O ensino e a pesquisa em
QUÍMICA

Cleiseano Emanuel da Silva Paniagua
(Organizador)

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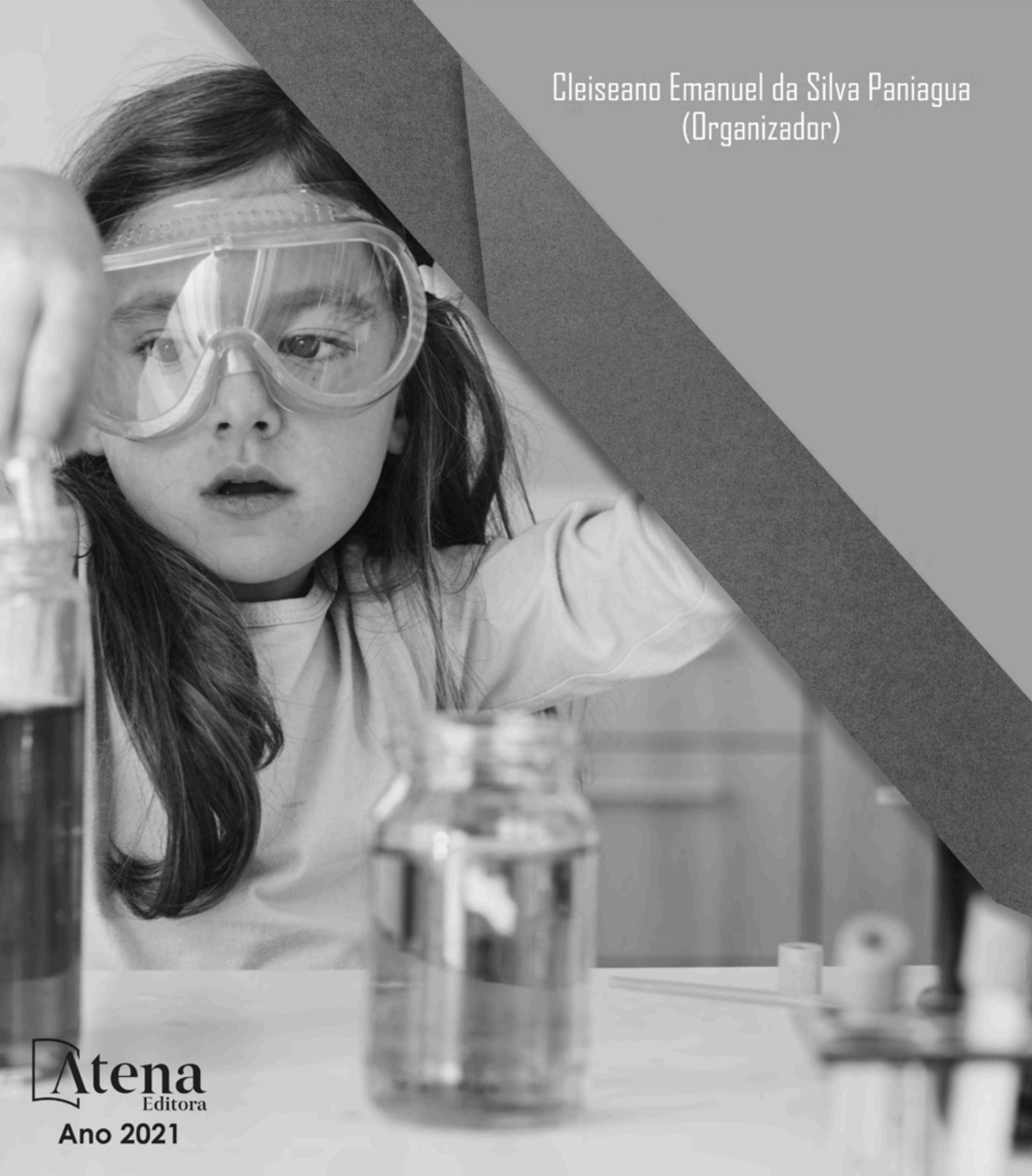

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APRESENTAÇÃO

O e-book: “O ensino e a pesquisa em química” volume I é constituído por quinze capítulos de livro que tratam das seguintes temáticas: processo de ensino-aprendizagem em química e desenvolvimento sustentável. Em relação a primeira temática, está é abordada em diferentes contextos e práticas que se encontram presente em doze dos quinze capítulos deste primeiro volume. Os trabalhos selecionados buscam investigar a diversidade de fatores que podem contribuir de forma positiva ou negativa nos diferentes processos de ensino-aprendizagem em química dentro ou fora do âmbito escolar. A disciplina de química é uma área das denominadas ciências da natureza ou ciências naturais que exigem uma grande capacidade de abstração para o entendimento de seus conceitos e como estes podem estar relacionados ao ambiente no qual o aluno se insere. Além disso, este campo do saber demanda a visualização de seus pressupostos teóricos em práticas por meio da experimentação que presume um espaço destinado à visualização ou o laboratório de química. Entretanto, este espaço não se faz presente em função da falta de recursos financeiros e projetos de políticas públicas voltadas para oferecer condições dos estabelecimentos da educação básica, manter um espaço destinado à experimentação química.

