Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2022.28125

248 (2022) 111–123
February

Adsorption of pollutants in sanitary landfill leachate using granular activated carbon and bentonite clay

Naiara Angelo Gomes[a,*], Elisângela Maria da Silva[a], Luisa Thaynara Muricy de Souza Silva[a], Danilo Brito da Costa[a], William de Paiva[b], Veruschka Escarião Dessoles Monteiro[a], Márcio Camargo de Melo[a]

[a]*Department of Civil Engineering, Federal University of Campina Grande, Paraíba, Brazil, emails: naiaraangeloccta@gmail.com (N.A. Gomes), elisa_maria18@hotmail.com (E.M. Silva), luisa.muricy12@gmail.com (L.T.M.S. Silva), danilo.b.costa@hotmail.com (D.B. Costa), veruschkamonteiro@hotmail.com (V.E.D. Monteiro), melomc90@gmail.com (M.C. Melo)*
[b]*Department of Sanitary and Environmental Engineering, Paraíba State University, Brazil, email: w.paiva461@gmail.com (W. Paiva)*

Received 5 August 2021; Accepted 30 December 2021

ABSTRACT

Organic and inorganic pollutants in sanitary landfill leachates are harmful to the environment and human health and must be removed before reaching receptive waterbodies. Thus, this study aimed to determine the adsorption capacity of granular activated carbon (GAC) mixed with bentonite clay (BC) for the removal of chemical oxygen demand (COD), ammoniacal nitrogen ($N–NH_3$), and total chromium (Cr) from the leachate generated in the Sanitary Landfill of Campina Grande, Paraíba, Brazil. Different compositions of these materials were tested, and the best one was determined based on central composite rotational design (CCRD) type 2^2. From this result, batch adsorption tests (isotherm and kinetics) were conducted using an adsorbing material:leachate ratio of 1:10, agitated at 130 rpm at 26°C ± 2°C. The isothermal behavior of the adsorption process was evaluated using linear, Langmuir, and Freundlich models, whereas the sorption mechanisms and rates were evaluated by pseudo-first-order and pseudo-second-order kinetic models. The CCRD results indicated that the best composition for the batch adsorption tests was 75% GAC + 25% BC. The maximum adsorption capacities obtained were approximately 29.00, 2.60, and 0.78 mg g^{-1} and the removal efficiencies were 80%–94%, 16.8%–30.4%, and 96.7%–99.7%, for COD, $N–NH_3$, and Cr, respectively. The Freundlich model exhibited the best adjustment for COD, $N–NH_3$, and Cr. Moreover, the pseudo-first-order kinetic model exhibited an acceptable adjustment only to COD, whereas the pseudo-second-order kinetic model was better adjusted to $N–NH_3$, and Cr results.

Keywords: Adsorption isotherms; Adsorption kinetics; Removal efficiency; Chemical oxygen demand; Ammoniacal nitrogen; Chromium

---

1. Introduction

The leachate of sanitary landfills contains several pollutants that are harmful to the environment and to public health [1–3], such as organic matter, ammoniacal nitrogen ($N–NH_3$), and heavy metals [4]. Thus, before disposal in water bodies, the leachate must be treated to reach the necessary conditions to avoid contamination. However, the adequate treatment of leachate is an expensive process that needs to be environmentally sustainable, which is a challenge for environmental sanitation professionals and sanitary landfill managers [5–7].

The disposal of inadequately treated leachate in the environment negatively impacts the soil and surface and groundwater [8–10] and may impact public health and the

---

* Corresponding author.

quality of life of the population [11]. Studies indicate that leachate pollutants produce cumulative and harmful effects to the growth of aquatic organisms, food chains disturbances, and severe public health problems, such as carcinogenic effects, acute toxicity, and genotoxicity [12–14]. Several studies have focused on different treatments (physical–chemical, biological, or their combination) to minimize the aforementioned impacts [1,15–22].

In the Sanitary Landfill of Campina Grande (SLCG), Paraíba State (PB), Brazil, the leachate undergoes natural evaporation and recirculation to cells in operation, which results in an effluent with high concentrations of chemical oxygen demand (COD), ammoniacal nitrogen ($N–NH_3$), and total chromium (Cr), in disagreement with the current environmental laws [6]. A frequently applied treatment to the reduction of COD, $N–NH_3$, and Cr concentrations in sanitary landfill leachates is the adsorption by activated carbon (AC) [7,11,23–26]. However, AC has a high cost and requires for periodical reactivations [14,27]. To address these issues, several low-cost adsorbents have been utilized, such as bentonite clay (BC) [28–32].

BC has a high cationic exchange capacity (CEC) and specific surface [33–35]; in addition, BC is a low-cost material available in several regions worldwide [36], which favors its use in the removal of heavy metals from aqueous systems [37,38]. In this regard, the city of Boa Vista, 17 km distant from the SLCG, is one of the main producers of BC in Brazil [39]. In contrast, AC is efficient in the removal of organic pollutants in aqueous phase [23,40,41] and can also reduce the amount of heavy metals when applied in the correct dosage [26].

Most part of the available studies focused on evaluating the adsorption of AC and BC individually [26,32,42–47], mainly utilizing synthetic solutions. Chen et al. [29] investigated the adsorption behavior of Cr^{3+} in aqueous solution by Gaomiaozi bentonite and obtained a maximum adsorption capacity of 4.68 mg g^{-1} at a pH 7 and equilibrium time of 120 min. Baylan and Meriçboyu [48] verified the adsorption of metals (Pb^{2+} and Cu^{2+}) in simple and binary solutions with bentonite and AC from grape seeds and observed that AC had a lower adsorptive capacity compared to that of bentonite. Mohammad-Pajooh et al. [26] evaluated the efficiency and adsorptive performance of several types of granular activated carbon (GAC) in the removal of COD and metals to identify the ideal experimental conditions and determine future strategies for leachate treatment. Ferraz and Yuan [46] used AC from spent coffee grounds to remove COD from synthetic and real leachates in adequate conditions (adsorbent dosage: 20 g L^{-1}, pH 4, temperature: 20°C) and obtained a removal percentage above 90% using real leachate.

Considering the exposed, studies evaluating the combined use of GAC and BC in an adequate dosage to the treatment of leachate pollutants from sanitary landfills, as well isotherm and kinetics adsorption studies, are still scarce, particularly in Brazilian semiarid regions. Therefore, this study aimed to investigate the adsorptive process of commercial GAC combined with calcium BC for the removal of COD, $N–NH_3$, and Cr from the leachate generated in the SLCG, such as to reduce the cost of the adsorption process and provide technical and scientific criteria to help professionals in the decision process related to the treatment of this effluent.

2. Materials and methods

2.1. Characterization of the sanitary landfill leachate

The leachate used in this study was collected in the SLCG (Fig. 1). This landfill has an area of 64 ha and started operating in July 2015 (age > 5 y); during this study, it received approximately 600 t d^{-1} of urban solid waste (USW) from 57 cities. In addition, it is located in the Brazilian semiarid region, which is characterized by: (i) average annual precipitation of 800 mm; (ii) aridity index up to 0.5; (iii) high risk of drought or extension of the dry season (>60%) [49]. Considering water resources, there is an intermittent natural watercourse in the direct influence area of this landfill, classified as class 3 according to resolution n° 357 of March 17, 2005 of the National Environment Council (CONAMA) [50].

The SLCG leachate was collected in April 2021. Approximately 5 L of effluent were collected from the leachate treatment lagoon No. 1 (L1) (Fig. 1), following the protocols recommended by the American Public Health Association (APHA), American Water Works Association (AWWA), and Water Environment Federation (WEF) [51]. The L1 has dimensions of 25 m × 36 m × 3 m (width, length, and depth), and stores the in nature effluent generated by all the USW confined in the SLCG, such that it evaporates.

After collecting, the leachate was transported to the Environment Geotechnics Laboratory (LGA) of the Federal University of Campina Grande (UFCG), in which tests of pH (method 4500-H^+), COD (method 5220 C), $N–NH_3$ (method 4500-NH_3 C), and Cr (method 3111 B) were conducted following the procedures of APHA, AWWA, and WEF [51].

2.2. Dosage of adsorbing materials

Commercial GAC and calcic BC were investigated for the removal of COD, $N–NH_3$, and Cr from the leachate collected at SLCG. The GAC was produced from the carbonization of wood, and had a grain size ranging from 1 to 4 mm. The BC was extracted from a quarry located in Boa Vista, Paraíba, and provided by the company Bentonit União Nordeste Industria e Comércio LTDA, with particles sizes ranging from 0.03 to 56 μm.

Several tests were conducted to characterize the commercial GAC and calcic BC, such as pH_{water}, pH_{KCl}, CEC [52], chemical composition by energy-dispersive X-ray fluorescence (EDX) (spectrometer Shimadzu, model EDX-720), and mineralogical composition by X-ray diffraction (DRX, Shimadzu, model XRD-6000).

An adsorption test was conducted for three compositions of GAC and BC with different proportions (m/m) using the central composite rotational design (CCRD) type 2^2, using software STATISTICA 12.0. The CCRD enabled to determine the removal efficiency for COD, $N–NH_3$, and Cr, and define the best dosage of adsorbent materials for the batch adsorption tests (isotherm and kinetics).

