Modified grape stem as a renewable adsorbent for cadmium removal

Daniel Schwantes, Affonso Celso Gonçalves Jr, Amarilis De Varennes and Alessandro Lucca Braccini

ABSTRACT

In order to aggregate value to the grape stem (wastes), this research aim was to increase the adsorption capacity of Cd^{2+} by chemical modifications on grape stems. The grape stems were milled and sieved, resulting in the biosorbent, which was used for the chemical modifications resulting in E. H_2O_2, E. H_2SO_4 and E. NaOH. These were characterized by such means as its pH_{PZC}, Fourier transform-infrared (FTIR) spectroscopy, porosimetry, thermal stability and scanning electron microscopy. The ideal adsorption dose, the pH influence on adsorption, kinetics, equilibrium and thermodynamics studies were carried out. The FTIR spectroscopy suggests the occurrence of carboxyl, amine, and phenolic acting in Cd^{2+} sorption. The modification on grape biomass caused small increase in pore volume and specific surface area. The grape-based adsorbents have similar thermal stability, with irregular appearance and heterogeneity. $5.0 \, g \, kg^{-1}$ is the best adsorption dose. The modified adsorbents exhibited increase in Cd^{2+} removal of 66% for E. NaOH, 33% for E. H_2O_2 and 8.3% for E. H_2SO_4. The use of grape stem as adsorbent is an attractive alternative, because its wastes have great availability, low cost and great potential for metal adsorption processes.

Key words | adsorption, biosorbent, remediation, water treatment

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INTRODUCTION

One of the major issues related to environmental problems is the preservation of freshwater in quantity and quality for current and future human consumption (Schwantes *et al.* 2018).

Several techniques are used for remediation of contaminated water; however, these techniques do not always present economic feasibility. Among the conventional methods mostly used for the wastewater treatment are chemical precipitation, oxidation or reduction, filtration, electrochemical treatment, membrane separation processes and solid phase extraction. Some of these technologies are infeasible due to technical or economic unfeasibility, especially when referring to the removal of toxic metals, since these are usually present in large volumes of water and in relatively low concentrations (Schwantes *et al.* 2016).

Among the toxic metals, cadmium (Cd) deserves attention because of its high toxicity and deleterious effects on humans and the environment, even at low concentrations. One of the main problems associated with Cd is its final destination in the food chain, as it can reach the soil or the air, by the burn of municipal waste or fossil fuels, thus polluting the environment and causing damage to the ecosystem (Nacke *et al.* 2017).

In humans, the inhalation of this heavy metal may cause problems in respiratory tract and kidneys, in the case of oral intoxication, when a significant amount of Cd is ingested, may generate an immediate poisoning and damage to the liver and kidneys; already in contact poisoning, genetic alterations may occur (Kim *et al.* 2018).

There are many modern techniques being developed for cadmium removal purposes, such the use of nanoscale zero valent iron (nZVI) (Dong *et al.* 2017), or reverse osmosis and nanofiltration membranes (Kheriji *et al.* 2015).

However, one of the most promising techniques in the removal of toxic metals from water is the use of natural adsorbents. According to Gonçalves *et al.* (2016), regarding the conventional water treatment, the use of biomass as adsorbents exhibit great advantages, due to its ability to

accumulate contaminants, to withstand several cycles of sorption and desorption, and also because they require little processing and are abundant in industry and agriculture, being considered materials of low cost.

Studies report the use of chemical modifications, whose purpose is to introduce functional groups into the structure of these adsorbents, or to increase their porosity and adsorption capacity (Dos Santos *et al.* 2010, 2011; Schwantes *et al.* 2016).

According to Hokkanen *et al.* (2016), methods of adsorbent modifications include physical modifications, chemical modifications and other methods. In order to make the biomass even more efficient, they suggest that chemical modifications should be carried out, for increasing adsorptive capacity.

In this scenario, the grape processing industry generates a large amount of residual biomass, that consists of bark, seeds, stems and, in smaller quantities, fruit pulp. Grape is produced either for consumption of grapes in natura or for the production of wine.

China leads the world production with 14,763,000 metric tons of grapes, while Brazil and Portugal produced, in 2016, respectively, 984,481 and 773,904 metric tons. The world grape production is around 77,438,929 metric tons (FAO 2016).

According to de Mello & da Silva (2014), the processing of grapes in winemaking and juice production generates approximately 20–25% of its weight in grapes solid wastes, especially grape stem. Thus, it can be estimated that the Brazilian, Portuguese and world annual production of grape solid wastes are respectively 246,120, 193,476 and 19,359,732 metric tons, respectively.

This research aimed to aggregate value to an agro-industrial waste, which occur worldwide, the grape stem, transforming it into adsorbents with high capacity of Cd^{2+} removal, and also to study the adsorption mechanisms of Cd^{2+} retention into the biomass.

MATERIAL AND METHODS

Obtaining the adsorbent materials

The grape stems were obtained in the agroindustry of wine production located at the School of Agriculture (ISA), located in Lisbon, Portugal. The stems were dried at 60 °C for 48 h, crushed and sieved in order to standardize the particle size (material retained between 14 and 65 mesh), resulting in biosorbent of stem or E. *in natura*.

Chemical modifications were applied to E. *in natura*, aiming to increase favorable characteristics for the adsorption of Cd^{2+}, such as surface contact area, porosity and the number of adsorption groups. For that purpose, the biosorbent of grape stems (E. *in natura*) was treated separately with H_2O_2, H_2SO_4 or NaOH 0.1 mol L^{-1} for 60 °C and 6 h (Schwantes *et al.* 2015, 2016). After that process, the residual treated biomass was washed with ultrapure water for the removal of any residue from the modifying solutions, and again dried at 60 °C for 48 h, resulting in the modified adsorbents called E. H_2O_2, E. H_2SO_4 and E. NaOH.

Characterization of the biosorbent and modified adsorbents

The point of zero charge (pH_{PZC}) of adsorbents, which refers to the pH at which the resultant of the surface charges of adsorbent is zero, was determined according to adaptations on Mimura *et al.* (2010) method, with 4 h of shaking samples.

The identification of functional groups of the biosorbents was performed by Fourier transform-infrared spectrophotometry (FTIR), with Shimadzu Infrared Spectrophotometer FTIR-8300 Fourier Transform, with a resolution of 4 cm. The morphological characterization of the adsorbents was evaluated by scanning electron microscopy (SEM), using a FEI Quanta 200 microscope (The Netherlands) operating at 30 kV voltage.

