show that setting pH of copper at 6.9, there is less metal removal, however setting the pH of chromium at 3.1 the metal removal percentage increase. In addition, setting the pH at 3.1, the adsorption of Cr (VI) onto cork surface improved and achieved the equilibrium faster. A comparative of metal removal percentages is showed at table 5.

Metal solution	% metal removal initial pH	% metal removal setting pH
Cu (II)	61.5	57.2
Cr (VI)	50.0	62.6

Table 5: Comparative % metal removal between both solutions in different pH.

There are many mechanisms to take into account when studying in pH effect such as: electrostatic forces, ion exchange, and chemical complexation. One of the most common mechanisms is electrostatic attraction/repulsion between sorbate and sorbent. Therefore, an increase of Cr (VI) sorption in acidic pH solution should be due electrostatic attractions between charged groups present in the surface of cork and the $HCrO_4^-$ anion, which is the most dominant anion at low pH.[20] This is due to the fact at low pH, biochar's surface is protonated and positively charged, favouring adsorption of anions. (Tan et al., 2015)[24] Otherwise, a decrease of the sorption increasing pH could be due to the competitiveness among chromium anionic species ($HCrO_4^-$ and CrO_4^{2-}) and OH^- ions in the bulk onto active sites of the cork surface. (Fiol, et al. 2003)[20] On the other hand, copper is present in solution in its cationic form Cu^{2+} so in acidic solution this species competes with H^+ when the pH value is low, for surface sites. Thus, copper presents better adsorption at neutral pH, because raw cork surface is negatively charged and cations are easily captured.(Fiol et al., 2006; Villaescusa et al., 2004; Chubar et al., 2004; Tan et al., 2015)[12, 13, 23, 24]At high pH, pH>7 Cu^{2+} coordinate with OH^- to form $Cu(OH)_2$ and precipitate.

Biochar kinetics batch experiments were investigated. The pH of Cr (VI) was set at 3.0 and Cu (II) was set at 6.0, where they show the strongest adsorption with sorbent. Results of kinetics are plotted on Figures 6.

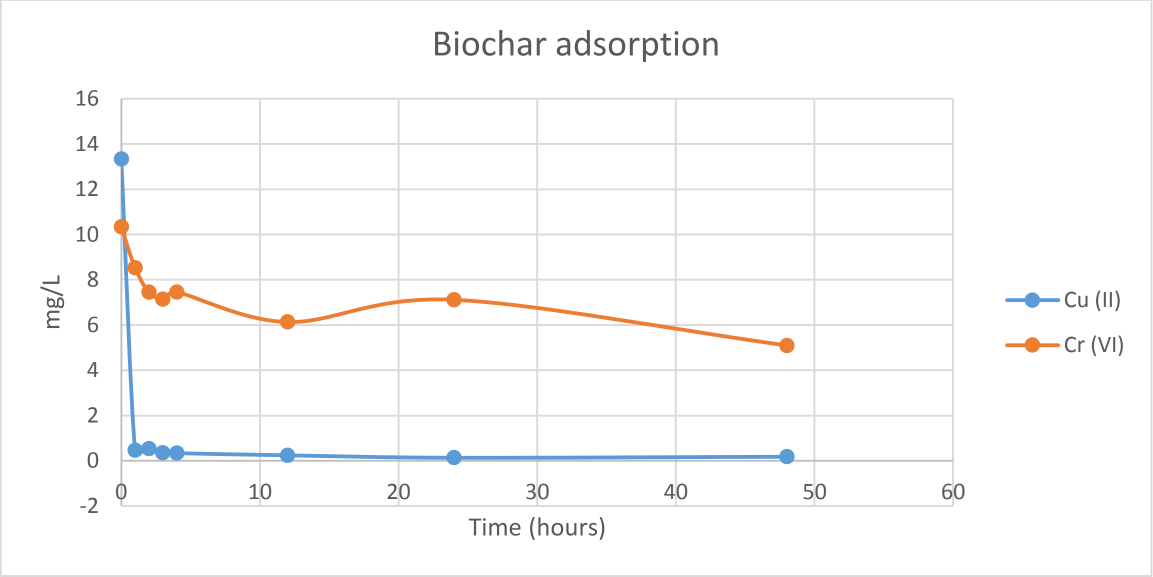

Figure 6. Biochar adsorption between Cu (II) and Cr (VI)

