Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.21417

90 (2017) 220–230
September

Comparison of the adsorptive action of hydrotalcite, *Moringa oleifera* and activated carbon in the treatment of landfill leachate

Nair Conde de Almeida*, Valdenilson José Alves de Oliveira,
Dejanira de Franceschi de Angelis

Department of Biochemistry and Microbiology, Institute of Biosciences, São Paulo State University, UNESP, Av. 24A, no. 1515, Bela Vista, CEP 13506-900, Rio Claro, São Paulo, Brazil, Tel. 55 19 35264184; emails: nairca2015@gmail.com (N.C. de Almeida), zito@rc.unesp.br (V.J.A. de Oliveira), dangelis@rc.unesp.br (D.F. de Angelis)

Received 14 February 2017; Accepted 6 September 2017

ABSTRACT

Landfill leachate is formed by organic and inorganic toxic compounds. It has high salt concentration and pathogenic organisms that can cause environmental harm. Hydrotalcite, activated carbon and *Moringa oleifera* seeds have been used for the adsorption of contaminants and the purification of water. In the present study, landfill leachate was submitted to physicochemical and microbiological analysis before and after treatment with these adsorbents. The characterization of the leachate revealed a small number of heterotrophic bacteria and fungi. Total coliforms and *Escherichia coli* reached mean values of 17,900 and 890 NMP/100 mL, respectively. The physicochemical analysis indicated high conductivity, color, turbidity, chemical oxygen demand (COD), biochemical oxygen demand in 5 d, ammonia, boron, sodium and chlorides. Treatment with hydrotalcite produced the best results regarding the improvement in these variables, but led to an increase in pH. Reused hydrotalcite (Hr) provided reasonable results, but with less efficiency than hydrotalcite. Moreover, Hr failed to remove boron and aluminum and magnesium levels increased. In addition, 4% activated carbon (AC4%) obtained better results regarding color and COD, but failed to remove boron and ammonia efficiently and 1% activated carbon achieved similar results to AC4%, but with lower degrees of removal. *M. oleífera* seed and extract achieved unsatisfactory results. All adsorbents, except *M. oleifera* extract, decreased the amount of heterotrophic bacteria approximately 10-fold. Total coliforms and *E. coli* did not resist the treatments. None of the adsorbents removed sodium, chloride or the toxicity of the leachate.

Keywords: Landfill leachate; Boron adsorption; Hydrotalcite; *Moringa oleifera*; Activated carbon

1. Introduction

Leachate is one of the most important problems found in landfills. Landfill leachate is a liquid residue with high amounts of organic and inorganic compounds, a dark color and bad smell produced by the physicochemical and microbiological decomposition of solid waste. The composition of leachate varies considerably depending on the nature of the solid waste, the configuration, management and age of the landfill as well as climatic factors, such as rainfall and temperature [1].

Landfill leachate contains toxic substances due to improper waste disposal by the population. Pathogenic organisms are also transmitted by leachate, which can cause environmental harm, affecting plants, animals and the human population. The high salt concentration in leachate causes problems with regard to biological treatment systems due to changes in the osmotic pressure of microbial cells [1]. Salt also corrodes pipes and exerts an influence on the natural characteristics of aquatic systems. The environmental damage caused by landfill leachate is significant and could

---

* Corresponding author.

1944-3994/1944-3986

contaminate surface water, soil and groundwater. Thus, the treatment of leachate is of considerable environmental importance [1].

In most Brazilian cities, leachate is collected from landfills and transported to sewage treatment plants, where it is subjected to microbiological degradation. After treatment, the leachate is released into surface water [1,2]. Since the compounds in the leachate are not properly identified, there is no way to predict whether such treatment is effective. Thus, the implantation of leachate treatment plants at landfills would be an advance in the search for solutions regarding the final disposal of this residue and would lead to improvements in environmental conditions.

Natural and synthetic adsorbents have been evaluated with regard to reducing the toxicity of leachate. Hydrotalcites are double lamellar hydroxides (DLHs) with a high anion exchange capacity that have been successfully used as adsorbents for contaminants and anions, such as borates in industrial effluents [3]. The structure of DLHs is derived from brucite ($Mg(OH)_2$). Mg^{2+} ions are octahedrally coordinated by hydroxyl groups, with octahedrons sharing edges and forming neutral layers that are maintained stacked by hydrogen bonds. DLHs have a wide variety of applications as heterogeneous catalysts [4], adsorbents [3,5] and anion exchangers [6] and are also employed in pharmaceutical products [7]. The removal of anions from a solution by DLHs usually occurs through the combination of two processes: anion exchange and adsorption [8]. Some examples of the removal process through anion exchange include the treatment of water for the removal of Cr(VI) compounds, phosphates and boron [8,9].

Moringa oleifera is a plant belonging to the family Moringaceae that is native to India and widely cultivated in tropical regions around the world [10]. This plant grows rapidly and is able to survive in poor soils as well as throughout long periods of drought [11]. According to Joly [12], *M. oleifera* is a tree with long green pods, winged seeds, small leaves and fragrant white flowers. The seeds have been used for the removal of organic matter and the clarification of river waters in regions where no conventional treatment is available. Studies involving the use of *M. oleifera* as a coagulant agent present significant results, demonstrating that this plant can be considered a water treatment option [13].

Activated carbon is a material with a complex pore structure, high surface area and several functional groups on the surface that contain oxygen, which favors adsorption [14]. Thus, activated carbon is a reference for the treatment of water and effluents.

The aim of the present study was to characterize the leachate composition from solid waste degradation at the Rio Claro landfill in the state of São Paulo (SP), Brazil, and to determine the absorbent efficiency of hydrotalcite, *M. oleifera* and activated carbon with regard to physicochemical and microbiological variables.

2. Materials and methods

2.1. Characterization of landfill leachate from Rio Claro Treatment Plant, São Paulo, Brazil

The leachate was subjected to the analysis determined by Article 18 of State Decree 8468-1976 [15], which stipulates standards of effluent emission and complementary analysis for the best characterization of samples. To determine the mean variation of leachate components, four samples were collected: two in dry periods (July 2014 and August 2015) and two in rainy periods (March 2015 and February 2016). The samples collected from the landfill were placed in ice-cooled thermal boxes with the temperature maintained between 5°C and 10°C.

2.1.1. Microbiological analysis

Microbiological analysis was performed immediately after samples' arrival at the laboratory.

Microbial count: Total heterotrophic bacteria were counted using the pour-plate technique in Plate Count Agar medium with addition of 5 ppm of actidione, following technical standard L. 5.201 [16]. For fungal counts, the spread-plate method was performed on a Sabouraud dextrose agar (SDA) medium with the addition of antibiotics (5 ppm of ampicillin and nalidixic acid). The plates with bacteria were kept at 35°C and those with fungi were kept at 28°C. For total coliform and *Escherichia coli* counts, the samples were diluted 100 times and analyzed using the COLILERT® method.