The surface analysis, size and pore volume was performed using Quantachrome Nova 1200e equipment. To this end, 500 mg of material were heated to 200 °C under vacuum for approximately 4 h. Subsequently, the processes of adsorption and desorption of N_2 were performed. The surface size and pore volume were calculated using the standard Brunauer, Emmett and Teller (BET) (Brunauer *et al.* 1938) and a pore size was obtained using the method of Barrett–Joyner–Halenda (BJH) (Barrett *et al.* 1951).

The thermal analysis was performed using a TGA 4000 Perkin Elmer thermogravimetric analyzer, where the materials were heated at a temperature ranging from 30 °C to 900 °C under heating rate 10 °C min^{-1} in nitrogen atmosphere.

The morphology of all adsorbents was evaluated by SEM using a JEO JSM 6360-LV microscope, equipped with dispersive energy microscopy.

Biosorption experiments

The adsorption studies were performed with solutions fortified with Cd^{2+}, prepared from salts of cadmium nitrate ($Cd(NO_3)_2$ $4H_2O$ P.A. $\geq 99.0\%$ Sigma-Aldrich) and ultrapure water.

Studies aiming to determine the ideal adsorbent dose and the pH influence on cadmium adsorption were carried

out. For this, a rotational composite central design was used, with mass values studied from 250 to 1,250 mg (proportion of 5.0 to 25 g L^{-1} of Kg m^{-3}). Experimentally, 50 mL of solution containing Cd^{2+} at 10 mg L^{-1} was added to Erlenmeyers with increasing masses of each adsorbent, which were then arranged in a thermostated Dubnoff system with constant stirring at 200 rpm and 25 °C for 1 h.

After the sorption process, the samples were centrifuged and aliquots were taken to determine the concentrations of remaining Cd^{2+} by EAA/Flame (Welz & Sperling 1999). The obtained results were evaluated by multivariate analysis using Statistica 5.0.

The adsorption kinetics of Cd^{2+} by grape adsorbents was evaluated by placing the adsorbent biomass in contact with solutions of Cd^{2+} in increasing amounts of time. For that, 200 mg of each adsorbent was separately placed in an Erlenmeyer flask with 50 mL of Cd^{2+} solution at 10 mg L^{-1}, pH 5.00, 25 °C and contact time from 10 to 180 min. After the centrifugation, the remained concentration of Cd^{2+} was determined by flame atomic absorption spectroscopy (FAAS) and the results linearized by the models of pseudo-first-order (Lagergren 1898), pseudo-second-order (Ho & McKay 1999), Elovich (Roginski 1948) and intraparticle diffusion (Weber & Morris 1963).

Adsorption isotherms were constructed using 200 mg of each adsorbent in Erlenmeyer flask containing 50 mL of Cd^{2+} solution at increasing concentrations (5 to 200 mg L^{-1}) at pH 5.00 and 25 °C at 200 rpm in thermostated Dubnoff system for 1 h. After centrifugation, the remaining concentration of Cd^{2+} was determined by FAAS, and the results linearized by Langmuir (1916), Freundlich (1906), Dubinin & Radushkevich (1947) and Sips (1948).

Thermodynamics parameters were also evaluated, using 200 mg of each adsorbent in an Erlenmeyer flask with 50 mL of Cd^{2+} solution at 10 mg L^{-1}, pH 5.00, 200 rpm with increasing temperatures of 15, 25, 35, 45 and 55 °C for 1 h. After the centrifugation, the remaining concentration of Cd^{2+} was determined by FAAS for the linearization and estimative of ΔG, ΔH and ΔS.

All equations and models used in this research are exhibited in Table 1 (supplementary material, available with the online version of this paper).

RESULTS AND DISCUSSION

Characterization of adsorbents

The values obtained for the pH$_{PZC}$ (Figure 1) of adsorbents are 4.28 to E. *in natura*, 4.09 for E. H$_2$O$_2$, 2.41 for E. H$_2$SO$_4$

Table 1 | SSA, volume and pore diameter for grape stem adsorbents

Biosorbent	SSA (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Pore diameter (nm)
E. *in natura*	0.148	9.43 × 10^{-4}	3.94
E. H$_2$O$_2$	0.470	18.49 × 10^{-4}	1.55
E. H$_2$SO$_4$	0.143	23.79 × 10^{-4}	64.73
E. NaOH	0.238	12.93 × 10^{-4}	1.93
Pinus barks (H$_2$O$_2$)[a]	0.760	56.00 × 10^{-4}	14.66
Cassava barks (H$_2$SO$_4$)[b]	0.464	17.9 × 10^{-4}	3.29
Cd^{2+} ions hydration radius[c]	0.275 nm		

[a]Schwantes *et al.* (2018).
[b]Schwantes *et al.* (2016).
[c]Tagliaferro *et al.* (2011).

and 7.10 for E. NaOH. The net charge on the adsorbent surface is positive when the pH of solution is inferior to the pH$_{PZC}$ value, and negative, when the pH of solution is superior to pH$_{PZC}$ value (Silveira Neta *et al.* 2012).

The change in pH$_{PZC}$ occurred according to the acidification or alkalization from each solution, causing protonation, deprotonation or hydroxylation of chemical groups of grapes biomass. Thus, when the pH$_{environment}$ > pH$_{PZC}$, the surface of the adsorbent is electronegative, favoring the adsorption of Cd^{2+}; however, if the pH$_{environment}$ < pH$_{PZC}$, the surface of the adsorbent is electropositive, in this state, the H$^+$ ions compete with Cd^{2+}, repelling or reducing the surface of adsorption (Schwantes *et al.* 2016).

It is possible to observe vibrational stretching at 3,395 to 3,422 cm^{-1}, 2,919 to 2,922 cm^{-1}, 1,735 to 1,738 cm^{-1}, 1,614 to 1,622 cm^{-1}, 1,513 to 1,522 cm^{-1}, 1,441 to 1,443 cm^{-1}, 1,390 to 1,400 cm^{-1}, 1,272 cm^{-1}, 1,060 cm^{-1} and 408 to 435 cm^{-1} (Figure 1).

The strong and broadband at 3,395 to 3,422 cm^{-1}, may result from a stretching asymmetric hydroxyl OH groups present in water and cellulose, and the symmetrical stretching of N-H bonds associated with primary (aliphatic and aromatic) and secondary amines (Barbosa 2007).