For the CCRD, the BC content and the reaction time (RT) were set as independent variables, whereas the removal

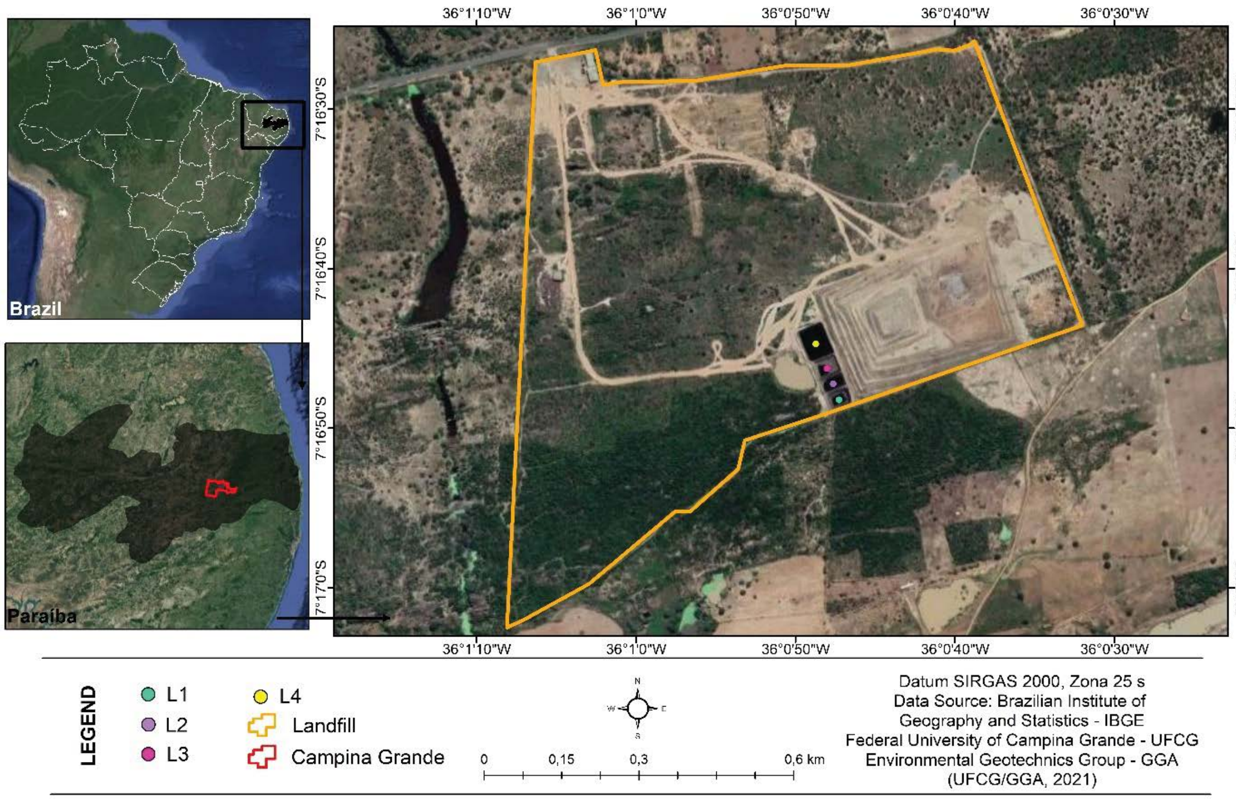

Fig. 1. SLCG location.

percentages of COD, N–NH_3, and Cr were set as dependent variables. The inferior and superior limits of the independent variables were 15% and 25% for the BC content and 25 and 120 min for the RT, respectively, which were set based on other studies [23,48,53,54].

Thus, the CCRD had two factors and two levels, with four axial points (P_A) and the triplicate of the central point (P_C) to ensure the reproducibility of the experimental data. A total of 11 tests were conducted, and the responses were the removal efficiencies of COD, N–NH_3, and Cr. Tables 1 and 2 present the variables and levels of CCRD and the test planning, respectively. The values –1, 0, +1, and ±1.41 refer to the inferior limit, P_C, superior limit, and P_A, respectively.

For the CCRD, suspensions were prepared in 125 mL Erlenmeyer flasks, with 10 g of the adsorbing compositions and 100 mL of the collected leachate, resulting in an absorbing material:leachate ratio of 1:10. In sequence, the suspensions were shaken (shaker table SOLAB, model SL 180) at 130 rpm and 26°C ± 2°C. In pre-established times (Table 1), the Erlenmeyer flasks were removed from the shaker table and let still for 30 min, to enable sedimentation of the solid fraction. In sequence, portions of the supernatant were pipetted to determine the corresponding COD, N–NH_3, and Cr concentrations, following the procedures of APHA, AWWA, and WEF [51]. The removal efficiency of these pollutants was calculated using Eq. (1):

$$\mathrm{RE}(\%) = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}$$

Table 1
Variables and levels defined for CCRD

Factors	Levels				
	–1.41	–1	0	+1	+1.41
BC content (%)	12.9	15.0	20.0	25.0	27.1
RC (min)	5.3	25.0	72.5	120.0	139.7

where RE is the removal efficiency (%), and C_0 and C_e are the initial and final concentrations (mg L^{-1}), respectively.

Although COD and N–NH_3 concentrations were analyzed, the composition for the batch adsorption tests (isotherm and kinetics) was determined based on the results for the removal of Cr, because of the higher affinity of the studied materials to adsorb cations. Detho et al. [7], Daud et al. [11] and Rosli et al. [55] also used a similar criterium to determine the best composition to be used for the batch adsorption test.

2.3. Batch adsorption test – adsorption isotherms

The methodology employed for the batch adsorption tests was adapted from the technical document EPA/530/SW-87/006-F [56] and Directive D4646 [57]. To estimate the adsorptive capacity of COD and N–NH_3, the leachate from SLCG was diluted in distilled water in concentrations (v/v) of 5%, 10%, 20%, 40%, 80%, and 100%, because there was a high concentration of these pollutants. For Cr,

Table 2
CCRD planning matrix

Experiments	Independent variables		Dependent variables		
	BC content (%)	RT (min)	COD removal (%)	$N–NH_3$ removal (%)	Cr removal (%)
1	–1	–1	R1	R1	R1
2	–1	1	R2	R2	R2
3	1	–1	R3	R3	R3
4	1	1	R4	R4	R4
5	–1.41	0	R5	R5	R5
6	1.41	0	R6	R6	R6
7	0	–1.41	R7	R7	R7
8	0	1.41	R8	R8	R8
9	0	0	R9	R9	R9
10	0	0	R10	R10	R10
11	0	0	R11	R11	R11

R: Response.

synthetic leachates (SL) were prepared from the dissolution of chromium(III) chloride analytical reagent grade ($CrCl_3·6H_2O$) in distilled water. Initially, a standard solution was prepared with 1 g L^{-1} of Cr. From this solution, pre-determined volumes, determined using stoichiometric calculations, were pipetted to prepare SL solutions with concentrations of 0.2, 7.0, 17.0, 33.0, 62.0, and 82.0 mg L^{-1}, named $SL_{0.2}$, $SL_{7.0}$, $SL_{17.0}$, $SL_{33.0}$, $SL_{62.0}$, and $SL_{82.0}$, respectively. As the pH of these solutions was below 6, which is the value recommended in D4646 [57], no correction was necessary. Although the Cr contents adopted were higher than those reported in the literature for sanitary landfill leachates [8,58], this extrapolation was necessary to evaluate the adsorption behavior and enable the measurement of this element by atomic absorption spectrometry (AAS, spectrometer Agilent, model AA240) after contact with the adsorbing material.

As the leachate studied had Ni (0.21–0.37 mg L^{-1}) and Cu (1.22–1.34 mg L^{-1}) [6] contents higher than the limits set by Brazilian environmental resolutions [50,59], these elements were added to $SL_{0.2}$ and $SL_{82.0}$ in the same concentrations as in Cr, such as to reproduce the ionic competition among these heavy metals. The stock solutions containing 1 g L^{-1} of nickel (N^{2+}) and copper (Cu^{3+}) were prepared with nickel(II) nitrate ($Ni(NO_3)_2·6H_2O$) and copper(II) chloride ($CuCl_2·2H_2O$) analytical reagent grade.

The batch adsorption tests were conducted by mixing 2 g of the combination of GAC and BC and 20 mL of the natural leachate or $SL_{0.2}$–$SL_{82.0}$ in 125 mL Erlenmeyer flasks, which were sealed with Parafilm and placed in a shaker table (SOLAB, model SL 180) at 130 rpm and 26°C ± 2°C during 24 h.

After the equilibrium time set (24 h), the suspensions were transferred from the Erlenmeyer flasks to 50 mL Falcon tubes and centrifuged (Centrifuge Novatecnica, model NT 815), at 605 g during 15 min. The resulting supernatants were filtered in a 0.45 µm membrane and the corresponding COD, $N–NH_3$, and Cr concentrations were determined, following the methods indicated by APHA, AWWA, and WEF [51]. The amount of solute (COD, $N–NH_3$, and Cr) adsorbed in the composition of commercial GAC and calcium BC was determined by Eq. (2):

$$q = \frac{\left(C_0 - C_e\right) \cdot V}{M} \tag{2}$$

where q is the adsorption capacity (mg g^{-1}), C_0 is the initial solute concentration, before exposure to the adsorbing material (mg L^{-1}), C_e is the equilibrium solute concentration, after exposure to the absorbing material (mg L^{-1}), M is the dry mass of the absorbing material (g), and V is the volume of the solution (L).