2.1.2. Physicochemical analysis

Conductivity was determined using a conductivity meter (Marte®, model MD-11), pH was determined using a pH meter (Digimed®, model DM-22) and turbidity was determined using a spectrophotometer (λ 433 nm, Nanocolor®, Macherey-Nagel, Germany). Regarding color, the samples were filtered (0.45-μm membrane filter kit) and analyzed using photometric determination (Nanocolor® spectrophotometer Macherey-Nagel). Sedimented solids were analyzed in an Imhoff cone. Chlorides were analyzed using Mohr's method [17]. Phenols, cyanides, sulfides, sulfates, aluminum, arsenic, boron, barium, cadmium, copper, chrome, hexavalent chromium, tin, soluble iron, fluorides, manganese, mercury, nickel, silver, selenium, sodium and zinc were analyzed at the São Lucas Laboratory of Environmental Analysis, Rio Claro, SP, Brazil (Table 1).

Biochemical oxygen demand in 5 d (BOD_5) and chemical oxygen demand (COD) were determined according to the Standard Methods for the Examination of Water and Wastewater [20].

2.2. Hydrotalcite synthesis

Hydrotalcite was prepared using the co-precipitation method with varied pH [23]. Two solutions (A and B) were prepared. Solution A: $Mg(NO_3)_2.6H_2O$ and $Al(NO_3)_3.9H_2O$ at respective concentrations of 1.0 and 0.5 mol/L. Solution B: Na_2CO_3 and NaOH at respective concentrations 1.0 and 2.5 mol/L. From these concentrations, the formation of a hydrotalcite with an Al/(Mg + Al) molar ratio of 0.33 was expected [8]. Solution B (200 mL) was placed in a Nalgene beaker with stirring (200 rpm). The same volume of solution A was added to solution B using a peristaltic pump at a rate of 1 mL/min. Stirring remained constant throughout the process with the aid of a mechanical stirrer. Homogenization performed for 2 h, producing a precipitate with a pH ~12. The precipitate

Table 1
Variables analyzed and methodology used at São Lucas Laboratory of Environmental Analysis

Variables	Methods
Total metals: arsenic and antimony	Antimony and Arsenic (atomic absorption, borohydride reduction) [18]
	Inductively Coupled Plasma-Atomic Emission Spectrometry [19]
Total metals	Inductively Coupled Plasma-Atomic Emission Spectrometry [19]
	APHA SMEWW, method: 3030E [20]
	APHA SMEWW, method: 3500 Cr B [20]
Dissolved metals	APHA SMEWW, method 3030E [20]
	Inductively Coupled Plasma-Atomic Emission Spectrometry [19]
Mercury	Mercury in Liquid Wastes (Manual Cold-Vapor Technique) [21]
	Inductively Coupled Plasma-Atomic Emission Spectrometry [19]
Anions	Determination of Inorganic Anions in Drinking Water by Ion Chromatography [22]
Cyanides	APHA SMEWW, method: 4500-Cn^-, D and E [20]
Sulfides	APHA SMEWW, method: 4500-$S2^-$ D [20]

was aged for 18 h in an oven at 60°C for the crystallization of hydrotalcite. The precipitate was then centrifuged and washed successively with deionized water at a temperature of 75°C ± 5°C until achieving pH 7. The crystals were dried in an oven at 100°C for 24 h and ground in a ball mill. The powdered sample was calcined at 500°C with a heating rate of 10°C min^{-1} for 3 h in a muffle furnace and stored in a desiccator.

2.2.1. Characterization of hydrotalcite

The hydrotalcite was analyzed at the Material Characterization and Development Center of the Federal University of São Carlos (CCDM-UFSCar), SP, Brazil. The crystalline phases of the hydrotalcite samples were determined using X-ray diffraction in a Rigaku Rotaflex diffractometer (model Ru200B) with a copper anode under the following conditions: scanning between 5° and 70° in 2θ, with step 0.02° and 3 s per step, 40 kV and 60 mA. Phase identification was performed by comparison with diffraction patterns using the Search-Match software (Crystallographica). X-ray fluorescence analysis was performed using the Ranger X-Flash Technology-Bruker S2 spectrometer calibrated with curves pre-established from international standards (NIST). The method consisted of oven drying at 110°C and calcination at 1,150°C to determine fire loss and analysis on lithium tetraborate-fused pellet equipment containing the sample. The surface area was determined using the Brunauer–Emmett–Teller (BET) method through the physical adsorption of nitrogen gas molecules on the sample surface using the FlowSorb II 2300 Micromeritics equipment. For the determination of thermogravimetry, the sample was heated from room temperature to 850°C in an inert atmosphere of nitrogen gas at flow rate of 50 mL/min (IT-LCP407 revision 001) and the mass was constantly monitored using a scale. The thermogravimetric curve and its derivative as a function of temperature were obtained in a TGA Q500 thermal analyzer (TA Instruments) with heating rate of 20°C min^{-1} and an alumina sample support.

2.3. Reused hydrotalcite

Hydrotalcite (synthesized as described in the item 2.2) was used for the treatment of the leachate and then submitted to drying in an oven at 100°C for 24 h and calcinations at 500°C with a heating rate of 10°C min^{-1} for 3 h in a muffle furnace to determine whether its adsorption capacity would be recovered after its use and calcination.

2.4. Preparation of *M. oleifera* seeds for use as clarifier

The husks of the seeds were removed. The cotyledons were milled and passed through a 60-mesh sieve.

2.5. Coagulant extraction of *M. oleifera* seed for use as clarifier

Various extraction procedures of the active component of *M. oleifera* are described in the literature and some are performed with saline, as cited by Okuda et al. [24]. However, due to the high concentrations of chlorides, sodium, etc. in the leachate, a method that did not add more salts to the system was employed, which was based on that described by Ribeiro [25] and Katayon et al. [26]. On average, 5 g of milled *M. oleifera* seeds were placed in 200 mL of distilled water and stirred rigorously for 2 min. The extract was filtered through a 16-μm pore filter and the volume was adjusted to 500 mL with distilled water. A filtrate sample was weighed, oven dried at 105°C and weighed again to determine the concentration of *M. oleifera* extract, which was 4 g/L. As the shelf life of the extract is limited due to biodegradation, the extract was produced on the days of the tests.

2.6. Activated carbon

Powdered activated carbon (PAC) from Labsynth Products Laboratories Ltd., Brazil.

2.7. Treatments

2.7.1. Application of hydrotalcite (LH) and reused hydrotalcite (LHr)

The removal experiments were carried out in flasks containing 100 mL of leachate with hydrotalcite with stirring (250 rpm/30 min) at 28°C ± 2°C and 2 h of decantation. The same procedure was performed for reused hydrotalcite. A preliminary test was performed with four hydrotalcite concentrations (2%, 4%, 8% and 12%) to determine the optimal concentration for boron removal.

2.7.2. Application of M. oleifera seeds (LMS)

The removal experiments were carried out in flasks containing 100 mL of leachate and 1% *M. oleifera* seed with stirring (250 rpm/30 min) at 28°C ± 2°C and 2 h of decantation. It was not possible to use a 4% concentration due to the excessive increase in turbidity, BOD_5 and COD.

