https://doi.org/10.1590/S1413-415220240097

Scientific Paper

Removal of anionic surfactant in a sequential batch fluidized bed biological reactor filled with polymeric hydrochar

Remoção de surfactante aniônico em um reator biológico de leito de hidrochar fluidizado funcionando em bateladas sequenciais

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ABSTRACT

Biological fluidized bed systems can be used to treat effluent contaminated with linear alkylbenzene sulfonate (LAS) and can also be made up of support materials produced from spent ion exchange resin residues. Therefore, the objective of this study was to evaluate the removal of anionic surfactants, specifically LAS, in a fluidized bed system filled with polymeric hydrochar and a consortium of microorganisms. For this purpose, the methodology was developed in the following phases: (I) production and characterization of the support medium; (II) implementation of the system in sequential batches and hydrodynamic tests; (III) inoculation, synthetic substrate supplementation, and adaptation of the inoculum to the system's LAS in sequential batches; and (IV) operation of the system in sequential batches to determine the LAS manipulation kinetics for three initial LAS concentrations from 17.51 to 41.89 mg L^{-1}. In phase I, polymeric hydrochar was obtained with an average diameter of 0.715 mm, an acidic surface, a low specific surface area, high sphericity, and characteristics of a nonporous or macroporous solid. The hydrodynamic tests resulted in a minimum fluidization velocity of 0.49 cm^{-1} in phase II. For the biological treatment system, the inoculation, feeding, and adaptation trials were extended for 29 days in Phase III. From the LAS treatment in the system in sequential batches, in Phase IV, removal efficiencies greater than 80.0% were obtained for both concentrations evaluated after 48 h of operation, and the degradation rate coefficients (k_{LAS}) decreased with increasing LAS concentration in the system.

Keywords: linear alkylbenzene sulfonate; hydrothermal carbonization; particle fluidization; biodegradation.

RESUMO

Sistemas biológicos de leito fluidizado podem ser usados no tratamento de efluentes contaminados com alquilbenzeno linear sulfonado (LAS) e ainda serem constituídos de materiais suporte produzidos a partir de resíduos de resinas de troca iônica exauridas. Desta forma, o objetivo deste estudo foi avaliar a remoção de surfactante aniônico, especificamente LAS, em sistema de leito fluidizado preenchido com hidrocarvão polimérico e consórcio de microrganismos. Para isso, a metodologia foi desenvolvida nas seguintes fases: (I) produção e caracterização do meio suporte; (II) implantação do sistema em bateladas sequenciais e ensaios hidrodinâmicos; (III) inoculação, suplementação de substrato sintético e adaptação do inóculo ao LAS do sistema em bateladas sequenciais; (IV) operação do sistema em bateladas sequenciais para determinação da cinética de degradação de LAS para três concentrações iniciais de LAS de 17,51 a 41,89 mg L^{-1}. Na fase I foi obtido o hidrocarvão polimérico com 0,715 mm de diâmetro médio, superfície ácida, baixa área superficial específica, alta esfericidade e características de sólido não poroso ou macroporoso. Os ensaios hidrodinâmicos resultaram em uma velocidade mínima de fluidização de 0,49 cm s^{-1} na fase II. Quanto ao sistema de tratamento biológico, os ensaios de inoculação, suplementação e adaptação foram conduzidos por 29 dias na Fase III. Do tratamento de LAS no sistema em bateladas sequenciais, na Fase IV obteve-se eficiências de remoção superiores a 80,0% para ambas as concentrações avaliadas após 48 h de operação e os coeficientes de taxa de degradação (k_{LAS}) reduziram conforme o aumento da concentração de LAS no sistema.

Palavras-chave: alquilbenzeno linear sulfonado; carbonização hidrotermal; fluidização de partículas; biodegradação.

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Conflicts of interest: the authors declare no conflicts of interest.
Funding: none.
Received on: 08/03/2024 – **Accepted on:** 05/15/2025
Editor: Melissa Gurgel Adeodato Vieira

INTRODUCTION

The anionic surfactant linear alkylbenzene sulfonate (LAS) has been used in the synthesis of cleaning, personal care, and laundry products (Corada-Fernández; González-Mazo; Lara-Martín, 2018) and is discharged in high concentrations into domestic and industrial wastewater (Siyal *et al*., 2020). These concentrations can range from 10.10 mg LAS L^{-1} in domestic sewage to 1,024.70 mg LAS L^{-1} in commercial laundry effluents (Braga; Varesche, 2014).