Based on the results of the batch adsorption tests, the experimental isotherms were plotted and adjusted by the theoretical models of linear adsorption, Langmuir, and Freundlich, as shown in Eqs. (3)–(5), respectively, using Excel 2019 and STATISTICA 12.0. The best model was chosen based on the analysis of the determination coefficient (R^2) and the sum of squared residuals (SSR).

$$q = K_d C_e \tag{3}$$

$$q = \frac{K_L b C_e}{1 + \left(K_L C_e\right)} \tag{4}$$

$$q = K_F C_e^N \tag{5}$$

where q is the adsorption capacity (mg g^{-1}), K_d, K_L, and K_F are the distribution (L g^{-1}), Langmuir (L mg^{-1}), and Freundlich (L g^{-1}) coefficients, respectively, C_e is the equilibrium concentration (mg L^{-1}), b is the maximum adsorption capacity (mg g^{-1}), and N is the slope of the curve, which reflects the sorption intensity with the increase of C_e (–).

2.4. Batch adsorption test – adsorption kinetics

The kinetics study was conducted for the combination GAC + BC with the highest removal percentage of Cr determined using CCDR. The methodology employed was similar to that in the isotherm study, in which the leachate from SLCG (characteristics in Table 3) was used for COD and N–NH_3, whereas $LS_{82.0}$ was used for Cr. Thus, 10 g of the adsorptive composition and 100 mL of the contaminant liquid (leachate with pH = 8.28 or $LS_{82.0}$ with pH = 3.37) were mixed in 125 mL Erlenmeyer flasks. In sequence, the mixture was agitated at 130 rpm during 5–200 min [60–62] at 26°C ± 2°C using a shaker table. In specific time intervals, the solutions were extracted and centrifuged at 605 g during 15 min. The COD and N–NH_3 were determined by the methods 5220 C and 4500-NH_3 C, respectively [51]. The measurement of the remaining Cr^{3+} was conducted by AAS (method 3111 B) [51].

Pseudo-first-order [Eq. (6)] [63] and pseudo-second-order [Eq. (7)] [64] kinetic models were adjusted to the experimental data to analyze the sorption rates and mechanisms of COD, N–NH_3, and Cr^{3+}:

$$\log\left(q_e - q_t\right) = \log\left(q_e\right) - \left(\frac{K_1}{2.303}\right)t \tag{6}$$

$$\frac{t}{q_t} = \left(\frac{1}{K_2 q_e^2}\right) + \left(\frac{1}{q_e}\right)t \tag{7}$$

where q_e and q_t are the adsorption capacities in equilibrium and time (mg g^{-1}), respectively, for COD, N–NH_3, and Cr^{3+}; t is the time (min); K_1 is the constant rate of pseudo-first-order (min^{-1}), determined from the slope of log(q_e – q_t) vs. t; and K_2 is the constant rate of pseudo-second-order (g mg^{-1} min^{-1}), calculated from the graph of t/q_t vs. t.

3. Results and discussion

3.1. Leachate characterization

The characterization of the leachate from the SLCG is presented in Table 3.

Table 3
Characterization of leachate from the SLCG

Indicator/Parameter	Values
pH	8.28
COD (mg L^{-1})	4,022.99
N–NH_3 (mg L^{-1})	1,512.00
Cr (mg L^{-1})	0.71

The characteristics of the studied leachate are typical of the methanogenic phase of USW degradation, as indicated by Souto and Povinelli [58]. The effluent has an alkaline pH and Cr concentration of 0.71 mg L^{-1}. pH values ranging from neutral to alkaline contribute to reducing the leaching of heavy metals in sanitary landfills [6,65]. The Cr content was lower than those obtained by Tsarpali et al. [66], Narayan et al. [67], and Chaouki et al. [68]. In contrast, the concentration was 14 times higher than the maximum concentration set by resolution n° 357 [50] for freshwater bodies class 3. Moreover, COD and N–NH_3 concentrations were 4,022.99 and 1,512.00 mg L^{-1}, respectively, and the N–NH_3 content was higher than the reference values set by Brazilian environmental resolutions n° 357 and 430 [50,59].

Thus, the disposal of this effluent in waterbodies can alter the water quality [67] and pollute surface and groundwater [69]. The toxicity of gaseous ammonia (NH_3) causes damages to cell tissues and potential risks to the human health and affects aquatic species [70,71].

3.2. Characterization of adsorptive materials

The chemical composition of GAC and BC is presented in Table 4. Both GAC and BC had as major oxides silicon dioxide (SiO_2), aluminum oxide (Al_2O_3), and iron oxide (Fe_2O_3). Low percentages of potassium (K_2O), magnesium (MgO), calcium (CaO), phosphorus (P_2O_5), titanium (TiO_2), sulfur (SO_3), and tungsten (WO_3) oxides were also obtained.

Table 4
Chemical composition of adsorptive materials

Elements	GAC (%)	BC (%)
SiO_2	63.71	61.50
Al_2O_3	10.70	20.58
Fe_2O_3	8.87	11.11
MgO	2.22	3.08
CaO	3.61	1.37
P_2O_5	2.38	ND
K_2O	5.90	0.66
TiO_2	0.76	1.26
SO_3	1.40	0.28
WO_3	0.29	ND
Other oxides	0.16	0.16

ND: Not detected.

Some of the properties of BC are listed in Table 5. As observed, the pH_{water} value was higher than the pH_{KCl} value, resulting in ΔpH = –0.98. This result indicates the predominance of negative charges in the surface of bentonite particles, favoring the adsorption of cations. The GAC had a ΔpH of 0.63 (pH_{water} = 9.39 and pH_{KCl} = 10.02), indicating the prevalence of anionic exchange. However, the GAC + BC composition in the proportion 3:1, employed in the adsorption test (isotherm and kinetics) and defined based on CCDR, exhibited a ΔpH = –0.49. The CEC of BC was 66.73 cmol kg^{-1}, with interlaying cations consisting mainly of Mg^{2+} and Ca^{+}, and in lower concentrations, Na^{+} and K^{+}, which can be easily exchanged by other cationic ions [72], such as NH_4^+ and heavy metals, resulting in the reduction of their content in liquid media.

The DRX test (Fig. 2) was conducted to evaluate the mineralogical properties of the adsorbents. The GAC spectrum exhibited an amorphous halo, with quartz peaks (Q) at 2θ = 20.70°, 26.51°, and 36.36°. For BC, montmorillonite (M) was detected in a content of 73.9% (2θ = 5.84°, 17.60°, 19.60°, 36.50°, and 54.26°), quartz with 11.5% (2θ = 20.83°, 26.61°, 34.45°, and 45.75°), and traces of vermiculite, albite, and feldspar. Mohajeri et al. [72] indicated that the high CEC of bentonite is a result of the high content of montmorillonite, which is responsible for its adsorptive capacity for heavy metals. Because of the water absorption in the layers

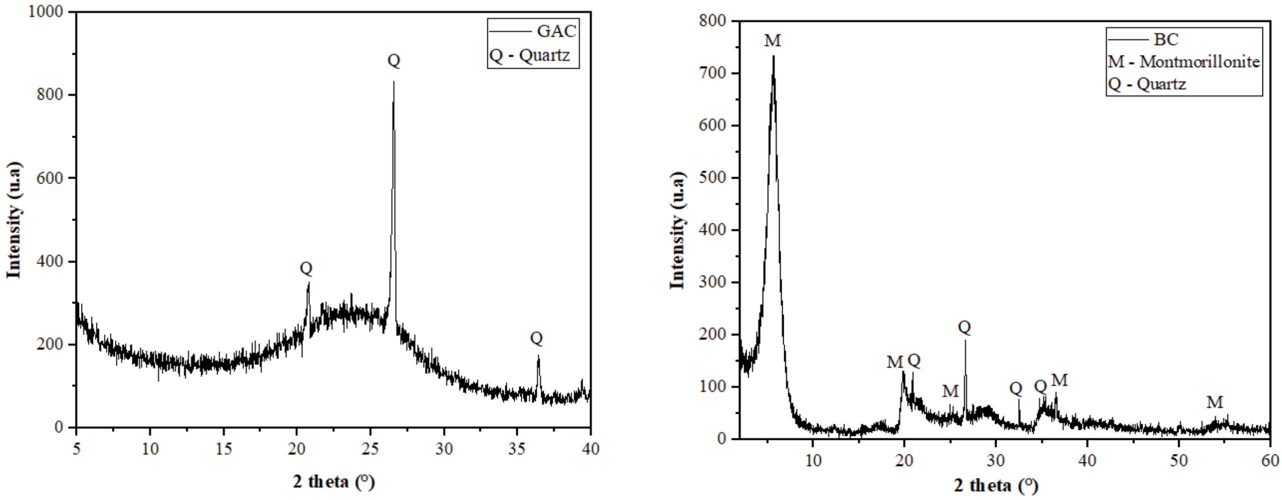

Fig. 2. DRX spectra of CAG and BC.

of this clay mineral, leading to a considerable swelling, the metal ions are adsorbed in the internal and external surfaces owing to the arrangement of Al–O and Si–O groups and the cationic exchange mechanism, respectively [60,61].

