ABSTRACT
A set of experiments were carried out in order to establish and evaluate the potential of activated carbon, produced from coffee waste in adsorption process, in the depuration of landfill leachate. Different reagents were studied in the activation of carbon: HCl, HCl + H2O2, H3PO4, H3PO4 + H2O2, all with an impregnation rate of 1:1. The activated carbon that showed the best global results was activated with H3PO4, obtaining a 51.0, 32.8, 66.0, 81.0 and 97.1% elimination of chemical oxygen demand, ammonia, total chlorine, bromine and copper, respectively. This activated carbon has a total pore area of 4.85 m²/g and a median pore diameter of 65.32 micrometers. When different loads of this carbon were placed in a stirrer system in contact with landfill leachate, with the aim of evaluating the effect of the adsorption load and contact time, the concentration of ammonia decreased from the beginning of the adsorption process to the end of it, and the removal of ammonia increased with the increase in the adsorbent load. However, the trend of the amount adsorbed per unit mass decreased with increased dosage. The model Freundlich equilibrium isotherm fits experimental data adequately, giving R² values of 0.95, 1/n of 0.5183, and a K value of 7.08*10⁻⁵ L/g, being favourable for adsorption process.

Keywords: landfill leachate; adsorption; waste; by-product.

INTRODUCTION
Landfilling is the most commonly used method for municipal solid waste (MSW) disposal around the world, though recycling, composting and incineration is currently being encouraged (XIE et al., 2014). One major worry in this waste management process is the generation of leachate by the waste within the system and/or the infiltration of groundwater/rainfall. Landfill leachate (LL) usually has high concentrations of organic pollutants, relatively high chemical oxygen demand (COD), toxic materials (xenobiotic organics), ammonia, heavy metals and inorganic salts, as well as refractory compounds such as humic substances and fulvic-like fractions, which are not easily degradable and cannot be effectively treated either by biological processes such as activated sludge, anaerobic filtration and anaerobic lagoons (MARTINS et al., 2012). In a study carried out by Alsiaibi, Mogheir and Afifi (2011), the degree of groundwater pollution near a landfill was evaluated due to the leachate effect. It was observed that the concentration of ammonia, nitrate, electric conductivity, chloride and COD exceed permissible limits, evidencing groundwater contamination.

If it is not properly collected and managed, it can potentially contaminate nearby surface and groundwater, affecting its quality and

RESUMO
Foi realizada uma série de experimentos para estabelecer e avaliar o potencial de carvão ativado produzido de resíduos de café por meio de um processo de adsorção na depuração do lixiviado de aterro sanitário. Foram estudados diferentes reagentes para a ativação do carvão. HCl, HCl + H2O2, H3PO4, H3PO4 + H2O2, todos com taxa de impregnação de 1:1. O carvão que apresentou os melhores resultados foi ativado com H3PO4, obtendo uma eliminação de 51,0; 32,8; 66,0; 81,0; e 97,1% de demanda química de oxigênio e concentração de amônia, cloro total, bromo e cobre, respectivamente. O referido carvão ativado tem uma área total de poro de 4,85 m²/g e diâmetro médio de poro de 65,32 micrômetros. Com o objetivo de avaliar o efeito da carga de adsorção e do tempo de contato, foram colocadas diferentes cargas desse carvão em um sistema de agitação em contato com o lixiviado de aterro sanitário. Observou-se que a concentração de amônia diminuiu e que sua remoção foi maior à medida que a carga adsorbente aumentava. No entanto, a quantidade adsorvida por unidade de massa diminuiu com o aumento da dosagem. Os dados experimentais adequaram-se corretamente ao modelo de isotermia de Freundlich, obtendo-se valores de R² de 0,95, 1/n de 0,5183, e um valor de K de 7,08*10⁻⁵ L/g, considerados favoráveis para o processo de adsorção.

Palavras-chave: lixiviado de aterro, adsorção, resíduos, subproduto.
compromising human health. For instance, the presence of metal ions in wastewater and their potential impact have been scientifically studied because of their extreme toxicity even at low concentrations, and their tendency to accumulate in the food chain (MOHAN; SINGH, 2002). In addition to groundwater contamination, soil quality alteration and ecosystem imbalance has been observed in landflling. Therefore, the removal of persistent LL pollutants is a significant and necessary challenge to be met (CORTÉS-LORENZO et al., 2014).

