

**LANDFILL LEACHATE TREATMENT BY WASTE-
DERIVED ACTIVATED CARBON**

by

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Abstract

This research evaluated the use of spent coffee grounds (SCG) and oat hulls as precursors for activated carbon applied for organic matter removal from leachate, a pollutant wastewater produced by landfills. These precursors were selected based on their global commercial significance. The high demand for the beverage coffee is directly proportional to the generation of SCG as organic waste. Similarly, oat is a popular cereal consumed worldwide, and its industrial processing generates hulls as organic waste. The activated carbon samples were produced by chemical activation with phosphoric acid (H_3PO_4), using distinct impregnation ratios: 50 and 100 % for SCG, and 60 and 100 % for oat hulls; followed by pyrolysis in an inert atmosphere, at 350 and 500 °C. The feasibility of the tested precursors as adsorbents was initially assessed in experiments with synthetic leachate. Afterwards, the results from the initial tests were compared with those obtained in real leachate treatment. The studies described in this thesis showed that the impregnation ratios and pyrolysis temperatures interfered with the surface areas of the formed adsorbents, consequently affecting the organic matter removal from leachate. Both oat hulls and SCG were successfully recovered as activated carbon, and efficiently treated synthetic and real leachate, removing more than 90 % of the organic matter. Therefore, this study highly encourages the use of SCG and oat hulls as precursors for activated carbon production and their application to treat leachate.

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- FMF and QY were responsible for the study conception and design. FMF was responsible for conducting the experiments, analysis and interpretation of the data, and writing the manuscript. QY was responsible for critical revision.

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List of Abbreviations

AC	Activated carbon
ACA	Activated carbon produced from cow dung ash
AS	Activated sludge
ATR	Attenuated total reflection
BET	Brunauer–Emmett–Teller
BOD	Biochemical oxygen demand
CA	Cow dung ash
COD	Chemical oxygen demand
Ce	Liquid-phase equilibrium concentration
C50-350	Spent coffee grounds activated carbon impregnated at 50% with H_3PO_4 and produced at 350°C
C50-500	Spent coffee grounds activated carbon impregnated at 50% with H_3PO_4 and produced at 500°C
C100-350	Spent coffee grounds activated carbon impregnated at 100% with H_3PO_4 and produced at 350°C
C100-500	Spent coffee grounds activated carbon impregnated at 100% with H_3PO_4 and produced at 500°C
DOC	Dissolved organic carbon
FTIR	Fourier transform infrared spectroscopy
GAC	Granular activated carbon
IUPAC	International Union of Pure and Applied Chemistry
OH	Oat hulls
OH60-350	Oat hulls activated carbon impregnated at 60% with H_3PO_4 and pyrolyzed at 350°C

OH60-500	Oat hulls activated carbon impregnated at 60% with H_3PO_4 and pyrolyzed at 500°C
OH100-350	Oat hulls activated carbon impregnated at 100% with H_3PO_4 and pyrolyzed at 350°C
OH100-500	Oat hulls activated carbon impregnated at 100% with H_3PO_4 and pyrolyzed at 500°C
PAC	Powder activated carbon
Q_{max}	Maximum adsorptive capacity
Q_e	Adsorptive capacity at the equilibrium
SCG	Spent coffee grounds

CHAPTER 1 Introduction and Objectives

Europe and North America have worked on waste minimization by encouraging recycling and waste diversion from landfills. Until the year of 2030, countries belonging to the European Union are expected to recycle 65 % of their municipal solid waste (European Commission 2017). In Canada, waste management authorities have encouraged the diversion of the food waste from landfills. Indeed, at Metro Vancouver disposal facilities, recyclable materials and food waste have been included on the list of banned materials that should be diverted from landfills (Metro Vancouver 2019). In Manitoba, the provincial government plans to completely ban organic waste from landfills until 2020 (Manitoba Conservation and Water Stewardship 2014). Meanwhile, municipal solid waste has been continuously disposed in sanitary landfills, contributing to greenhouse gases emissions and to the formation of a wastewater named leachate (Renou et al. 2008).

Leachate can be treated by several technologies, including biological processes, advanced oxidation processes, and physico-chemical methods (Renou et al. 2008). Nonetheless, these processes may have to be combined to attend strict discharge limits, which potentially increases the operational costs associated with leachate treatment (Renou et al. 2008).

As a low-cost alternative for leachate treatment, organic waste has been recovered as activated carbon, being primarily tested for heavy metals removals (Ghani et al. 2017). On the other hand, limited information is available about the efficiency of waste-derived activated carbon to remove the organic matter from leachate (Ghani et al. 2017), which motivated this study. Therefore, the objectives of this study were to determine the efficiency of spent coffee grounds (SCG; Chapter 3) and oat hulls

(Chapter 4) activated carbon on the organic matter removal from synthetic and real landfill leachate.

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CHAPTER 2 Literature Review

2.1. Landfill leachate: characteristics and environmental impacts

Leachate is a wastewater produced by sanitary landfills due to factors such as waste decomposition and infiltration of water (Ren and Yuan 2015; Renou et al. 2008). General characteristics of leachate include the following: dark colour; pH ranging from 5 to 9; alkalinity (carbonate, bicarbonate and hydroxide); low concentration of heavy metals; high concentrations of organic matter; high concentration of ammonia; and xenobiotic compounds (pesticides, phenols, etc) (Ferraz et al. 2013; Kjeldsen et al. 2002; Ren et al. 2017; Renou et al. 2008). In addition, leachate characteristics comprise useful information for its classification, i.e, leachate can be referred to as “young” and “old”. Leachate classified as “young” presents characteristics such as low pH and a high content of easily biodegradable organic matter. On the other hand, “old” leachate refers to a wastewater with high pH, high concentration of ammonia and organic matter mostly non-biodegradable or refractory. The physico-chemical parameter biochemical oxygen demand (BOD) and chemical oxygen demand (COD) can be used to classify leachate as young or old, as follows: if the ratio BOD/COD is 0.5 or higher, leachate is classified as young due to the high content of easily biodegradable organics; whereas if the ratio BOD/COD is below 0.5, leachate is classified as old due to the high content of refractory organics (Renou et al. 2008).

The refractory organic content in leachate is primarily constituted by humic substances, which causes the dark colour of this wastewater (Kang et al. 2002; Renou et al. 2008). Accordingly, studies referring to synthetic leachate usually report recipes based on humic or tannic acids (Campos et al. 2014; Ren et al. 2017). Humic substances comprise a complex and heterogenous matrix of particulate and dissolved substances found not only in leachate, but also in drinking water (Crittenden et al. 2012; Piccolo

2001; Sillanpaa et al. 2018) Humic substances can be classified according to their solubility (Frimmel 2005; Nuzzo et al. 2013). The fraction insoluble in acidic pH is represented by humic acids, whereas regardless the pH fulvic acids account for the soluble fraction and humin for the insoluble fraction (Frimmel 2005; Nuzzo et al. 2013). Humic substances can be further fractionated in hydrophobic/hydrophilic portions and their respective acidic, neutral or alkaline nature (Crittenden et al. 2012).

Ammonia toxicity to the aquatic life and oxygen depletion are examples of potential impacts caused by leachate discharge in water bodies (Kjeldsen et al. 2002). Depending on the level and duration of exposure, lethal and sublethal effects may be observed for fish and benthic invertebrates living in an aquatic environment contaminated by leachate. Water contamination by leachate can also affect fish population, causing mortality or abnormal behaviour (Budi et al. 2016; Fauziah et al. 2013; Makaras et al. 2018)

Leachate release to the environment also is a public health issue. In case of drinking water contamination, humic substances in leachate could deteriorate water quality causing colour, odour, and taste (Renou et al. 2008). Additionally, humic substances in leachate may react with disinfectants such as chlorine, forming carcinogenic by-products such as trihalomethanes (Crittenden et al. 2012). Leachate also contains xenobiotic compounds (i.e, phenol, pesticides, phtalates) that might be harmful to human health depending on their concentration and availability (Gao et al. 2013; Kjeldsen et al. 2002; Renou et al. 2008). Drinking water contamination by leachate would also cause inconveniences in locations where water treatment plants are not provided with advanced treatment methods, which would be the case of First Nations communities living in isolated areas in Canada. Recent statistics, published in 2016, showed that 55 % of First Nations water systems present high or moderate risk of

interrupting the public supply whether an eventual contamination of the water source is identified, causing hassle to the community (Environment and Climate Change Canada, 2016).

2.2. Leachate treatment by adsorption-based processes

Adsorption is a mass-transfer process commonly used in water and wastewater treatment, in which target substances (adsorbate) can be removed from the aqueous phase as they are adsorbed onto the surface of a solid phase (adsorbent) (Crittenden et al. 2012). The adsorbate can be attached to the surface of the adsorbent by means of chemical or physical attraction. The first implies in the removal of the adsorbate from the aqueous phase by means of a chemical reaction (generally, an irreversible process), where electrons are transferred between the adsorbent and adsorbate. Physical attraction is the most common mechanism for removal of the adsorbate from water and wastewater. By means of van der Waals forces, the adsorbate is attracted to the surface of the adsorbent, which is a reversible process allowing the regeneration of the adsorbent for future applications (Crittenden et al. 2012).

Activated carbon is the most commonly used adsorbent for organic matter removal from water and wastewater, presenting a high surface area. It can be classified as powder activated carbon (PAC) and granular activated carbon (GAC) (Crittenden et al. 2012). The prior consists of small-sized particles (20-50 μm) with a high surface area (1400 to 1800 $\text{m}^2 \text{g}^{-1}$). PAC is used as suspensions applied seasonally when it is necessary to remove odour, taste and contaminants in low concentration. On the other hand, compared to PAC, GAC consists of larger particles (0.5 to 3 mm) with surface area ranging from 950-1075 $\text{m}^2 \text{g}^{-1}$, usually applied for the removal of dissolved organic

matter. Differently from PAC, GAC can be regenerated and reused after its adsorptive capacity is reached (Crittenden et al. 2012).

Carbon-based adsorbents such as activated carbon may present a negative or positive surface charge in function of the pH. Usually, the surface of these adsorbents is negatively charged at neutral to high pH, whereas it is neutral at low pH (Bjelopavlic et al. 1999; Zhang et al. 2016). Therefore, if carbon-based adsorbents are intended to remove humic substances, adsorption will be more efficient at low pH. The adsorbent will present a neutral surface charge able to attract humic substances, whereas at high pH functional groups pertaining to humic substances will be ionized and their negative charge will repulse the negative charge of the adsorbent (Bjelopavlic et al. 1999; Zhang et al. 2016).

The efficiency of the adsorption process can be assessed by the adsorptive capacity, a parameter estimated by isotherm plots. The latter are obtained from series of tests where known concentrations of adsorbate in a certain volume of solution are mixed with different dosages of the adsorbent. Once the equilibrium is reached, the adsorbate concentration in solution is measured and compared to the initial concentration (Crittenden et al. 2012; Marsh and Reinoso 2006). The Langmuir and Freundlich isotherms are generally used for adsorption modelling: the former considers that a molecule of adsorbate can be attached to only one adsorption site, whereas the Freundlich model accepts the adsorption of more than one molecule of adsorbate by each adsorption site (Crittenden et al. 2012).

2.2.1. Leachate treatment by commercial activated carbon

Rivas et al. (2006) evaluated the use of activated carbon for the organic matter removal from an old leachate mostly composed of humic substances. Adsorption isotherms were performed at the following conditions: adsorbent Norit 0.8 (surface area,

1150 m² g⁻¹) at concentrations varying from 0 to 100 g L⁻¹; temperature of 20°C; pH 8 (i.e, the pH of the tested leachate); and organic matter removal was assessed by COD measurements. For equilibrium concentrations varying in a range between 250 to 3000 gCOD L⁻¹, the maximum adsorptive capacities determined by Langmuir model varied from 500 to 700 g COD g⁻¹ Norit 0.8.

Koumaki et al. (2011) also tested PAC adsorption for an old leachate mostly composed of humic substances. The adsorbents were described as PAC WP5 and WP7 presented surface areas of 650 and 900 m² g⁻¹, respectively. Isotherms tests were performed with the two PACs at 0.01 to 6 g L⁻¹, pH 8, temperature of 23 °C, equilibrium time of 24 hours and organic matter removal determined by COD measurements. As the old leachate presented a COD as high as 5500 mg L⁻¹, PAC doses lower than 1 g L⁻¹ were not effective. On the other hand, at the maximum dose of 6 g L⁻¹, COD removals for PACs WP5 and WP7 were 45 and 62 %, respectively. The isotherms were better fitted by Freundlich model: the adsorptive capacities estimated for WP5 and WP7 by the parameter K_F were 2.36.10⁻⁶ and 7.10⁻⁷, respectively.