The peaks among 2,919 to 2,922 cm^{-1} can be referred to the stretching vibration of C-H bonds, and may be symmetrical or asymmetrical, due to the presence of alkanes, acyl, aliphatic acids and lipids (Abidi *et al.* 2014).

The peaks between 1,735 to 1,738 cm^{-1}, tend to be axial stretching of C = O bonds of aldehydes and esters groups, originating from polysaccharide, lipid and hemicellulose (Barbosa 2007).

The vibrational waves between 1,614 to 1,622 cm^{-1}, may refer to C-C phenyl ring stretch, but can also be
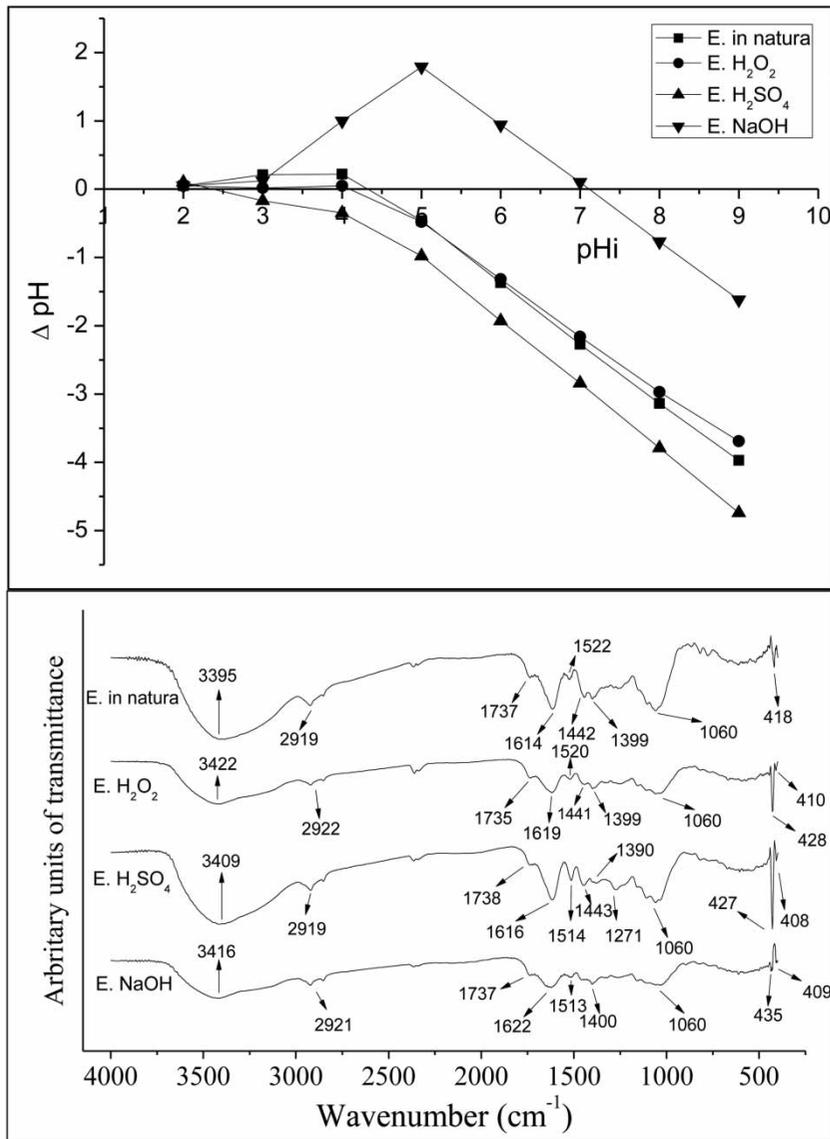
Figure 1 │ pH$_{PZC}$ (above) and FTIR spectroscopy, for grape stem adsorbents (below).

associated with nucleic acids peaks due to carbonyl and carboxyl groups (Schulz & Baranska 2007). The peaks among 1,513 to 1,522 cm^{-1}, may be related to the N-H group, referring to secondary amide, probably of protein degradation.

The stretching vibrational around 1,441 to 1,443 cm^{-1}, tend to angular deformation of C-H$_2$ or C-H$_3$, related to lipids and fatty acids, and aromatic compounds, respectively (Barbosa 2007).

The wave in 1,390 cm^{-1} can be related to carbon particles, as the peaks present in E. *in natura* and E. H$_2$SO$_4$, the 1,399 cm^{-1}, arise mainly from the vibrational modes of methyl and methylene groups of proteins, lipids and amino groups being a symmetric bending mode of CH$_3$. The adsorbent E. NaOH exhibits a peak at 1,440 cm^{-1}, derived from

symmetric stretching vibration of the COO$^-$ group linked to fatty acids and amino acids, and symmetrical stretching of CH$_3$ protein.

The stretching vibration at 1,060 cm^{-1} may be related to the group CO deoxyribose from nucleic acids or cellulose and polysaccharide degradation bonds such as CO, CC and OCH (Barbosa 2007).

Importantly, new groups, not previously seen in adsorbent E. *in natura* can be observed, such as vibrational stretch in 1,271 cm^{-1}, found only in E. H$_2$SO$_4$, which refers to a mass balance in the C-H bond (Schulz & Baranska 2007). A peak at 1,514 cm^{-1} is possibly related to the presence of a carotenoid structure that may be a cellular pigment.

The chemical modifications with H_2O_2 and NaOH caused a small increase in the specific surface area (SSA) of grape stem (Table 1). In addition, it is observed that the pore volume increased significantly when compared to the biosorbent (E. *in natura*), with increases of 1.9× for E. H_2O_2, 2.5× for E. H_2SO_4 and 1.8 for E NaOH.

The adsorbent E. H_2SO_4 exhibits the higher pore diameter (64.73 nm) which, according to IUPAC (1972) constitutes a macroporous material, while E. *in natura* is generally mesoporous (~2–50 nm) and E. H_2O_2 predominantly microporous (0–2 nm). These results are similar to other biosorbent materials (1–2) after simple chemical modification as *Pinus* barks treated with H_2O_2 and H_2SO_4.

The thermogravimetric analysis (TG and DTG) was performed to verify the thermic stability of grape stems *in natura* and after the treatments with H_2O_2, H_2SO_4 and NaOH. The TG and DTG curves can be seen in Figure 2.