The treatment processes of LL are very complicated, expensive and generally require various process applications because of their high loading, complex chemical composition and seasonally variable volume (BU et al., 2010). Biological treatment can also partially remove contaminants, but their removal efficiencies are generally found to be low to moderate because of the fact that several of the emerging contaminants are relatively resistant to biodegradation (LIU et al., 2012).

The combination of biological, chemical, and physicochemical processes has the ability to synergize the advantages of each single process, and has been documented as being effective for treating stabilized LL (WANG et al., 2009).

The activated carbon (AC) adsorption process has emerged to be a technological strategy for wastewater treatment, due to its simplicity of design, ease of operation, insensitivity to toxic substances and high ability to removing a wide range of pollutants (FOO; LEE; HAMEED, 2013). AC are materials containing large surface areas, well-developed porosity and rich surface groups. Therefore, it has been widely used for the separation of gases, the recovery of solvents, the removal of organic pollutants from drinking water, and as a catalyst support (DE RIDDER et al., 2013; ELMOUWAHIDI et al., 2012).

Adsorption onto AC has been reported as an effective method for removing high molecular weight refractory organic matter from aqueous solutions (HALIM et al., 2010). AC has been widely used as adsorbent, catalyst and catalyst support in a variety of environmental applications like hazardous pollutant removal (SANDOVAL et al., 2011). However, studies have been complicated by a wide range of experimental conditions and variability of the constituents of LL (FOO; HAMEED, 2009).

Various non-conventional low cost adsorbents have shown good adsorption capacities in removing COD from wastewater (LIM; SHAABAN; YIN, 2009; KALDERIS et al., 2008). To obtain AC, different precursors of vegetable origin (wood, oils, husks, pits and seeds of plants and fruits) and polymeric materials can be used. The use of agricultural residues presented significant advantages, because of their low cost, and because they come from renewable sources and allow their reuse. Hence, in recent years many studies have been reported involving the production of AC using agricultural residues, such as apricot and/or cherry pits, wheat straw, bean and rice husks, nut husks, and corn husks (GUO; ROCKSTRAW, 2007).

Production of activated carbon (AC) from agricultural byproducts is a research field that has gained increased interest in recent years because of its potential for the disposal of agro-residues. At the same time, a beneficial byproduct that can be used in a number of environmental applications is produced. This paper surveys the developments in the production processes of AC from agricultural byproducts in the past 7 years from 2005 to 2012 via conventional and microwave heating. Emphasis is placed on the applied methodology and the influences of activating conditions, such as carbonization temperature, retention time, and impregnation ratio. From the review of AC production processes, agricultural wastes produced by a chemical method with microwave heating can be a source of AC with relatively higher surface area than that produced via conventional heating.

One potential source of AC is coffee, which is produced all over the world and has a high annual production (REFFAS et al., 2010), generating a large volume of residues; in fact, every year, about 30 million tons of solid waste from coffee industry are produced, and most is inadequately disposed off. However, AC produced from coffee waste has shown interesting capacities in retaining iron and orthophosphate (OLIVEIRA et al., 2009), 4-chloro-2-methyl phenoxy acetic acid (CHING et al., 2011; AL-ZABEN; MEKHAMER, 2017).

The aim of this study was to evaluate the potential of AC obtained from coffee waste using different activation reagents, adsorbent loads, and adsorption treatment times to depurate LL, in order to reduce its concentration of iron, copper, ammonia, COD and chloride in this kind of water. The application of this waste would add value to coffee wastes, enabling reuse and decreasing the waste disposal cost and environmental pollution associated with this process, and also allow evaluate the treatment of LL.