Old leachate treatment by adsorption/coagulation was also evaluated by Hur and Kim (2000), who focused on the removal of organic matter (i.e, humic substances). Tests with PAC were performed at concentrations ranging from 0.1 to 2 g L⁻¹. After mixing with PAC for 20 minutes, leachate was post-treated with alumn for other 20 minutes, followed by a 2-h settling period. COD removal due to PAC adsorption was about 15%, whereas the adsorptive capacity of PAC at 100 mg L⁻¹ was up to 6.5 mg COD L⁻¹. Combining adsorption with PAC at 200 mg L⁻¹ with coagulation using 500 mg L⁻¹ of alumn, COD removal was enhanced to 30 %. Isotherms were best fitted by Freundlich model, and the adsorptive capacity estimated by the K_F parameter was 1.35.10⁻³.

Li et al. (2010) applied coagulation/flocculation combined with PAC adsorption to remove refractory organic matter from an old leachate. Raw leachate presenting 2817 mg L⁻¹ of COD was pretreated by coagulation/flocculation with polyferric sulphate (0.3 g Fe⁺³ L⁻¹), which removed 70 % of its initial COD. Subsequently, leachate containing 855 mg L⁻¹ of COD was treated by adsorption. Isotherms tests were performed with PAC at doses of 0.5 to 50 g L⁻¹, pH 4, temperature of 20 °C and a 6-h equilibrium period. Corroborating the results presented by Koumaki et al. (2011), PAC dose as low as 0.5 g L⁻¹ was insufficient for a significant COD removal, which in this case was only 7 %. COD removal was enhanced to 53 % when PAC was used at 10 g L⁻¹. The adsorptive capacity was estimated by Freundlich model, which resulted a KF parameter of 2.45.10⁻⁵.

Aktas and Çeçen (2001) treated an old leachate combining the activated sludge (AS) process with adsorption using PAC, focusing on the organic matter removal. Adsorption isotherms were performed as follows: the adsorbent was Norit 4 (650 m² g⁻¹ of surface area) at concentrations of 1, 5 and 15 g L⁻¹; temperature of 20 °C; leachate diluted (1:20) in water; and stirring for 3 days, when the COD removal was in equilibrium. The authors considered satisfactory the application of Freundlich model to experimental data using such a complex wastewater as leachate (correlation coefficients varying from 0.88 to 0.95). According to the authors, a low adsorptive capacity (estimated in terms of the parameter K_F in the Freundlich model, 0.0038 mg COD mg⁻¹ PAC (L mg⁻¹)^{1/n}) was observed for humic substances in leachate. Consequently, the difference in organic matter removal by PAC+AS and AS was only 6%.

Rivas et al. (2003) combined ozonation with adsorption using PAC to remove humic substances comprising the organic matter of an old leachate. Raw leachate (COD 3500 mg/L) was pretreated for one hour with O₃ 1 mMol L⁻¹, which resulted in 30 % of

COD removal. The pretreated leachate was further treated with 30 g L⁻¹ of Norit 0.8 (surface area, 1150 m² g⁻¹), which could successfully remove 90 % of the COD in 2h. The adsorptive capacities estimated by Sips model for COD and UV absorbance at 254 nm were 200 mg g⁻¹ and 3220 mg g⁻¹, respectively.

2.2.2. Leachate treatment by waste-derived activated carbon

Several types of organic waste have been tested as precursors for biochar and activated carbon, and promising results have been reported for colour removal from dyes and heavy metals from wastewaters and aqueous solutions (Gisi et al. 2016; Shehzad et al. 2015).

Jung et al. (2015) tested biochar produced from *Pinus taeda* pyrolyzed at 300 °C in an inert atmosphere (N₂) to remove natural organic matter from aqueous solution. The authors tested the adsorption of a solution containing 10 mg L⁻¹ of humic acid and varying doses of the biochar (20 to 100 mg L⁻¹). The solution was in contact with the adsorbent for 7 days. Regardless the dose used for the adsorbent, the remaining amount of humic acid in the liquid phase was very similar to the initial concentration (10 mg L⁻¹).

Activated carbon produced from cow dung ash (ACA) has been compared to cow dung ash (CA) as adsorbent for leachate treatment (Kaur et al. 2016). Whereas both adsorbents have been dried at 105 °C, active cow dung was impregnated with acetic acid for 12 h prior to drying. Using 20 g L⁻¹ of adsorbents and a 3-h agitation time, the authors reported COD removals of 61 % for CA, 73% for ACA, and 94 % for a commercial biochar. Although ACA was more efficient for COD removal rather than CA, it presented a smaller adsorptive capacity estimated by Langmuir model, 53 mg g⁻¹, whereas for CA this parameter was calculated as 47 mg g⁻¹. This result could be

possibly associated to a higher surface area of CA compared to ACA, which was not presented by the authors.

Ghani et al. (2017) produced activated carbon from banana pseudo-stem and tested it for old leachate treatment without pH adjustment. The precursor was impregnated with ZnCl_2 (4.5:1 ratio) and presented a surface area of $1329 \text{ m}^2 \text{ g}^{-1}$. Leachate was shaken with the adsorbent for 24 h, and at the end of the test colour and COD removals were about 90 %. This result would not be expected considering that leachate presented a high pH range (8-9), at which the humic substances would be ionized and the adsorbent presented a negatives surface charge, resulting in repulsion between adsorbent/adsorbate. However, the authors associated the high organic matter removal with the formation of humic substances-heavy metal complexes, whereas heavy metals positively charged were attracted to the negatively charged surface of the activated carbon.

Azmi et al. (2015) treated old leachate with activated carbon produced from sugarcane bagasse, focusing on organic matter and ammonia removal. The precursor was impregnated with KOH (2.59:1 ratio), and presented a surface area of $100 \text{ m}^2 \text{ g}^{-1}$. Without any pH adjustment, old leachate was shaken with 50 g L^{-1} of activated carbon for 3h. The results indicated 38 % of ammonia removal, whereas the removals of colour and COD were 74 and 86 %, respectively.

The efficiency of waste-derived activated carbon is not limited for organic matter and colour removal from leachate but it has also been reported in studies related to heavy metals removal (Ching et al. 2011; Foo et al. 2013). Ching et al. (2011) treated old leachate with activated carbon produced from spent coffee grounds, focusing on total iron and orthophosphate removal. Spent coffee grounds were impregnated with H_2SO_4 at ratios varying from 0.5 to 2.5 and shaken with leachate at the dose of 100 g L^{-1}

¹, for an equilibrium time of 1.5 h. The activated carbon impregnated at the ratio 0.5 (surface area, 121.5 m² g⁻¹) resulted in optimum removals of iron, 77 %, and orthophosphate, 84 %.

Foo et al. (2013) evaluated the boron and total iron removal from old leachate using activated carbon produced from banana frond. The later was carbonized at 700 °C, impregnated with KOH at a 1:1.75 ratio, and heated in a microwave. The adsorbent produced presented a surface area of 848 m² g⁻¹ and the mesopore volume corresponded to 77 % of total pore volume. Significant removals of boron (87 %) and total iron (93 %) were observed in a very short contact time (about 10 min) when leachate was shaken with 30 g L⁻¹ of banana frond activated carbon.

From the literature review herein presented, only few studies have reported the application of waste-derived activated carbon for leachate treatment, evidencing the importance of further investigations (Ghani et al. 2017).

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CHAPTER 3 Organic matter removal from landfill leachate by adsorption using spent coffee grounds activated carbon

Abstract

This study aimed to treat landfill leachate using spent coffee grounds (SCG) activated carbon, determining its efficiency for organic matter and colour removal, as well as its maximum adsorptive capacity. Synthetic leachate containing only humic acid and ammonium chloride was used in adsorption batch tests to determine the experimental conditions (adsorbent dose, pH, temperature, and contact time) favouring chemical oxygen demand (COD) and colour removals. SCG activated carbon was also tested for real leachate treatment. The samples were prepared by impregnating SCG with phosphoric acid (H_3PO_4) at the ratios of 50 and 100 %. Afterwards, the samples were submitted to pyrolysis (350 and 500 °C) at an inert atmosphere (N_2 at a flow rate of 0.1 L min⁻¹), for a 1-hour period. The results indicated that samples impregnated at 50 % presented higher surface areas (300-2118 m² g⁻¹) compared to those impregnated at 100% (188-1209 m² g⁻¹). The most efficient sample was produced at an impregnation ratio of 50 % and at a pyrolysis temperature of 500 °C. Its maximum adsorptive capacity was 40 mg of COD per gram of activated carbon. In addition, outstanding performances were observed for real landfill leachate treatment. COD removal was 94±3 % and colour was entirely removed, proving the high efficiency of SCG activated carbon for real landfill leachate.

Keywords: activated carbon; adsorption; landfill leachate; organic matter removal; spent coffee grounds

3.1. Introduction

Coffee is a favored beverage worldwide and impressive numbers are assigned for coffee grounds global production: recent statistics shows that 169.7 million 60 kg-bags were produced in 2018, whereas between 2017 and 2018, 161.3 million 60 kg-bags were consumed worldwide (International Coffee Organization 2019). During the brewing process, massive amounts of organic waste is generated, i.e., spent coffee grounds (SCG) (Campos-Vega et al. 2015; Fernandes et al. 2017). The latter can be toxic to aquatic organisms in case of long-term exposure, due to constituents such as caffeine, fatty acids and metals (Fernandes et al. 2017). However, if sanitary landfills are the final disposal for SCG, like any other organic waste landfilled, they may contribute to the formation of leachate, a pollutant wastewater (Foo and Hameed 2009; Renou et al. 2008).

Leachate composition may be influenced by several factors, such as the landfilled waste, precipitation and temperature (Foo and Hameed 2009; Renou et al. 2008). Nonetheless, leachate is typically composed by high concentration of ammonia, biodegradable and refractory organic matter (i.e, humic substances), dissolved solids, and heavy metals in low concentration (Foo and Hameed 2009; Kjeldsen et al. 2002; Renou et al. 2008). The high concentrations of organic matter and ammonia (that can be as high as 800 to 5000 mg L⁻¹) comprise the major concerns, whereas heavy metals comprise the minor concerns about this wastewater. Due to its pollutant composition, leachate may cause deleterious effects to the environment if discharged to water bodies without proper treatment (Foo and Hameed 2009; Kjeldsen et al. 2002; Renou et al. 2008).

Treatment technologies available for leachate include traditional methods such aerobic processes (Campos et al. 2014; Ren et al. 2017), air stripping (Ferraz et al.

2013; Yuan et al. 2016), and adsorption using commercial activated carbon or biochar (Aktas and Çeçen 2001; Foo and Hameed 2009; Huang et al. 2019; Li et al. 2010; Renou et al. 2008; Rivas et al. 2006). Alternatively, sophisticated methods such as adsorption using graphene (Pang et al. 2019; Saleh et al. 2017) and $[Sb(TPP)Cl_2]SbCl_6$ (Soury et al. 2019), or advanced oxidation processes using CeO_2 -based photocatalysts (Ma et al. 2019) have recently been tested to remove organic contaminants from wastewaters. Despite the high level of wastewater purification provided by combining sophisticated treatment methods, high operational costs may limit real-scale applications (Foo and Hameed 2009; Renou et al. 2008).

Focusing on cost-effective alternatives for leachate treatment, low-cost adsorbents produced from organic waste have been tested (Foo and Hameed 2009; Kumar and Jena 2016). For instance, organic wastes such as SCG can be diverted from landfills and recovered as adsorbents (Campos-Vega et al. 2015; Shehzad et al. 2015). Although recent studies have confirmed the feasibility of using SCG for activated carbon production (Ahsan et al. 2018; Campos-Vega et al. 2015; Ching et al. 2011; Janissen and Huynh 2018; Poblete et al. 2017; Reffas et al. 2010; Tehrani et al. 2015), the literature is still lacking the application of SCG-derived activated carbon for landfill leachate treatment. So far, the most relevant studies on this topic have addressed two distinct goals: while Ching et al. (2011) were focused on iron and orthophosphate removal from leachate using SCG activated carbon, Poblete et al. (2017) studied the combination of adsorption (SCG activated carbon)/advanced oxidation processes for organic matter removal from leachate. These studies confirmed the effectiveness of SCG activated carbon for their target contaminants, encouraging further investigations.

Considering the importance of sustainable alternatives for leachate treatment, this study aimed to treat landfill leachate using SCG activated carbon, determining its

efficiency for organic matter and colour removal, as well as its maximum adsorptive capacity. This study also aimed to contribute to the literature dedicated to waste-derived activated carbon applied for the organic matter removal from landfill leachate.