The adsorbent E. *in natura* (Figure 2) exhibited three events, the first at 76 °C with mass loss of 6%, possibly related to the loss of water and volatiles. In the second event, with 211 °C and with mass loss of 12%, with the decomposition of hemicellulose. The third event is exhibited at 325 °C, with a mass loss of 62%, possibly related to cellulose breakage (Melzer *et al.* 2013).

For adsorbent E. H_2O_2, it is exhibited the first mass loss at 64 °C, with a reduction of 9% of mass, possibly due to loss of water. The second event occurred at 352 °C, due to the degradation of cellulose, lignin, hemicelluloses, minerals and condensed tannins, reaching 60% of its mass.

For adsorbent E. H_2SO_4, the first event occurred at 75 °C, with mass loss of 8%, possibly due to volatiles and water content. Another event is exhibited at 321 °C, with decomposition of 63% of mass, due to the breakdown of carbohydrates, such as hemicellulose and cellulose (Rambo *et al.* 2015).

The adsorbent E. NaOH exhibited three distinct events, the first at 76 °C, possibly related to the evaporation of water and volatile compounds, resulting in mass loss of 8%. The
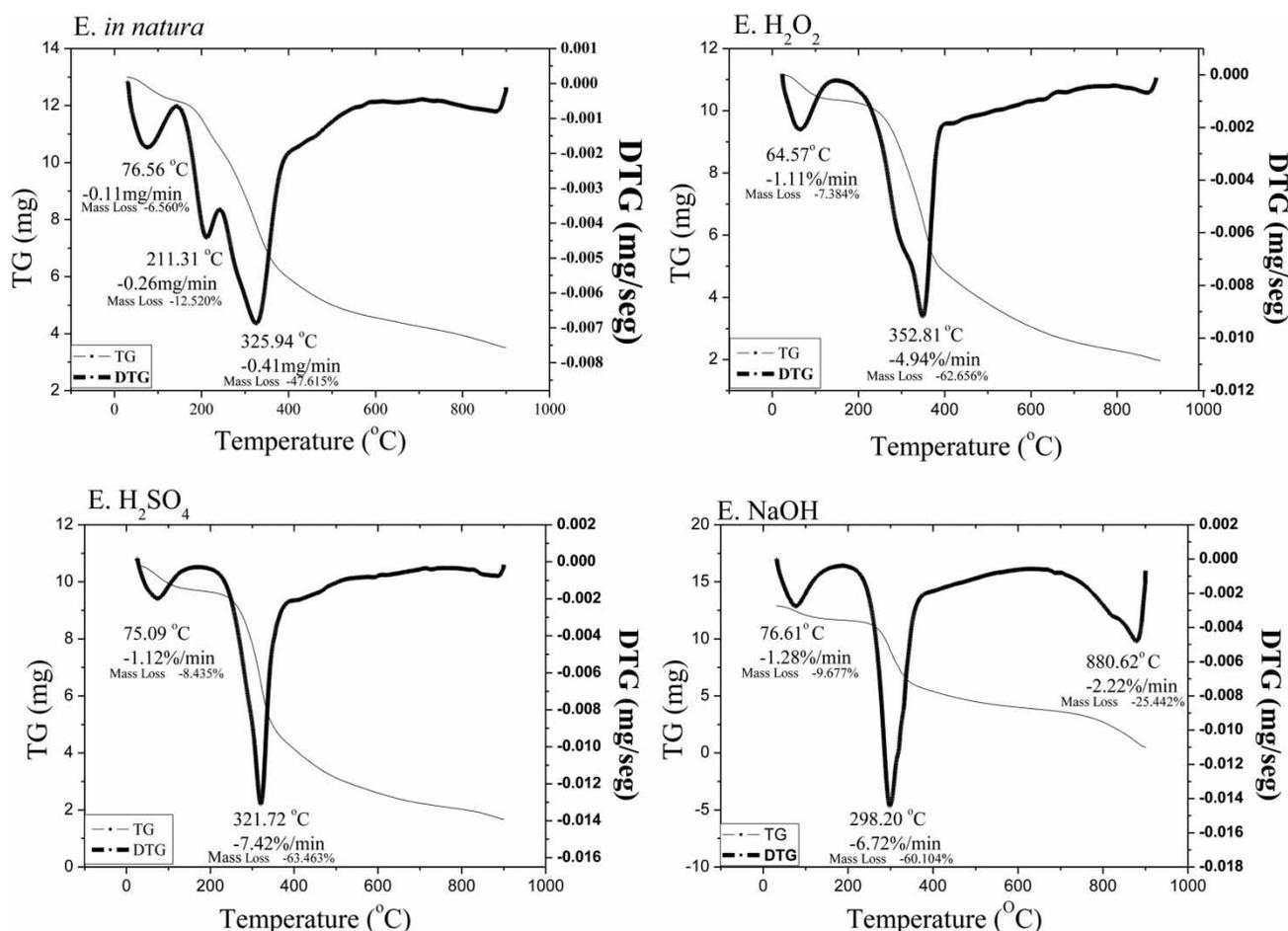

Figure 2 | TG and DTG curves for the grape stem adsorbents.

second mass loss (60%) occurred at 298 °C, with probable degradation of compounds such as cellulose and hemicellulosis. The third event occurred at 880 °C, with 25% of mass loss, probably due to the incineration of the remaining material, resulting in ash formation (Melzer *et al.* 2013).

The SEM at Figure 3 illustrates, for E. *in natura*, an irregular and heterogeneous surface. The SEM for E. H_2O_2, which resulted from a modification with a powerful oxidizing agent, reveals an area with many cavities, and heterogeneous, spongy and tubular aspects.

The micrograph for E. H_2SO_4, which resulted from a strong acid treatment, known also as a powerful dehydrating agent, exhibits a heterogeneous surface, though with numerous cavities of spongy appearance.

For E. NaOH, which was treated with a strong base, known for its corrosion and solubilization of numerous organic compounds, the SEM exhibits a heterogeneous surface, however irregular, also with numerous cavities.

As noted, all the obtained adsorbents exhibit heterogeneous morphologic characteristics that resemble the biomass origin (E. *in natura*); however, each applied chemical treatment generated adsorbents with particular characteristics, according to the employed modifying agent.

According to Nacke *et al.* (2016, 2017) irregular appearance, heterogeneity, many cavities, are generally characteristics that generate high SSA, which are usually characteristic of adsorbents with high adsorption capacity of ions in solution.

Rubio *et al.* (2015) in evaluating crambe biosorbents obtained SEM with an irregular and heterogeneous structure, which, according to the authors, was experimentally demonstrated to be a primordial characteristic for high adsorption rates of Pb^{2+} ions in the aqueous medium.