MATERIALS AND METHODS

Preparation and analysis of adsorbents

Coffee waste was collected from local coffee shops in Coquimbo, Chile. The coffee used was roasted coffee and was sampled after preparing coffee drink. The coffee wastes were washed with boiled water to eliminate the impurities, dust and water-soluble substances followed by washing with distilled water. The washed coffee was oven-dried at 105°C for 24 h prior to activation. The dried coffee grounds were separated in four quantities of 50 g and placed in a porcelain flask of 200 mL. After that, they were activated using different reagents:

- HCl;
- HCl + H₂O₂;
**Landfill leachate characterization**

The LL samples used in this study were obtained from a landfill in Chile that manages municipal solid waste. The landfill has an area of 16.7 ha. General characteristics of the raw LL collected and studied were: COD: 13,460 mg/L, pH: 9.25, total copper: 204.00 mg/L, total chlorine: 50.00 mg/L, ammonia: 6.00 mg/L, conductivity: 33.61 mS/cm, total solids (TS): 559.00 mg/L, and bromine: 21.00 mg/L. The LL samples were obtained from different points of the landfill, and after that, they were stored in darkness at 4ºC with minimum exposure to the surrounding air to maintain their characteristics.

Measurement of pH was performed by a pH meter (WTW 3150i unit). COD was determined according to the EPA 410.4 method using the Colorimetric Method. Ammonia was determined using the Nessler method (D1426-92). Bromide was measured using the DPD method. Total chloride was measured using the Standard method 4500-Cl. Total copper was measured using the Bicichoninate Acid Method (HI-93702-01).

**Batch adsorption experiments**

This study was divided into two steps of adsorption experiments in batch conditions. The first one was designed to evaluate which of the AC achieved higher levels of contaminant removal. The second one was to study the load of the chosen AC that improves removal of ammonia and its optimal contact time. Therefore, the study was focused on the identification of the condition that provides the best treatment performance. The LL was filtered using a 5 mm pore size filter before being submitted to an adsorption process. Both batch experiments were carried out without pH adjustment.

**Evaluation of activated carbons performance**

Adsorption experiments were carried out by adding 4 g/L of different ACs in 500 mL of LL placed in 1 L glass flasks. The 4 flasks were placed in orbital shakers (PROTECH Model 720) and agitation was carried out at 150 rpm for 120 min. The LL samples were taken each 30 min, and concentration of COD, ammonia, total copper, chloride and bromide were measured. The removal percentage of those parameters was calculated using Equation 1:

\[
\text{Removal} \% = \left( \frac{C_0 - C_e}{C_0} \right) \times 100
\]

In which:
- \(C_0\) and \(C_e\) (mg/L): the concentration of COD, ammonia, total copper and chloride at the beginning and at the end of the runs, respectively.

The amount of pollutants adsorbed by AC during the batch adsorption process \(q_e\) was determined using Equation 2:

\[
q_e = \frac{(C_0 - C_e) \times V}{m}
\]

In which:
- \(V\): volume of solution (L);
- \(m\) = dry weight of AC (g) used.

Microstructure of the AC that showed better results were examined using a scanning electron microscope (SM) LEO 1420VP.

**Evaluation of contact time and adsorbent load**

Adsorbent load and contact adsorption time are important parameters affecting the adsorption process. Therefore, to determine the effect of these factors in the elimination of contaminants is essential in order to optimize the results and reduce costs. The AC that improved elimination of pollutants of LL investigated in this study was selected for evaluation of the contact time in the adsorption process and the adsorbent load that achieves an adequate removal of parameters. The temperature of the adsorption process was 19ºC. To do this, a sample of homogenized LL was taken, divided into four parts and placed in a 1 L glass flask. In each flask a different load of the chosen AC was also placed. The 4 flasks were placed in the same shakers described in topic “Evaluation of activated carbons perform”, and agitation was done at 150 rpm for 120 min. The LL samples were taken each 30 min, and the concentration of ammonia was measured.

To determine the ammonia adsorption capacity of the chosen AC, the Freundlich and Langmuir models were used. The amounts of ammonia adsorbed onto AC were calculated from the difference between the initial and the remaining concentrations in the solution. The amount of ammonia adsorbed per gram of AC \(X/m\) (mg/g) was given by Equation 2.
The Langmuir isotherm is a useful and simple tool for describing both physical and chemical adsorption. The Langmuir isotherm model (see Equation 3) was developed based on the assumption that adsorption takes place at a fixed number of accessible homogeneous surfaces that are identical, with no transmigration of adsorbates in the plane of the neighbouring surface, leading to the conclusion that the adsorption was monolayer in nature:

$$q = \frac{Q_0 b C}{1 + b C}$$

In which:

- $Q_0$ = the Langmuir monomolecular layer capacity (mg/g);
- $b$ = the Langmuir isotherm constant.