3.2. Material and Methods

3.2.1. Adsorbents preparation

SCG were collected from a local coffee shop, and the activated carbon was produced by adapting the methodology described by previous studies (Azmi et al. 2015; Ching et al. 2011; Tehrani et al. 2015). The precursor (SCG) was initially washed with deionized water, dried at 105 °C for 24 h, cooled down to room temperature, and sieved at 250 µm. For the purpose of chemical activation, SCG were weighed (40 g) and impregnated with H₃PO₄ 85 % at the mass ratios (w w⁻¹, %) 50 and 100 %. Afterwards, the samples were sonicated for 1 h, dried at 105 °C for 24 h, cooled down to room temperature and weighed. The next process applied to the samples was pyrolysis in an inert atmosphere (N₂, at a flow rate of 0.1 L min⁻¹), which was performed using a Lindberg Blue M box furnace. In this study, the SCG activated carbon samples were produced at 350 and 500 °C. Therefore, once the selected temperature was reached, the samples were kept in the furnace for 1 h, under a continuous flow of N₂ (0.1 L min⁻¹). At the end of the process, the samples were cooled down to room temperature (20 °C) and weighed. Focusing on ash removal, the activated carbon samples were initially washed with deionized water, and then washed with 0.1 M hydrochloric acid (HCl) and 0.1 M sodium bicarbonate (NaHCO₃), until its pH was neutral (Azmi et al. 2015; Ching et al. 2011; Tehrani et al. 2015). Afterwards, the samples were dried at 105 °C for 24 h, cooled down to room temperature and weighed. The activated carbon yield, burn-off

and ash content were determined according to previous studies (Azmi et al. 2015; Ching et al. 2011; Tehrani et al. 2015).

3.2.2. Adsorbate: synthetic and real landfill leachate

Synthetic leachate recipe was adapted from previous studies (Bardi et al. 2017; Ren et al. 2017): 1000 mg L⁻¹ of humic acid and 1500 mg L⁻¹ of ammonium chloride (NH₄Cl) were dissolved in deionized water. Synthetic leachate was transferred to an amber flask and stored at 4 °C. Therefore, synthetic leachate presented approximately 1000 mg L⁻¹ of COD, 393 mg L⁻¹ of NH₄⁺ and 996 mg L⁻¹ of Cl⁻, which corresponds to a similar composition compared to real leachate used in this study (Demchenko et al. 2018). Real leachate was collected from Brady Road Landfill, located in Winnipeg-MB, Canada, and stored at 4 °C prior to its use for the experiments. This landfill is in operation since 1973 receiving both residential and commercial wastes (Berenjkar et al. 2019; Islam et al. 2019). According to previous studies, the leachate collected in the Brady Road landfill can be classified as old, due to the high content of refractory organic matter, pH 8, and high concentrations of ammonia (Bardi et al. 2017; Berenjkar et al. 2019; Islam et al. 2019; Ren et al. 2017; Xu et al. 2018).

3.2.3. Adsorption experiments

Adsorption batch tests were adapted from previous studies (Azmi et al. 2015; Ching et al. 2011; Kaur et al. 2016; Reffas et al. 2010), using 100 mL of leachate. Blanks containing only leachate and no adsorbent were also tested. An orbital shaker was used to keep the samples constantly agitated at 125 rpm. To determine the interference of the adsorbent dose (10 and 20 g L⁻¹), pH (4 and 8), and temperature (20 and 50 °C) on the organic matter removal from synthetic leachate, the samples were

kept under agitation for 3 hours. As the best conditions (adsorbent dose, pH and temperature) for synthetic leachate treatment were verified, kinetic tests and adsorption isotherms were also performed. For the isotherms test, samples were kept in agitation for 24 h, using a fixed dose of activated carbon (20 g L⁻¹), whereas the COD of synthetic varied from 300 to 3000 mg L⁻¹. To verify whether the results obtained with synthetic leachate were comparable with the real wastewater treatment, adsorption batch tests were also performed on real leachate. After each test was completed, the samples were centrifuged (12000 rpm for 5 minutes), filtered (0.45 µm filter), and COD and colour were determined (Azmi et al. 2015; Ching et al. 2011; Kaur et al. 2016; Reffas et al. 2010).

3.2.4. Data analysis

The adsorption tests were performed in triplicates, and the results obtained were reported as averages and their correspondent standard deviations. Colour and COD removals were calculated as per Ching et al. (Ching et al. 2011). The maximum adsorptive capacities were determined using the Langmuir model, as follows:

$$Q_e = (Q_{\max} b C_e) / (1 + b C_e) \quad \text{Equation 1}$$

where Q_e is the adsorbent-phase concentration of the adsorbate, Q_{\max} is the maximum adsorptive capacity (mg g⁻¹), b is the Langmuir adsorption constant (L mg⁻¹), and C_e is the equilibrium concentration of the adsorbate in the liquid-phase (Ching et al. 2011).

3.2.5. Analytical methods

Colour and COD analysis were performed on filtered samples of both synthetic and real leachate before and after the adsorption tests, as per Standard Methods (APHA et al. 2012). The SCG activated carbon samples were characterized by Fourier transform infrared spectroscopy (FTIR) in attenuated total reflection (ATR) mode using a Nicolet

TM iS10 FTIR Spectrometer (40 scans, 4 cm⁻¹ resolution). Using a Quantachrome Autosorb-1 BET analyzer, N₂ adsorption-desorption isotherms at 77 K were performed to determine the surface area and pore volume (Banerjee et al. 2016; Ching et al. 2011; Reffas et al. 2010). While surface area was calculated by Brunauer- Emmett-Teller (BET) equations, pore volume was determined by t-plot method (Banerjee et al. 2016; Ching et al. 2011; Reffas et al. 2010).

3.3. Results and Discussions

3.3.1. Adsorbent characterization

SCG activated carbon samples presented yields in the range of 40 %, burn-off around 60 %, whereas ash content varied from 28 to 37 % (Table 3.1). Indeed, lignocellulosic materials would result in a maximum yield of 48 %, which corresponds to their typical carbon content that would remain after pyrolysis, while oxygen and hydrogen would be removed during this process (Marsh and Reinoso, 2006). Therefore, SCG activated carbon samples herein presented were efficiently produced by chemical activation/pyrolysis, and the results presented in Table 3.1 are comparable to those reported by previous studies (Ching et al. 2011; Reffas et al. 2010; Tehrani et al. 2015).

SCG activated carbon samples presented average pore diameters varying from 2.5 to 3.8 nm (Table 3.1), which indicates the formation mesoporous materials. According to the International Union of Pure and Applied Chemistry (IUPAC), diameters ranging from 2 to 50 nm refer to mesopores, whereas those smaller than 2 nm correspond to micropores (Rouquerol et al. 1994).

Table 3.1 Physical properties of spent coffee grounds activated carbon impregnated at 50 % with H₃PO₄ and produced at 500 °C (C50-500) and at 350 °C (C50-350), and impregnated at 100 % with H₃PO₄ and produced at 500 °C (C100-500) and at 350 °C (C100-350).

Parameter	Sample			
	C50-350	C100-350	C50-500	C100-500
Yield (%)	40±3.3	40±1	41±3.6	40±3.4
Burn-off (%)	60±3.3	60±0.7	59±3.6	60±3.4
Ash content (%)	28±5	37±3	35±7.5	35±8
Particle size (µm)	250	250	250	250
BET surface area (m ² g ⁻¹)	300	188	2118	1209
Micropore surface area (m ² g ⁻¹)	245	140	1815	1090
External surface area (m ² g ⁻¹)	55	47	302	119
Total pore volume (cm ³ g ⁻¹)	0.038	0.030	0.182	0.127
Micropore volume (cm ³ g ⁻¹)	0.021	0.017	0.127	0.097
Mesopore volume (cm ³ g ⁻¹)	0.017	0.013	0.055	0.030
Average pore diameter (nm)	3.4	3.8	2.5	2.6

*BET: Brunauer–Emmett–Teller

Activated carbon samples produced at 500 °C developed higher porosity and BET surface area in comparison with those produced at 350 °C (Table 3.1). For instance, samples produced at 500 °C presented total pore volumes up to 5 times greater than those observed for samples produced at 350 °C (Table 3.1). The impregnation ratios also interfered with the development of porosity: samples impregnated at 100 %

presented smaller total pore volumes than those impregnated at 50 % (Table 3.1). The reduced formation of porosity resulted in smaller BET surface area for samples impregnated at 100 %, in comparison with those impregnated at 50 % (Table 3.1). Similar observations were reported by Ching et al. (2011) and Kumar and Jena (2016). Therefore, the activation process does not seem to require an impregnation ratio as high as 100 % in order to produce a porous adsorbent. The BET surface areas obtained in this study were comparable with the values reported in the literature (1000 to 2700 m² g⁻¹) for activated carbon produced from diverse food waste precursors (Shehzad et al. 2015).

The FTIR/ATR characterization of the activated carbon samples indicated that they presented similar functional groups (Figure 3.1). The absence of peaks at 3400 cm⁻¹ associated with hydrogen-bonded OH from water confirmed the dehydration of all the samples during the activated carbon production. Typical groups present in SCG were identified, as follows: C-H stretching vibration was observed at 2900 cm⁻¹, whereas C \equiv C stretching vibration in alkyne was observed at 2100 cm⁻¹, anhydrides were associated with the band at 1880 cm⁻¹, C=O stretching vibration in carboxyl and C=C stretching vibration in aromatic rings at 1500 cm⁻¹ (Chen and Wu 2004; Ching et al. 2011; Marsh and Reinoso 2006; Reffas et al. 2010; Saleh, 2018).

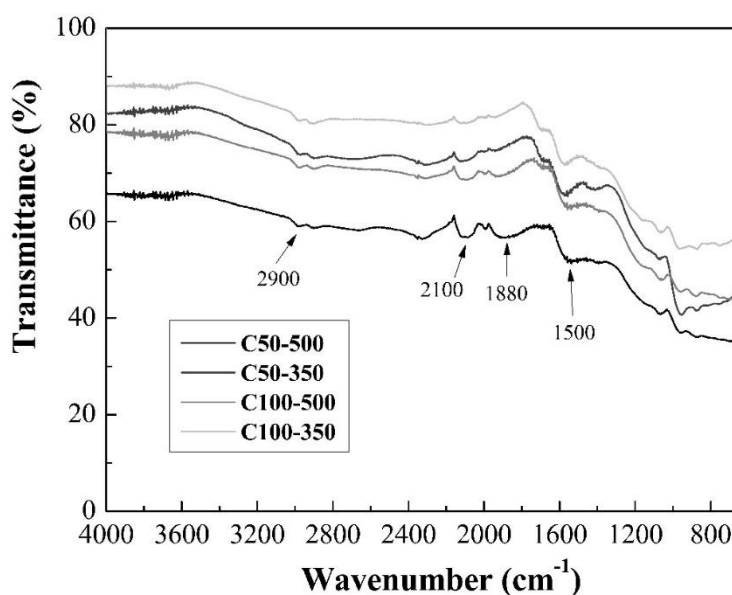


Figure 3.1 Fourier transform infrared spectroscopy/attenuated total reflection (FTIR/ATR) spectra for spent coffee grounds activated carbon samples impregnated at 50 % with H_3PO_4 and produced at 500 °C (C50-500) and at 350 °C (C50-350), and impregnated at 100 % with H_3PO_4 and produced at 500 °C (C100-500) and at 350 °C (C100-350).

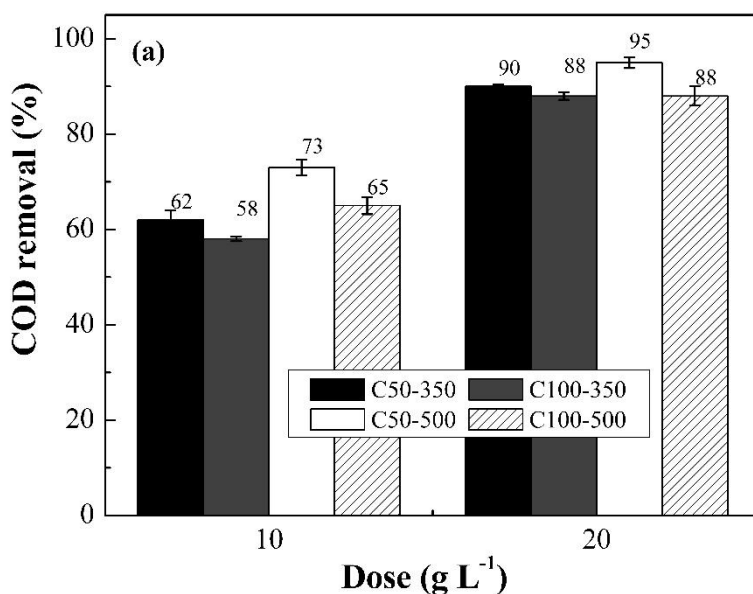
3.3.2. Adsorption batch tests with synthetic leachate

3.3.2.1. Interference of SCG activated carbon dose on COD removal

For all tested samples, higher COD removals were obtained when the activated carbon dose was 20 g L⁻¹ instead of 10 g L⁻¹ (Figure 3.2a). Samples impregnated at 50 % and produced at 500 °C provided an average COD removal of 73±1.2 % at the dose of 10 g L⁻¹, whereas at 20 g L⁻¹, the average COD removal increased to 95±1 % (Figure 3.2a). In contrast, samples impregnated at 100 % and produced at 500 °C provided an average COD removal of 65±1.8 % at the dose of 10 g L⁻¹, increasing its performance to 88±2 % at the dose of 20 g L⁻¹ (Figure 3.2a). Regarding the adsorbents produced at 350

°C, samples impregnated at 50 % provided COD removals of 62 ± 2 % and 90 ± 0.5 % when tested at the doses of 10 and 20 g L⁻¹, respectively (Figure 3.2a). Samples impregnated at 100 % and tested at the doses of 10 and 20 g L⁻¹ provided COD removals of 58 ± 0.5 % and 88 ± 0.8 %, respectively (Figure 3.2a). Therefore, 20 g L⁻¹ was the selected dose for the subsequent experiments.