Neste contexto, os professores de química são desafiados a buscar alternativas para a experimentação a ser desenvolvida dentro do ambiente de sala ou em áreas abertas sem infra- estrutura necessária. Neste sentido, os trabalhos trazem abordagens sob diferentes óticas de experiências relatadas por intermédios de Práticas Pedagógicas Inovadoras (PPI), metodologias ativas de ensino e propostas de pesquisas realizadas na busca por materiais alternativos para substituir os tradicionais de alto custo e de difícil acesso. Tais experiências também são relatadas por meio de olimpíadas de química no México e práticas para alunos recém ingressos em instituições de ensino superior no Brasil.

A segunda temática apresenta três trabalhos que apresentam resultados pela busca de metodologias que possibilitem o desenvolvimento da Química Sustentável (Química Verde) e o desenvolvimento de adsorventes naturais para a remoção de metais pesados e/ou tóxicos em diferentes matrizes aquáticas, visando uma melhor qualidade tanto o ambiente quanto para o próprio homem.

Nesta perspectiva, a Atena Editora vem trabalhando por meio do incentivo de publicações de trabalhos de pesquisadores de todas as regiões do Brasil e de outros países com o intuito de colaborar com a publicação de e-books e, consequentemente, sua divulgação de forma gratuita em diferentes plataformas digitais de fácil acesso. Logo, a Atena Editora contribui para a divulgação e disseminação do conhecimento cientifico gerado dentro de instituições de ensino e pesquisa e que pode ser acessado de qualquer lugar e em tempo real por qualquer pessoa interessada na busca pelo conhecimento.

Cleiseano Emanuel da Silva Paniagua

SUMÁRIO

CAPÍTULO 15

PASSION FRUIT PEEL FLOUR AS ARSENIC BIOSORBENT FOR WATER TREATMENT

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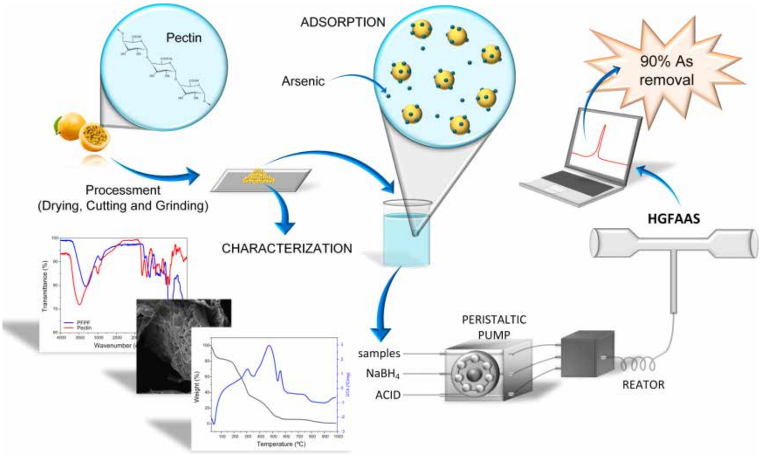
ABSTRACT: Recent work has shown that peels from passion fruit and other fruits can be successfully used for the removal of inorganic contaminants from water and wastewater. This work describes the chemical characterization of passion fruit (*Passiflora* sp.) peel flour (PFPF) and its use as an efficient and low-cost sorbent for As(III) removal in water treatment. Under experimental conditions, PFPF showed an As(III) adsorption capacity of 10.2 ± 0.6 mg g^{-1} and As(III) removal performance of 90%. The main difference between FTIR spectra acquired before and after As(III) adsorption was a band at around 1342 cm^{-1}, which could be attributed to interaction between As(III) and the carboxyl groups of PFPF. The thermal decomposition profiles of PFPF before and after As(III) adsorption showed significant differences, which could be explained by the desorption of arsenic oxide or fusion of the arsenic oxides. The adsorption of As(III) by PFPF was a spontaneous process. SEM images revealed an amorphous structure of PFPF, with large clusters of soft fibers favoring physical adsorption.

KEYWORDS: Inorganic contaminants; Biosorption; Wastewater, *Passiflora* sp.

GRAPHICAL ABSTRACT (GA)



GA Figure:

GA Text: Passion fruit peel flour is an efficient and low-cost sorbent for As removal from water. Passion fruit peel flour presented a performance of 90% for As removal.