The empirically-derived Freundlich isotherm model (see Equation 4) is widely applied to multilayer adsorption, with non-uniform distribution of adsorption heat and affinity over the heterogeneous surface. The Freundlich model shows that the ratio of pollutant adsorbed to the adsorbent is a function of the equilibrium liquid phase solute concentration.

$$q = \frac{x}{m} = K C^{1/n}$$

In which:

- $K$ (L/g) and $n$: the Freundlich isotherm constants.

The Freundlich coefficient $K$ represents an indicator of adsorption capacity; $1/n$ indicates the adsorption intensity, while its reciprocal $n$ represents the affinity factor for the Freundlich model.

**RESULTS AND DISCUSSION**

**Analysis of porosity**

Table 1 shows the porosity of samples measured as total mercury intrusion volume, the total pore area, the median pore diameter, and the percentage of pores of a certain size. As can be seen in Table 1, porosities of samples ranged from 0.367 to 0.5389 mL/g, similar than other activated carbon obtained in other works (YAKOUT; SHARAF EL-DEEN, 2016; YAVUZ et al., 2010). Samples activated with HCl show higher total pore area than samples activated with H₃PO₄. Also, the addition of H₂O₂ to the attack solution produces in both cases (HCl and H₃PO₄) an increase, at the same time, of the total pore area and total intrusion volume. However, a reduction in the mesopore volumes is observed.

Figure 1 shows the cumulative intrusion volume versus mercury pressure. Curves of samples B, C and D are representative of samples consisting of relatively coarse grains. Accordingly, the curves exhibit two distinct parts: the relatively steep initial rise at low pressure, due to void spaces created around the contact points among the grains, and the second rise, due to the pores within the grains. Curve A is representative of samples with a wide distribution of pore sizes.

To increase our understanding of the microstructure of samples, a pore size distribution (PSD) study intrusion Log-differential volume (mL/g) versus pore diameter (µm) was carried out (Figure 2). Two zones can be differentiated in all samples: the small pores range from 0.005 to 0.1 µm that are related with the grain pores, and the zone from 10 to 400 µm, that correspond with the air void between grains. It should be noted that sample A shows pores in the medium zone (0.1–10 µm).

**Evaluation of activated carbon performance**

The four CA developed from coffee waste were studied in order to evaluate which obtains higher levels of contaminant removal in LL. Figure 3 shows the evolution of the concentration of COD over time, when contaminated water was exposed to different AC.

<table>
<thead>
<tr>
<th>Activated carbon</th>
<th>A (HCl)</th>
<th>B (HCl+H₂O₂)</th>
<th>C (H₃PO₄)</th>
<th>D (H₃PO₄+H₂O₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total intrusion volume (mL/g)</td>
<td>0.3670</td>
<td>0.5389</td>
<td>0.3888</td>
<td>0.4652</td>
</tr>
<tr>
<td>Total pore area (m²/g)</td>
<td>20134</td>
<td>28528</td>
<td>4856</td>
<td>6358</td>
</tr>
<tr>
<td>Median pore diameter (µm)</td>
<td>30103</td>
<td>884825</td>
<td>653230</td>
<td>775385</td>
</tr>
</tbody>
</table>

Figure 1 – Cumulative intrusion volume versus pressure.
It can be observed that the concentration of COD decreased with an increase in the adsorption time, and it can also be seen that the AC which obtained the highest removal of COD was C, followed by B, D and A. Also, considering Equation 1, 51.3, 44.7, 43.0 and 36.1% of elimination were achieved, respectively. Results obtained in the elimination of COD using the AC are in agreement with the literature. There was reported relatively low level of removal of COD using AC (LI et al., 2010). This behaviour could be due to the fact that LL has various constituents with different adsorption affinities. The adsorption sites will be filled first with those constituents of higher adsorption affinity, leaving those with lower adsorption affinity poorly adsorbed (ADINATA; WAN DAUD; AROUA, 2007). In addition, the AC that showed the best performance throughout this study was C.

The AC which obtained the highest elimination of ammonia was D, followed by C, B and A, with removal of 46.9, 32.8, 21.9 and 12.5%, respectively (see Figure 4). These results are attributed to the mass-transfer differences of ammonium ions between the liquid and the surface of AC.