3.3. Dosage of adsorptive materials

Table 6 presents the results of the CCRD. The removal efficiencies varied from 10.0% to 42.9% for COD, 5.0%–12.5% for N–NH_3, and 45.2%–69.0% for Cr for the different experimental conditions analyzed. The higher removal percentages in the RTs considered in the CCRD were achieved for Cr, reaching a value of 69.0% in experiment 6 (Table 6) for the composition 72.9% GAC + 27.1% BC. As observed, the Cr removal was directly proportional to the increase in the BC percentage. This behavior may be explained by the availability of sorption sites and the chemical affinity between the Cr^{3+} ions and the predominantly negative surfaces of BC clay minerals [37]. Chen et al. [29] observed that the removal of Cr^{3+} in aqueous solution for a Chinese bentonite was proportional to the increase in the bentonite content, from 79% to 96% when the amount of bentonite increased from 0.4 to 2.0 g in 50 mL of solution. Ray et al. [60] also observed a similar behavior for two Indian bentonites using a synthetic solution of Pb^{2+}, with a gradual increase in the removal from 50.4% to 98.0% (bentonite 1) and from 28.7% to 97.3% (bentonite 2).

The lowest removal percentages were observed for N–NH_3, with no significant relation with the BC content and RT (Table 7). This may have occurred because of the nature of the adsorptive materials employed: the BC has a negative charge and tends to adsorb cations, whereas GAC has an a polar surface because of the high-temperature fabrication process, and exhibits a weak interaction with some polar adsorbents, such as N–NH_3 [23]. Moreover, the GAC surface is hydrophobic, which favors the adsorption of organic substances [23], resulting in higher removal percentages of COD compared to those of N–NH_3.

Table 7 shows the p-values obtained from analysis of variance (ANOVA). From the table, the factors BC content and RT, in both quadratic and linear fractions, had a significant influence ($p < 0.1$) on the removal efficiency of COD, N–NH_3, and Cr. The BC content had a significant influence on the removal of COD, whereas this influence was not significant for N–NH_3 ($p > 0.1$). However, this variable favored the removal of Cr, which was defined as the reference to choose the composition to be adopted to the batch adsorption tests.

Table 5
Properties of BC

Property	BC
pH_{water}	7.82
pH_{KCl}	6.84
Mg^{2+}, cmol kg^{-1}	31.91
Ca^{2+}, cmol kg^{-1}	26.83
Na^{+}, cmol kg^{-1}	7.65
K^{+}, cmol kg^{-1}	0.34
H^{+}, cmol kg^{-1}	0.00
Al^{3+}, cmol kg^{-1}	0.00
CEC, cmol kg^{-1}	66.73
OC, g kg^{-1}	3.60
OM, g kg^{-1}	6.20
EC, µS cm^{-1}	1,300.00

CEC: cationic exchange capacity (CEC); OC: organic carbon; OM: organic matter; EC: electrical conductivity.

Fig. 3 shows the response surfaces, indicating the influence of the variables BC content and RT on the removal efficiencies of COD, N–NH_3, and Cr. For higher BC contents, there was a slight reduction in the removal of COD (Fig. 3a); the increase in RT contributed to higher removal percentages of N–NH_3 (Fig. 3b); the increase in the BC content and RT favored Cr removal (Fig. 3c), reaching efficiencies of 45% to 69%. These results validate the choice of a composition with high BC content (75% GAC + 25% BC) for the batch adsorption tests (isotherm and kinetics).

Table 6
CCRD responses

Experiments	Factors		Responses		
	BC content (%)	RT (min)	COD removal (%)	N–NH$_3$ removal (%)	Cr removal (%)
1	15.00	25.00	14.30	6.30	55.00
2	15.00	120.00	10.00	7.50	62.00
3	25.00	25.00	14.30	12.50	64.80
4	25.00	120.00	28.60	12.50	67.70
5	12.90	72.50	14.30	8.80	62.00
6	27.10	72.50	14.30	5.00	69.00
7	20.00	5.32	14.30	11.30	45.20
8	20.00	139.70	42.90	12.50	65.10
9	20.00	72.50	28.60	6.30	63.60
10	20.00	72.50	35.70	8.80	59.10
11	20.00	72.50	42.80	6.30	61.60

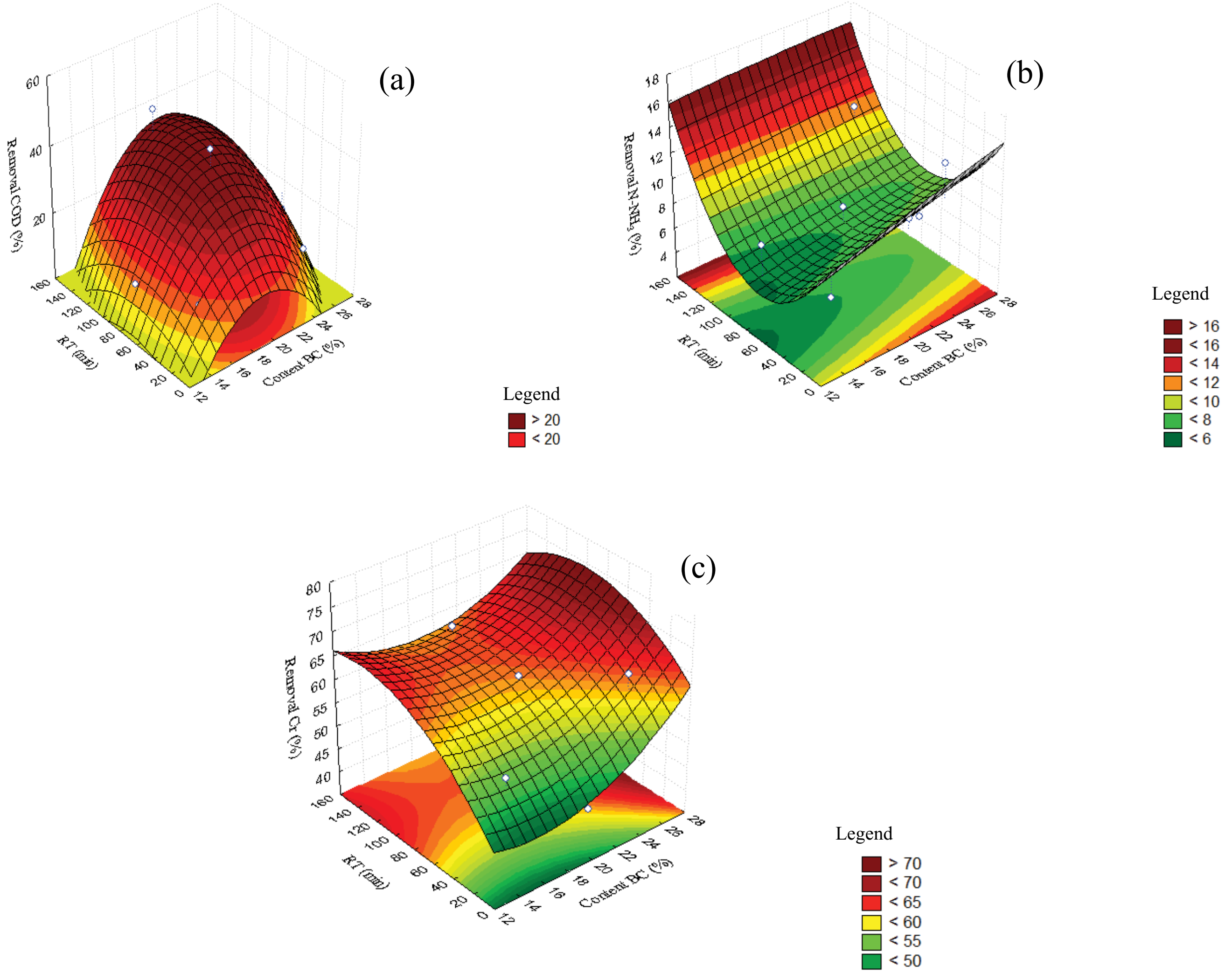

Fig. 3. Response surfaces: (a) COD removal, (b) N–NH$_3$ removal and (c) Cr removal.

Table 7
p-values obtained from ANOVA for CCRD

Variable	DF	*p*-value		
		COD removal (%)	$N–NH_3$ removal (%)	Cr removal (%)
BC content (L)	1	0.4550	0.2790	0.0576
BC content (Q)	1	0.0585	0.9596	0.1134
RT (L)	1	0.1300	0.5331	0.0269
RT (Q)	1	0.2560	0.0546	0.1092
BC content with RT	1	0.3232	0.7045	0.4484
Lack of adjustment	3	0.4587	0.1546	0.2267

DF: Degree of freedom.

The R^2 values for the models analyzed were 0.8048, 0.5320, and 0.8529 for COD, $N–NH_3$, and Cr, respectively, for a significance level of 10% ($p < 0.1$), indicating that approximately 80%, 53%, and 85% of the variability of the removal processes of these pollutants can be explained by the models.

3.4. Batch adsorption test – adsorption isotherm

The experimental isotherms of COD, $N–NH_3$, and Cr adjusted using linear, Langmuir, and Freundlich models, as well as the removal percentages obtained for the composition 75% GAC + 25% BC, are shown in Figs. 4–6. The Langmuir model did not provide a good adjustment for COD and $N–NH_3$; thus, these isotherms were not plotted in Figs. 4a and 5a.

From Figs. 4a, 5a, and 6a, the maximum adsorption capacities experimentally obtained for COD, $N–NH_3$, and Cr were 28.97, 2.59, and 0.84 mg g^{-1}, respectively, and the removal efficiencies (Figs. 4b, 5b, and 6b) were in the ranges 80%–94%, 16.8%–30.4%, and 96.7%–99.7%, respectively. The high removal percentages, particularly for Cr^{3+}, may be related to BC characteristics (Table 5 and Fig. 2), such as the high CEC and montmorillonite content [60,61,72]. Moreover, the high values of adsorption capacity and removal efficiency obtained for COD and Cr^{3+} indicate that these pollutants are less likely to leach and contaminate soils and surface and groundwater [73].