Using biochar as sorbent of Cu (II) the equilibrium was achieved very fast, in less than 10 minutes. One possible reason is the pH_{pzc} that is around 8.1. At this pH the competiveness of Cu^{2+} against H^+ for negative biochar surface area is extremely low, and it can bond fast to the surface. The samples pH were above 8.1. Another possible reason is the precipitation of copper occurs at pH 7 and probably most of the copper precipitated.

By other hand Cr (VI) is presented as anionic form. As experimented before, biochar has negatively charged surface area that is mean that $HCrO_4^-$ and CrO_4^{2-} have weak interaction with biochar. Ups and downs represented in plot might be due to adsorptions and desorptions between chromium and biochar functional groups.

Table 6 show a comparative of metal removal among raw cork without setting pH, setting pH and biochar.

Metal solution	% metal removal without setting pH	% metal removal setting pH	% metal removal Biochar
Cu (II)	58.0	54.3	99.0
Cr (VI)	50.0	62.6	50.7

Table 6. Compartaive % metal removal between raw material without setting bH, setting pH and biochar.

In order to investigate the sorption rate of metals pseudo-first-order and pseudo-second-order equations is used to describe better the adsorption mechanism. The lineal form of pseudo-first-order equation is: (Sillerová et al., 2013)[3]

$$Ln\ (S_e - S_t) = LnS_e - k_1 t$$

The differential equation that describes the pseudo-second-order is the following:

$$\frac{dS_t}{dt} = k_2(S_e - S_t)^2$$

Where q_e (mg g^{-1}) is the amount of metal sorbed at equilibrium, k_1 (min^{-1}) is the rate of pseudo-first-order constant of sorption, k_2 (g mg^{-1} min^{-1}) is the rate of pseudo-second-order constant of sorption and q_t (mg g^{-1}) is the amount of metal sorbed on the surface of the sorbent at any time t. Separating the variables and integrating for the initial conditions t=0, q_o=0 gives:

$$\frac{1}{(S_e - S_t)} = \frac{1}{S_e} + kt$$

Integrated form of pseudo-second order reaction. Can be rearranged to obtain the linear form: (Fiol et al., 2012)[12]

$$\frac{t}{S_t} = \frac{1}{kS_e^2} + \frac{1}{S_e}t$$

The experimental kinetic data were fitted to these two equations in order to better describe the adsorption mechanisms. The kinetic models parameters for Cu and Cr uptake by raw cork and biochar are summarized in Table 7.

Adsorbent	Metal	First-order kinetic model			Second-order kinetic model		
		k_1 (min^{-1})	S_e ($mg \cdot g^{-1}$)	R^2	k_2 ($g \cdot mg^{-1} \cdot min^{-1}$)	S_e ($mg \cdot g^{-1}$)	R^2
Raw cork	Cu	0.002	0.233	0.8788	0.0701	0.749	0.9999
Raw cork	Cr	0.0026	0.282	0.9287	0.0433	0.646	0.9993
Biochar	Cu	-0.0004	0.052	0.0262	-0.0983	3.944	1
Biochar	Cr	0.0023	2.141	0.8307	0.004	3.199	0.9796

Table 7. Kinetic model parameters for Cu and Cr uptake by raw cork and biochar

The raw cork results show that pseudo-second-order describe better kinetic data for both metals. The adsorption of copper using biochar do not show good results because negative rate constants do not exist. A possible reason may be biochar pH, it is too much high for copper and it makes precipitate as hydroxide Cu $(OH)_2$. According to kinetic data the adsorption of chromium using biochar is the best option for removing this metal from water.