LAS is the most representative sales and purchase subsegment of the anionic surfactant class (Felipe; Dias, 2017) because of its cleaning properties and relatively low cost (Cowan-Ellsberry *et al*., 2014). Despite its biodegradability in effluent treatment plants, the presence of LAS in surface waters and sediments has been identified (Corada-Fernández; González-Mazo; Lara-Martín, 2018), and it can cause serious pollution and toxic effects on aquatic organisms (Felipe; Dias, 2017).

In surface waters, concentrations of up to 4.50 mg LAS L^{-1} (Silva *et al*., 2017) have been reported, whereas studies have indicated the ecotoxicological potential of concentrations greater than 0.10 mg LAS L^{-1} (Liu; Wu, 2017)—for plants and animals, 0.25 mg LAS L^{-1} (Cansu; Deniz, 2019). However, Brazilian regulations establish maximum values of 0.20 and 0.50 mg LAS L^{-1} for saline and fresh water, respectively (Brasil, 2005), indicating the need to review these values for environmentally safe concentrations (Jones-Costa *et al*., 2018). This toxicity of LAS is related to its complex structure and high molecular weight (Siyal *et al*., 2020).

The removal of surfactants in wastewater can be performed via treatment methods such as adsorption, flocculation and coagulation, aerobic and anaerobic biodegradation, and advanced oxidation (Palmer; Hatley, 2018). Compared with other treatment processes, biological treatment technologies are viable, economical, and efficient alternatives for the removal of biodegradable contaminants (Hamza; Iorhemen; Tay, 2016). Several studies have been conducted using fluidized bed reactors for the removal of LAS, especially via anaerobic pathways (Oliveira *et al*., 2010; Macedo *et al*., 2015; Motteran *et al*., 2018).

In the operation of fluidized bed reactors, the most used support medium is sand (Oliveira *et al*., 2010; Carosia *et al*., 2014; Motteran *et al*., 2014; Braga *et al*., 2015; Macedo *et al*., 2015). Despite being a low-cost and easily accessible material, sand particles have a high specific mass, requiring a high ascent velocity for their fluidization and thus resulting in a high operating cost of the system (Saucedo-Terán *et al*., 2004). Therefore, materials with low specific gravity, such as polymeric particles, may be an alternative to reduce operating costs related to energy (Tavares, 1995; Saucedo-Terán *et al*., 2004).

Thus, polymeric waste, such as exhausted ion exchange resins, can be subjected to recycling processes, such as hydrothermal carbonization, to produce new inert materials with different applications, resulting in a viable and environmentally friendly alternative (Spinacé; Paoli, 2005; Antero *et al*., 2015). These exhausted resins are considered hazardous solid waste, so companies must perform specialized disposal, such as incineration or disposal in controlled industrial landfills, which requires high costs (Wei *et al*., 2016) and, if discarded in inappropriate places, can impact the environment (Spinacé; Paoli, 2005).

One of the possibilities for LAS removal is the use of polymeric hydrochar as the support medium of a biological fluidized bed reactor produced by hydrothermal carbonization. Thus, the depleted ion exchange resin residues can be transformed by hydrothermal carbonization into a material with physical, chemical, and textural characteristics suitable for the development of biofilms, thus resulting in a technology for the treatment of effluents contaminated with LAS. The objective of this study was to evaluate the removal of LAS in a batch fluidized bed reactor filled with polymeric hydrochar and a consortium of microorganisms.