The main removal mechanisms of the pollutants analyzed are physical or chemical adsorption, hydrogen bonds, ionic exchange, and hydrophobic bonds [23,62,72]. Seruga et al. [62] used bentonite with 85% montmorillonite (a higher content than that of the BC in this study) and achieved a $N–NH_3$ removal efficiency of 52.3% after agitation during 180 min at 120 rpm and initial concentration of 0.8 ± 0.2 g L^{-1}. Halim et al. [23] used AC to remove COD and $N–NH_3$ from the leachate of the sanitary landfill Pulau Burung, Malaysia, and obtained maximum adsorptive capacities of 37.88 and 6.08 mg g^{-1}, respectively.

From Figs. 4b, 5b and 6b, the removal efficiencies started to reduce from the third concentration of the leachate from SLCG and SL, which was caused by the increase in the concentrations of COD, $N–NH_3$, and Cr in solution. Thus, the active sites for the adsorption of these pollutants in the adsorbent surfaces were not sufficient [35,74].

Based on the adjustment criteria for the linear, Langmuir, and Freundlich models, presented in Table 8, it is observed that the Freundlich model exhibited the best

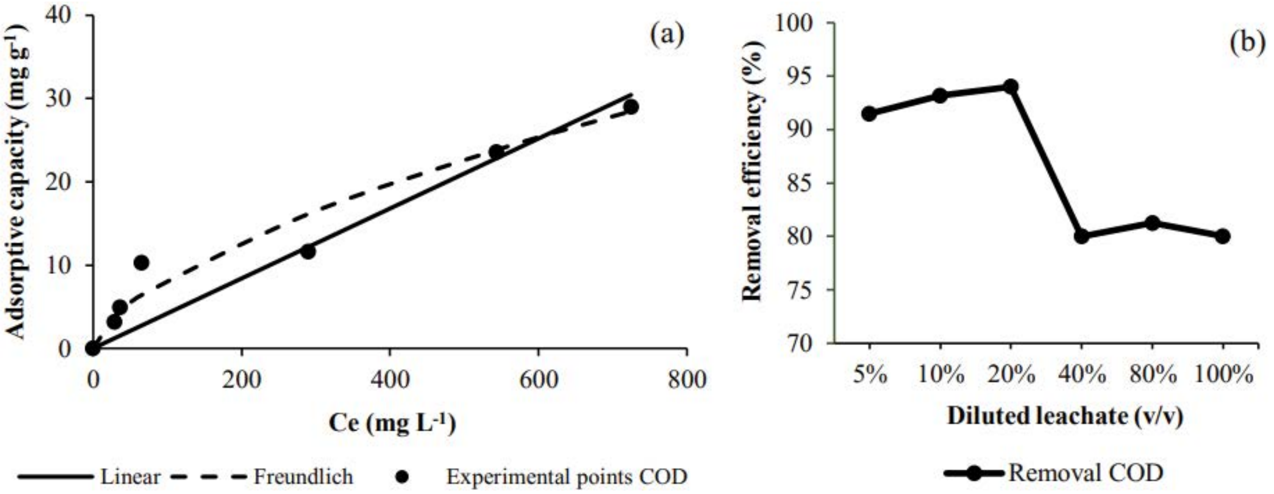

Fig. 4. COD: (a) linear and Freundlich isotherm models (b) removal efficiencies.

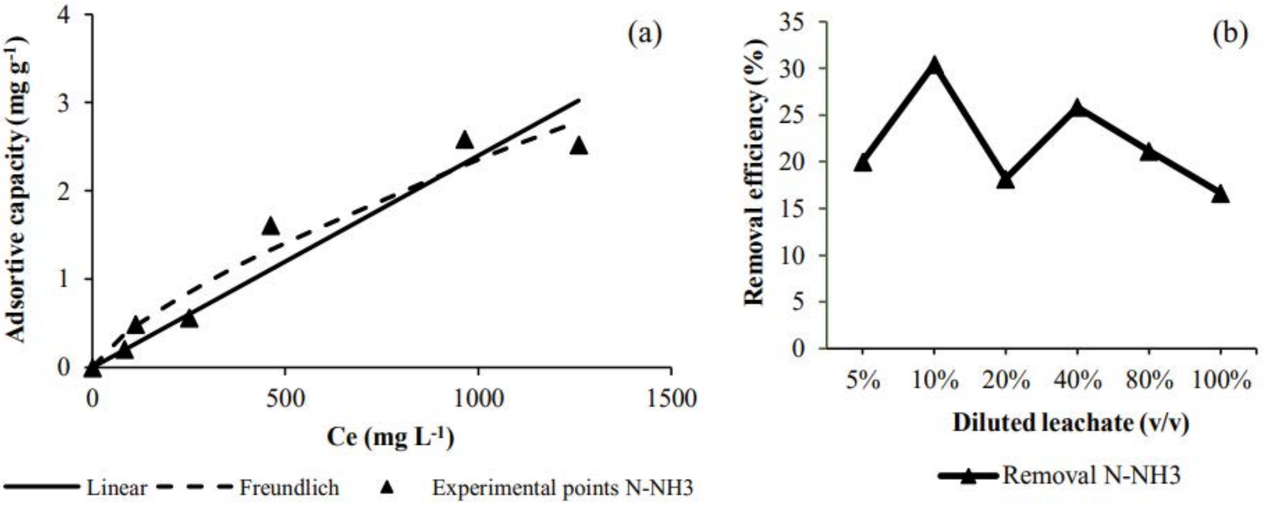

Fig. 5. $N–NH_3$: (a) linear and Freundlich isotherm models (b) removal efficiencies.

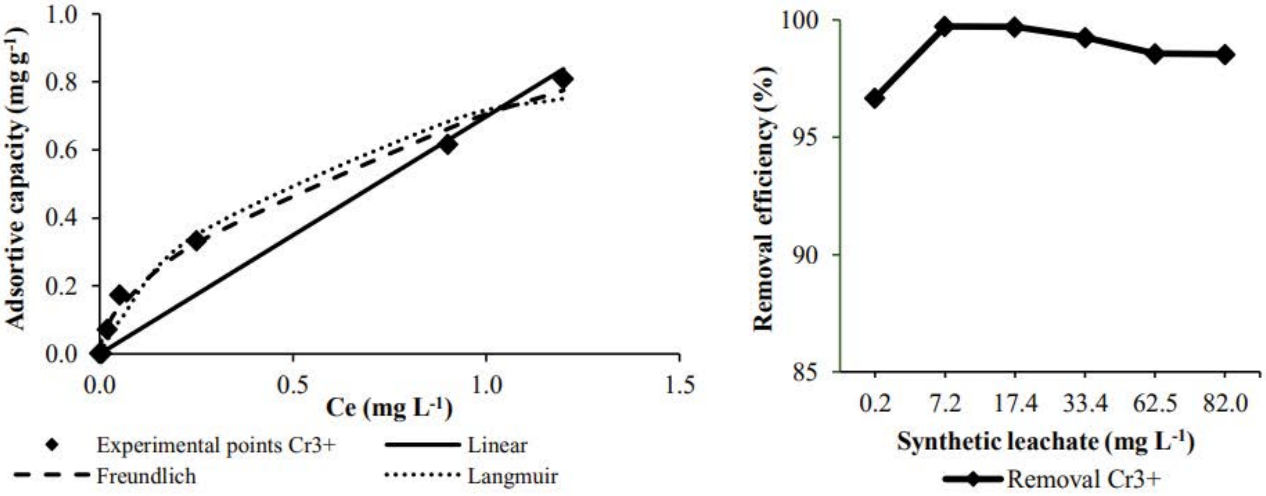

Fig. 6. Cr: (a) linear, Langmuir, and Freundlich isotherm models (b) removal efficiencies.

adjustment for the data of COD, $N–NH_3$, and Cr, with R^2 values of 0.996, 0.968, and 0.994, and SSR values of 35.352, 0.352, and 0.006, respectively. The Freundlich model describes the process in a heterogeneous level, in which the concentration of the adsorbate in the adsorbent increases with the increase of the initial concentration of the solution [7,75].

Based on the Langmuir coefficients (Table 8), the dimensionless separation factor (R_L) was calculated to analyze whether the adsorptive process of composition 75% GAC + 25% BC was favorable or not. The R_L values for COD, $N–NH_3$, and Cr^{3+} were -1.05×10^{-7}, -2.05×10^{-7}, and 0.302, respectively, indicating irreversible ($R_L < 0$) and favorable ($0 < R_L < 1$) adsorption [60,61,76]. Moreover, the values of the parameter N of the Freundlich model were within 0 and 1, which represents a favorable adsorption behavior of the chemicals analyzed, as indicated by Lázaro et al. [77] and Bavaresco et al. [78]. Although one model provided better results compared to the others, all the isotherm models evaluated significantly represented the adjusted data, as all the p-values were lower than the adopted significance level ($p < 0.05$) [79], except Langmuir for COD and $N–NH_3$.

The results indicate that the composition of GAC and BC analyzed can be potentially applied in reactive barriers for the treatment of the SLCG leachate, and can also be considered for other sanitary landfills in Brazilian semiarid regions. In addition, this composition is a sustainable, low-cost alternative for the reduction of pollutants concentration in leachates, particularly Cr, such that the leachate can reach adequate concentrations to be disposed in waterbodies.