2.7.3. Application of M. oleifera extract (LME)

In flasks containing 100 mL of leachate, 4% *M. oleifera* extract was mixed with stirring (120 rpm/4 min) and the mixture was then stirred slowly (30 rpm/25 min). Due to the good results achieved in previous studies, the technique employed by researchers Ribeiro [25] and Katayon et al. [26] was used.

2.7.4. Application of activated carbon

The removal experiments were carried out in flasks containing 100 mL of leachate with 1% activated carbon (LAC_1) and 4% activated carbon (LAC_4) with stirring (250 rpm/30 min) at 28°C ± 2°C and 2 h of decantation. Normally, the percentage of activated carbon used in effluent treatment varies from 1% to 2% [27,28]. In this experiment, the 1% concentration was used as reference and 4% was used to establish a comparison with hydrotalcite (4%).

All treatments were performed in triplicate and subsequently filtered through 8-μm paper filter to remove residues from the adsorbents. The results are expressed as mean values.

2.8. Toxicity test with Daphnia similis

The tests with *D. similis* were conducted in accordance with NBR Norm 12713 [29].

3. Results and discussion

3.1. Characterization of landfill leachate

The characterization of the landfill leachate is presented in Tables 2–4. Variables that increase the toxicity of the leachate and fail to comply with legislation were found in the four samples regardless of the period analyzed (dry or rainy).

3.1.1. Microbial count

Table 2 displays the data on heterotrophic bacteria and fungi, demonstrating lower values in comparison with effluents from domestic sewage. One may therefore infer that the conditions of this leachate are not favorable to microbiological growth and may hinder biological treatment based only on biodegradation. With regard to total coliforms and *E. coli*, the values are above the maximum permitted for disposal in class 2 rivers according to Article 11 [15].

3.1.2. Physicochemical analysis

Among the variables displayed in Table 3, pH and sedimentable solids are in compliance with values determined by legislation. Regarding the other variables, although legislation does not determine maximum indices for the release of effluents, the values found to have a high probability of causing impacts on microbiological treatment or the environment

Table 2
Quantification of fungi, bacteria, total coliforms and *E. coli* in four samples of landfill leachate

Variables	Samples				MVPr
	1	2	3	4	
Heterotrophic bacteria (CFU/mL)	2.4×10^4	2.8×10^4	1.8×10^4	1.3×10^5	NA
Fungi (CFU/mL)	2.6×10^5	8×10^3	10	5	NA
Total coliforms (MPN/100 mL)	16,500	14,280	19,500	21,430	5,000
E. coli (MPN/100 mL)	980	940	900	740	100

NA, not applicable; MVPr, maximum value permitted for class 2 rivers by Article 11 [15]; MPN, most probable number.

Table 3
pH, conductivity, true color, turbidity, sedimentable solids, COD and BOD_5 of landfill leachate

Variables	Samples				MVP
	1	2	3	4	
pH	7.75	8.11	7.72	7.62	6–9
Conductivity (mS/cm)	26.05	22.21	28.92	32.73	NA
True color (Pt Co/L)	5,340	5,660	6,400	6,980	NA
Turbidity (NTU)	89.8	98.2	88.5	102	NA
Sedimented solids (mL/L)	<0.1	<0.1	<0.1	<0.1	<0.1
COD (mg/L)	3,600	2,720	4,576	2,677	NA
BOD_5 (mg/L)	624	636	516	643	60

NA, not applicable; MVP, maximum value permitted by Article 18 [15].

Table 4
Chemical analysis of metals and non-metals in landfill leachate (mg/L)

	Samples (mg/L)				MVP	MVPr
	1	2	3	4		
Metals						
Arsenic	0.046	0.045	0.044	0.025	0.2	0.1
Barium	0.210	0.198	0.220	0.173	5.0	1.0
Boron	*7*	*7.68*	*8.24*	*7.2*	*5*	*5*
Cadmium	<0.001	<0.001	<0.001	<0.001	0.2	0.01
Lead	<0.005	<0.005	<0.005	<0.005	0.5	0.1
Copper	<0.005	<0.005	<0.005	<0.005	1	1
Chrome	0.300	0.198	0.259	0.151	5.0	0.05
Hexavalent chromium	<0.100	<0.100	<0.100	0.05	0.1	0.1
Tin	0.038	0.039	0.075	0.038	4.0	2.0
Soluble iron	1.80	1.86	1.8	0.966	15	15
Fluoride	<10.000	<10.000	<10.000	<2.000	10	10
Manganese	0.280	0.188	0.151	0.208	1	1
Mercury	<0.0002	<0.0002	<0.0002	<0.0002	0.01	0.002
Nickel	<0.130	0.186	0.251	0.119	2	2
Silver	<0.005	<0.005	<0.005	<0.005	0.02	0.02
Sodium	*1,823*	*1,747*	*1,905*	*1,719*	*NA*	*NA*
Selenium	<0.005	<0.005	<0.005	<0.005	0.02	0.01
Zinc	0.310	0.153	0.219	0.100	5	5
Non-metals						
Chlorides	*3,201*	*2,856*	*3,802*	*2,625*	*NA*	*NA*
Cyanide	<0.004	<0.004	<0.004	<0.002	0.2	0.2
Sulfide	<0.002	<0.002	<0.002	<0.002	NA	NA
Sulfate	<50.000	<50.000	<50.000	<10.000	NA	NA
Phenol	0.066	0.042	0.061	<0.006	0.5	0.001
Ammonia	*2,525*	*3,570*	*2,250*	*2,627*	*NA*	*0.5*

NA, not applicable; MVP, maximum value permitted by Article 18; MVPr, maximum value permitted for class 2 rivers by Article 11 [15].

in which this leachate is eventually discarded. The conductivity of freshwater rivers ranges from 0 to 800 µS/cm, conductivity of water from marginal rivers ranges from 800 to 1,600 µS/cm, conductivity of brackish water ranges from 1,600 to 4,800 µS/cm, conductivity of saline water is above 4,800 µS/cm and conductivity of sea water is around 51,500 µS/cm [30]. The values displayed in Table 3 are above those for freshwater rivers and are situated between values for saline and sea water. As conductivity is directly related to salinity [31], the introduction of an effluent with high salinity may destabilize the osmotic equilibrium of the biota in rivers in the region where the leachate is released.

The values for true color were high (Table 3) considering the maximum permitted for water distributed to the population (151 UC) [32]. A change in water color in rivers may be due to the presence of natural substances, such as humic and fulvic acids and metals due to the process of local rock dissolution, turning the water a yellowish color. According to Oliveira et al. [31], 75 PtCo/L is higher than acceptable for a class 2 river.

Maximum turbidity permitted in the public water supply is 5.0 NTU [32]. The turbidity of the leachate reached values higher than 88 NTU (Table 3).