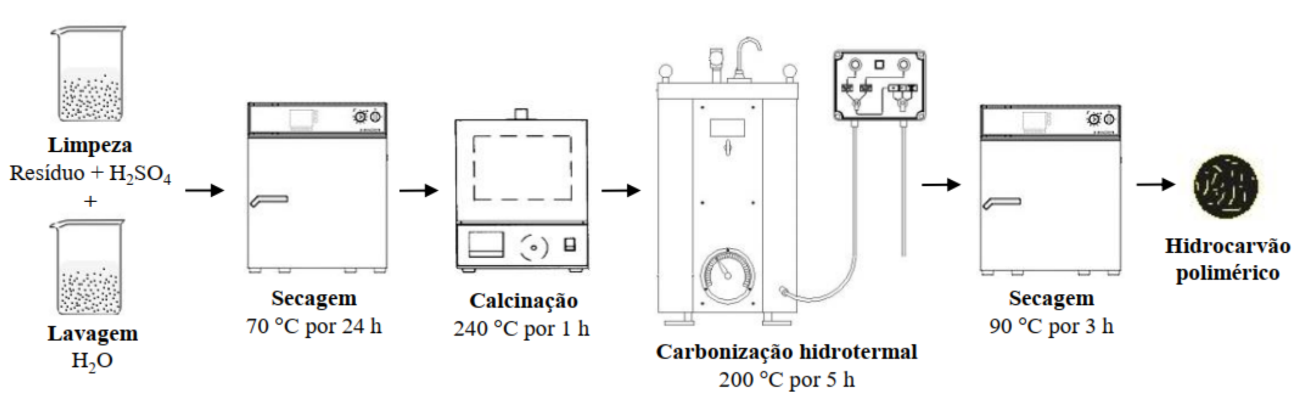
METHOD

Production of the support medium

The support medium was produced from samples of depleted ion exchange resin residues of the strongly acidic cationic type, consisting of a sulfonated styrene--divinylbenzene copolymer (Sty-DVB-SO_3 H). The chemical reagents used in the analyses were of analytical grade. Figure 1 illustrates the steps conducted for the production of the polymeric hydrochar.

The wet particles were cleaned with a 6.0% (v/v) for analysis (PA) (H_2SO_4) sulfuric acid solution (DuPont, 2019) because of the greater release of hydrogen ions ($2H^+$). For this purpose, 5.0 kg of exhausted and wet resin was placed in a glass fiber-reinforced polyvinyl chloride (PVC) vessel, with a volume of 11.62 L, in the cleaning stage. A total of 4.0 L of H_2SO_4 solution (6% v/v) was slowly added, and the reaction was continued for 24 h, with sporadic manual agitation.

At the end of this period, the particles were washed with distilled water until the pH of the solution stabilized. After cleaning, the excess water was



Source: Prepared by the author (2020).

Figure 1 – Scheme of the steps to produce the polymeric hydrocharcoal.

removed with the aid of a sieve for subsequent drying on metal trays at 70°C for 24 h. After this process, the particles were calcined in an oven under the second treatment conditions at 240°C for 1 h. Calcination was performed to eliminate interstitial water from the polymer matrix due to the decomposition of sulfonic groups (Oliveira; Rabelo; Rangel, 2005).

Next, hydrothermal carbonization of the pretreated particles was conducted in an autoclave with a total volume of 11.65 L. Considering 60.0% autoclave capacity, 700.0 g and 7.0 L of distilled water were added. The system was programmed for a working temperature of 200 °C and a reaction time of 5 h. These values of temperature and reaction time were adopted, according to the study by Antero *et al.* (2015), who used depleted resins for the production of polymeric activated carbon. During the reaction, the external temperature and pressure parameters were continuously recorded. The sample was then dried on metal trays at 90 °C for 3 h.

Characterization of the support medium

The characterization of the polymeric hydrochar was performed via the particle density (ρ_s) (Viana *et al.*, 2017), apparent specific gravity (ρ_a) (adaptation from Aversa *et al.*, 2014), and production yield of this material (Alves *et al.*, 2019) via quantitative methods, in addition to the sphericity (ψ) of the sample via qualitative methods.

In addition, the specific surface area and pore volume of the polymeric hydrochar were evaluated via nitrogen adsorption–desorption isotherms (-196°C) in a relative pressure range of 10^{-6-1} via ASAP 2020 equipment (Micromeritics Plus). The total pore volume was obtained from the desorption isotherm from the volume of N2 desorbed at a relative pressure of 0.95. The functional groups were investigated via Fourier transform infrared (FTIR) spectroscopy via a spectrometer (Perkin Elmer, model Spectrum 400). The polymeric hydrocharcoal sample was mixed with potassium bromide (KBr) (1.0%, by weight) at a pressure of 6 tons to form the analysis disc. The spectra were obtained in the mid-infrared region with wavenumbers between 400 and 4,000 cm^{-1}, a resolution of 4 cm^{-1}, and a scan number (*scans*) equal to 32 accumulations. Both analyses were performed at the Analytical Center of the Institute of Chemistry of the Universidade Federal de Goiás.

Fluidized bed reactor

The sequential batch system (Figure 2) was operated with a reaction volume of 3.5 L, and this volume was measured based on the samples collected during the sequential batch operation tests, as well as for immersion of the particles in the synthetic effluent when the system was at rest in the stages of inoculation, supplementation, and adaptation to the LAS inoculum. For the reaction volume of the system, 2.5 L corresponds to the volume of the reactor, 0.5 L corresponds to the recirculation system, and 0.5 L corresponds to the reservoir. Therefore, the total capacity of the reservoir was not used, contributing to the proper functioning of the system.

For inoculation, the reactor was filled with 100.0 g of polymeric hydrochar and fed 2.8 L of aqueous solution of synthetic substrate, with one-third of the concentration added in the first 3 days, and 0.7 L of sieved sludge, representing 20% of the reaction volume. During this stage, the consumption of organic matter by the microorganisms was monitored via chemical oxygen demand (COD) analysis. When this decrease was identified in the system, a new substrate was prepared and added to the synthetic effluent.