4.4. Adsorption isotherm

Sorption capacity of raw cork and biochar were determined using Langmuir and Freundlich equations.

The Langmuir sorption isotherm assumes monolayer adsorption onto surface containing a finite number of adsorption sites. Once is filled, no more sorption can take place at this site. This indicate that the surface reaches a saturation point where the maximum adsorption on the surface will be achieved (Desta M.B., 2013)[43]. Can be expressed as follows:

$$S = \frac{S_{max} \times K_L \times C}{1 + K_L C}$$

Where S (mg kg^{-1}) is the amount of sorbate sorbed per unit mass of sorbent, S_{max} (mg kg^{-1}) is the maximum metal uptake per unit mass of sorbent, C (mg l^{-1}) the equilibrium concentration of sorbate in solution and K_L (l mg^{-1}) is the Langmuir constant. S_{max} and K_L are constants related to energy of adsorption and maximum adsorption capacity.

The Freundlich isotherm is an empirical equation based on sorption on heterogeneous surface. This equation is commonly presented as:

$$S = K_F C^n$$

Where K_F (mg^{1-n} L^n kg^{-1}) is the Freundlich sorption coefficient, represent adsorption capacity and n (-) are empirical constant, that represent adsorption intensity (Sillerová et al., 2013)[3]. The n value indicate the degree of nonlinearity between solution concentration and adsorption as follows: if n=1, then adsorption is linear; if n<1, then adsorption is chemical process; if n>1, then adsorption is a physical process (Desta M.B., 2013)[43].

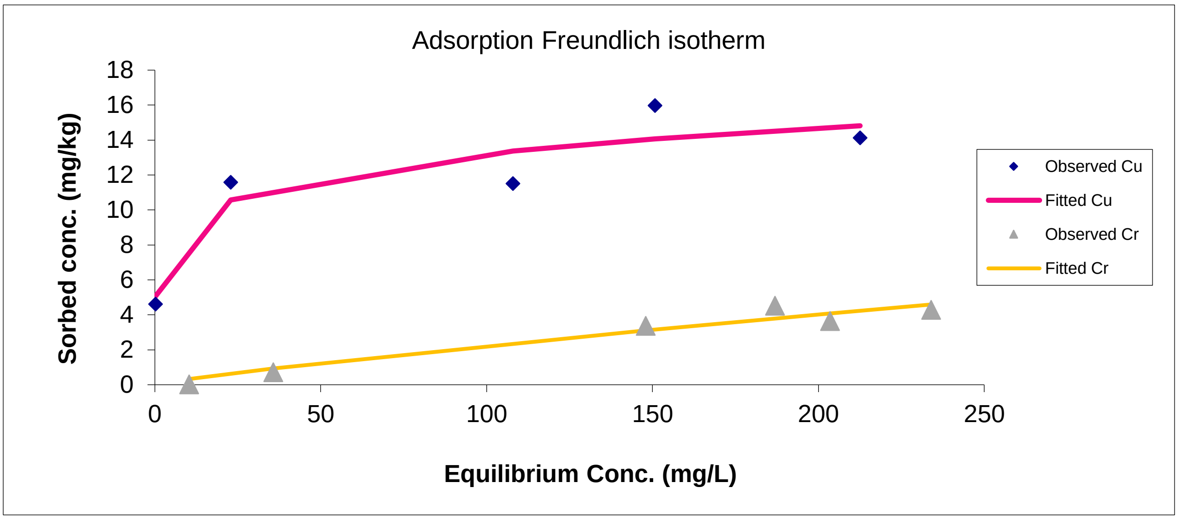

Figure 7. Fitted of the Freundlich isotherm equation (lines) to the gathered from the experiment (symbols)