According to Amor et al. [33], the leachate of a young landfill (<5 years) is usually characterized by high concentrations of BOD$_5$ (4,000–15,000 mg O$_2$/L) and COD (25,000–60,000 mgO$_2$/L), ammonia concentration of 500–2,000 mg/L, BOD$_5$/COD ratio of 0.15 to 0.25 and pH 4. The values displayed in Table 3 show that the leachate is in an intermediate stage of aging (methanogenic phase), with mean COD and BOD$_5$ around 3,400 and 600 mg/L, respectively, a BOD/COD ratio of 0.17 and pH above 7.

Table 4 displays results of the metal and non-metal analysis. Based on Article 18 [15], only boron is above the limit established by legislation. Boron is found in the composition of glass, fiberglass additives, ceramics, insecticides and fertilizers. The appearance of this element at an amount above that expected in the leachate is likely due to the inclusion of industrial waste in the landfill. Rio Claro and neighboring cities, such as Santa Gertrudes and Cordeirópolis, are part of an important ceramic production center in the state of São Paulo. Until 2002, all the urban waste collected from the municipality of Santa Gertrudes (approximately 2.1 ton/d) was sent to the Rio Claro landfill [34]. Moreover, fiberglass factories are located in the municipality of Rio Claro. While industrial waste is not currently mixed with household waste, the leachate is the product of both old and new landfills and this excess of boron may come from old landfills.

Legislation does not establish maximum sodium and chloride values in effluents, but science demonstrates that these elements can cause an osmotic imbalance in receiving bodies of water at the point of release as well as the destabilization of soil, thereby affecting plant growth. Sodium is present in almost all waters in the form of highly soluble salts and is considered one of the most abundant elements on earth [35]. In the landfill leachate, the sodium concentration reached values higher than 1,700 mg/L. The limit established by the World Health Organization for sodium in drinking water is 200 mg/L [36]. High levels of chlorides were also found in the samples analyzed (Table 4). Ordinance 2914/2011 of the Brazilian Ministry of Health [37] establishes 250 mg/L as the maximum value for chloride in drinking water. The high levels of ammonia demonstrate that the leachate is in an intermediate phase of aging, acquiring characteristics of the methanogenic phase, in which ammoniacal nitrogen levels can be between 3,000 and 5,000 mg/L [33].

3.2. *Characterization of hydrotalcite*

Fig. 1 displays the X-ray diffractograms of the hydrotalcite. Characteristic peaks of hydrotalcite-like compounds were found in the sample, demonstrating that hydrotalcite was used as a precursor for the sample. All peaks in the diffractogram confirm the Mg-Al-CO_3 structure reported in the literature [8].

The X-ray fluorescence analysis demonstrated fire loss (31.90%) and the hydrotalcite chemical composition, with 23.27% Al_2O_3 and 43.93% MgO.

A number of factors, such as aging and the hydrothermal treatment of synthesized DLHs as well as the degasification used prior to the measurement of adsorption–desorption isotherms, play an important role in determining textural properties [8]. Delazare et al. [8] obtained a surface area of 68.9 m^2/g, but the hydrotalcite in the experiment had a BET surface area of 34.9 m^2/g.

In the present study, the thermogravimetric analysis was consistent with data described by Delazare et al. [8], revealing two stages of mass loss with endothermic energy variations. The first stage started at room temperature and ended at approximately 200°C, suggesting the release of interlayer water and water molecules that may have been adsorbed to the surface of the material. The second stage of decomposition occurred at 200°C–450°C, suggesting hydrotalcite decomposition via the release of interlayer carbonates and hydroxyls from the brucite-like layers. At 600°C, the curve indicated the presence of approximately 65% inorganic compound residues, such as mixed oxides of aluminum and magnesium (Fig. 2).

3.3. *Preliminary test to determine best hydrotalcite (DLH) concentration to be used in boron removal*

Fig. 3 shows the effects of the four concentrations of hydrotalcite on pH, conductivity and boron adsorption. An increase in pH was found in the control sample, which was probably due to the stirring of the sample, enabling the dissolution of atmospheric CO_2 in the system, which would promote the formation of salts that tend to alkalinize the medium, such as calcium and sodium carbonates. Some changes in the variables occurred when the concentration

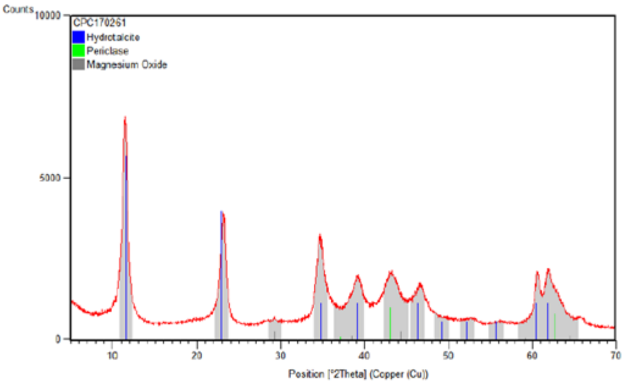

Fig. 1. Diffractogram with phases identification: hydrotalcite (magnesium aluminum carbonate hydroxide hydrate, JCPDS 14-0191 $Mg_6Al_2CO_3(OH)_{16}.4H_2O$) and magnesium oxide (periclase, JCPDS 3-0998 and 30-0794 MgO).

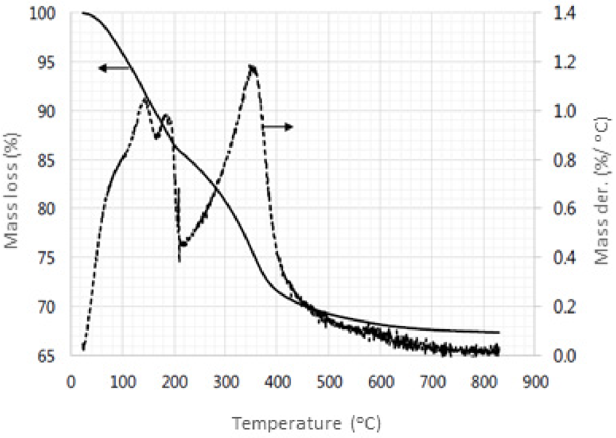

Fig. 2. Thermogravimetric curve and derivative curve as function of temperature.