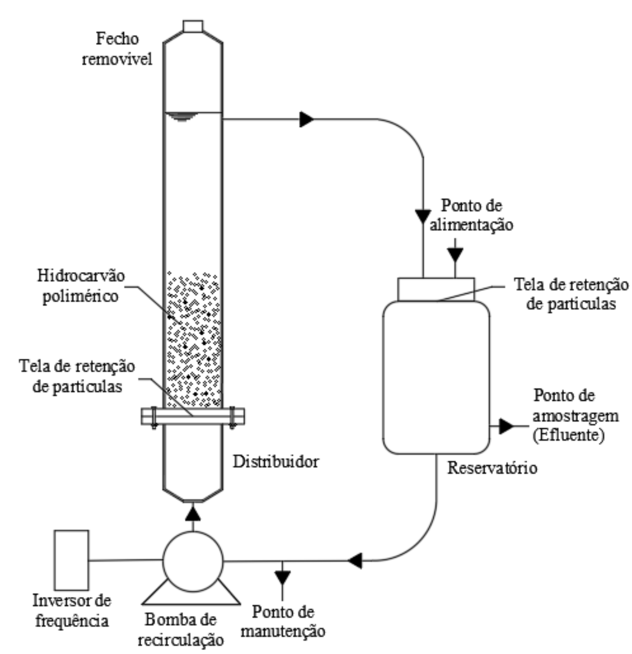
Sludge from a upflow anaerobic sludge blanket (UASB) reactor, which treats wastewater from the food industry in Nerópolis (GO), was used as the starting inoculum of the fluidized bed system. The culture medium formulated by Oliveira *et al.* (2010) was used as the base for the composition of the synthetic substrate and consisted of yeast extract (500 mg L^{-1}), sucrose (80 mg L^{-1}), sodium bicarbonate (400 mg L^{-1}), and 5.0 mL L^{-1} salt solution (50.0 g L^{-1} NaCl, 1.4 g L^{-1} $MgCl_2 \cdot 6H_2O$ and 0.9 g L^{-1} $CaCl_2 \cdot 2H_2O$).

When the minimum concentration of organic matter in the synthetic effluent was identified, the addition of a contaminant was performed in the adaptation phase. The anionic surfactant used as a contaminant was sodium dodecylbenzene sulfonate (Neon, CAS No. 25155-30-0), with a molecular formula of $CH_3(CH_2)_{11}C_6H_4SO_3Na$ and an active substance content between 49 and 52%. Phases I, II, and III were operated with increasing LAS concentrations in the system. Table 1 shows the operation steps of the fluidized bed system in sequential batches.

According to the batch of each assay, the global kinetics were estimated via LAS analyses performed temporally from the beginning to the end of the experiment. To determine the order of the reaction and kinetic coefficient in the batch reactor, the data were linearized via the integral method for zero-order, first-order, and second-order models (Von Sperling; Verbyla; Oliveira, 2020).

Physical, chemical, and biological analyses

According to the stages of inoculation, synthetic substrate supplementation, and adaptation of the inoculum to the LAS, the physical-chemical and biological analyses presented in Table 2, as well as the methods and references adopted, were performed. The equipment used was a spectrophotometer (Hach, model DR/2010), a benchtop pH meter (Tecnopon), and a microprocessor oven for bacteriological culture (SP Labor, model SP-200).



Source: Prepared by the author (2020).

Figure 2 – Schematic diagram of the fluidized bed system operated in sequential batches.

The Gram staining method was performed only for the characterization of bacteria in the sludge before the inoculation stage, and a light microscope (Bioval) without an image capture system was used. In addition, the heterotrophic bacteria were qualitatively analyzed via liquid synthetic effluent samples on plates with plate count agar to evaluate the growth of the microorganisms in the system.

The concentration of LAS was determined by the method of active substances that react with methylene blue (MBAS) (APHA; AWWA; WEF, 2017). The calibration curve for LAS quantification was generated via the use of a standard solution of 100 mg LAS L^{-1} prepared with deionized water. Solutions of 0.5, 1.0, 1.5, 2.0, and 2.5 mg LAS L^{-1} were used to construct the curve.