Other studies have also reported better removal efficiencies of target contaminants when the adsorbent dose was increased. For instance, the efficiency of phosphorus removal from landfill leachate was increased along with the increase on SCG activated carbon dose (5 to 250 g L⁻¹) (Ching et al. 2011). When cow dung activated carbon was applied for leachate treatment, COD removal efficiency almost doubled when the adsorbent dose was increased from 10 to 20 g L⁻¹ (Kaur et al. 2016).



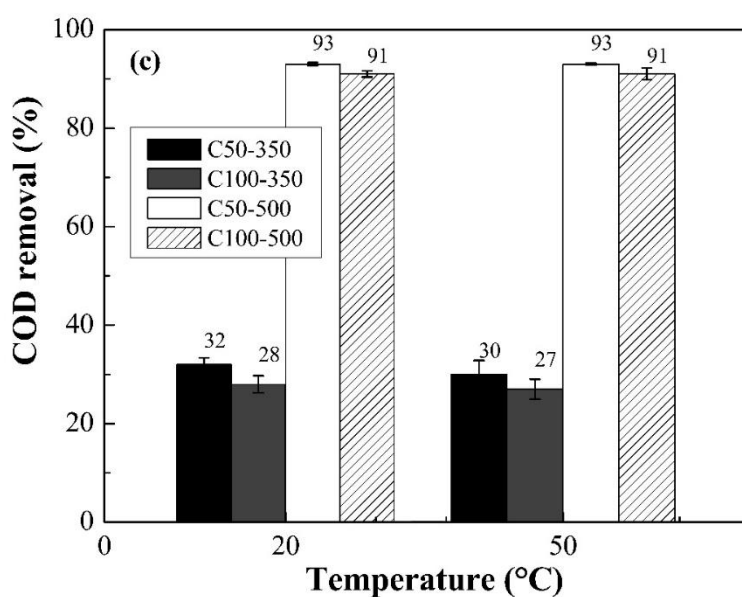
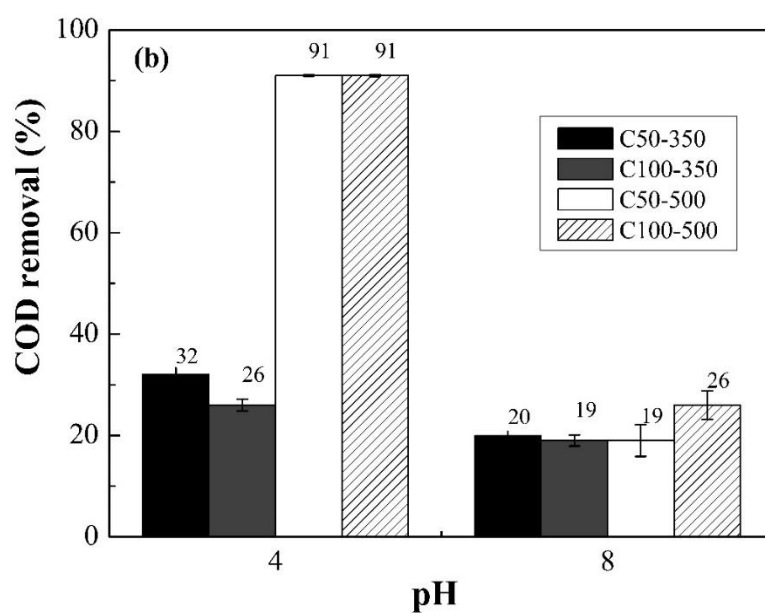


Figure 3.2 Interference of (a) the adsorbent dose, (b) pH, and (c) temperature on COD removal by spent coffee grounds activated carbon impregnated at 50 % with H_3PO_4 and produced at 500 °C (C50-500) and at 350 °C (C50-350), and impregnated at 100 % with H_3PO_4 and produced at 500 °C (C100-500) and at 350 °C (C100-350).

3.3.2.2. Interference of pH on COD removal by SCG activated carbon

Adjusting the pH to 4 improved COD removal from synthetic leachate (Figure 3.2b). For samples impregnated at 50 % and produced at 500 °C, COD removals at pH 4 exceeded up to 5 times the values observed at pH 8. The same trend was observed for activated carbon samples prepared at 350 °C. This result is in agreement with the literature (Bjelopavlic et al. 1999; Reffas et al. 2010; Zhang et al. 2016), indicating that SCG activated carbon most probably exhibited a neutral surface charge at acidic pH rather than at alkaline pH, favoring humic acid adsorption. In contrast, at alkaline pH the surface of the activated carbon was most likely negative, repelling potentially ionized groups pertaining to humic acid (Bjelopavlic et al. 1999; Reffas et al. 2010; Zhang et al. 2016). This could explain the lower COD removals observed in tests at pH 8, compared with those observed for tests at pH 4 (Figure 3.2b). Therefore, subsequent experiments were performed using an adsorbent dose of 20 g L⁻¹ and synthetic leachate at pH 4.

It is worthwhile mentioning that the pH was rigorously controlled throughout the experiments, to guarantee it would not drop to ranges that could favor the precipitation of humic acid (pH < 2). In this case, the latter could have been partially removed by precipitation, and the overall adsorption efficiencies could have been overestimated. Hence, by controlling the pH to 4, the reported results were indeed related to the adsorption process.

3.3.2.3. Interference of temperature on COD removal by SCG activated carbon

Whereas previous studies were conducted at temperatures between 25 and 30 °C (Aktas and Çeçen, 2001; Huang et al. 2019), in the current research tests were

performed at 20 °C (room temperature) and at 50 °C. The results shown in Figure 3.2c indicated that the adsorption of humic acid by SCG activated carbon does not seem to be favored by increasing the temperature. For all tested samples, COD removals were in the same range for both tested temperatures. This result suggests that the synthetic leachate treatment can be performed without additional costs associated with heating the wastewater. Other studies reporting on waste-derived activated carbon also observed that increasing the temperature did not enhance COD removal from leachate (Kaur et al. 2016) or methyl orange from aqueous solutions (Saleh et al. 2014).

3.3.2.4. Contact time interference on COD and colour removals

COD and colour were mostly removed from synthetic leachate during the first 30 minutes, for all tested samples (Figure 3.3). As expected, blank samples did not present any variation on its organic matter content after the treatment, therefore, COD remained around 1100 mg O₂ L⁻¹, while colour remained around 35,000 Pt-Co units. SCG activated carbon impregnated at 50 % and produced at 500 °C removed 67±10 % of COD and 69±11 % of colour, in the first 30 minutes treating synthetic leachate. At the end of a 3-h monitoring period, 80±3 % of the COD and 90±1.5 % of colour were removed (Figure 3.3). Therefore, this sample was the most efficient among all tested adsorbents in this study, but also resulted in higher COD removal compared to a previous study (Kaur et al. 2016). Kaur et al. (2016) treated leachate using cow dung activated carbon, and reported 40 % of COD removal in the first hour, and approximately 70 % after 3h.

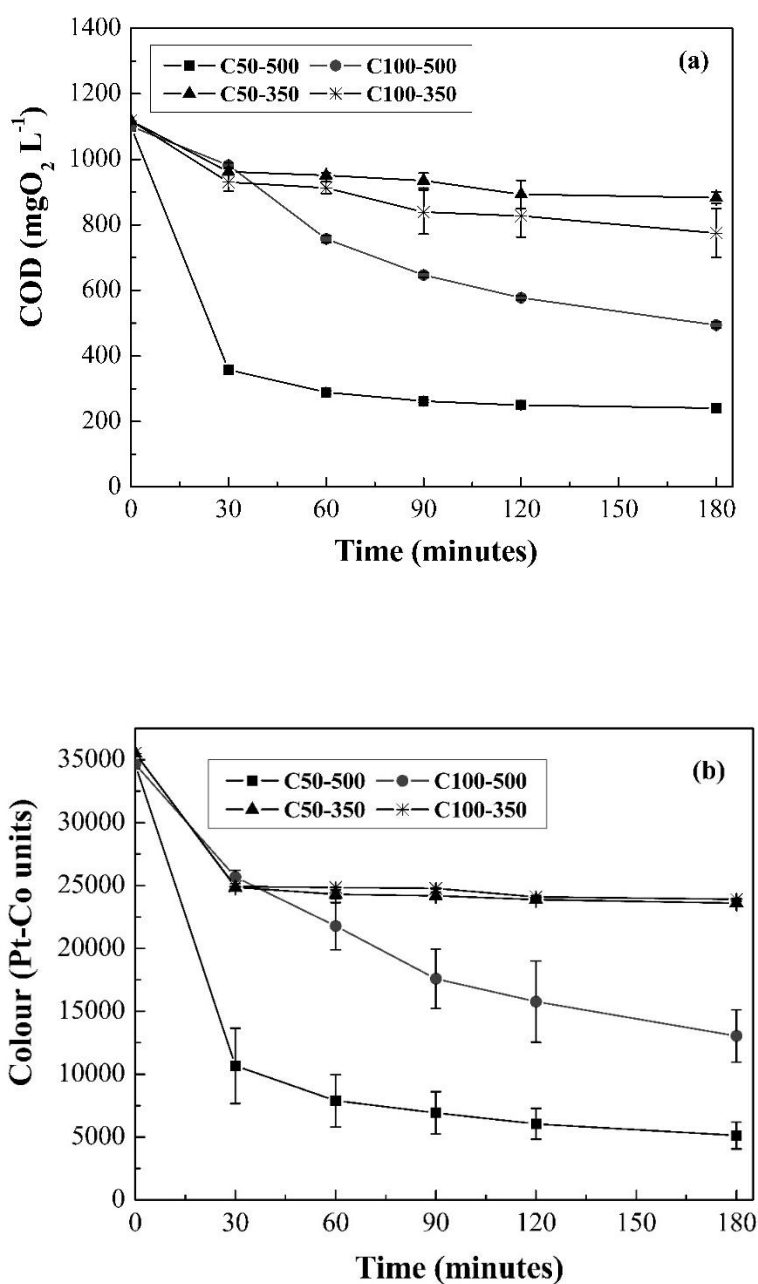


Figure 3.3 Effect of contact time on (a) COD and (b) colour removals from synthetic leachate by spent coffee grounds activated carbon impregnated at 50 % with H₃PO₄ and produced at 500 °C (C50-500) and at 350 °C (C50-350), and impregnated at 100 % with H₃PO₄ and produced at 500 °C (C100-500) and at 350 °C (C100-350).

SCG activated carbon impregnated at 100 % and produced at 500 °C removed only 11 ± 3 % of COD and 26 ± 2 % of colour from synthetic leachate in the first 30 minutes (Figure 3.3). At the end of a 3-h monitoring period, 55 ± 9 % of COD and 62 ± 8 % of colour were removed from synthetic leachate. Whereas the best performances on organic matter removal were observed for adsorbents produced at 500 °C, the opposite was observed for those produced at 350 °C. Colour and COD removals did not exceed 30 % after a 3-h monitoring period, due to the significantly lower surface area of these adsorbents, compared to adsorbents produced at 500 °C (Figure 3.3).

3.3.2.5. Adsorption isotherms

Activated carbon samples produced at 500 °C exhibited a higher adsorptive capacity (Figure 3.4a) compared to those produced at 350 °C (Figure 3.4b). In addition, increasing the impregnation ratio from 50 to 100 % did not increase the adsorptive capacities. For samples produced at 500 °C, the maximum adsorptive capacity determined by the Langmuir model was 40 mg COD g^{-1} for the sample impregnated at 50 % and 31 mg COD g^{-1} for the sample impregnated at 100 %. This result is in agreement with the physical properties (Table 3.1) previously discussed: the activated carbon samples produced at 500 °C consisted of mesoporous materials provided with significantly higher BET surface area in comparison with those produced at 350 °C. Consequently, activated carbon samples produced at 500 °C were provided with more adsorption sites where humic acid could be retained. For samples produced at 350 °C, the maximum adsorptive capacities determined by the Langmuir model were 17 mg COD g^{-1} and 11 mg COD g^{-1} for SCG impregnated at 50 and 100 %, respectively.