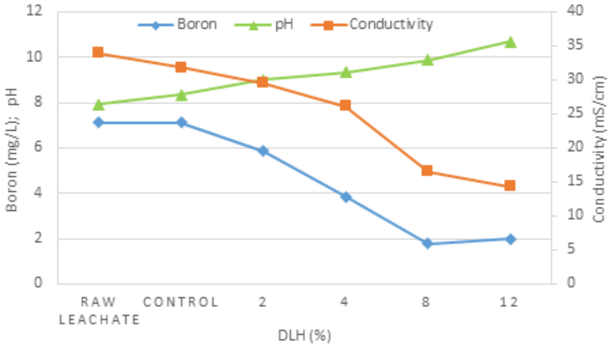

Fig. 3. Boron concentration, conductivity and pH in raw landfill leachate, control (without hydrotalcite) and with addition of 2%, 4%, 8% and 12% hydrotalcite (DLH).

of hydrotalcite was increased. There was a gradual increase in the sample pH and the conductivity decreased by about 20% when 4% DLH was used, 49% when 8% DLH was used and 66% when 12% DLH was used. Analyzing Fig. 3, the ideal concentration of hydrotalcite would be 4% to adjust the boron concentration in the landfill leachate studied to comply with legislation. Starting from a solution of 30 mg/L of boron, Delazare et al. [8] report a maximum removal rate of 25.9 mg/L using 4% hydrotalcite. The high efficiency of boron removal (86%) was due to the number of adsorption sites. The surface of hydrotalcite has residual positive charges that are compensated by adsorbed anionic species, which, in this case, is the borate ion. In the landfill leachate tested, the efficiency of the process was lower, with the removal of about 3.4 mg/L of boron (47%), probably due to the numerous compounds and ions in this type of sample, as indicated by the characterization of the leachate (Tables 3 and 4). The composition of leachate is complex, with other anions capable of being adsorbed to hydrotalcite and competing with boron. When the hydrotalcite concentration was increased to 8%, boron adsorption was approximately 75%, but the boron removal remained around 72% when the concentration was increased to 12%. According to Delazare et al. [8], there is a concentration limit at which the conversion of $B(OH)_3$ to $B(OH)_4^-$ no longer occurs. Thus, the amount of boron removed would be the same even with an increase in the number of adsorption sites, since hydrotalcite cannot remove $B(OH)_3$.

In total, 4% hydrotalcite was chosen to continue the tests because it reduced boron to a level in compliance with legislation.

3.4. Comparative experiment with landfill leachate treated with hydrotalcite (LH), reused hydrotalcite (LHr), M. oleifera seed (LMS), M. oleifera extract (LME) and activated carbon (LAC_1 and LAC_4)

The analyses were performed only for variables with results in disagreement with legislation or values that could impact the balance of the natural environment.

3.4.1. Microbial count

Table 5 displays the number of total coliforms and *E. coli*, indicating that these bacteria did not resist the treatments and were also not found in the control. The adsorbents demonstrated good clarification and precipitation capacity, dragging the microorganisms in the samples to the sludge and reducing the initial number to about 10^2 CFU/mL, except the *M. oleifera* extract, which maintained the count at 10^4 CFU/mL, like the control. The leachate used as control in the experiments was subjected to agitation and filtration processes as well as the treatments tested. Thus, some variables underwent alterations differing from the crude leachate. The number of fungi was small in the landfill leachate and none were detected in the treatments.

3.4.2. Physicochemical analysis

Leachate agitation and filtration procedures were sufficient to induce changes in several variables. The pH of the control increased in relation to the value of the leachate in nature, whereas the conductivity, turbidity, BOD_5 and COD decreased and no change occurred in the true color (Fig. 4).

All adsorbents maintained the pH of the leachate within the limits established by legislation (Fig. 4), but the use of hydrotalcite made the leachate more alkaline than the other adsorbents studied. Depending on the initial leachate pH, the use of hydrotalcite could exceed the maximum limit permitted for effluent emission (pH 9).

All adsorbents decreased conductivity. The best results were achieved by hydrotalcite and 4% activated carbon, with reductions of 51.5 and 50.2%, respectively (Fig. 4). However, conductivity around 15 mS/cm is very high compared with the receiving bodies of water (freshwater rivers), in which conductivity ranges from 0 to 800 μS/cm [30].

The best result for true color was achieved with 4% activated carbon (98% removal rate). Hydrotalcite removed about 70%. Paterniani et al. [13] used a coagulant solution obtained from *M. oleifera* seeds to treat water and found a 90% apparent color reduction in a simple sedimentation process. In the landfill leachate treatment, however, the *M. oleifera* extract was the adsorbent with the lowest removal rate (19%; Fig. 4).

Treatment with *M. oleifera* seed increased the turbidity of the leachate approximately 10-fold. This may have been due to the alkaline pH, which hindered the precipitation of the pulverized *M. oleifera* seed, making the leachate turbid. Beginning with initial turbidity of 102 NTU, the *M. oleifera* extract reduced the turbidity of the leachate by approximately 44%. Using *M. oleifera* extract for water treatment, Ribeiro [25] obtained approximately 90% removal rates starting with initial turbidity of 22.5 NTU, but also found that the increase in pH led to a decrease in turbidity removal capacity. The best results were achieved in the treatment with hydrotalcite, which reduced the turbidity of the leachate by approximately 58% (Fig. 4).

The greatest reduction in BOD_5 was achieved by hydrotalcite (approximately 95%), followed by 4% activated carbon (81%). These adsorbents adapted the leachate to the norm established by Article 18 [15], which determines that treatment should reduce BOD_5 by at least 80%. Thus, the effluent

Table 5
Microbial quantification of the landfill leachate in nature, control (without adsorbent) and treated with hydrotacite (LH), reused hydrotalcite (LHr), *M. oleifera* seed (LMS), *M. oleifera* extract (LME), 1% activated carbon (LAC_1) and 4% activated carbon (LAC_4)

	Landfill leachate	Control	LH	LHr	LMS	LME	LAC_1	LAC_4
Fungi (CFU/mL)	10	<10	<10	<10	<10	<10	<10	<10
Bacteria (10^3 CFU/mL)	130	30	2.0	4.0	5.0	36	4.0	3.5
Total coliforms (MPN/100 mL)	21,430	–	–	–	–	–	–	–
E. coli (MPN/100 mL)	740	–	–	–	–	–	–	–