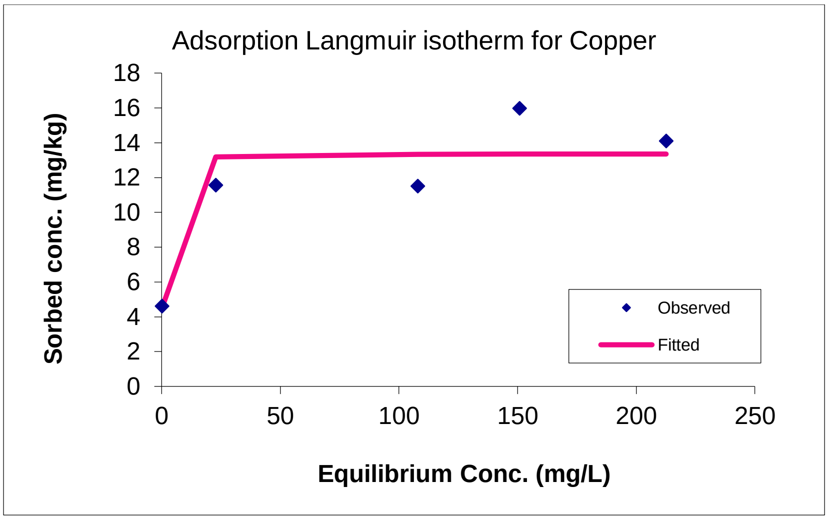

Figure 8. Fitted of the Langmuir isotherm equation (lines) to the gathered from the experimental (symbols)

Obtained results (Figure 7 and Figure 8) suggest that biochar is able to sorb copper and chromium. The Langmuir model is not able to fit the experimental values for Cr, nevertheless is able to fit Cu, where the maximum adsorption was 13.4 mg kg^{-1}.

Freundlich model can fit the experimental values for both metals. Where Cu maximum adsorption was 14.8 mg kg^{-1} and Cr maximum adsorption was 4.6 mg kg^{-1}.

The Langmuir and Freundlich parameters are summarized in Table 8.

	Freundlich		R (%)	Langmuir		R (%)
Metal	K_F (mg^{1-n} L^n kg^{-1})	n (-)		K_L (L mg^{-1})	S_{max} (mg kg^{-1})	
Cu	6.59	0.151	0.881	2.924	13.4	0.820
Cr	0.05	0.843	0.944	-	-	-

Table 8. Freundlich and Langmuir parameters (K_F, K_L, n and S_{max}) and model efficiencies (R) obtained for both metals (Cu and Cr) using biochar.

Freundlich constants (K_F) was higher in the case of copper removal. The adsorption of chromium is affected by desorption process the weak interactions between the Cr anion and functional groups presents in biochar surface.

In both solutions n parameter is below one, that indicate chemical sorption onto biochar surface and electro attraction may be the main adsorption mechanism (Desta M.B., 2013)[43].

5. CONCLUSIONS

Raw cork was used for Cr (VI) and Cu (II) removal from aqueous solutions. Based on the results obtained, raw cork is able to adsorb Cr and Cu from aqueous solutions.

Metal sorption is pH-dependent and maximum adsorption for chromium was found to occur at pH 3. In case of copper better adsorption was found at 6. In these pH, the maximum adsorption were 61.5% and 55.6% respectively. No significant difference was found between the two particle fractions (0.5 and 2 mm) in the adsorption efficiency.

Biochar was successfully prepared from the raw cork. The specific surface area of the biochar is very high (300 $m^2 g^{-1}$) in comparison with other biochar.

Chromium adsorption using biochar is affected by random desorption process, which may be due weak interactions between the biochar surface and the chromium. The adsorption kinetics results showed very fast removal of copper. It has to be pointed out that due to high value of pH (around 8) of the final solution, precipitation of Cu is involved in the Cu removal process. The Freundlich isotherm model showed that the K_F value is higher in case of copper indicating that the interaction between biochar and copper are better than chromium, which may be due a negatively charged biochar surface. The Langmuir isotherm model does not fit the experimental data of Cr (VI) very well.

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