As can be seen in Table 1, the median pore diameter for sample B was higher than C and D while it has the lowest removal of COD and NH-N. It was unexpected because the adsorption capacity of COD and NH₃-N is due to the catalytic oxidation, which causes the widening of micropore to mesopores, thus increasing the adsorption capacity (MOHAMED; MOHAMMADI; NAJAFPOUR, 2010). During pyrolysis process, non-carbon elements such as hydrogen, oxygen and nitrogen released in the form of tars and gases leave a rigid carbon skeleton with a rudimentary pore structure formed from the aromatic compound. Therefore, activation by physico-chemical process enhanced the pore structure of sugarcane-derived activated carbon (FAROOQ et al., 2012).

Figure 5 shows the evolution of chlorine of the LL studied, under the use of different AC.

As can be observed in Figure 5, the AC which obtained the highest elimination of chlorine was C, followed by A, D and B, achieving removal of 66.2, 60.4, 56.1 and 54.2%, respectively.

As shown in Figure 6, the removal of bromine for the various AC was 81%, 47.6, 38.1 and 14.3% for C, D, B and A, respectively. The higher bromine removal for C is in agreement with the results
found in literature (FAROOQ et al., 2012), which reported elimination of 80% with a similar pH that was used in the present study.

Figure 7 depicts the evolution of the concentration of total copper in the LL throughout the adsorption process, using different AC. As can be observed, the AC which obtained the highest elimination of copper was C, followed by A, B and D, achieving removal of 97.5, 96.1, 95.6 and 85.8%, respectively. These results were higher than those obtained by Imamoglu and Tekir (2008), who reported 40% copper elimination when the initial concentration of this metal was similar to that used in this investigation (200 mg/L). These results could be due to the researchers’ application of a lower load of AC.

Also, the results obtained in this study are a bit lower than obtained for Alslaibi et al. (2013), who get 100% of elimination of cooper using AC produced from olive lump stone waste, with a Brunauer-Emmett-Teller (BET) surface area, area, mesopore surface area, total pore volume, and average pore diameter of the prepared AC of 886.72 m²/g, 740.66 m²/g, 0.507 cm³/g, and 4.92 nm, respectively. The differences could be due to the characteristic of the carbon and also to the higher contact time used in the adsorption process, of 4 h.

The maximum adsorption capacity (q_e) for copper was 50 mg/g, higher than that obtained by Bouhamed, Elouaer and Bouzid (2012), who used a lower concentration adsorbent in the adsorption processes. The dominating copper removal mechanisms by AC could have been due to cation interaction with surface sites and immobilization of metal together with organic matter being adsorbed to the adsorbent.

Although, from the results, it is possible to observe that the AC which achieved the best elimination percentage of COD and NH-N was D, considering the global results obtained at this step of the investigation, and the AC that achieved the best elimination percentage was C (AC activated with H₃PO₄).

It is well known that the adsorption capacity may decrease because of competition by natural organic matter with different organic contaminants through direct site competition and pore entrance blockage (APUL et al., 2013), and also the pore size distribution of AC in relation to the molecular weight of natural organic matter and the target pollutants plays an important role in determining the competitive
behaviour (NEWCOMBE et al., 2002). However, this issue is going to be studied in a future investigation.

Figure 8 depicts a scanning electron microscope (SEM) image of AC activated with H$_3$PO$_4$. The surface morphology appeared to have very little pores and a fluffy and irregular porous texture with a large and accessible surface area.

**Evaluation of contact time and adsorbent load**

Considering the results of the previous section, the AC that obtained the best global results of pollutant removal was C, followed by D. Therefore, this AC was selected for evaluation of the contact time in the adsorption process and the adsorbent load that achieves an adequate removal of ammonia, in order to establish their influence, because ammonia was the parameter that gets the lower elimination. Consequently, different loads of the chosen AC were applied to four beakers filled with 500 mL of LL and stirred, taking samples periodically to measure the evolution of ammonia concentration during the adsorption time.

Figure 9 shows the evolution of ammonia concentration present in LL throughout the adsorption process, using different AC loads:
- 3 g/L;
- 5 g/L;
- 7 g/L;
- 9 g/L.