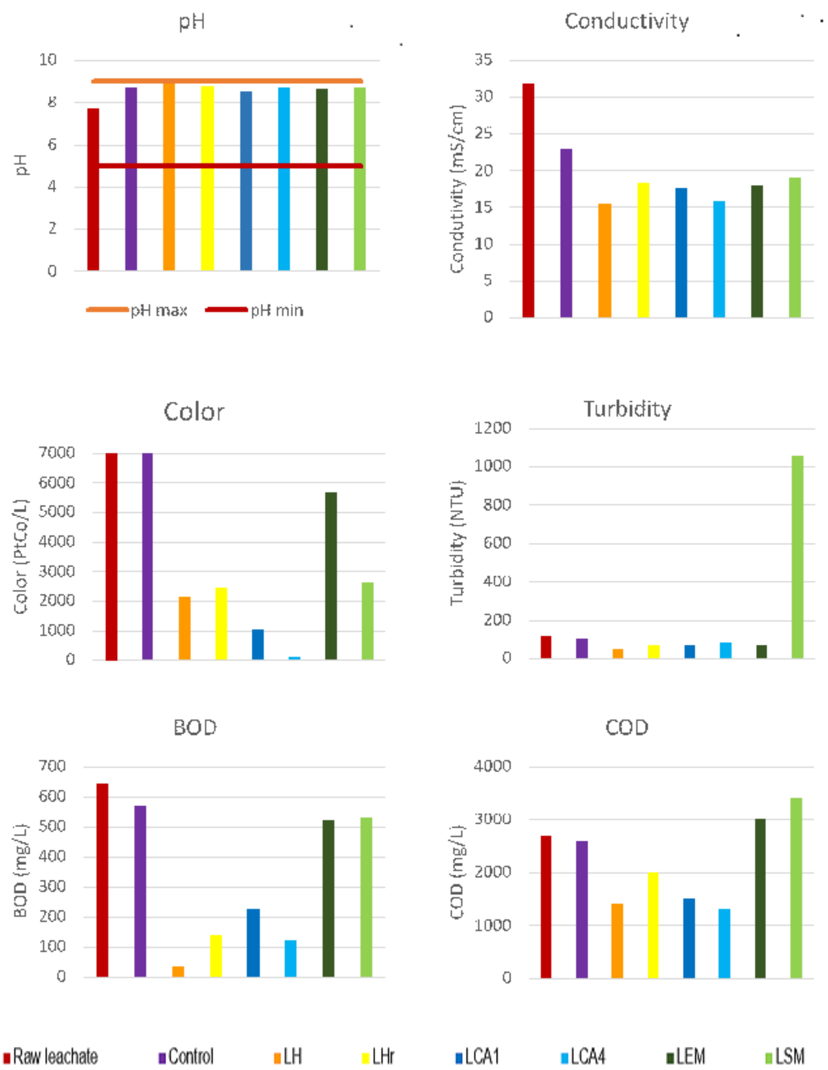

Fig. 4. Results of pH, conductivity, true color, turbidity, COD and BOD_5 analysis of the landfill leachate in nature, control (without adsorbent) and treated with hydrotacite (LH), reused hydrotalcite (LHr), *M. oleifera* seed (LMS), *M. oleifera* extract (LME), 1% activated carbon (LAC_1) and 4% activated carbon (LAC_4).

after treatment with these adsorbents could be released into a receiving body of water. These reductions are comparable with the rates described by Hashemi et al. [38] using filter membranes. The reused hydrotalcite reduced BOD_5 by approximately about 78%, which is near the rate required by legislation. Neither the *M. oleifera* extract nor seeds seed reached satisfactory levels of BOD_5 reduction (Fig. 4). Regarding COD, hydrotalcite and 4% activated carbon were the adsorbents that achieved the best results, with reductions of about 48% and 43%, respectively. The *M. oleifera* extract and seed led to an increase in COD by 12% and 27%, respectively (Fig. 4). Thus, *M. oleifera* only lowered BOD_5 by 18% and increased the COD of the leachate.

Fig. 5 shows that only hydrotalcite was effective at removing boron, adjusting the boron level of the leachate to legislation. In contrast, 4% activated carbon did not remove boron satisfactorily. According to Farrokhzadeh et al. [39], *M. oleifera* is a relatively efficient biosorbent for heavy metal removal from aqueous solutions. However, *M. oleifera* was not efficient with regard to boron adsorption from landfill leachate.

The agitation and filtration procedures caused a decrease in the ammonia level when the control was compared with the leachate in nature (Fig. 5). Hydrotalcite and reused hydrotalcite removed approximately 35% of ammonia. Activated carbon at two concentrations (LAC_1 and LAC_4) maintained the ammonia levels close to that of the control, indicating that this adsorbent was unable to adsorb ammonia. The *M. oleifera* adsorbents added ammonia to the system, with higher indices than the control.

As hydrotalcite has magnesium and aluminum in its constitution, additional analyses were performed to determine whether excessive amounts of these two elements would be added to the leachate. Fig. 5 shows that treatment with reused hydrotalcite led to an increase in aluminum concentration in the leachate from 0.22 to 4.5 mg/L. The reuse of hydrotalcite may destabilize the adsorbent, causing the

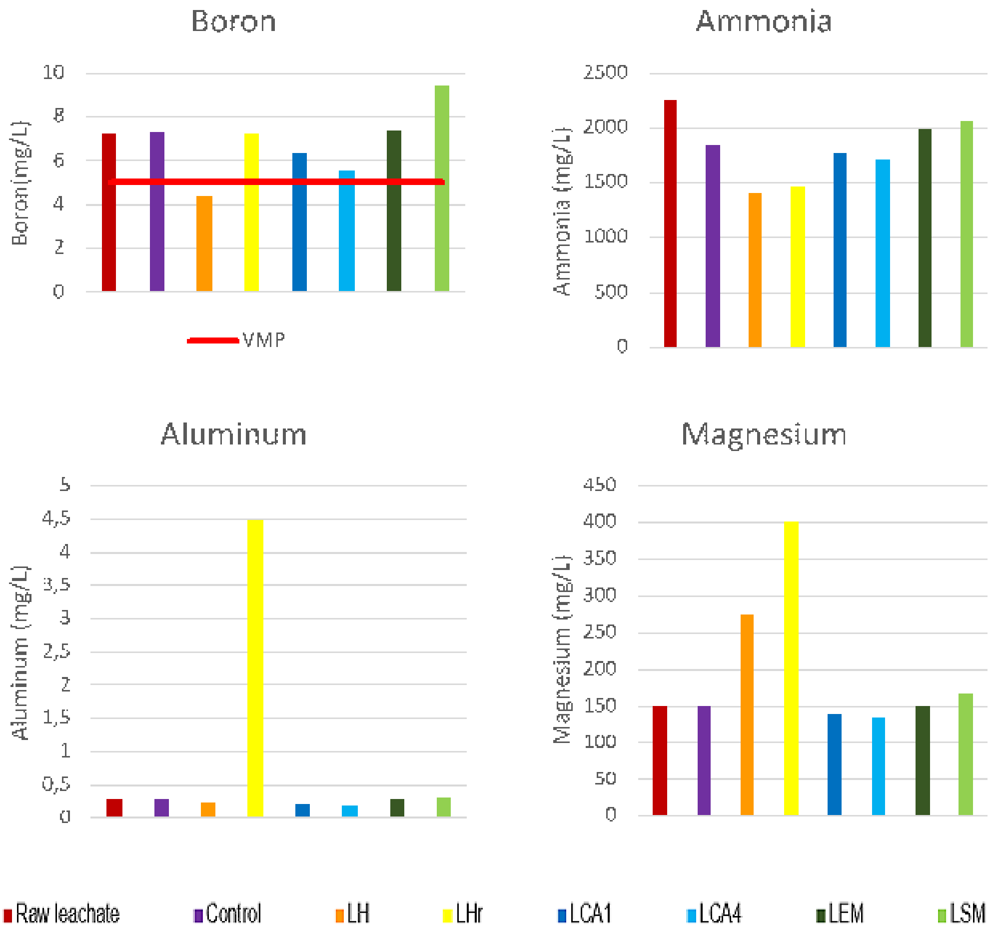

Fig. 5. Results of boron, magnesium, aluminum, and ammonia analysis of the landfill leachate in nature, control (without adsorbent) and treated with hydrotacite (LH), reused hydrotalcite (LHr), *M. oleifera* seed (LMS), *M. oleifera* extract (LME), 1% activated carbon (LAC$_1$) and 4% activated carbon (LAC$_4$).

release of the aluminum contained in its octahedral structure. With the other adsorbents, including hydrotalcite, aluminum levels remained close to that of the control. An increase in magnesium was found in the treatments with the two types of hydrotalcite, with the higher index found when the reused hydrotalcite was employed (400 mg/L).