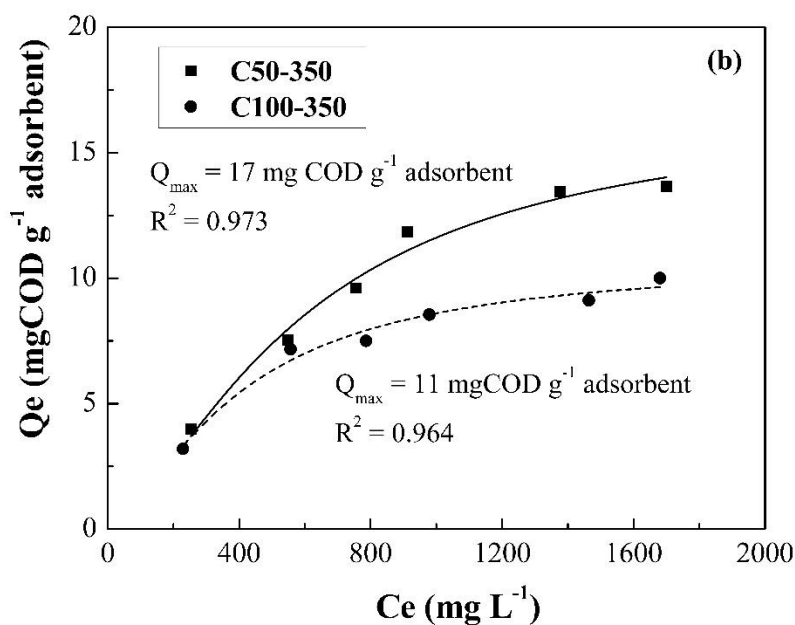
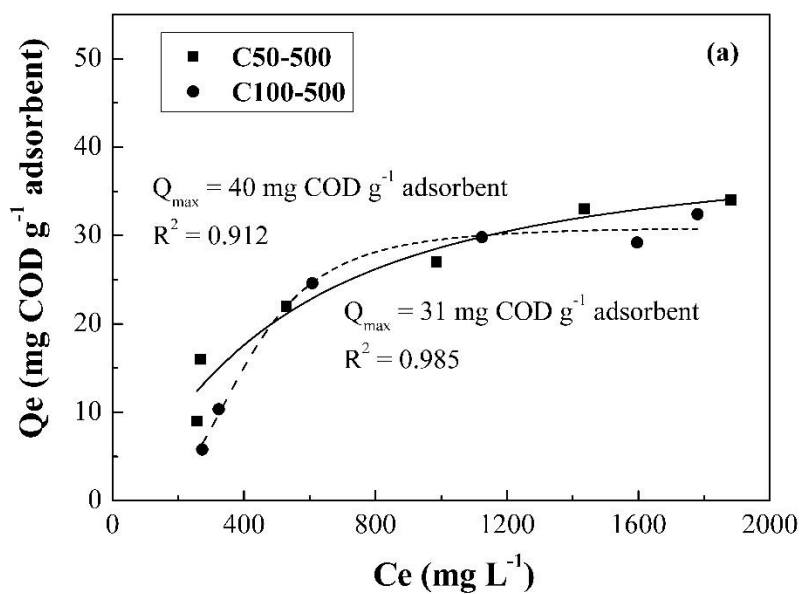


Figure 3.4 Adsorption isotherms obtained for spent coffee grounds activated carbon (a) impregnated at 50 and 100 % with H₃PO₄ and produced at 500 °C (C50-500 and C100-500) and (b) impregnated at 50 and 100 % with H₃PO₄ and produced at 350 °C (C50-350 and C100-350).

Previous studies have reported that several mechanisms may drive the adsorption of humic substances onto activated carbon surface, including hydrophobic forces, Van der Waals forces, and polar interactions by functional groups on the surface of the adsorbent (Ghani et al. 2017; Jung et al. 2015). Additionally, humic substances may combine with heavy metals also present in leachate, forming complexes positively charged that can be attracted to the surface of the activated carbon, enhancing the organic matter removal by adsorption (Ghani et al. 2017; Jung et al. 2015).

3.3.3. Adsorption batch tests with real leachate

When tested for real leachate treatment, SCG activated carbon produced at 500 °C successfully removed the organic matter (Figure 3.5). Samples impregnated at 50 % removed 61 ± 0.2 % of COD and 74 ± 1.2 % of colour in the first 30 minutes, whereas 76 ± 0.8 % of COD and 91 ± 2 % of colour were removed at the end of a 3-h monitoring period. After 24 h, both COD and colour were further removed, and the efficiencies were 94 ± 3 % and 100 %, respectively. This COD removal corresponded to an adsorptive capacity of 41 mg COD g^{-1} , which was similar to the maximum adsorptive capacity (40 mg COD g^{-1}) obtained for synthetic leachate by the Langmuir model (Figure 3.4a). When the impregnation ratio was increased to 100 %, the activated carbon removed 40 ± 9 % of COD and 72 ± 1.4 % of colour in the first 30 minutes, whereas 67 ± 1.5 % of COD and 83 ± 2.5 % of colour were removed at the end of a 3-h monitoring period. No further removals were observed after 24 h. The adsorptive capacity at the equilibrium was 33 mg COD g^{-1} , which was equal to the value determined by the Langmuir model in tests with synthetic leachate (Figure 3.4a).

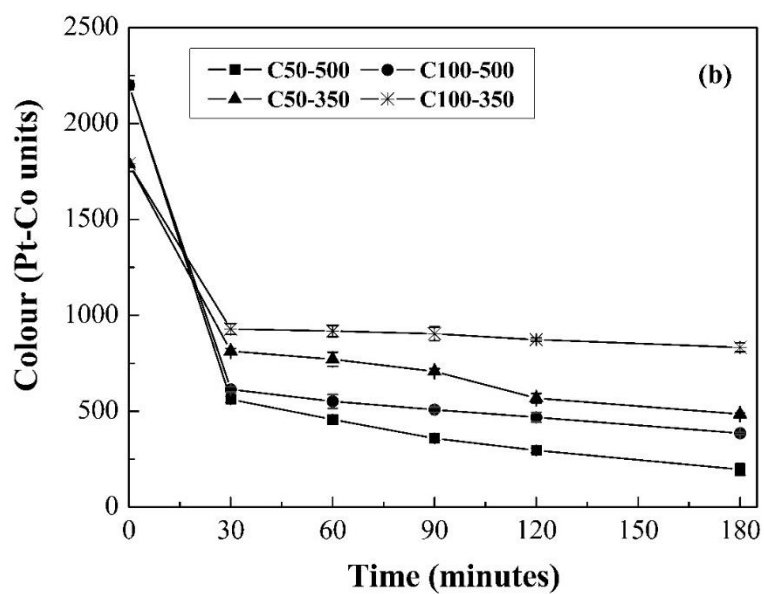
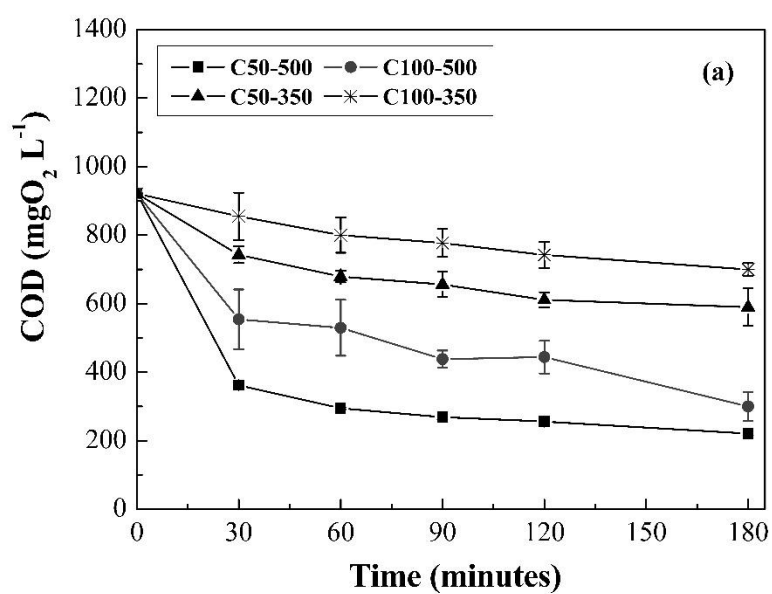


Figure 3.5 Effect of contact time on (a) COD and (b) colour removals from real leachate by spent coffee grounds activated carbon impregnated at 50 % with H_3PO_4 and produced at 500 °C (C50-500) and at 350 °C (C50-350), and impregnated at 100 % with H_3PO_4 and produced at 500 °C (C100-500) and at 350 °C (C100-350).

In contrast to the great performance obtained with activated carbon produced at 500°C, samples produced at 350°C presented modest removals of COD and colour (Figure 3.5). When impregnated at 50%, the adsorbent removed 36 ± 4 % of COD and 73 ± 3.5 % of colour, after 3 hours. Increasing the impregnation ratio to 100 % did not improve the organic matter removal from real leachate: COD and colour removals were 24 ± 1.5 % and 54 ± 5 %, respectively. Blank samples did not present any variation on COD and colour from the start to the end of the test. The adsorptive capacities at the equilibrium were in the same range previously determined by the Langmuir model in tests with synthetic leachate (Figure 3.4b).

3.4. Conclusion

The current research was dedicated to a topic that is still lacking in the literature, i.e., the specific application of SCG activated carbon for the organic matter removal from landfill leachate. Mesoporous activated carbon samples were produced from SCG impregnated with H_3PO_4 , and they were successfully applied for COD and colour removal from synthetic leachate. Tests with synthetic leachate indicated that the most appropriate conditions for organic matter removal comprised of a 20-g L^{-1} adsorbent dose, liquid-phase at pH 4, and batch tests carried out at 20 °C. Under these experimental conditions, it was obtained the maximum adsorptive capacity: 40 mg COD g^{-1} of SCG activated carbon impregnated at 50 % and produced at 500 °C. Batch tests performed for real landfill leachate presented outstanding efficiencies: 94 ± 3 % for COD removal, while colour was entirely removed. This research encourages the diversion of SCG from landfills, as they can be reused as alternative precursor for activated carbon. SCG activated carbon was proven efficient not only to treat synthetic wastewater, but also real landfill leachate. Focusing on real-scale applications, future

studies could further investigate alternatives methods to produce activated carbon with high surface areas, using reduced amounts of chemicals and energy for this process. In addition, the feasibility of regenerating exhausted adsorbents should also be investigated.

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CHAPTER 4 Performance of oat hulls activated carbon for COD and colour removal from landfill leachate

Abstract

This research aimed to recover oat hulls as activated carbon, using the produced adsorbent to remove the organic matter removal from landfill leachate. The organic matter content in leachate was determined by measurements of chemical oxygen demand (COD) and colour. In addition, the maximum adsorptive capacities associated with the adsorbents were also determined. Adsorption batch tests were initially performed with synthetic leachate, and variables such as pH, activated carbon dose, temperature and contact time were evaluated. The effectiveness of the adsorbents was also verified for real landfill leachate. Oat hulls samples were chemically activated with phosphoric acid (impregnation ratios, 60 and 100 %) and pyrolyzed (N_2 atmosphere) at 350 and 500 °C. The 100 % impregnation ratio resulted in adsorbents with higher surface areas ($1090\text{--}3880\text{ m}^2\text{ g}^{-1}$) rather than the ratio 60 % ($123\text{--}731\text{ m}^2\text{ g}^{-1}$). It was found that the organic matter removal from synthetic leachate was favored by performing the adsorption tests at 20 °C, pH 4, and using a 20-g L^{-1} activated carbon dose. Under these experimental conditions, the activated carbon sample impregnated at 100 % with phosphoric acid and pyrolyzed at 500 °C completely removed the colour from leachate, and COD removal was up to 90 %. Therefore, oat hulls comprise a suitable precursor for activated carbon, and its application for leachate treatment should be encouraged.

Keywords: activated carbon; adsorptive capacity; COD removal; colour removal; landfill leachate; oat hulls

4.1.Introduction

Although municipal solid waste can be safely disposed in sanitary landfills, the operation of these facilities is challenged by emissions of greenhouse gases and leachate (Renou et al. 2008). Landfill leachate is reported by the literature as a high-strength wastewater containing easily and hardly biodegradable organic matter, ammonia in high concentrations, dissolved solids, and heavy metals (Ferraz et al. 2016; Kjeldsen et al. 2002; Ren et al. 2017; Renou et al. 2008).