As it was expected, the concentration of ammonia decreased from the beginning of the adsorption process to the end, and it was more pronounced at minute 60 of the experiment and then reached a plateau. This phenomenon is attributed to the reduction of immediate solute adsorption due to the lack of available open sites for pollutant adsorption, which in turn supported film diffusion (HAMEED, 2009).

Also, the results obtained at the end of experimentation indicate that the removal percentage of ammonia increased with an increase in the adsorbent load from 3 to 9 g/L. For a load of 3, 5, 7 and 9 g/L, the ammonia removal was 32.8, 43.8, 48.4 and 51.6%, respectively. These results are explained by the fact that with an increase of adsorbent dosage the available adsorption surface and availability of more adsorption sites increase, which results in more adsorbate attached to the surfaces (EL-ZAHHAR et al., 2013). Although an increase in adsorption occurred with respect to an increase in dosage, the trend of amount adsorbed per unit mass decreased with increasing dosage. In fact, the amount of ammonia adsorbed by mass unit of AC during the batch adsorption process, determined using Equation 2, was 700.0, 560.0, 442.9 and 377.6 mg/g for 3, 5, 7, 9 g/L, respectively.

A higher adsorbent load than the used in this investigation can enhance the probability of collision between adsorbent particles, and therefore create particle aggregation, leading to a decline in the total surface area and an increase in diffusion path length, both of which contribute to the decrease of adsorption (SEMERJIAN, 2010; NAMASIVAYAM; SANGEETHA, 2004; RAO et al., 2008) resulting from high sorbent concentration, which would lead to a decrease in the total surface area of the adsorbent. Similar observations were made by Foo, Lee and Hameed (2013) who established that an increase in the adsorbent dosage over an optimal did not produce an appreciable improvement in the removal of pollutants.

Data of ammonia adsorption to AC were analysed with the Langmuir and Freundlich models (see Figure 10) at 19ºC for AC range of 3 to 9 g/L.

As can be seen, the linear form of the Langmuir isotherm does not fit adequately to the experimental data, giving a R$^2$ lower than 0.9 (0.7653). The model Freundlich equilibrium isotherms fit experimental data adequately, giving R$^2$ values higher than 0.95 (0.9528). Also 1/n (intensity of the reaction) was 0.5183 and k was 7.08*10$^{-5}$ L/g, conditions favourable for the adsorption process.
The interesting results obtained with coffee waste transformed in AC using phosphoric acid could be due to the fact that this method allows the development of mesopores in the resulting carbon structure (MOLINA-SABIO; RODRÍGUEZ-REINOSO, 2004). Among the activation agents, H₃PO₄ offers several advantages: it is non-polluting, it is eliminated by leaching with water, and it is recyclable for further use after water washing (IOANNIDOU; ZABANIOTOU, 2007). H₃PO₄ is known to transform upon heating into different polycondensed forms; pyrophosphoric acid at 213°C and metaphosphoric acid around 300°C (SUÁREZ-GARCÍA; MARTÍNEZ-ALONSO; TASCÓN, 2004). The volatilization of H₃PO₄ can produce new channels (pores) in the carbon structure, which leads to an increase in the porosity at high temperature. Phosphoric acid activation of precursors results in the formation of highly porous carbon with acid surface groups (PUZIY et al., 2005). This advantage could explain the better results obtained using the carbon activated with H₃PO₄, even considering that it has less total pore area with respect to the other ones.

CONCLUSIONS
The AC that produced the best global results of elimination of ammonia, COD, copper, bromine and chlorine was the coffee waste that was activated using H₃PO₄, with an impregnation ratio of 1:1. The study carried out using this AC in order to evaluate the effect of adsorption time and the load of adsorbent reveals that the concentration of ammonia suffers a pronounced reduction from the beginning to minute 60 of the experiment. Also, the removal of this pollutant increased with an increase in the adsorbent load; however, the load that maximizes the removal of ammonia per mass unit of adsorbent was 3 g/L. The ammonia adsorption data obtained are successfully modelled by the Freundlich isotherm. The quality of the LL can be improved applying adsorption process using waste obtained from coffee as AC. These results allow consider to coffee waste as a by-product with add value.

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REFERENCES


Landfill leachate treatment using activated carbon obtained from coffee waste


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