3.5. Batch adsorption test – adsorption kinetics

The pseudo-first-order and pseudo-second-order kinetic models are illustrated in Fig. 7a and b, respectively. Table 9 presents the sorption kinetic coefficients determined for COD, $N–NH_3$, and Cr^{3+} using the composition 75% GAC + 25% calcium BC.

Table 8
Adjustment criteria for the isotherm models

Indicator	Models	Coefficients	Estimated value	Standard deviation	p	R^2	SSR
COD	Linear	K_d (L g^{-1})	0.042	0.004	0.0001	0.928	74.088
	Langmuir	K_L (L g^{-1})	–13,137.700	2.859×10^9	0.1034	0.000	536.228
		b (mg g^{-1})	13.700	6.912			
	Freundlich	K_F (mg g^{-1})	0.480	0.360	0.0004	0.966	35.352
		N	0.620	0.120			
$N–NH_3$	Linear	K_d (L g^{-1})	0.002	0.0002	0.0001	0.943	0.624
	Langmuir	K_L (L g^{-1})	–3,864.600	8.184×10^8	0.1203	0.000	5.635
		b (mg g^{-1})	1.330	1.000			
	Freundlich	K_F (mg g^{-1})	0.015	0.014	0.0005	0.968	0.352
		N	0.736	0.138			
Cr^{3+}	Linear	K_d (L g^{-1})	0.698	0.064	0.0001	0.952	0.048
	Langmuir	K_L (L g^{-1})	1.929	0.889	0.0002	0.985	0.015
		b (mg g^{-1})	1.075	0.194			
	Freundlich	K_F (L g^{-1})	0.701	0.025	0.00003	0.994	0.006
		N	0.553	0.054			

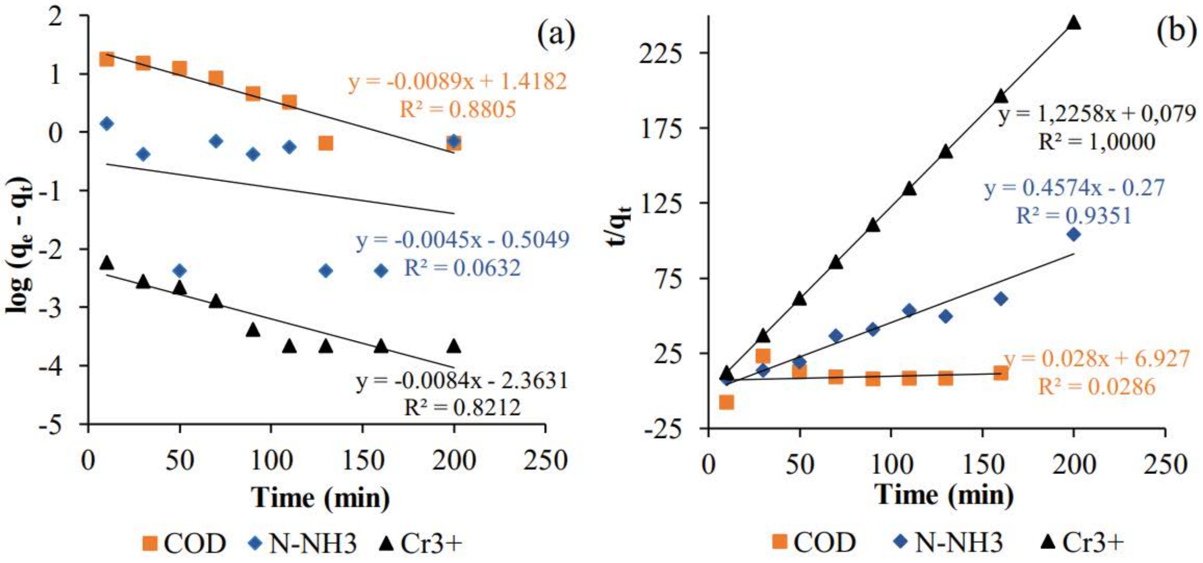

Fig. 7. Kinetic models applies to composition 75% GAC + 25% calcium BC: (a) pseudo-first-order and (b) pseudo-second-order.

Table 9
Kinetic coefficients of pseudo-first-order and pseudo-second-order models

Kinetic model	Coefficients	COD	$N–NH_3$	Cr^{3+}
Pseudo-first-order	q_e (mg g^{-1})	26.1939	0.3127	0.0043
	K_1 (min^{-1})	0.0205	0.0104	0.0193
	R^2	0.8805	0.0632	0.8212
Pseudo-second-order	q_e (mg g^{-1})	35.7143	2.1858	0.8158
	K_2 (g mg^{-1} min^{-1})	0.0001	–0.7752	19.0201
	R^2	0.0286	0.9351	1.0000
Practical acquisition	Experimental q_e	16.2218	2.6158	0.8156

According to the results in Fig. 7a and Table 9, the R^2 values obtained for the pseudo-first-order kinetic model were 0.88, 0.06, and 0.82, and the calculated adsorptive capacities (q_e) were 26.19, 0.31, and 0.04 mg g^{-1}, for COD, DQO, N–NH$_3$, and Cr^{3+}, respectively. Thus, the pseudo-first-order model exhibited an acceptable adjustment only for COD, considering the R^2 value (0.88) and the agreement between the calculated and experimental q_e (16.22 mg g^{-1}) values. N–NH$_3$ and Cr^{3+} were better adjusted to the pseudo-second-order (Fig. 7b and Table 9), with R^2 values of 0.94 and 1.00 and estimated adsorptive capacities of 2.19 and 0.82 mg g^{-1}, respectively, which is in agreement with the adoption equilibrium values obtained experimentally (2.62 mg g^{-1} for N–NH$_3$ and 0.82 mg g^{-1} for Cr^{3+}). These data indicate that the adsorption of N–NH$_3$ and Cr^{3+} for the composition 75% GAC + 25% calcium BC completely follows the pseudo-second-order kinetic reaction, which is based on the assumption that the chemisorption is the limiting phase of the sorption rate, directly depending on the adsorption capacity rather than the adsorbate concentration [80]. Halim et al. [23] and Foo et al. [44] also observed good adjustment to the pseudo-first-order model for COD using GAC or BC, and to the pseudo-second-order model for N–NH$_3$ [62] and Cr^{3+} [29].

4. Conclusions

The study demonstrated that the combination of GAC and calcium BC in the proportion 3:1 (GAC:BC) exhibited the following tendency for pollutants removal: Cr > COD > N–NH$_3$. The maximum experimental adsorption capacities of the 75% GAC + 25% BC composition were 29.0 mg g^{-1} (COD), 2.6 mg g^{-1} (N–NH$_3$), and 0.84 mg g^{-1} (Cr^{3+}), and Cr^{3+} was the pollutant with the highest removal percentage (96.7% to 99.7%).

The removal percentages of COD and N–NH$_3$ from the sanitary landfill leachate were better adjusted using the Freundlich isotherm model. For the removal of Cr^{3+}, Langmuir and Freundlich models exhibited good adjustments, with similar determination coefficients, but the Freundlich model was more representative.

The pseudo-first-order kinetic model exhibited acceptable adjustment (R^2 = 0.88) to the adsorption of COD for the materials analyzed; in contrast, pollutants N–NH$_3$ Cr^{3+} were better adjusted to the pseudo-second-order model.

The composition 75% GAC + 25% calcium BC showed potential to be used to the removal of COD and Cr from the leachate of sanitary landfills located at the Brazilian semiarid region. Nonetheless, column studies are recommended to provide more details regarding other important parameters.

References

[1] C.R. Klauck, A. Giacobbo, C.G. Altenhofen, L.B. Silva, Á. Meneguzzi, A.M. Bernardes, M.A.S. Rodrigues, Toxicity elimination of landfill leachate by hybrid processing of advanced oxidation process and adsorption, Environ. Technol. Innovation, 8 (2017) 246–255.

[2] S.M. Iskander, R. Zhao, A. Pathak, A. Gupta, A. Pruden, J.T. Novak, Z. He, A review of landfill leachate induced ultraviolet quenching substances: sources, characteristics, and treatment, Water Res., 145 (2018) 297–311.

[3] B.P. Naveen, J. Sumalatha, R.K. Malik, A study on contamination of ground and surface water bodies by leachate leakage from a landfill in Bangalore, India, Int. J. Geoeng., 9 (2018) 1–20.

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

[5] E. Toufexi, V. Tsarpali, I. Efthimiou, M.-S. Vidali, D. Vlastos, S. Dailianis, Environmental and human risk assessment of landfill leachate: an integrated approach with the use of cytotoxic and genotoxic stress indices in mussel and human cells, J. Hazard. Mater., 260 (2013) 593–601.

[6] N.A. Gomes, E.M. Silva, S.C. Nascimento, N.T.H. Calixto, L.S. Ribeiro, Composição do lixiviado armazenado em uma lagoa de evaporação natural implantada no Aterro Sanitário em Campina Grande-PB. In: V Congresso Nacional de Pesquisa e Ensino em Ciência, 2020, pp. 1–11.

[7] A. Detho, Z. Daud, M.A. Rosli, M.B. Ridzuan, H. Awang, M.A. Kamaruddin, A.A. Halim, COD and ammoniacal nitrogen reduction from stabilized landfill leachate using carbon mineral composite adsorbent, Desal. Water Treat., 210 (2021) 143–151.