Depending on the level of purification required for leachate prior to its release into the environment, it can be treated by stand-alone or combined methods, such as: air stripping (Ferraz et al. 2013; Yuan et al. 2016), advanced oxidation processes (Poblete et al. 2017), biological processes (Ferraz et al. 2016; Ren et al. 2017), and adsorption (Li et al. 2010; Renou et al. 2008). Significant removals of heavy metals and organic matter have been attributed to the use of commercial activated carbon for leachate treatment (Aktas and Çeçen 2001; Li et al. 2010; Renou et al. 2008; Rivas et al. 2006). Nonetheless, as part of the efforts to divert organic wastes from landfills, these materials have been tested as precursors for activated carbon production and applied for wastewater treatment (Gisi et al. 2016).

Oat is one the most popular cereals consumed worldwide, and during its processing for human consumption, massive amounts of hulls are produced. The latter is a lignin-cellulosic waste that corresponds to about 25% of the oat grain weight. Oat hulls can be reused as animal feed, biomass for fuel production, or ultimately disposed in landfills (Banerjee et al. 2016; Thompson et al. 2000). Alternatively, oat hulls can be recovered as activated carbon, being successfully applied for dye (Banerjee et al. 2017) and arsenic (Chuang et al. 2005) removals from aqueous solutions.

While limited information is available for oat hulls activated carbon applied for water purification, the literature lacks their application for landfill leachate. Therefore, this study aimed to contribute to the literature by using oat hulls as precursors for activated carbon and testing these adsorbents to remove colour and COD from landfill leachate.

4.2. Material and Methods

The methodology used in this section was the same the one presented in Chapter 3, subsection 3.2. Therefore, experimental procedures previously described will be reintroduced and briefly mentioned in the subsections below.

4.2.1 Oat hulls activated carbon

Oat hulls were collected from a milling industry located in Emerson-MB, Canada. Oat hulls activated carbon were produced as per Chapter 3 (Subsection 3.1), and based on previously published papers (Azmi et al. 2015; Banerjee et al. 2016; Chuang et al. 2005; Tehrani et al. 2015). In brief, the adsorbents were prepared by means of chemical activation with phosphoric acid (impregnation ratios 60 and 100 %), followed by pyrolysis for 1 hour, under a N₂ atmosphere. The temperatures tested for pyrolysis were 350 and 500 °C (Azmi et al. 2015; Banerjee et al. 2016; Chuang et al. 2005; Tehrani et al. 2015).

4.2.2 Landfill leachate

Synthetic and real leachate were obtained as described in Chapter 3 (subsection 3.2). In brief, synthetic leachate consisted of a mixture containing 1000 mg L⁻¹ of humic acid and 1500 mg L⁻¹ of NH₄Cl (Ren et al. 2017; Bardi et al. 2017). The same municipal

landfill cited in Chapter 3, Section 3.2, provided the real leachate used in the experiments with oat hulls activated carbon.

4.2.3 Batch tests

Blanks and samples (100-mL volume) were evaluated in batch tests as per Chapter 3 (Section 3.3) and previous studies on waste-derived activated carbon (Azmi et al. 2015; Banerjee et al. 2016; Ching et al. 2011; Chuang et al. 2005; Kaur et al. 2016; Reffas et al. 2010). Tests with synthetic leachate were run for 3 h, and the organic matter removal was evaluated by varying the following parameters: oat hulls activated carbon dose (10 and 20 g L⁻¹), pH (4 and 8), and temperature (20 and 50 °C). The adsorptive capacities were determined in 24-h tests using 20 g L⁻¹ of oat hulls activated carbon, and different initial concentrations of synthetic leachate COD (300 to 3000 mg O₂ L⁻¹). The performance of the oat hulls activated carbon was also tested on real leachate using the best experimental conditions in terms of adsorbent dose, pH and temperature. Prior to COD and colour determinations, the adsorbents were removed from the treated samples by centrifugation followed by filtration carbon (Azmi et al. 2015; Banerjee et al. 2016; Ching et al. 2011; Chuang et al. 2005; Kaur et al. 2016; Reffas et al. 2010).

4.2.4 Experimental data analysis

Analogously to Chapter 3, subsection 3.4, the experiments were run in triplicates, and data was reported as mean and standard deviations (Ahsan et al. 2018; Ching et al. 2011; Jung et al. 2015; Kaur et al. 2016; Martinez et al. 2019; Poblete et al. 2017). The Langmuir model was applied for determination of the maximum adsorptive capacities (Chuang et al. 2005).

4.2.5 Physico-chemical and spectroscopic analysis

The analyses and instruments described Chapter 3 (subsection 3.5) were also applied for the current subsection. Colour and COD were determined according to Standard Methods (APHA et al. 2012). Functional groups on the surface of the oat hulls activated carbon were determined by FTIR/ATR (Nicolet TM iS10 FTIR Spectrometer). A Quantachrome Autosorb-1 BET analyzer was used to determine the surface area and pore volume of the oat hulls activated carbon samples.

4.3. Results and Discussions

4.3.1 Physico-chemical and spectroscopic properties of oat hulls activated carbon

The yields obtained for oat hulls activated carbon were about 38 %, whereas burn-off was around 60 %, and ash content 30 % (Table 4.1). As reported by Hildago-Oporto et al. (2019), oat hulls are lignocellulosic materials composed by nitrogen (0.6 %), carbon (43 %), hydrogen (6 %), and oxygen (50.4 %). During pyrolysis, hydrogen and oxygen atoms are removed from lignocellulosic materials, and the formed porous adsorbent is mainly composed by carbon atoms. Therefore, the maximum yield for activated carbon produced from lignocellulosic materials would be 40-48 %, which corresponds to its carbon content (Hildago-Oporto et al. 2019; Marsh and Reinoso 2006). Hence, the yields obtained for oat hulls activated carbon corresponded to 80 % of the maximum theoretical yield, confirming the high efficiency of chemical activation/pyrolysis under the conditions tested in this study.

The BET surface area was affected by both the tested impregnation ratios and pyrolysis temperature (Table 4.1). Samples that were impregnated with H_3PO_4 at the ratio 100 % presented much higher surface areas (1090 and 3880 $\text{m}^2 \text{g}^{-1}$) compared to those impregnated at the ratio 60 % (123 and 731 $\text{m}^2 \text{g}^{-1}$; Table 4.1). In addition,

samples pyrolyzed at 500 °C presented higher BET surface areas than those pyrolyzed at 350 °C.

Table 4.1 Characterization of the oat hulls activated carbon samples: impregnated at 60 % with H₃PO₄ and pyrolyzed at 500 °C (OH60-500) and 350 °C (OH60-350), and impregnated at 100 % with H₃PO₄ and pyrolyzed at 500 °C (OH100-500) and 350 °C (OH100-350).

Parameters	Samples			
	OH60-	OH100-	OH60-	OH100-
	350	350	500	500
Particle size (μm)	250	250	250	250
Yield (%)	38±0.8	38±4.2	39±3	38±0.4
Burn-off (%)	62±0.8	62±4.0	61±1.9	62±0.4
Ash content (%)	33±2.2	30±4.2	33±3.6	29±6.8
BET surface area (m ² g ⁻¹)	123	1090	731	3880
Micropore surface area (m ² g ⁻¹)	1.68	910	1815	3187
External surface area (m ² g ⁻¹)	121	179	302	693
Total pore volume (cm ³ g ⁻¹)	0.044	0.153	0.182	0.316
Micropore volume (cm ³ g ⁻¹)	0.004	0.097	0.127	0.188
Mesopore volume (cm ³ g ⁻¹)	0.040	0.057	0.055	0.128
Average pore size (nm)	8.3	3.0	2.5	3.7

*BET: Brunauer–Emmett–Teller

The values herein reported are greater than the BET surface areas published by previous studies (Chuang et al. 2005; Fan et al. 2004; Movasaghi et al. 2019). Steam

activation applied to the production of oat hulls activated carbon resulted in BET surface areas varying from 349 to 625 m² g⁻¹ (Chuang et al. 2005; Fan et al. 2004). Oat hulls activated carbon impregnated at 100 % with H₃PO₄ and heated by microwave presented BET surface area of 460-m² g⁻¹ (Movasaghi et al. 2019).

Similarly to the BET surface area, the development of porosity in the samples was affected by both the impregnation ratios and pyrolysis temperatures (Table 4.1). The oat hulls activated carbon samples presented pore diameters from 2.5 to 8.3 nm, as a result of mesopores formation (Rouquerol et al. 1994).

Functional groups pertaining to oat hulls were identified by FTIR/ATR, as follows (Figure 4.1): bands at 2100 cm⁻¹ were attributed to C≡C stretching vibration in alkyne; bands at 1500 cm⁻¹ were assigned to C=O stretching vibration in carboxyl and C=C stretching vibration in aromatic rings; and bands at 1024 cm⁻¹ were assigned to C-O stretching (Abedi and Dalai, 2019; Banerjee et al. 2016; Ching et al. 2011; Marsh and Reinoso, 2006; Movasaghi et al. 2019).

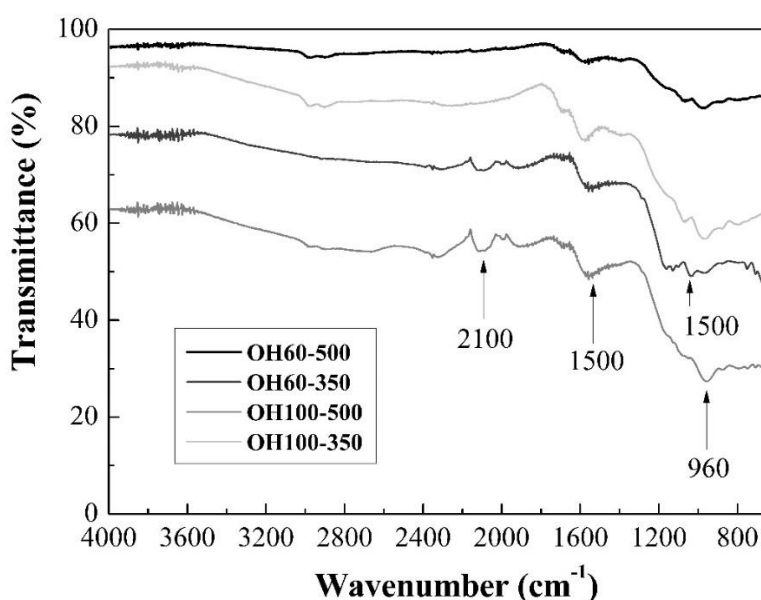


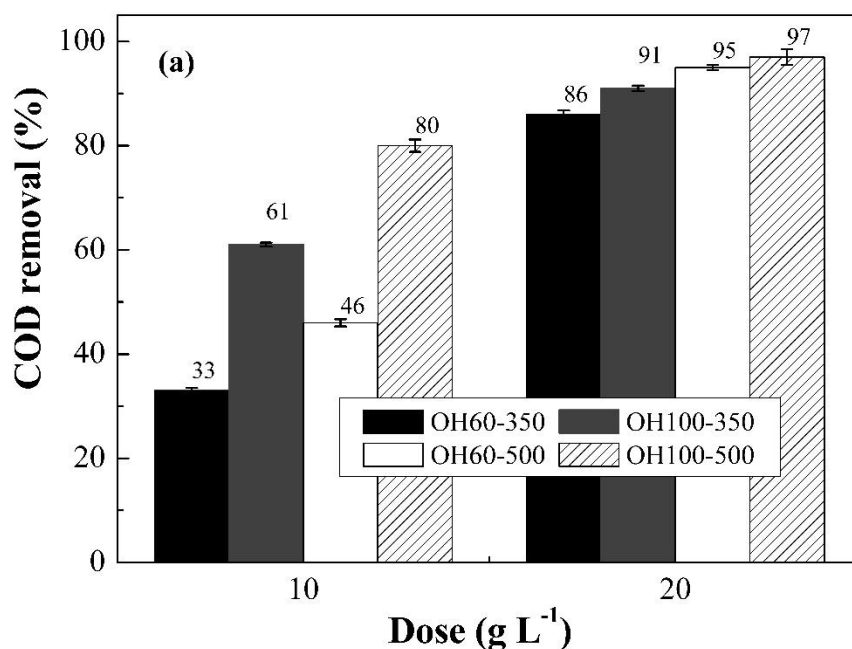
Figure 4.1 Fourier transform infrared spectroscopy/attenuated total reflection (FTIR/ATR) spectra for oat hulls activated carbon samples: impregnated at 60 % with

H₃PO₄ and pyrolyzed at 500 °C (OH60-500) and at 350 °C (OH60-350), and impregnated at 100 % with H₃PO₄ and pyrolyzed at 500 °C (OH100-500) and at 350 °C (OH100-350).