Experiments with Cd^{2+} adsorption

Significant differences were found at 1% for adsorbent E. *in natura*, E. H_2O_2, E. H_2SO_4 and E. NaOH regarding the source of variation 'adsorbent mass' (for linear and quadratic models), indicating that the amount of adsorbent mass influences the process of adsorption of Cd^{2+} (Table 2).

Significant difference at 5% was found for E. H_2SO_4, for the '*pH of Cd^{2+} solution*' (for linear and quadratic models), indicating that for this specific adsorbent, the pH range has influence in the adsorption process of Cd^{2+}. For other adsorbents, no significant differences for pH ranges were found, suggesting that in the evaluated range (3.00 to 7.00), the pH of the solution does not cause influence on Cd^{2+} adsorption.

This result is extremely favorable, because it demonstrates grape stem adsorbents can remedy Cd^{2+} from aquatic environments with high removal capacity within the pH range of 3.00 to 7.00, without requiring any adjustment to the pH of the liquid medium (Figure 4).

As can be seen at Figure 4 and in Table 1, the pH ranges do not cause significant variation in Cd^{2+} adsorption, except for adsorbent E. $H_2SO_{4.}$ In general, the greater Cd^{2+} removal rates (measured by the adsorbed amount Q_{eq} or Q_{ads}), were obtained for adsorbents masses close to 200 mg (ratio of 5.0 g L^{-1} or Kg m^3).

In this way, it can be estimated that at least 50% of the grape stem produced in Brazil in 2016 were used in the manufacture of biosorbents, about 123,000 tons of adsorbents would be produced, with the possibility of removing an enormous amount of cadmium from contaminated water. As already mentioned, the availability of plant waste is one of the factors that makes its use so attractive.

According to Meneghel *et al.* (2013) and Rubio *et al.* (2013), the relation between adsorbent mass and volume of contaminated water is critical. In certain cases, a decrease in the adsorbed amount occurs due to the formation of agglomerates, which will reduce the total surface area and therefore the number of available active sites.

Grape stem materials exhibited the following Cd^{2+} adsorption capacity: E. *in natura* 1.20, E. H_2O_2 1.60, E. H_2SO_4 1.20 and E. NaOH 2.00 mg g^{-1}, i.e. an increase of the adsorption capacity of 33% for E. H_2O_2 and 66% for E. NaOH, when compared to the biosorbent E. *in natura*.

Although only tested in laboratory scale, several authors have already reported the use of modified biosorbents in bed columns, aiming the removal of metals such as Cd from industrial effluents (Ahmad & Haydar 2016), various heavy metals from wastewater (Abdolali *et al.* 2017), Ni^{2+} and Cu^{2+} (Barquilha *et al.* 2017), and many others.

In 20 min of contact-time, the adsorption system enters in chemical equilibrium, not exhibiting great variations on the Cd^{2+} adsorption rate after this time interval (Figure 5 left), i.e. the adsorption of Cd^{2+} by grape stem materials is a fast process.

Elovich, pseudo-first-order and intraparticle diffusion models don't fit well to the experimental data (Table 3), however, good adjustments (R^2 values) are exhibited for pseudo-second-order model, suggesting the occurrence of Cd^{2+} chemisorption by E. *in natura*, E. H_2O_2, E. H_2SO_4 and E. NaOH (Ho & McKay 1999). In addition, the calculated adsorption capacity predicted by pseudo-second ($Q_{eq\ (cal.)}$) approach the experimental values ($Q_{eq\ (exp.)}$).
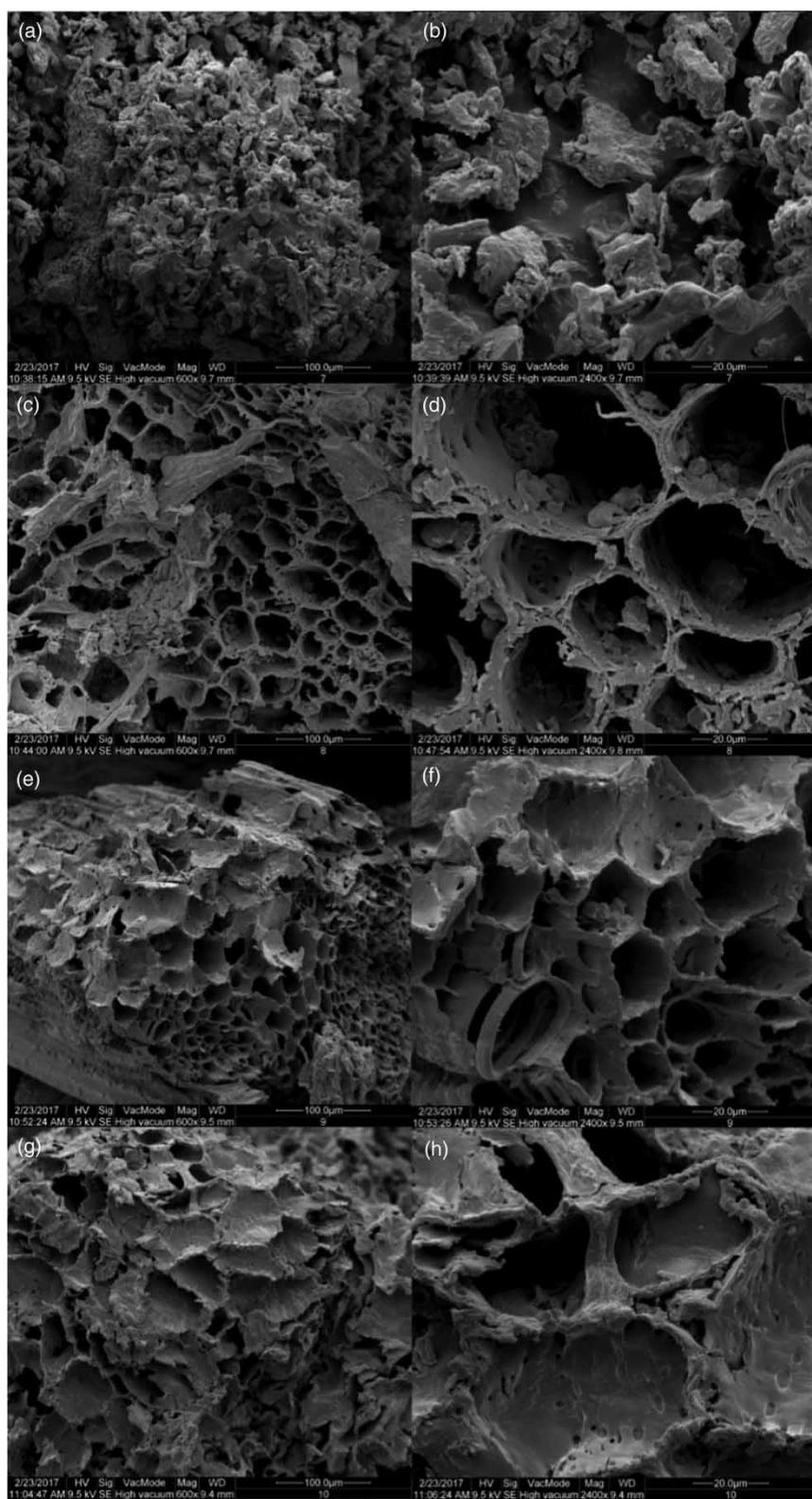
Figure 3 │ SEM for adsorbents E. *in natura* at 600 (a) and 2,400× (b), E. H_2O_2 at 600 (c) and 2,400× (d), E. H_2SO_4 at 600 (e) and 2,400× (f), and E. NaOH at 600 (g) and 2,400× (h).