None of the adsorbents analyzed removed chlorides or sodium efficiently. Souza [40] found that hydrotalcite was able to remove the anions F$^-$, SO$_4^{-2}$and PO$_4^{-3}$, but not Cl$^-$, Br$^-$ or NO$_3^-$. Competition between anions for the hydrotalcite adsorption sites leads to less removal. The site preference was for the anion with the highest effective load, which is in agreement with data described by Das et al. [41] and Tong et al. [42]. Due to the complex composition of the leachate, this type of competition must also occur.

3.5. Landfill leachate toxicity tests with D. similis

A bioindicator test was performed to evaluate the toxicity of the leachate studied. The results of the acute toxicity test showed that, despite the efficiency of the adsorbents regarding the reduction of important variables, none was able to decrease the toxicity to *D. similis* (Table 6).

The EC$_{50}$ of the treatments was around 1.75, showing a small improvement over the control, but still demonstrating a high level of toxicity.

4. Conclusions

The characterization of the landfill leachate demonstrated that the variables that increase toxicity and are in disagreement with legislation were maintained in the four samples tested, regardless of the analyzed period (dry or rainy). Low values were found for heterotrophic bacteria and fungi, indicating that the conditions of this leachate do not favor microbiological growth and could therefore hinder biological treatment. Total coliforms and *E. coli* values were above those permitted for receiving bodies of water. The physicochemical analysis demonstrated high conductivity, color, turbidity, COD, BOD$_5$, ammonia, boron, sodium and chlorides.

The treatment with hydrotalcite achieved the best results regarding reductions in conductivity, turbidity, COD, BOD$_5$, boron and ammonia as well as the second best result regarding the removal of color from the leachate. While pH was increased, the value was within the limit permitted by legislation.

Table 6
Results of toxicity test with *Daphnia similis* with landfill leachate control (without adsorbent) and treated with hydrotacite (LH), reused hydrotalcite (LHr), *M. oleifera* seed (LMS), *M. oleifera* extract (LME), 1% activated carbon (LAC_1) and 4% activated carbon (LAC_4)

	EC_{50}[a]
Control	1.23
LH	1.78
LHr	1.75
LAC_1	1.76
LAC_4	1.73
LMS	1.77
LME	1.73

[a] EC_{50}: minimum concentration capable of causing harmful effect in 50% of test organisms.

Reused hydrotalcite achieved good results regarding reductions in conductivity, color, turbidity, BOD_5 and ammonia, although its efficiency was lower than hydrotalcite and 4% activated carbon. Moreover, reused hydrotalcite was unable to remove boron from the leachate and both aluminum and magnesium levels were increased.

The use of 4% activated carbon resulted in better color and COD removal rates and adequate reductions in conductivity, turbidity and BOD_5, but did not remove boron or ammonia satisfactorily. Treatment with 1% activated carbon achieved similar results, but with less reduction.

When compared with the other adsorbents, treatments with *M. oleifera* seed and extract were less efficient. This type of adsorbent produces important results for the treatment of water, but is not indicated for the treatment of landfill leachate.

All adsorbents were able to decrease the amount of heterotrophic bacteria approximately 10-fold, except the *M. oleifera* extract, for which the count remain close to the control. Total coliforms and *E. coli* did not resist the treatments.

The adsorbents were not able to remove sodium or chloride from the leachate or to reduce the toxicity to *D. silmilis*.

This is a preliminary study that evaluated the possibility of using adsorbents for the treatment of landfill leachate. Hydrotalcite proved to be very efficient in the improvement of several variables; however, further studies are needed to determine methods for the effective removal of the toxicity of the leachate.

Acknowledgments

The authors are grateful to Rio Claro City Hall for the permission to collect the landfill leachate samples. This work was financially supported by CAPES.

References

[1] S. Renou, J.G. Givaudan, S. Poulain, F. Dirassouyan, P. Moulin, Landfill leachate treatment: review and opportunity, J. Hazard. Mater., 150 (2008) 468–493.

[2] I. Nascimento Filho, C. Von Mühlen, E.B. Caramão, Estudo de compostos orgânicos em lixiviado de aterros sanitários por EFS e CG/EM, Quim. Nova, 24 (2001) 554–556.

[3] N.K. Lazaridis, D. D. Asouhidou, Kinetics of sorptive removal of chromium (VI) from aqueous solutions by calcined Mg–Al–CO_3 hydrotalcite, Water Res., 37 (2003) 2875–2882.

[4] A. Béres, I. Pálinkó, I. Kiricsi, J.B. Nagy, Y. Kiyozumi, F. Mizukami, Layered double hydroxides and their pillared derivatives–materials for solid base catalysis; synthesis and characterization, Appl. Catal., A, 182 (1999) 237–247.

[5] Y. Seida, Y. Nakano, Removal of phosphate by layered double hydroxides containing iron, Water Res., 36 (2002) 1306–1312.

[6] L.D. Conceição, S.B. Pergher, C.C. Moro, L.C. Oliveira, Magnetic composites based on hydrotalcites for removal of anionic contaminants in water, Quím. Nova, 30 (2007) 1077–1081.

[7] L. Costa, C. Ladeira, A. Colli Badino, Overproduction of clavulanic acid by extractive fermentation, Electron. J. Biotechnol., 18 (2015) 154–160.

[8] T. Delazare, L.P. Ferreira, N.F. Ribeiro, M.M. Souza, J.C. Campos, L. Yokoyama, Removal of boron from oilfield wastewater via adsorption with synthetic layered double hydroxides, J. Environ. Sci. Health, 49 (2014) 923–932.

[9] T. Wajima, Removal of boron from geothermal water using hydrotalcite, Toxicol. Environ. Chem., 92 (2010) 879–884.

[10] R.V. Karadi, N.B. Gadge, K.R. Alagawadi, R.V. Savadi, Effect of *Moringa oleifera* Lam. root-wood on ethylene glycol induced urolithiasis in rats, J. Ethnopharmacol., 105 (2006) 306–311.

[11] G.L. McConnachie, G.K. Folkard, M.A. Mtawali, J.P. Sutherland, Field trials of appropriate hydraulic flocculation processes, Water Res., 33 (1999) 1425–1434.

[12] A.B. Joly, Botânica: introdução à taxonomia vegetal, Companhia Editora Nacional, São Paulo, 1979.

[13] J.E.S. Paterniani, M.C. Mantovani, M.R. Sant'Anna, Uso de sementes de *Moringa oleifera* para tratamento de águas superficiais, Revista Brasileira de Eng. Agríc. Ambiental, 13 (2009) 765–771.

[14] C.S. Barbosa, S.A.A. Santana, C.W.B. Bezerra, H.A. dos Santos Silva, Remoção de compostos fenólicos de soluções aquosas utilizando carvão ativado preparado a partir do aguapé (*Eichornia crassipes*): estudo cinético e de equilíbrio termodinâmico, Quím. Nova, 37 (2014) 447–453.