RESULTS AND DISCUSSION

Morphology and physical properties of the polymeric hydrochar

Table 3 shows that the average diameter and specific mass of the polymeric hydrocharcoal particles were lower than those of the materials used by Oliveira (2010) in a fluidized bed reactor, such as sand (mean Ø, 1.55 mm; ρ_s, 2.30 g cm^{-3}), activated carbon (average Ø, 1.55 mm; ρ_s, 1.80 g cm^{-3}) and glass beads (average Ø, 1.55 mm; ρ_s, 2.20 g cm^{-3}). In addition, artificial support materials, consisting of plastic particles, also had significantly lower apparent specific gravities (1.36 to 1.55 g cm^{-3}) than clay mineral particles did (2.50 to 2.68 g cm^{-3}). For example, natural and volcanoclastic zeolites result in both lower ascension

Table 1 – Operational steps of the LAS biodegradation kinetics in the fluidized bed system in sequential batches.

Operation phase	Duration (h)	Step description
Inoculation and supplementation	17	Feeding the fluidized bed system with inoculum (20% of the reaction volume) (Andrade *et al.*, 2017) and synthetic substrate (Oliveira *et al.*, 2010) under intermittent fluidization every 1 h and 30 min for 5 min, using a digital timer, with a fluidization flow rate of 71.34 cm^3 s^{-1} (256.82 L h^{-1}), a fluidization velocity of 1.66 cm s^{-1}, and bed expansion above 50%.
Adaptation	12	Feeding the fluidized bed system, containing synthetic effluent (inoculum and synthetic substrate), with the contaminant LAS at a concentration of 11.45 mg LAS L^{-1} under intermittent fluidization every 1 h and 30 min for 5 min by means of a digital timer, with a fluidization flow rate of 71.34 cm^3 s^{-1} (256.82 L h^{-1}), a fluidization rate of 1.66 cm s^{-1}, and bed expansion above 50%.
I	6	Feeding the fluidized bed system containing synthetic effluent (inoculum and synthetic substrate) with the contaminant LAS at a concentration of 17.51 mg LAS L^{-1} under a fluidization flow rate of 71.34 cm^3 s^{-1} (256.82 L h^{-1}), fluidization velocity of 1.66 cm s^{-1}, and bed expansion above 50%.
II	7	Feeding the fluidized bed system containing synthetic effluent (inoculum and synthetic substrate) with the contaminant LAS at a concentration of 20.31 mg LAS L^{-1} under a fluidization flow rate of 71.34 cm^3 s^{-1} (256.82 L h^{-1}), fluidization velocity of 1.66 cm s^{-1}, and bed expansion above 50%.
II	7	Feeding the fluidized bed system containing synthetic effluent (inoculum and synthetic substrate) with the contaminant LAS at a concentration of 41.89 mg LAS L^{-1} under a fluidization flow rate of 71.34 cm^3 s^{-1} (256.82 L h^{-1}), fluidization velocity of 1.66 cm s^{-1}, and bed expansion above 50%.

Source: Prepared by the authors.

Table 2 – Analyses performed in the tests of the fluidized bed system in sequential batches.

Parameters	Frequency of analysis	Method	References	Reference code
Heterotrophic bacteria	Weekly	Spread sowing	APHA, AWWA and WEF (2017)	9215C
gram-positive and gram-negative bacteria [a]	-	Gram stain	Madigan *et al.* (2016)	-
Apparent color (PtCo)	Daily rate	Spectrophotometric	APHA, AWWA and WEF (2017)	2120C
Raw and filtered COD (mg L^{-1})	Weekly	Spectrophotometric	APHA, AWWA and WEF (2017)	5220C
LAS (mg L^{-1})[b]	Weekly	Spectrophotometric	APHA, AWWA and WEF (2017)	5540C
pH	Daily rate	Potentiometric	APHA, AWWA and WEF (2017)	4500-H^+
Series of solids [a]	-	Gravimetric	APHA, AWWA and WEF (2017)	2540
Temperature (°C)	Daily rate	-	APHA, AWWA and WEF (2017)	2550
Turbidity (FAU)	Daily rate	Spectrophotometric	APHA, AWWA and WEF (2017)	2130

[a]Parameter evaluated in the sludge used as starting inoculum; [b]Parameter evaluated only in the stage of adaptation of the inoculum to the LAS.
Source: Prepared by the authors.

Table 3 – Physical characteristics of the support medium of the fluidized bed reactor.

Half support	Diameter (mm)	Mean diameter (mm)	Specific mass of particles (g cm^{-3})	Apparent specific gravity (g cm^{-3})	Sphericity
Polymeric hydrocharcoal	0.59–0.84	0.715	1.43	0.87	0.90

Source: Prepared by the authors.

velocities and lower recirculation rates in the system and, consequently, lower costs of energy required for fluidization (Eldyasti; Nakhla; Zhu, 2012).