Table 2 | Summary of the analysis of variance (ANOVA) for tests involving adsorbent mass and pH of Cd^{2+} solution

Sources of variation	Degrees of freedom	Average squares			
		E. *in natura*	E. H_2O_2	E. H_2SO_4	E. NaOH
Mass (L)	1	0.658324[a]	1.059795[a]	0.563293[a]	1.886175[a]
Mass (Q)	1	0.171143[a]	0.201129[a]	0.140963[a]	0.409658[a]
pH (L)	1	0.002291[ns]	0.010476[ns]	0.078108[b]	0.000035[ns]
pH (Q)	1	0.00338[ns]	0.002326[ns]	0.030001[ns]	0.001817[ns]
Mass × pH	1	0.002113[ns]	0.002002[ns]	0.01655[ns]	0.00001[ns]
Residue	6	0.00498	0.002645	0.006695	0.010799
Total	11				

[ns], not significant.
[a]Significant at 1%.
[b]Significant at 5%.

Many other studies aiming the use of biosorbents for metal removal found excellent adjustments for pseudo-second-order: Schwantes *et al.* (2016) using cassava barks for adsorption of Cd^{2+}, Pb^{2+} and Cr^{3+}; Schwantes *et al.* (2015) with crambe pie for Cd^{2+}, Pb^{2+} and Cr^{3+} removal; Schwantes *et al.* (2018) with *Pinus* barks aiming Cd^{2+}, Pb^{2+} and Cr^{3+} removal; Ngabura *et al.* (2018) using durian peels for Zn^{2+} adsorption; Nacke *et al.* (2016, 2017) using *Jatropha curcas* L. biosorbents for Cu^{2+} and Zn^{2+} removal.

These results demonstrates that numerous lignocellulosic-based adsorbents, when in contact with heavy metals in liquid phase, undergo chemisorption. In all these cited biosorbents is recurrent the existence of carboxylic, hydroxyl, methoxy, and phenolic groups that are potentially active in metals binding (Hokkanen Bhatnagar & Sillanpaa 2016).

For pseudo-first-order, K_1 assumes negative values, indicating that the concentration of solutes in solution decreases with increasing time (Table 3). However, the observed data fit to pseudo-second-order model. The pseudo-second-order kinetics describes well the processes of chemical adsorption, involving donation or exchange of electrons between the adsorbate and the adsorbent, as covalent and ion exchange forces (Ho & McKay 1999). In this type of adsorption, the molecules are not attracted by all the points of the surface of the solid, but specifically to the active sites, forming a single layer initially, and other layers may be formed by physisorption.

A mechanistic study was carried out to evaluate the diffusion of the adsorbate using the Morris–Weber model for the studied system and, despite the low porosity of the adsorbent material (Table 1), there is an occurrence of intraparticle diffusion. Cd^{2+} ions hydration radius of 0.275 nm (Tagliaferro *et al.* 2011), i.e. lower than the average pore diameter at the surface of the adsorbents, allows the diffusion of Cd^{2+} ions into the adsorbent pores. In spite of this fact, the low obtained adjustments (R^2) suggest that intraparticle diffusion is not the governing mechanism of the adsorption process in this case.

According to equilibrium tests, E. NaOH was the adsorbent with the higher values of Cd^{2+} removal (Figure 5 right), with an average of 70% of metal removal in the interval of 5 to 200 mg L^{-1} of Cd^{2+} in solution.

Grape stem adsorbents presented good fit (R^2) to Langmuir model (Table 4), which suggests adsorption of Cd^{2+} in monolayers. It should also be noted that the adsorption process predicted by Langmuir model was favorable since R_L values ranged from 0 to 1, for E. *in natura*, E. H_2SO_4 and E. NaOH (Langmuir 1916).

In this context, the adsorbent E. NaOH, which had the best value of Q_m, 14.9 mg g^{-1}, i.e. with an increase of 8.4× in the precursor biosorbent. Good fit was also obtained by Freundlich for E. NaOH, suggesting the simultaneous occurrence of mono and multilayer Cd^{2+}. In this case, n is higher than 1, indicating, for E. NaOH, active sites of high reactivity (Schwantes *et al.* 2018).

The Qm obtained for E. NaOH (14.9 mg g^{-1}) is higher than obtained by Lo *et al.* (2012) using bamboo active coal (0.67 mg g^{-1} for Pb^{2+}) and obtained by Schwantes *et al.* (2018) using *Pinus* biosorbent (10.83 mg g^{-1} for Cd^{2+}).

E. *in natura* and E. NaOH exhibit good fit for D-R, with E (sorption energy) values greater than 8 KJ mol^{-1}, indicating Cd^{2+} chemisorption (Dubinin & Radushkevich 1947).