4.3.2 Synthetic leachate treatment

4.3.2.1. COD removal in function of the tested adsorbent dose

It was observed in all experiments that the activated carbon dose of 20 g L⁻¹ resulted in the highest efficiencies of COD removal (Figure 4.2a). For instance, samples impregnated at 60 % and pyrolyzed at 500 °C removed 46±0.7 % of COD when the 10- g L⁻¹ dose was used, and this value was increased to 95±1.5 % when the adsorbent dose was 20 g L⁻¹ (Figure 4.2a). The comparison of the results herein presented with the literature is limited due to the lack in similar studies with oat hulls published so far.



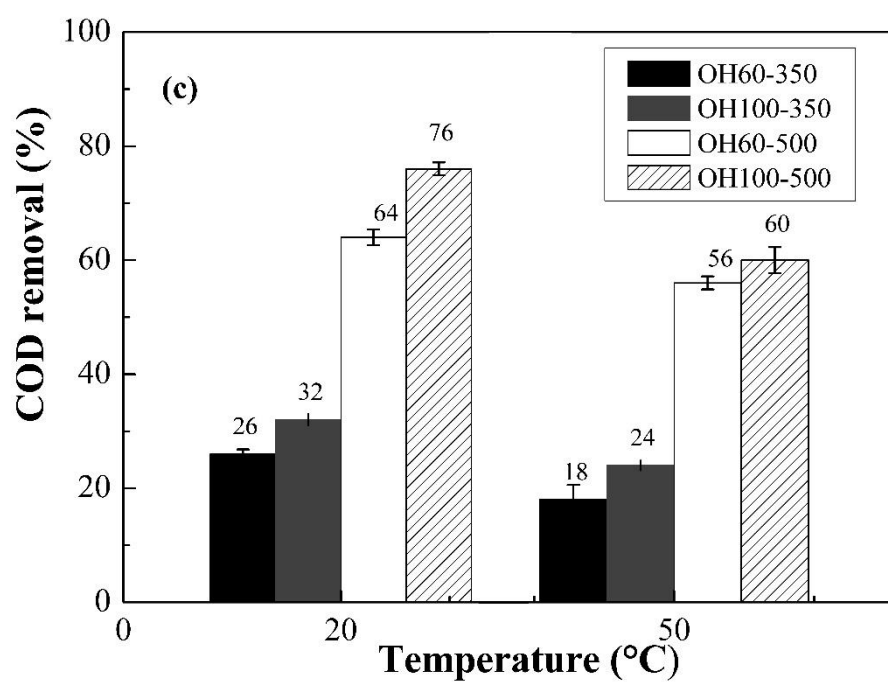
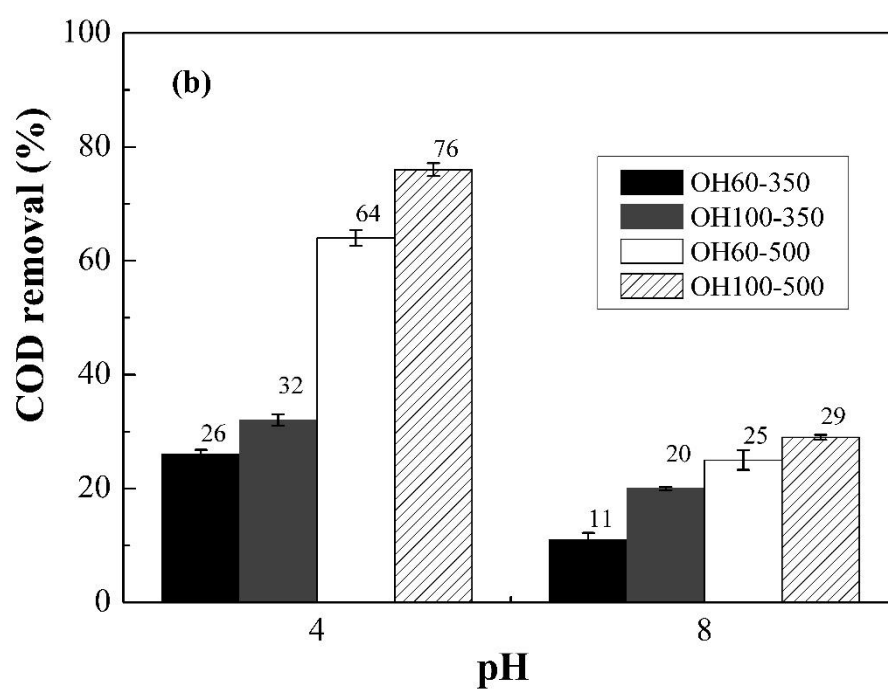


Figure 4.2 COD removal in function of (a) the adsorbent dose, (b) pH, and (c) temperature, using oat hulls activated carbon samples: impregnated at 60 % with H_3PO_4

and pyrolyzed at 500 °C (OH60-500) and at 350 °C (OH60-350), and impregnated at 100 % with H₃PO₄ and pyrolyzed at 500 °C (OH100-500) and at 350 °C (OH100-350).

4.3.2.2. COD removal in function of the pH

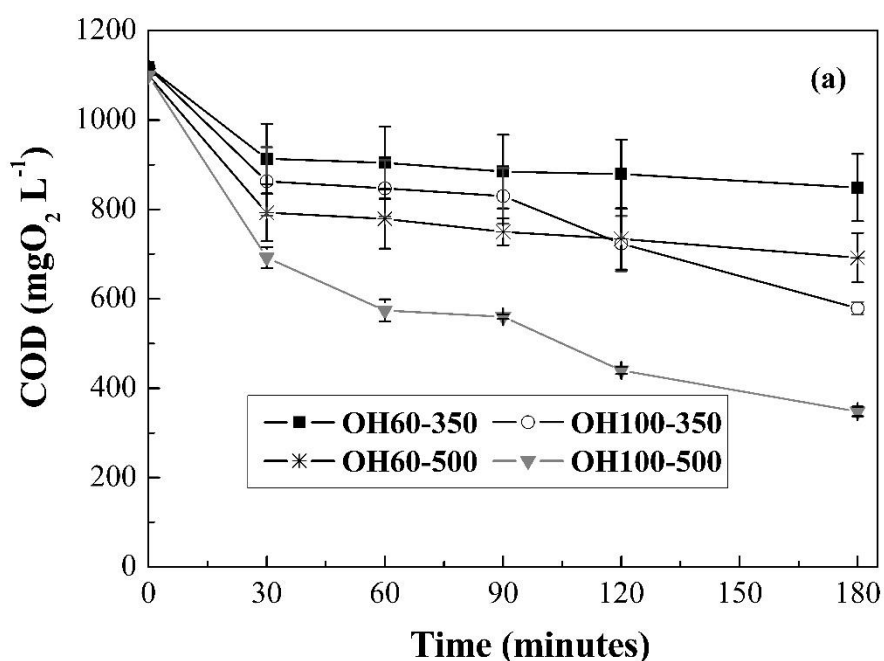
Oat hulls activated carbon samples performed better when the pH of synthetic leachate was adjusted to pH 4 instead of 8 (Figure 4.2b). Consequently, COD removals obtained at pH 4 were almost twice the values obtained for synthetic leachate treatment at pH 8. Previous studies related to carbon-based adsorbents also observed improved removals of organic matter at low pH (Bjelopavlic et al. 1999; Reffas et al. 2010; Zhang et al. 2016). According to the literature, the charges on the activated carbon surface tend to be neutralized at pH 4, enhancing the adsorption of humic acid. On the contrary, at pH higher than 7 the activated carbon tends to present a negative charge, repulsing ionized humic acid molecules (Bjelopavlic et al. 1999; Reffas et al. 2010; Zhang et al. 2016).

4.3.2.3. COD removal in function of the temperature

Increasing the temperature to 50 °C did not improved COD removal by the tested oat hulls activated carbon samples (Figure 4.2c). In contrast, the highest COD removal, 76±1.14 %, was obtained in tests performed at 20 °C using the sample impregnated at 100 % and pyrolyzed at 500 °C. If heating leachate does not favour COD removal, then the use of oat hulls activated carbon becomes more advantageous in terms of operational costs.

4.3.2.4. COD and colour removals in function of the contact time

Oat hulls activated carbon impregnated at 100 % and pyrolyzed at 500 °C exhibited the highest performance on COD and colour removals when compared to the other tested adsorbents (Figure 4.3). In the first hour, COD and colour removals were 48 ± 2 % and 37 ± 0.8 %, respectively. After 3 h, these values increased to 68 ± 2 % for COD and 45 ± 0.5 % for colour. The adsorbent impregnated at 60 % and pyrolyzed at 500 °C removed approximately 30 % of COD and colour in the first hour. After 3 h, this value increased to approximately 40 %. Regarding the adsorbents pyrolyzed at 350 °C, the sample impregnated at 100 % removed up to 45 % of COD and colour from synthetic leachate. On the other hand, the lowest efficiency was observed for the sample impregnated at 60 %: COD and colour removals were 24 ± 6 % and 35 ± 1.4 %, respectively (Figure 3.3). As expected, blank samples presented the same COD (approximately, $1100 \text{ mg O}_2 \text{ L}^{-1}$) and colour (approximately, 35,000 Pt-Co units) at the beginning and at the end of the experiment.



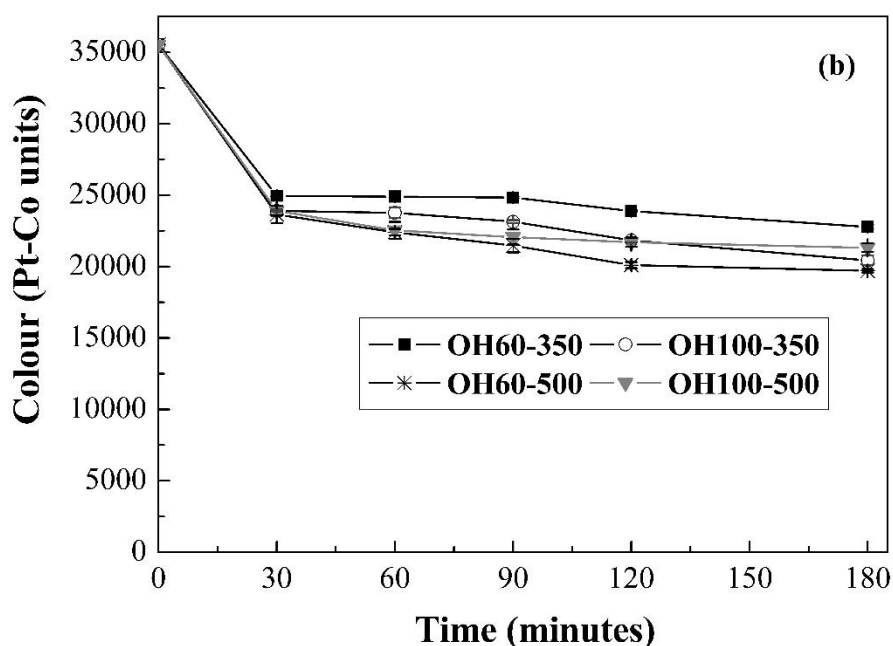


Figure 4.3 (a) COD and (b) colour removals from synthetic leachate along with time, using oat hulls activated carbon samples: impregnated at 60 % with H_3PO_4 and pyrolyzed at 500 °C (OH60-500) and at 350 °C (OH60-350), and impregnated at 100 % with H_3PO_4 and pyrolyzed at 500 °C (OH100-500) and at 350 °C (OH100-350).

4.3.2.5. Isothermal tests for oat hulls activated carbon

Higher adsorptive capacities were obtained for activated carbon samples impregnated at 100 %, rather than for those impregnated at 60 % (Figure 4.4). For instance, the maximum adsorptive capacities for samples impregnated at 100 % and pyrolyzed at 500 °C and 350°C were 41 and 30 mg COD g⁻¹ adsorbent, respectively. On the other hand, samples impregnated at 60 % and pyrolyzed at 500 °C and 350°C, presented maximum adsorptive capacities of 27 and 14 mg COD g⁻¹ adsorbent, respectively. Therefore, the impregnation ratio 100 % favoured the formation of high

BET surface area adsorbents, which in turn improved the COD removal from synthetic leachate.