1 | INTRODUCTION

The contamination of groundwater and soils by arsenic is a serious environmental problem and a health risk worldwide (BONDU et al., 2017; KUMAR et al., 2016; MIRLEAN; BAISCH; DINIZ, 2014; ZHOU et al., 2017). Due to this contamination, the accumulation of arsenic in plants is recognized as a serious problem in several countries, especially in Southeast Asia, where the contamination of rice with arsenic is a major public health issue (RITCHIE; MEKJINDA, 2016; WILLIAMS et al., 2009; ZHAO et al., 2009).

The Iron Quadrangle, a very important mining area in Brazil, is located in the State of Minas Gerais, where the region gained global notoriety after the Bento Rodrigues and Brumadinho Dam disasters. Since the major natural source of arsenic in soil is the weathering of rocks containing the element (KUMAR et al., 2016), mining can lead to arsenic contamination, especially in regions with gold occurrence because gold is often found together with minerals that contain arsenic. In this region, concentrations of arsenic 10-fold higher than the Brazilian legal limit have been reported, with several studies showing that contaminated water is used for consumption (BORBA et al., 2003; BORBA; FIGUEIREDO; CAVALCANTI, 2004; GARDENAL, 2002; GONÇALVES et al., 2007). The occurrence of arsenic in water is therefore a matter of concern, necessitating frequent monitoring and the development of methods for the removal of arsenic from groundwater and wastewater. Inorganic arsenic can be found in the environment in several forms, including As (0), As (III) and As (V), being that As (III) is 60 times more toxic than As (V). (HADIANI; KHOSRAVI-DARANI; RAHIMIFARD, 2019)

Techniques for arsenic decontamination that have been reported in the last decade include reverse osmosis (XU; CAPITO; CATH, 2013), adsorption (REN et al., 2014), coagulation and filtration (FEISTEL et al., 2016), ion exchange (LEE et al., 2017) and photocatalysis/complexation-ultrafiltration (MOLINARI; ARGURIO, 2017). However, these methods can be sophisticated and expensive. As an alternative, biosorption is a very promising nonconventional process, offering the advantages of an abundant availability of biomass, low cost, and high efficiency for toxic element removal. Biosorption is the ability of some types of biomass to remove substances from solution by means of processes of adsorption, ion exchange, coordination complexation, chelation, or microprecipitation (FEBRIANTO et al., 2009). Recent studies have described the use of various biomasses for the removal of arsenic from water (CHIBAN et al., 2016; CHRISTOBEL; LIPTON, 2015; HADIANI; KHOSRAVI-DARANI; RAHIMIFARD, 2019; SIBI, 2014; SINGH; SINHA; SRIVASTAVA, 2015).

According to the Brazilian Service for the Support of Micro and Small Companies (SEBRAE), Brazil is the world's largest producer of passion fruit (*Passiflora* sp.). The fruit is often consumed fresh, but its main economic importance is for juice manufacture. The pulp is also used for the preparation of ice creams, wines, liqueurs, and sweets. Work has sought to find ways to exploit industrial juice manufacturing residues, which are usually discarded or used as animal feed and organic fertilizer (SEBRAE, 2016). Waste peel from agroindustry can be a major environmental problem, so the use of this waste to remove toxic elements from water may be highly advantageous, since it solves two problems simultaneously and at low cost. In recent studies, the peels of passion fruit and other fruits were successfully used for the biosorption of Cu(II), Cd(II), Ni(II), and Pb(II) (CHAO; CHANG; NIEVA, 2014) as well as Zr(IV) (BHATTI et al., 2016).

Bearing in mind the principles of green chemistry, the large generation of agro-industrial residue and the problems of public health caused by arsenic contamination, this work presents a chemical characterization of passion fruit peel and investigates its use as sorbent for As(III) removal in water treatment, with a brief discussion of the mechanisms involved in the adsorption.

2 | EXPERIMENTAL

2.1 Preparation of passion fruit peel flour (PFPF)

The samples of passion fruit (PF) without pulp were from a pulp juice factory located in Ouro Preto, a city in the State of Minas Gerais, Brazil. After washing and removing the flavedo, the albedo of the PF was dried in a kiln at 60 °C, followed by manually cutting and grinding in a knife mill (A11 Basic, IKA). The flour obtained from this procedure was denoted PFPF.

2.2 Extraction of pectin from the PFPF

Since pectin is a major component of PF peel, it was extracted from the PFPF according to a procedure adapted from Pinheiro et al. (2008), using (5.0000 ± 0.0001) g of PFPF and 0.01 mol L^{-1} citric acid solution, under reflux at 97 °C for 1 h in a condensation system. The hot extract was filtered using qualitative filter paper (Unifil), under reduced pressure, and was then cooled to 4 °C. Ethanol solution (1:2 v v^{-1}) was added to the filtrate and the pectin precipitate was separated by centrifugation at 400 rpm for 15 min (Excelsa 3 Model 280 centrifuge, Fanem).