Additionally, as shown in Table 3, the mean diameter and specific mass of the polymeric hydrochar particles were lower than those of the materials used by Oliveira (2010) in a fluidized bed reactor, such as sand (mean Ø, 1.55 mm; ρ_s, 2.30 g cm^{-3}), activated carbon (average Ø, 1.55 mm; ρ_s, 1.80 g cm^{-3}) and glass beads (average Ø, 1.55 mm; ρ_s, 2.20 g cm^{-3}). In addition, artificial support materials, consisting of plastic particles, also had significantly lower apparent specific gravities (1.36 to 1.55 g cm^{-3}) than clay mineral particles did (2.50 to 2.68 g cm^{-3}). For example, natural and volcanoclastic zeolites result in both lower ascension velocities and lower recirculation rates in the system and, consequently, lower costs of energy required for fluidization (Eldyasti; Nakhla; Zhu, 2012).

The particles maintained high sphericity after the treatment processes, which is suitable for the formation of biofilms (Eldyasti; Nakhla; Zhu, 2012). Eldyasti, Nakhla and Zhu (2012) reported that particles with greater sphericity, equal to 0.90, contributed to the growth of microbial biofilms, resulting in biofilms with greater thickness, greater active biomass, and lower rates of biofilm detachment in the fluidization system.

With respect to the hardness of the particles, Antero *et al.* (2015) used exhausted ion exchange resins to produce polymeric activated carbon and subjected it to compression tests, and these resins were similar to the materials used for the production of polymeric hydrochar. These authors reported that the mechanical properties of poly

meric activated carbon (PAC) subjected to thermal treatments and hydrothermal activation were not altered in relation to those of the precursor. The hardness and structural integrity of the particles in the bed are important so that their disintegration during fluidization does not occur, thus avoiding costs associated with operational problems (Gomide, 1980) and the replacement of support material (Eldyasti; Nakhla; Zhu, 2012).

Textured properties of polymeric hydrocharcoal

The adsorption and desorption isotherms of nitrogen (N_2) at 77 K of the polymeric hydrochar, according to the IUPAC classification (IUPAC, 1985), are type III (absence of hysteresis); the adsorbent–adsorbate interactions are relatively weak, and the molecules adsorbed are grouped in favorable regions of the surface of a nonporous or macroporous solid (Thommes *et al.*, 2015).

According to the single-point method, the specific surface area of the polymeric hydrochar was 2.20 m^2 g^{-1}, which is considered relatively low (IUPAC, 1985). The Brunauer–Emmett–Teller (BET) method was disregarded because it is not applicable for type III isotherms (Thommes *et al.*, 2015). Despite the low specific surface area, Oliveira (2010) used expanded clay with a specific surface area of 1.08 m^2 g^{-1} as the support medium of a fluidized bed reactor for the treatment of LAS, resulting in removal efficiencies of 81 ± 15% for an influent concentration of 13.4 ± 3 mg LAS L^{-1}.

In the Barrett–Joyner–Halenda (BJH) method, a relatively low total pore volume of 0.029 cm^3 g^{-1} was observed compared with that of activated carbons produced with ion exchange resin residues, which varied from 0.1801 to 0.5330 cm^3 g^{-1} (Wei *et al.*, 2016). Therefore, the low surface area obtained, as well as the low degree of pore formation, is inherent to the hydrothermal carbonization process (Antero *et al.*, 2020).

Although textural characteristics are important for the rapid formation of biofilms on particles (Oliveira, 2010), Eldyasti, Nakhla and Zhu (2012) reported that the micropores of natural zeolite particles do not affect biofilm growth, as the surface area of these particles is 15 times greater than that of plastic particles. Both had the same sphericity values, equal to 0.90, resulting in approximate biofilm thicknesses and lower rates of biofilm detachment.

Chemical properties of the polymeric hydrocharcoal

According to the FTIR spectrum, the functional groups of the hydrochar resulted in strong and broad absorption bands in the range of approximately 3,468 cm^{-1}, which were attributed to the vibration of stretching in the hydroxyl groups (O–H) and the presence of water in the sample (Hongtao *et al.*, 2018). The peak observed at 1,638 cm^{-1} is associated with the vibrational stretching of double bonds (C═C) in aromatic groups (Taskin *et al.*, 2019), inherent to the polymeric material (Kumar *et al.*, 2011). A weak and broad band was also observed between 900 and 400 cm^{-1}, indicating the stretching of single bonds between carbons (C–C) (Yihunu *et al.*, 2019).

The functional groups of the particles can influence the treatment efficiency, improving the low bioaffinity caused by the smooth surface. The hydrophilicity of the particle aids in the growth of the microbial biofilm. This occurs via the formation of hydrogen bonds between the components of the particle surface and the bacterial cell wall (Zhao *et al.*, 2019). Therefore, the hydroxyl groups identified in the polymeric hydrochar are favorable for the formation of biofilms on the particles.