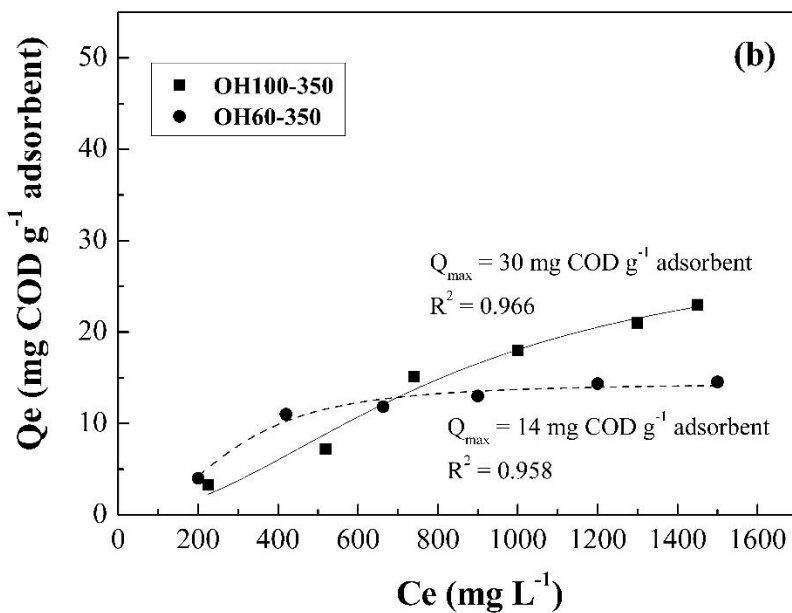
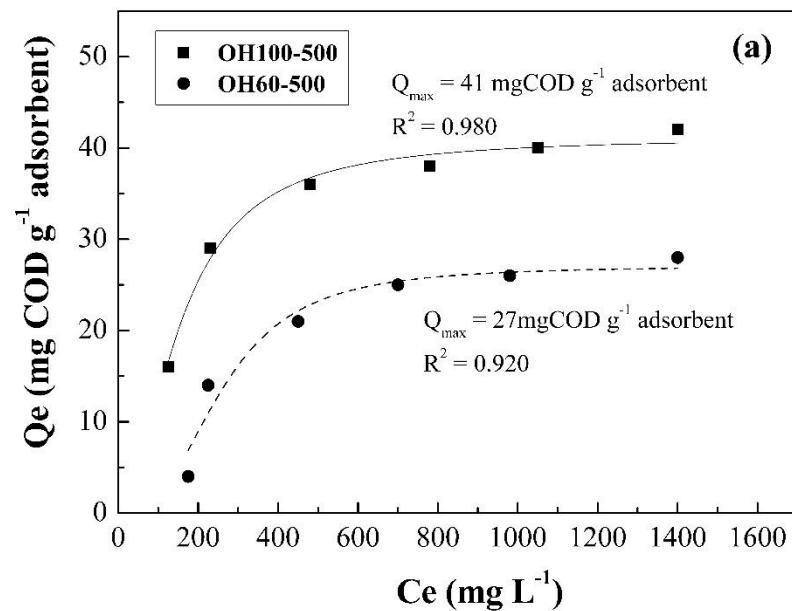


Figure 4.4 Isotherms obtained in adsorption tests with synthetic leachate and oat hulls activated carbon samples (a) impregnated at 60 (OH60-500) and 100 % (OH100-500)

with H_3PO_4 and pyrolyzed at 500 °C, and (b) impregnated at 60 (OH60-350) and 100 % (OH100-350) with H_3PO_4 and pyrolyzed at 350 °C.

4.3.3 Real leachate treatment

In accordance with synthetic leachate tests, tests performed with real leachate confirmed that adsorbents impregnated at 100 % provided the best removals of COD and colour (Figure 4.5). The oat hulls activated carbon pyrolyzed at 500 °C removed 75 ± 5 % of COD and 85 ± 1.6 % of colour from real leachate in only 30 minutes, while additional removals were observed at the end of the test. After 3 h, colour was completely removed, and COD removal was 90 ± 0.5 %. The COD removal herein reported was equivalent to an adsorptive capacity of 40 mg COD g^{-1} adsorbent, confirming the values calculated by the Langmuir model for synthetic leachate. The oat hulls activated carbon pyrolyzed at 350 °C removed 45 ± 3 % of COD and 73 ± 3 % of colour from real leachate in only 30 minutes. After 3 h, COD and colour removals were 63 ± 0.5 % and 90 ± 0.5 %, respectively. Lower performances were obtained in tests with the adsorbents impregnated at 60 %. At the end of the treatment (3 h), COD and colour removals were around 30 and 70 %, respectively, for the adsorbents pyrolyzed at 500 °C. On the other hand, adsorbents pyrolyzed at 350 °C removed approximately 24 % of COD and 60 % of colour after 3 h. The initial levels of COD and colour in blank samples remained unaffected after 3 h.

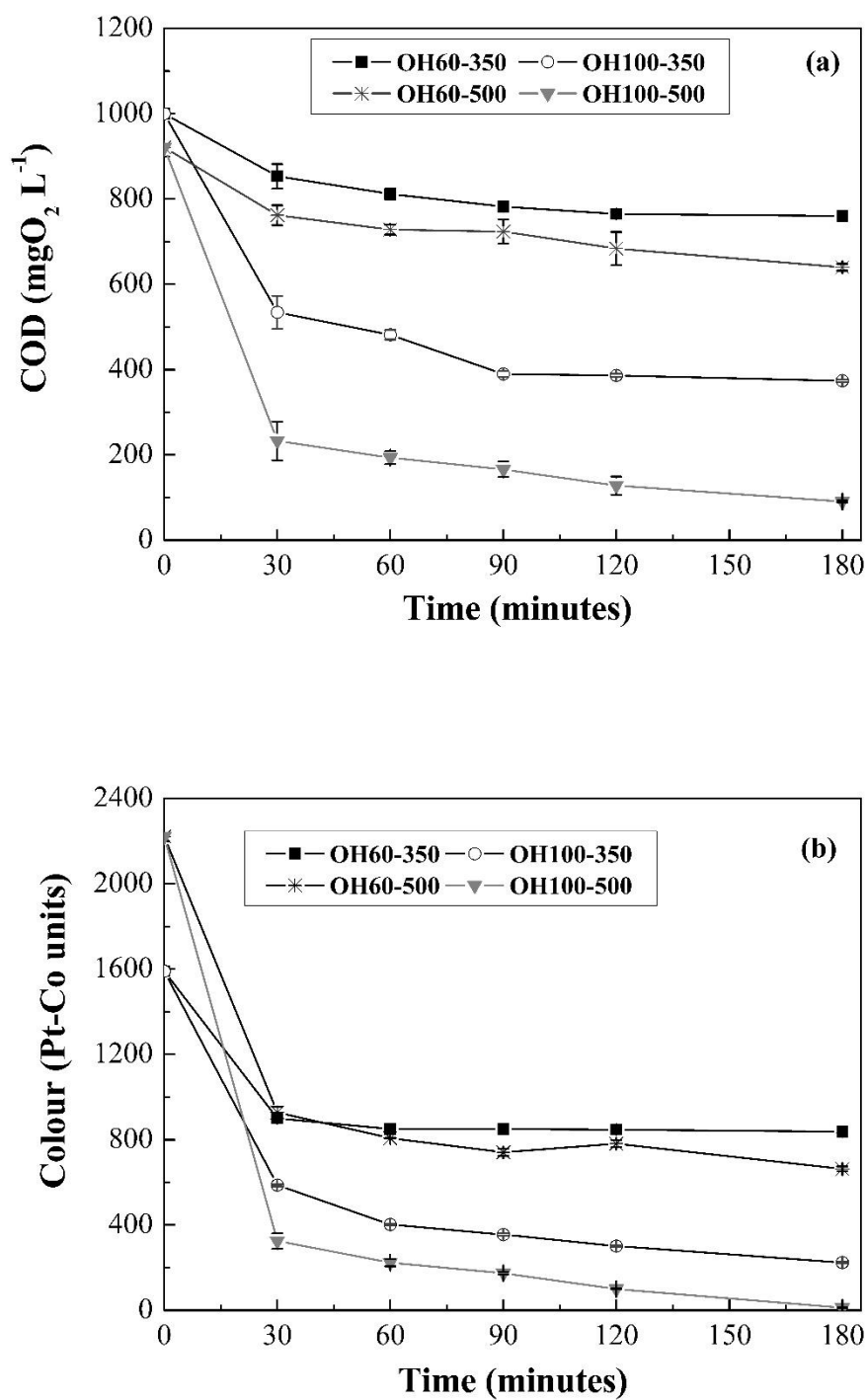


Figure 4.5 Interference of the contact time on (a) COD and (b) colour removals from real leachate using oat hulls activated carbon samples: impregnated at 60 % with H₃PO₄ and pyrolyzed at 500 °C (OH60-500) and at 350 °C (OH60-350), and impregnated at 100 % with H₃PO₄ and pyrolyzed at 500 °C (OH100-500) and at 350 °C (OH100-350).

4.4. Conclusion

The adsorbents produced at different impregnation ratios and pyrolysis temperatures presented average pore diameters varying from 2.5 to 8.3 nm, indicating that mesoporous activated carbon samples were successfully produced. The BET surface area was dependent on both the tested impregnation ratios and pyrolysis temperatures. Adsorption was favoured by running the batch tests at 20 °C, using a 20-g L⁻¹ adsorbent dose, and adjusting the pH of leachate to 4. Due to their high BET surface areas, oat hulls activated carbon samples impregnated at 100 % presented higher adsorptive capacities (30-41 mg COD g⁻¹ adsorbents) compared with those impregnated at 60 % (14-27 mg COD g⁻¹ adsorbents). Oat hulls activated carbon also presented high efficiencies for organic matter removal from real leachate in a short time. Adsorbents impregnated at 100% and pyrolyzed at 500 °C removed 75±5 % of COD and 85±1.6 % of colour from real leachate in only 30 minutes. After 3h, colour was completely removed, and COD removal was 90±0.5 %. Therefore, the recovery of oat hulls as precursor for activated carbon should be highly encouraged, once promising results were obtained for the organic matter removal from landfill leachate.

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CHAPTER 5 General Conclusions

SCG and oat hulls were efficiently recovered as precursors for activated carbon production, generating mesoporous adsorbents that were successfully applied for leachate treatment. For both tested precursors, using the pyrolysis temperature of 500 °C favoured the formation of high BET surface areas, but different responses were obtained with respect to the impregnation ratios. SCG presented a reduced demand for chemicals in comparison with oat hulls. The impregnation ratio 50 % resulted in SCG activated carbon samples with higher BET surface areas, compared to those produced at the ratio 100 %. In contrast, oat hulls required an impregnation ratio of 100 % to produce activated carbon samples with high BET surface areas. For all tested adsorbents, the organic matter removal from leachate was highest using an activated carbon dose of 20 g L⁻¹, pH 4, and temperature of 20 °C. Whereas using pH 8 instead of 4 was not helpful for the adsorption of organic matter in leachate, the improper control of pH in the acidic range could be misleading, as the adsorption efficiency could be overestimated. For instance, humic acid precipitates at pH below 2 (Frimmel 2005; Nuzzo et al. 2013), so the organic matter removal in samples treated at such low pH would be caused by two mechanisms, precipitation and adsorption. In conclusion, this study highly recommends the recovery of SCG and oat hulls to generate activated carbon used for leachate treatment, as both materials presented high performances for synthetic and real landfill leachate treatment, removing more than 90 % of COD and 100 % of colour.

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CHAPTER 6 Engineering Significance

According to the critical literature review presented in Chapter 2, significant environmental impacts may result from the discharge of leachate into water bodies. Organic waste is being gradually banned from landfills in Canada, requiring alternative options for its disposal (Metro Vancouver 2019; Manitoba Conservation and Water Stewardship 2014). One possible alternative for organic waste diversion from landfills is its use as precursor for activated carbon. Waste-derived activated carbon has been successfully tested to remove contaminants from wastewater, but very limited information is available for their application for leachate treatment. As mentioned in Chapter 3, coffee is a highly consumed beverage worldwide, and SCG comprise the main organic waste produced during the brewing process. As per Chapter 4, oat is one of the most consumed and commercialized cereal, being Canada the largest exporter in the world (Government of Manitoba, 2019; Prairie Oat Growers Association). The production of oat cereal results in significant amounts of hulls as organic waste. Analogously to SCG, the ultimate fate for oat hulls is their final disposal in landfills, which may contribute to the formation and emissions of greenhouse gases and landfill leachate, impacting the environment (Renou et al., 2008).

Currently, while only few studies have been published reporting SCG activated carbon for leachate treatment, the literature is lacking the use of oat hulls activated carbon for that purpose. Therefore, this thesis aimed to contribute to the literature, combining solid waste recovery and leachate treatment; and concluded that high efficiencies for organic matter removal were obtained when leachate was treated with activated carbon derived from both SCG and oat hulls. Other studies should be conducted to investigate the feasibility of producing high-surface area activated carbon from SCG and oat hulls in large scale, reducing the amounts of chemicals for activation,

and minimizing chemical waste. In addition, activated carbon can be regenerated and reused to treat water and/or wastewater (Yuen and Hameed, 2009), which should be further investigated for SGC and out hulls activated carbon.

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