[15] Estado de São Paulo, Decreto Estadual nº 8468, de 8 de setembro de 1976: aprova o regulamento da lei nº 997, de 31 de maio de 1976, que dispõe sobre a prevenção e controle da poluição do meio ambiente, Diário Oficial do Estado de São Paulo, São Paulo (SP), 1976.

[16] CETESB, Companhia Ambiental de São Paulo, Norma técnica L. 5.201 – Bactérias Heterotróficas – Contagem em placas: método de ensaio, São Paulo, 1986, p. 26.

[17] Titrations. info. Mohr Method. Available at: http://www.titrations.info/precipitation-titration-argentometry-chlorides-Mohr (Accessed November 2016).

[18] US EPA, Method 7062: Antimony and Arsenic (Atomic Absorption, Borohydride Reduction), part of Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Revision 00, 1994. Available at: https://www.epa.gov/sites/production/files/2015-12/documents/7062.pdf.

[19] US EPA, Method 6010C (SW-846): Inductively Coupled Plasma-Atomic Emission Spectrometry, Revision 3, 2007. Available at: https://www.epa.gov/homeland-security-research/epa-method-6010c-sw-846-inductively-coupled-plasma-atomic-emission.

[20] APHA, Standard Methods for the Examination of Water and Wastewater, 22nd revised ed., American Public Health Association, American Water Works Association, Water Environment Federation, 2012.

[21] US EPA, Method 7470A (SW-846): Mercury in Liquid Waste (Manual Cold-Vapor Technique), Revision 1, 1994. Available at https://www.epa.gov/homeland-security-research/epa-method-7470a-sw-846-mercury-liquid-wastes-manual-cold-vapor-technique.

[22] US EPA, Method 300.1: Determination of Inorganic Anions in Drinking Water by Ion Chromatography, Revision 1.0, 1997. Available at https://www.epa.gov/homeland-security-research/epa-method-3001-revision-10-determination-inorganic-anions-drinking-water.

[23] E.L. Crepaldi, J.B. Valim, Hidróxidos duplos lamelares: síntese, estrutura, propriedades e aplicações, Quím. Nova, 21 (1998) 300–311.

[24] T. Okuda, A.U. Baes, W. Nishijima, M. Okada, Isolation and characterization of coagulant extracted from *Moringa oleifera* seed by salt solution, Water Res., 35 (2001) 405–410.

[25] A.T. Ribeiro, Aplicação da *Moringa oleifera* no tratamento de água para consumo humano, Remoção de poluentes por coagulação-floculação, (2012) 69f, Dissertação de mestrado – Universidade do Porto, Faculdade de Engenharia, 2012.

[26] S. Katayon, M.J. Megat Mohd Noor, M. Asma, L.A. Abdul Ghani, L.A. Thamer, I. Azni, J. Ahmad, B.C. Khor, A.M. Suleyman, Effects of storage conditions of *Moringa oleifera* seeds on its performance in coagulation, Biorsour. Technol., 97 (2006) 1455–1460.

[27] D.C. Costa, F.A. Medeiros Rodrigues, G.A. Thurler Fontoura, J.C. Campos, M. Dezotti, Tratamento do efluente de uma indústria química pelo processo de lodos ativados convencional e combinado com carvão ativado, Eng. Sanit. Ambiental, 8 (2003) 274–284.

[28] R.C. Tomasella, E.G. de Oliveira, D.F. de Angelis, M.L. Garcia, Avaliação do potencial de compostos naturais (argila, turfa e carvão) na remoção do chumbo (Pb) e da toxicidade de um efluente industrial, Eng. Sanit. Ambiental, 20 (2016) 251–258.

[29] ABNT, Associação Brasileira de Normas Técnicas, NBR 12713:2016 Ecotoxicologia Aquática – Toxicidade aguda – Método de ensaio com *Daphnia* spp. (Crustacea, Cladocera), Rio de Janeiro, 2016, p. 21.

[30] AGSOLVE, Como e porque medir a Condutividade Elétrica com sondas muiltiparâmetros. Available at https://www.agsolve.com.br/noticias/como-e-porque-medir-a-condutividade-eletrica-ce-com-sondas-muiltiparametros (Accessed November 2016).

[31] C.N. Oliveira, V.P. Campos, Y.D. Pinto Medeiros, Avaliação e identificação de parâmetros importantes para a qualidade de corpos d'água no semiárido baiano, Estudo de caso: bacia hidrográfica do rio Salitre, 2010.

[32] SABESP, Companhia de saneamento básico de São Paulo, Qualidade de água. Available at http://site.sabesp.com.br/site/interna/Default.aspx?secaoId=40 (Accessed November 2016).

[33] C. Amor, E. De Torres-Socías, J.A. Peres, M.I. Maldonado, I. Oller, S. Malato, M.S. Lucas, Mature landfill leachate treatment by coagulation/flocculation combined with Fenton and solar photo-Fenton processes, J. Hazard. Mater., 286 (2015) 261–268.

[34] A.E. Domingos, Avaliação do meio ambiente de Santa Gertrudes – SP e propostas para uma agenda local. 2004. vii, 144 f. Dissertação de mestrado – Universidade Estadual Paulista, Instituto de Geociências e Ciências Exatas, 2004.

[35] CETESB, Companhia Ambiental do Estado de São Paulo, Qualidade das águas interiores no estado de São Paulo, Significado ambiental e sanitário das variáveis de qualidade das águas e dos sedimentos e metodologias analíticas e de amostragem, 2009 p. 43.

[36] WHO, Guidelines for Drinking-Water Quality: Recommendations, World Health Organization, 2004.

[37] Brasil, Portaria nº 2914 de 12 de dezembro de 2011, Ministério da Saúde, Brasília, 2011.

[38] H. Hashemi, Y. Hajizadeh, M.M. Amin, B. Bina, A. Ebrahimi, A. Khodabakhshi, A. Ebrahimi, H.R. Pourzamani, Macropollutants removal from compost leachate using membrane separation process, Desal. Wat. Treat., 57 (2016) 7149–7154.

[39] H. Farrokhzadeh, E. Taheri, A. Ebrahimi, A. Fatehizadeh, M.V. Dastjerdi, B. Bina, Effectiveness of *Moringa oleifera* powder in removal of heavy metals from aqueous solutions, Fresenius Environ. Bull., 22 (2013) 1516–1523.

[40] L.G. Souza, Estudo da remoção de ânions de soluções aquosas por meio de sorção em hidróxidos duplos lamelares, Dissertação de mestrado, Universidade Federal do Rio de Janeiro, Escola de Química, 2008, 132 p.

[41] J. Das, B.S. Patra, N. Baliarsingh, K.M. Parida, Adsorption of phosphate by layered double hydroxides in aqueous solutions, Appl. Clay Sci., 32 (2006) 252–260.

[42] X. Tong, Z. Yang, P. Xu, Y. Li, X. Niu, Nitrate adsorption from aqueous solutions by calcined ternary Mg-Al-Fe hydrotalcite, Water Sci. Technol., 75 (2017) 2194–2203.