[8] P. Kjeldsen, M.A. Barlaz, A.P. Rooker, A. Baun, A. Ledin, T.H. Christensen, Present and long-term composition of MSW landfill leachate: a review, Crit. Rev. Env. Sci. Technol., 32 (2002) 297–336.

[9] S. Mishra, D. Tiwary, A. Ohri, Leachate characterisation and evaluation of leachate pollution potential of urban municipal landfill sites, Int. J. Environ. Waste Manage., 21 (2018) 217–230.

[10] H. Luo, Y. Cheng, D. He, E.H. Yang, Review of leaching behavior of municipal solid waste incineration (MSWI) ash, Sci. Total Environ., 668 (2019) 90–103.

[11] Z. Daud, A. Detho, M.A. Rosli, M.H. Abubakar, K.A. Samo, N.F.M. Rais, H.A. Tajarudin, Ammoniacal nitrogen and COD removal from stabilized landfill leachate using granular activated carbon and green mussel (*Perna viridis*) shell powder as a composite adsorbent, Desal. Water Treat., 192 (2020) 111–117.

[12] G. Gajski, V. Oreščanin, V. Garaj-Vrhovac, Chemical composition and genotoxicity assessment of sanitary landfill leachate from Rovinj, Croatia, Ecotoxicol. Environ. Saf., 78 (2012) 253–259.

[13] S. Budi, B.A. Suliasih, M.S. Othman, L.Y. Heng, S. Surif, Toxicity identification evaluation of landfill leachate using fish, prawn and seed plant, Waste Manage., 55 (2016) 231–237.

[14] H. Luo, Y. Zeng, Y. Cheng, D. He, X. Pan, Recent advances in municipal landfill leachate: a review focusing on its characteristics, treatment, and toxicity assessment, Sci. Total Environ., 703 (2020) 135468.

[15] A.B. Castilhos Junior, R.L. Dalsasso, F. Rohers, Landfill leachate pre-treatment by upflow direct filtration and column of activated carbon (in Portuguese), Engenharia Sanitária e Ambiental, 15 (2010) 385–392.

[16] F. Kawahigashi, M.B. Mendes, V.G.D. Assunção, V.H. Gomes, F. Fernandes, E.Y. Hirooka, E.K. Kuroda, Post-treatment of landfill leachate using activated carbon (in Portuguese), Engenharia Sanitária e Ambiental, 19 (2014) 235–244.

[17] L.G. Lucena, E.M.R. Rocha, Solar photo-Fenton process for the treatment of landfill leachate, Revista DAE, 63 (2015) 49–63 (in Portuguese).

[18] F. Campos, R.P. Piveli, Evaluation of reduction of recalcitrant organic matter in landfill leachate by the combined process of coagulation/flocculation and powdered activated carbon adsorption, Revista DAE, 205 (2016), 45–53 (in Portuguese).

[19] F.A. El-Gohary, G. Kamel, Characterization and biological treatment of pre-treated landfill leachate, Ecol. Eng., 94 (2016) 268–274.

[20] A. Mojiri, L. Ziyang, R.M. Tajuddin, H. Farraji, N. Alifar, Co-treatment of landfill leachate and municipal wastewater using the ZELIAC/zeolite constructed wetland system, J. Environ. Manage., 166 (2016) 124–130.

[21] N.M. Trautmann, J.H. Martin, K.S. Porter, K.C. Hawk, Use of Artificial Wetlands for Treatment of Municipal Solid Waste Landfill Leachate, D.A. Hammer, Eds., Constructed Wetlands

for Wastewater Treatment: Municipal, Industrial, and Agricultural, CRC Press, Boca Raton, 2020, pp. 245–251.

[22] F. Ghanbari, J. Wu, M. Khatebasreh, D. Ding, K.-Y.A. Lin, Efficient treatment for landfill leachate through sequential electrocoagulation, electrooxidation and PMS/UV/$CuFe_2O_4$ process, Sep. Purif. Technol., 242 (2020) 116828, doi: 10.1016/j.seppur.2020.116828.

[23] A.A. Halim, H.A. Aziz, M.A.M. Johari, K.S. Ariffin, Comparison study of ammonia and COD adsorption on zeolite, activated carbon and composite materials in landfill leachate treatment, Desalination, 262 (2010) 31–35.

[24] H. Modin, K.M. Persson, A. Andersson, M. van Praagh, Removal of metals from landfill leachate by sorption to activated carbon, bone meal and iron fines, J. Hazard. Mater., 189 (2011) 749–754.

[25] A.R. Ishak, F.S. Hamid, S. Mohamad, K.S. Tay, Removal of organic matter from stabilized landfill leachate using coagulation–flocculation-Fenton coupled with activated charcoal adsorption, Waste Manage. Res., 35 (2017) 739–746.

[26] E. Mohammad-Pajooh, A.E. Turcios, G. Cuff, D. Weichgrebe, K.H. Rosenwinkel, M.D. Vedenyapina, L.P. Sharifullina, Removal of inert COD and trace metals from stabilized landfill leachate by granular activated carbon (GAC) adsorption, J. Environ. Manage., 228 (2018) 189–196.

[27] A.H. Jawad, M.A.M. Ishak, A.M. Farhan, K. Ismail, Response surface methodology approach for optimization of color removal and COD reduction of methylene blue using microwave-induced NaOH activated carbon from biomass waste, Desal. Water Treat., 62 (2017) 208–220.

[28] E.K. Putra, R. Pranowo, J. Sunarso, N. Indraswati, S. Ismadji, Performance of activated carbon and bentonite for adsorption of amoxicillin from wastewater: mechanisms, isotherms and kinetics, Water Res., 43 (2009) 2419–2430.

[29] Y.G. Chen, Y. He, W.M. Ye, C.H. Lin, X.F. Zhang, B. Ye, Removal of chromium(III) from aqueous solutions by adsorption on bentonite from Gaomiaozi, China, Environ. Earth Sci., 67 (2012) 1261–1268.

[30] S.A. Wanees, A.M.M. Ahmed, M.S. Adam, M.A. Mohamed, Adsorption studies on the removal of hexavalent chromium-contaminated wastewater using activated carbon and bentonite, Asian J. Chem., 25 (2013) 8245–8252.

[31] R. Foroutan, R. Zareipour, R. Mohammadi, Fast adsorption of chromium(VI) ions from synthetic sewage using bentonite and bentonite/bio-coal composite: a comparative study, Mater. Res. Express, 6 (2018) 025508, doi: 10.1088/2053-1591/aaebb9.

[32] X. Xu, X. Liu, M. Oh, J. Park, Y.F. Chen, Adsorption properties of heavy metal ions in landfill leachate by Na-bentonite, Mater. Test., 61 (2019) 81–87.

[33] J.N. Putro, S.P. Santoso, S. Ismadji, Y.H. Ju, Investigation of heavy metal adsorption in binary system by nanocrystalline cellulose–bentonite nanocomposite: improvement on extended Langmuir isotherm model, Microporous Mesoporous Mater., 246 (2017) 166–177.

[34] F. Massad, Mecânica dos solos experimental, Oficina de Textos, São Paulo, 2016.

[35] C.B. Gupt, S. Bordoloi, S. Sekharan, A.K. Sarmah, A feasibility study of Indian fly ash-bentonite as an alternative adsorbent composite to sand-bentonite mixes in landfill liner, Environ. Pollut., 265 Part A (2020) 114811, doi: 10.1016/j.envpol.2020.114811.

[36] Departamento Nacional de Produção Mineral (DNPM), Sumário Mineral, 2013, 148 p. Available at: http://www.anm.gov.br/dnpm/publicacoes/serie-estatisticas-e-economia-mineral/sumario-mineral/sumario-mineral-brasileiro-2013

[37] N.D. Mu'azu, M.H. Essa, S. Lukman, Augmenting granular activated carbon with natural clay for multicomponent sorption of heavy metals from aqueous solutions, Water Sci. Technol., 76 (2017) 2213–2221.

[38] M.K. Uddin, A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade, Chem. Eng. J., 308 (2017) 438–462.

[39] G.F. Silva, Environmental recovery of the bentonite extraction areas in the Boa Vista/PB region, Holos Environ., 20 (2020) 88–99 (in Portuguese).

[40] J. Wiszniowski, D. Robert, J. Surmacz-Gorska, K. Miksch, J.V. Weber, Landfill leachate treatment methods: a review, Environ. Chem. Lett., 4 (2006) 51–61.

[41] N.F. Campos, G.A.J.C. Guedes, L.P.S. Oliveira, B.M.V. Gama, D.C.S. Sales, J.M. Rodríguez-Díaz, C.M.B.M. Barbosa, M.M.M.B. Duarte, Competitive adsorption between Cu^{2+} and Ni^{2+} on corn cob activated carbon and the difference of thermal effects on mono and bicomponent systems, J. Environ. Chem. Eng., 8 (2020) 104232, doi: 10.1016/j.jece.2020.104232.

[42] H.J. Lu, M.T. Luan, J.L. Zhang, Y.X. Yu, Study on the adsorption of Cr(VI) onto landfill liners containing granular activated carbon or bentonite activated by acid, J. China Univ. Min. Technol., 18 (2008) 125–130.

[43] I. Chaari, M. Medhioub, F. Jamoussi, Use of clay to remove heavy metals from Jebel Chakir landfill leachate, J. Appl. Sci. Environ. Sanit., 6 (2011) 143–148.