The values of ΔH indicate endothermic reactive systems ($\Delta H > 0$) or exothermic ($\Delta H < 0$) (Wan Ngah &
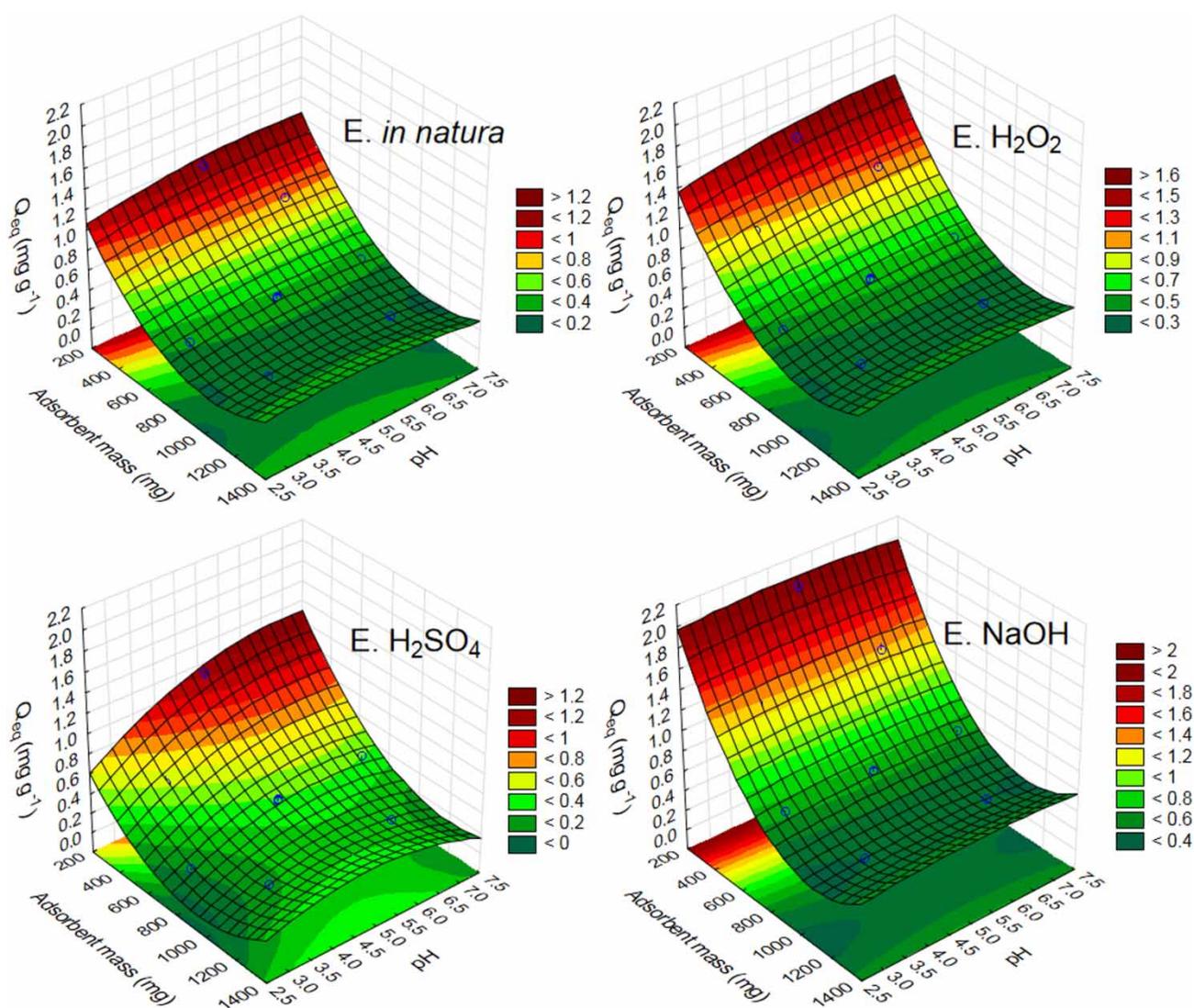
Figure 4 | Surface of response for adsorbed amount at equilibrium (Q_{eq}) *versus* pH of Cd^{2+} solution *versus* mass of grape stem adsorbents. x = adsorbent mass, from 250 to 1,250 mg (5.0 to 25 g L^{-1} or Kg m^3), y = pH of the solution containing Cd^{2+} at 10 mg L^{-1}, z = quantity of adsorbed Cd^{2+} at equilibrium (mg g^{-1}). E. *in natura* z = 1.20239 − 0.00254378x + 0.0000013077x^2 + 0.161047y − 0.0114731y^2 − 0.000045822xy R^2: 98.1%. E. H_2O_2 z = 1.58617 − 0.00293286x + 0.000001417x^2 + 0.154181y − 0.00951766y^2 − 0.000044605xy R^2: 98.8%. E. H_2SO_4 z = −0.0634065 − 0.00188951x + 0.0000011868x^2 + 0.507761y − 0.0341814y^2 0.00012824xy R^2: 94.5%. E. NaOH z = 2.61556 − 0.00442359x + 0.0000020232x^2 + 0.083276y − 0.00841089y2 + 0.000003090xy R^2: 97.9%.

Fatinathan 2010). The results of Table 5 indicate that the adsorption of Cd^{2+} by E. *in natura* and E. H_2O_2 is endothermic, whereas the adsorption by E. H_2SO_4 and E. NaOH is exothermic.

According to Wan Ngah & Hanafiah (2008), when ∆G assumes negative values this is indicative of the spontaneous nature of the reaction, whereas positive values for ∆S indicate an increase in the disorder and randomness of the solid interface/solution during the sorting process.

Thus, due to the values assumed by ∆G, the adsorption of Cd^{2+} by E. *in natura* and E. H_2O_2 constitute non-spontaneous sorption processes, whereas E. H_2SO_4 and E. NaOH constitute spontaneous adsorptive processes.