System operation

Table 4 describes the operating conditions of the assays used to evaluate the LAS degradation kinetics. In assays I, II, and III, the initial LAS concentrations were 17.51, 20.31, and 41.89 mg LAS L^{-1}, respectively. The temperature was between 26.1 and 35.1°C, and the pH ranged between 7.5 and 7.9, within the ideal range for bacterial growth (Tortora; Funke; Case, 2017).

Furthermore, no synthetic substrate supplementation was performed during these assays. There was no change in the concentration of total organic matter (total COD) in the system effluent, which ranged from 307 to 305 mg L^{-1}. The remaining organic matter (filtered COD) was lower in assays II and III than in assay I; however, the values were below the detection limit of the method.

A marked reduction in the contaminant concentration in the system occurred after an operating time of 96 h. Thereafter, the assay was maintained

Table 4 – Results obtained in the kinetic tests of biodegradation of LAS.

Assay	Operating time (h)	LAS initial (mg L^{-1})	Residual LAS (mg L^{-1})	LAS removal (%)	Total COD (mg L^{-1})	Filtered COD (mg L^{-1})	pH	Temperature (°C)
I	147	17.51	2.00	88.6	307	153	7.8 ± 0.1	31.4 ± 1.8
II	167	20.31	1.91	90.5	307	< 150	7.8 ± 0.1	33.7 ± 1.4
III	168	41.89	2.79	93.3	305	< 150	7.6 ± 0.1	28.1 ± 2.0

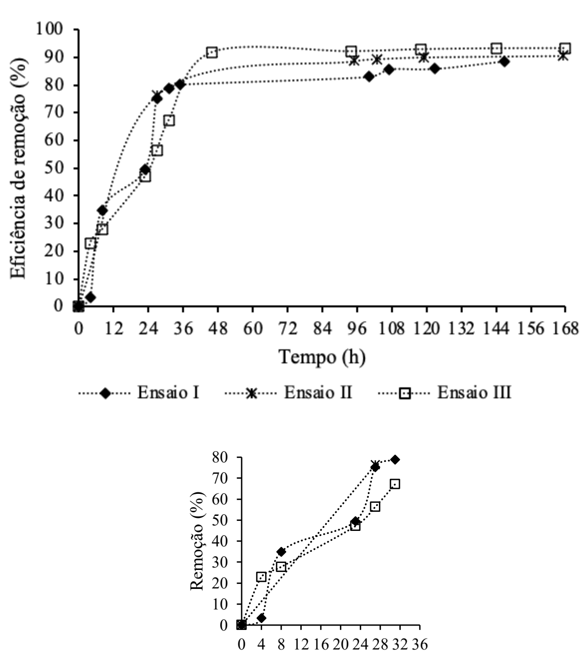
Source: Prepared by the authors.

until there was no change in the residual concentration of LAS. The residual LAS concentrations were 2.00, 1.91, and 2.79 mg LAS L^{-1} for initial concentrations of 17.51 (assay I), 20.31 (assay II), and 41.89 mg LAS L^{-1} (assay III), respectively.

As shown in Figure 3, the LAS removal efficiency reached values higher than 60.0% at 32 h of operation, and after 48 h of operation, the efficiency shifted to 80.0%. Furthermore, increasing the concentration of LAS reduced the efficiency of contaminant removal in the system after 32 h of operation. Assay I resulted in an LAS removal efficiency of 67.1%, whereas assays I and II resulted in removals of 78.8% and 76.4%, respectively. At the end of each batch operation, the LAS removal efficiencies were 88.6%, 90.5%, and 93.3% for initial concentrations of 17.51 (assay I), 20.31 (assay II), and 41.89 mg LAS L^{-1} (assay III), respectively.

Therefore, the LAS removal rates in the sequential batch system were above 88.0% for concentrations of 17.51 to 41.89 mg LAS L^{-1}, with operating times of 147 to 168 h. Macedo *et al.* (2019) investigated the LAS degradation kinetics by operating batch reactors with concentrations of 8.7 to 63.5 mg LAS L^{-1} and 171 to 289 mg COD L^{-1}, respectively, for 144 h. At the end of the operation, the authors obtained removal rates above 95.0% for concentrations between 8.7 and 24.0 mg LAS L^{-1}. However, LAS removal was reduced to 77.5 and 56.1% for concentrations of 40.4 and 63.5 mg LAS L^{-1} and 465 and 520 mg COD L^{-1}, respectively (Macedo *et al.*, 2019).