[44] K.Y. Foo, L.K. Lee, B.H. Hameed, Preparation of activated carbon from sugarcane bagasse by microwave assisted activation for the remediation of semi-aerobic landfill leachate, Bioresour. Technol., 134 (2013) 166–172.

[45] K. Atkovska, B. Bliznakovska, G. Ruseska, S. Bogoevski, B. Boskovski, A. Grozdanov, Adsorption of Fe(II) and Zn(II) ions from landfill leachate by natural bentonite, J. Chem. Technol. Metall., 51 (2016) 215–222.

[46] F.M. Ferraz, Q. Yuan, Organic matter removal from landfill leachate by adsorption using spent coffee grounds activated carbon, Sustainable Mater. Technol., 23 (2020) e00141, doi: 10.1016/j.susmat.2019.e00141.

[47] H. Lu, M. Luan, J. Zhang, Transport of Cr(VI) through clay liners containing activated carbon or acid-activated bentonite, Appl. Clay Sci., 50 (2010) 99–105.

[48] N. Baylan, A.E. Meriçboyu, Adsorption of lead and copper on bentonite and grapeseed activated carbon in single- and binary-ion systems, Sep. Sci. Technol., 51 (2016) 2360–2368.

[49] Instituto Nacional do Semiárido (INSA), O semiárido brasileiro: riquezas, diversidade e saberes, 1st ed., Campina Grande: Ed. INSA/MCTI, 2013, 39 p.

[50] BRASIL, Resolution n. 357, March 17, 2005, Establishes Provisions for the Classification of Water Bodies as Well as Environmental Directives for Their Framework, Establishes Conditions and Standards for Effluent Releases and Makes Other Provisions, Published in Official Gazette on March 18, 2005, Available at: http://www2.mma.gov.br/port/conama/legiabre.cfm?codlegi=459

[51] APHA, AWWA, WEF, Standard Methods for the Examination of Water and Wastewater, 22nd ed., American Public Health Association, Washington, 2017, 1203 p.

[52] Brazilian Agricultural Research Corporation (Embrapa), Manual of Soil Analysis Methods, 2 Ed. Rio de Janeiro-RJ, Centro Nacional de Pesquisa de Solos, 2011, 212 p (in Portuguese).

[53] A.S. Mollamahmutoglu, G. Kanat, F.I. Turkdogan, Pollution removal from leachate using bottom ash-bentonite-zeolite liner, Desal. Water Treat., 160 (2019) 178–184.

[54] M.A. Budihardjo, B. Zaman, I.B. Priyambada, D. Ramadani, A.R. Rizaldianto, The Potential of Semi-permeable Bentonite and Zeolite Composite on the Reduction of Pb(II) Concentration in Landfill, The 6th Environmental Technology and Management Conference (ETMC) in Conjunction with The 12th AUN/SEED-Net Regional Conference on Environmental Engineering (RC EnvE), E3S Web Conf., 148 (2020) 01005.

[55] M. Rosli, Z. Daud, M. Ridzuan, N. Abd Aziz, H. Awang, A.O. Adeleke, Equilibrium isotherm and kinetic study of the adsorption of organic pollutants of leachate by using micro peat-activated carbon composite media, Desal. Water Treat., 160 (2019) 185–192.

[56] W.R. Roy, Technical Resource Document: Batch-Type Procedures for Estimating Soil Adsorption of Chemicals, Office of Solid Waste and Emergency Response, US Environmental Protection Agency, 1992.

[57] American Society for Testing and Materials (ASTM), Designation D4646: Standard Test Method for 24-h Batch-Type Measurement of Contaminant Sorption by Soils and Sediments, ASTM, Philadelphia, 2016.

[58] G.D'A.B. Souto, J. Povinelli, Tabelas de características típicas do lixiviado de aterros sanitários brasileiros: fases ácida e metanogênica, In: 26° Congresso Brasileiro de Engenharia Sanitária e Ambiental, 2011, pp. 1–22.

[59] BRASIL, Resolution n. 430, May 13, 2011. Provisions the Conditions and Standards of Effluents and Complements and Changes Resolution 357 from March 17, 2005 Issued by the National Environment Council (CONAMA), Published in Official Gazette on May 16, 2011, Available at: http://www.mma.gov.br/port/conama/legiabre.cfm?codlegi=646, Access: 05 July 2021.

[60] S. Ray, A.K. Mishra, A.S. Kalamdhad, Equilibrium, kinetic and hydraulic study of different Indian bentonites in presence of lead, Eur. J. Environ. Civ. Eng., 1 (2020) 1–20.

[61] S. Ray, A.K. Mishra, A.S. Kalamdhad, Evaluation of equilibrium, kinetic and hydraulic characteristics of Indian bentonites in presence of heavy metal for landfill application, J. Cleaner Prod., 317 (2021) 128396, doi: 10.1016/j.jclepro.2021.128396.

[62] P. Seruga, M. Krzywonos, J. Pyżanowska, A. Urbanowska, H. Pawlak-Kruczek, Ł. Niedźwiecki, Removal of ammonia from the municipal waste treatment effluents using natural minerals, Molecules, 24 (2019) 3633, doi: 10.3390/molecules24203633.

[63] S. Lagergren, Zur theorie der sogenannten adsorption geloster stoffe, Handlingar, 24 (1898) 1–39.

[64] Y. Ho, G. Mckay, Pseudo-second-order model for sorption processes, Process Biochem., 34 (1999) 451–465.

[65] A. Król, K. Mizerna, M. Bożym, An assessment of pH-dependent release and mobility of heavy metals from metallurgical slag, J. Hazard. Mater., 384 (2020) 121502, doi: 10.1016/j.jhazmat.2019.121502.

[66] V. Tsarpali, M. Kamilari, S. Dailianis, Seasonal alterations of landfill leachate composition and toxic potency in semi-arid regions, J. Hazard. Mater., 233 (2012) 163–171.

[67] R.B. Narayan, B.I. Zargham, A. Ngambia, A.R. Riyanto, Economic and environmental impact analysis of ammoniacal nitrogen removal from landfill leachate using sequencing batch reactor: a case study from Czech Republic, J. Water Supply Res. Technol. AQUA, 68 (2019) 816–828.

[68] Z. Chaouki, M. Hadri, M. Nawdali, M. Benzina, H. Zaitan, Treatment of a landfill leachate from Casablanca city by a coagulation–flocculation and adsorption process using a palm bark powder (PBP), Sci. Afr., 12 (2021) e00721, doi: 10.1016/j.sciaf.2021.e00721.

[69] M. Hussein, K. Yoneda, Z. Mohd-Zaki, A. Amir, N. Othman, Heavy metals in leachate, impacted soils and natural soils of different landfills in Malaysia: an alarming threat, Chemosphere, 267 (2021) 128874, doi: 10.1016/j.chemosphere.2020.128874.

[70] A.S. Silva, Analysis of Toxic Components in Solid Urban Wastes, Thesis, Universidade Federal de Campina Grande, Campina Grande, 2016, 155 p (in Portuguese).

[71] S. Dasarathy, R.P. Mookerjee, V. Rackayova, V.R. Thrane, B. Vairappan, P. Ott, C.F. Rose, Ammonia toxicity: from head to toe?, Metab. Brain Dis., 32 (2017) 529–538.

[72] P. Mohajeri, M.R. Selamat, H.A. Aziz, C. Smith, Removal of COD and ammonia nitrogen by a sawdust/bentonite-augmented SBR process, Clean Technol., 1 (2019) 125–140.

[73] J. Sobti, S.K. Singh, Sorption behaviour of heavy metals in sand-bentonite-coal ash mixes for use as a liner material in landfills, Int. J. Geotech. Eng., 13 (2019) 411–424.

[74] M.D. Meitei, M.N.V. Prasad, Adsorption of Cu(II), Mn(II) and Zn(II) by *Spirodela polyrhiza* (L.) Schleiden: equilibrium, kinetic and thermodynamic studies, Ecol. Eng., 71 (2014) 308–317.

[75] I. Ghorbel-Abid, M. Trabelsi-Ayadi, Competitive adsorption of heavy metals on local landfill clay, Arabian J. Chem., 8 (2015) 25–31.

[76] S. Ahmadi, C.A. Igwegbe, Adsorptive removal of phenol and aniline by modified bentonite: adsorption isotherm and kinetics study, Appl. Water Sci., 8 (2018) 1–8.

[77] D.A. Lázaro, M.B. Mansur, A.S. Franca, L.S. Oliveira, S.D.F. Rocha, Performance of cold-pressed cake from *Raphanus sativus* (L. Var.) oilseeds, a solid residue from biodiesel production, as adsorbent for basic dyes, Int. J. Chem. Eng., 1 (2008) 289–302.

[78] J. Bavaresco, M.L.K. Rodrigues, C. Gianello, V. Barrón, J. Torrent, Chromium adsorption in different mineralogical fractions from subtropical soils, Pedosphere, 27 (2017) 106–111.

[79] R.A.F. Silva, D.B. Costa, W. Paiva, M.C. Melo, V.E.D. Monteiro, Correlations between physico-chemical properties and nickel adsorption parameters in soils used in sanitary landfill liners, Águas Subterrâneas, 34 (2020) 275–284.

[80] Z. Zhao, W. Sun, M.B. Ray, Adsorption isotherms and kinetics for the removal of algal organic matter by granular activated carbon, Sci. Total Environ., 1 (2021) 150885, doi: 10.1016/j.scitotenv.2021.150885.