CONCLUSION

The grape stem biosorbent, after simple chemical modification with H_2O_2, H_2SO_4 and NaOH, exhibit different values for pH_{PZC}, possible functional groups such as carboxyl, amine, phenolic and other groups, modifications on adsorbents texture, but with similar thermal stabilities, and these results suggest that treatments carried out with
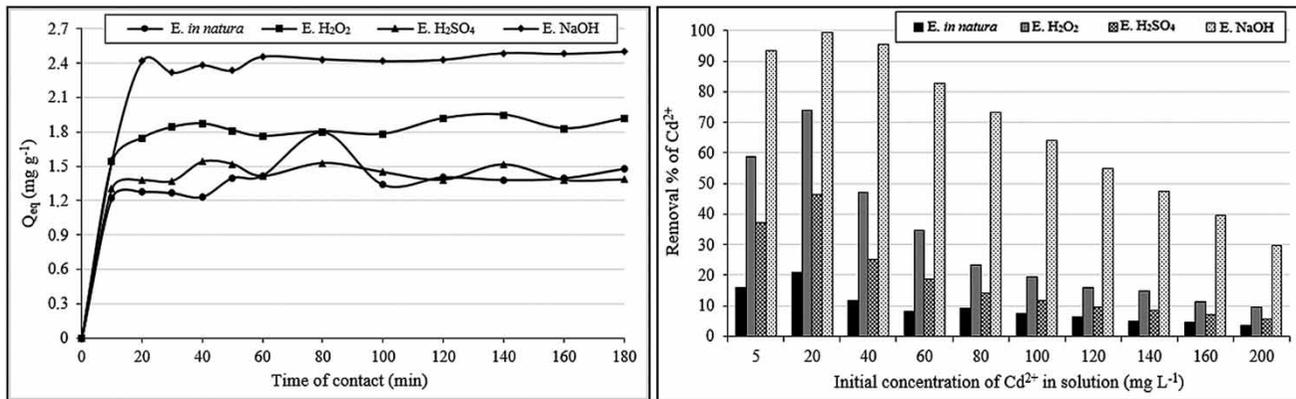
Figure 5 | (*left*) Kinetics of Cd^{2+} adsorption by grape stem materials. Experimental conditions: Initial concentration of Cd^{2+} of 10 mg L^{-1}, 200 rpm, 25 °C, pH of 5.00, mass of adsorbent/ volume of solution relation of 5.0 g L^{-1}. (*right*) Cd^{2+} removal percentage at increasing concentrations. Experimental conditions: 200 rpm, 25 °C, pH of 5.00, mass of adsorbent/ volume of solution relation of 5.0 g L^{-1}, 60 min of contact time.

Table 3 | Parameters of pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion for the removal of Cd^{2+} by E. *in natura*, E. H_2O_2, E. H_2SO_4 and E. NaOH

Models/Adsorbents	E. *in natura*	E. H_2O_2	E. H_2SO_4	E. NaOH
Pseudo-first-order				
K_1 (min^{-1})	−0.0031	−0.0037	−0.0094	−0.0149
$Q_{eq\ (cal.)}$ (mg g^{-1})	0.5961	0.2209	0.2250	0.2845
R^2	0.914	0.847	0.927	0.853
Pseudo-second-order				
K_2 (g mg^{-1} min^{-1})	0.1740	0.1877	−0.3335	0.1584
$Q_{eq\ (cal.)}$ (mg g^{-1})	1.4511	1.9170	1.3777	2.5176
R^2	0.997	0.997	0.998	1.000
Elovich				
a (mg g^{-1} h^{-1})	1.0891	1.5396	1.1460	1.8762
b (g mg^{-1})	0.0596	0.0606	0.0696	0.1202
R^2	0.939	0.642	0.930	0.892
$Q_{eq\ (exp.)}$ (mg g^{-1})	1.3823	1.8133	1.4302	2.3511
Adsorbents	**Intraparticle diffusion**	**Line A**	**Line B**	
E. *in natura*	K_{id} (g mg^{-1} $min^{-1/2}$) C_i (mg g^{-1}) R^2	0.0308 1.0350 0.905		
E. H_2O_2	K_{id} (g mg^{-1} $min^{-1/2}$) C_i (mg g^{-1}) R^2	0.1069 1.2290 0.937	0.0118 1.6776 0.735	
E. H_2SO_4	K_{id} (g mg^{-1} $min^{-1/2}$) C_i (mg g^{-1}) R^2	0.0223 1.2505 0.9594		
E. NaOH	K_{id} (g mg^{-1} $min^{-1/2}$) C_i (mg g^{-1}) R^2	0.0248 2.1707 0.971		

H_2O_2, H_2SO_4 and NaOH caused certain modifications on the biomass grape stems.

The modified adsorbents of grape stem exhibited superior adsorption rates to its precursor biosorbent, especially E. H_2O_2, with 33% of increase in adsorptive capacity, and E. NaOH, with adsorption elevation by 66%.

The use of such solid residues (grape stems) as raw material for the production of modified adsorbents appears

Table 4 | Linear parameters of Langmuir, Freundlich, D-R and Sips for adsorption of Cd^{2+} by E. *in natura*, E. H_2O_2, E. H_2SO_4 and E NaOH

Parameters		E. *in natura*	E. H_2O_2	E. H_2SO_4	E. NaOH
Langmuir	Q_m (mg g^{-1})	1.785	4.591	2.881	14.923
	K_L (L mg^{-1})	1.592	−0.036	0.441	0.000
	R_L	0.003	−0.159	0.011	0.988
	R^2	0.993	0.996	0.999	0.993
Freundlich	K_f (mg g^{-1})	0.061	3.128	1.886	7.797
	N	1.358	9.573	12.367	5.074
	R_2	0.959	0.894	0.910	0.992
D-R	Q_d (mol L^{-1})	9.017E-05	4.762E-05	4.885E-05	2.495E-04
	E (KJ mol^{-1})	8.853	36.140	32.308	17.961
	R^2	0.984	0.580	0.604	0.997
Sips	n	0.607	0.818	0.720	1.795
	K_s (L mg^{-1})	0.070	0.222	0.106	1.578
	R^2	0.995	0.885	0.999	0.999

Table 5 | Thermodynamic parameters for adsorption of Cd^{2+} by E. *in natura*, E. H_2O_2, E. H_2SO_4 and E. NaOH

Adsorbents	Temp. °C	Q_{eq} (mg g^{-1})	ΔG (KJ mol^{-1})	ΔH (J mol^{-1})	ΔS (J mol^{-1} K^{-1})	R^2
E. *in natura*	15	0.00	45.44	15.58	−103.71	0.93
	25	0.11	46.48			
	35	0.17	47.52			
	45	0.14	48.56			
	55	0.10	49.59			
E. H_2O_2	15	1.51	9.29	5.67	12.57	0.98
	25	1.57	9.41			
	35	1.61	9.54			
	45	1.56	9.67			
	55	1.67	9.79			
E. H_2SO_4	15	0.92	−30.05	−29.71	1.20	0.87
	25	0.93	−30.05			
	35	0.99	−30.05			
	45	1.03	−30.05			
	55	1.02	−30.05			
E. NaOH	15	2.40	−33.68	−21.71	41.55	0.91
	25	2.39	−33.68			
	35	2.37	−33.68			
	45	2.46	−33.68			
	55	2.38	−33.68			

as an excellent alternative for the disposal of these residues, allowing added value to a currently discarded residue.

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