Macedo (2018) reported that an increased concentration of LAS inhibits the growth of microorganisms, as do the xenobiotic components present in the wastewater from commercial laundry and domestic sewage used in the study. In the present study, the removal of LAS at high concentrations was not impaired, which may be related to the use of synthetic effluent in the treatment, which was composed of a substrate (yeast extract, sucrose, and salt solution), inoculum (total COD of 307 mg L^{-1} and filtered COD of 105 mg L^{-1}) and commercial LAS (41.89 mg LAS L^{-1}).



Source: Prepared by the authors.

Figure 3 – LAS removal efficiencies in the kinetic tests of biodegradation in the fluidized bed system in sequential batches.

According to the results presented in Figure 3, the reaction equations, the coefficients of determination (R^2), and the degradation rate coefficients (k_{LAS}) for the initial concentrations of LAS evaluated. Through the linearization of the kinetic test data, the equations of the zero-order, first-order, and second-order reactions were estimated.

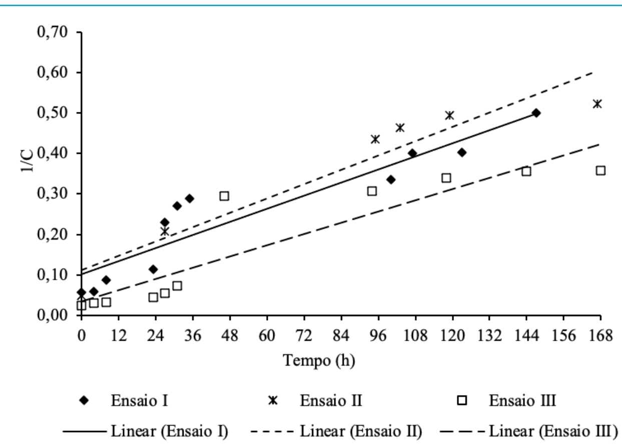
As shown in Figure 4, the second-order model better fits the experimental results obtained in this study, resulting in R^2 values between 0.84 and 0.91. Thus, the second-order equations show that the k_{LAS} coefficients were the same for initial concentrations of 17.51 (assay I) and 20.31 mg LAS L^{-1} (assay II); however, there was a minimal reduction in k_{LAS} at the initial concentration of 41.89 mg LAS L^{-1} (assay III). Macedo (2018), by operating batch reactors for 144 h at various concentrations ranging from 8.3 to 66.9 mg LAS L^{-1}, obtained k_{LAS} values close to 8.3 and 24.2 mg LAS L^{-1}, but these coefficients decreased at concentrations higher than 34.8 mg LAS L^{-1}.

The removal of LAS at concentrations above 34.8 mg LAS L^{-1} is impaired by the inhibition of microorganisms caused by contaminants and by excess substrate in the system, requiring the addition of cosubstrates to improve degradation (Macedo, 2018). Andrade *et al.* (2017) reported that the kinetic behavior of k_{LAS} decreased from 0.054 h^{-1} (27 mg LAS L^{-1}) in a 96 h batch to 0.011 h^{-1} (60 mg LAS L^{-1}) in a 120 h batch due to the increase in the LAS concentration and excess substrate. Therefore, the increase in LAS concentration may have impaired the reaction rate, according to the estimated LAS coefficients k, concomitant with the LAS removal efficiencies obtained for the different concentrations at 32 h of operation.

CONCLUSIONS

Considering the methodology used in the production of hydrochar, a nonporous or macroporous solid with an average diameter of 0.715 mm, a low specific surface area, a specific gravity of the particles of 1.43 g cm^{-3}, high sphericity, and adequate hardness, in addition to the chemical functionalities inherent to hydroxyl groups and polymeric materials, was obtained.

The biological system of a fluidized bed filled with polymeric hydrochar operated in sequential batches was efficient at removing LAS, with values greater than 80.0% for concentrations ranging from 17.51 to 41.89 mg LAS L^{-1} after 48 h of operation. According to the LAS biodegradation kinetics, the different



Source: Prepared by the authors.

Figure 4 – Graphical analysis of LAS biodegradation for the second-order equation.

concentrations mentioned above caused a minimal reduction in the reaction rate as the concentration of LAS in the system increased.

AUTHORS' CONTRIBUTIONS

Silveira, J.R.: Conceptualization, Investigation, Methodology, Project administration, Validation, Visualization, Writing–review and editing. Teran, F.J.C.: Conceptualization, Investigation, Methodology, Project administration, Validation, Visualization, Writing–review and editing. Oliveira, S.B.: Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Resources, Supervision, Validation, and Writing–original draft.

DATA AVAILABILITY STATEMENT

The datasets generated and/or analyzed during the current study are available from the corresponding author upon reasonable request.

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