2.3 PFPF characterization

2.3.1 Spectroscopic and surface characterization

Fourier transform infrared spectroscopy (FTIR) analyses were made of the PFPF (before and after As(III) adsorption) and the extracted pectin (for comparison). The sample was placed directly on the crystal for attenuated total reflectance (ATR) analysis. The ATR-FTIR spectra were recorded from 500 to 4000 cm^{-1}, using a spectrometer (Model MB3000, ABB Bomen, Quebec, Canada) with ZnSe optics and a DTGS detector, at a resolution of 4 cm^{-1} and with 32 scans.

The surfaces of the PFPF and PFPF-As were studied using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS), employing a Vega3 SB instrument (Tescan/Oxford Instruments) equipped with a tungsten filament and a secondary electron detector. The instrument was operated at 15-20 keV. The samples were attached to a sample holder fitted with a graphite ribbon and were coated with gold, under vacuum, using a Q150R ES system (Quorum Technologies).

The point of zero charge (PZC) of the PFPF was determined as described by Teodoro et al. (2016) with minor modifications. Solutions of 0.01 mol L^{-1} $NaNO_3$ with initial pH values of 3, 6, and 11 were used as background electrolyte. The pH was adjusted using solutions of 1 mol L^{-1} NaOH and 1.0 mol L^{-1} HCl (Merck, analytical grade). Aliquots (20.0 mL) of 0.01 mol L^{-1} $NaNO_3$ solution, at pH 3, 6, or 11, were transferred to 125 mL Erlenmeyer flasks, together with PFPF, to give suspensions with PFPF concentrations of 0.5, 1.0, 3.0, and 5.0 % (w v^{-1}). The twelve flasks were mechanically stirred for 24 h at 130 rpm and 25 ºC (TE-424, TECNAL) and the equilibrium pH was measured using a pH meter (Kasvi).

2.3.2 Thermal characterization

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of the PFPF (before and after As(III) adsorption) employed a TA Instruments SDT 2960 analyzer operated with a 20 mL min^{-1} flow of nitrogen and heating from 25 to 1000 °C, at a rate of 10 °C min^{-1}. The measurements were performed in triplicate, using (6.0 ± 0.2) mg of sample.

2.4 Adsorption experiments

The experiments of As(III) adsorption on the PFPF were carried out in batch mode, with evaluation based on the initial As(III) concentration and the contact time, enabling determination of the kinetics of the process and evaluation of the performance of PFPF as an arsenic adsorbent.

Adsorption and desorption experiments were performed in triplicate, at 25 °C, using an incubator-shaker (TE-424, TECNAL). The diluted solutions were prepared from a 1000 mg L^{-1} As (III) standard (SpecSol code SQ31355-250, matrix: NaOH). The pH of the diluted solutions was adjusted to pH 5.0, using 1.0 mol L^{-1} and 0.1 mol L^{-1} HNO_3.

The solutions were analyzed by hydride generation-flame atomic absorption spectrometry (HG-FAAS), using a Buck Scientific Model 420 hydride generator and a flame atomic absorption spectrometer (APHA Method 3114). The material obtained after As(III) adsorption was denoted PFPF-As.

For kinetics experiments, aliquots of 25.00 mL of 2.42 mg L^{-1} As(III) solution were added to (0.0200 ± 0.0001) g of PFPF in Erlenmeyer flasks, followed by stirring at 150 rpm for different times (0.50, 1.0, 2.0, 3.0, 4.0, 5.0, and 6.0 h).

For equilibrium experiments, aliquots of 25.00 mL of As(III) solutions at different concentrations (0.800, 1.000, 1.300, 1.500, 1.800, 2.000, 2.300, 3.200, 4.000, 6.000, 8.000, 15.00, 20.00, 25.00, 30.00, and 40.00 mg L^{-1}) were added to (0.0200 ± 0.0001) g of PFPF, followed by stirring the systems at 150 rpm for 4 h (the time selected from the kinetics assays). The samples were then filtered through qualitative filter paper (Unifil) and the arsenic concentrations in the supernatants were quantified. The amount of As(III) adsorbed at equilibrium (q, mg g^{-1}) and the percentage adsorption (*%Ads*) were calculated using Equations (1) and (2), respectively:

$$q = \frac{C_0 - C_{eq}}{m} V \qquad (1)$$

$$\% Ads = \frac{C_0 - C_{eq}}{C_0} 100 \qquad (2)$$

where, C_0 and C_{eq} are the initial and equilibrium As(III) concentrations (mg L^{-1}), respectively, V is the solution volume (L), and m is the mass (g) of adsorbent.

The experimental adsorption data were fitted with the Langmuir model (Equation (3)), using OriginPro 8.0 software to fit nonlinear equations to the adsorption results, hence reducing the errors resulting from linearization of the experimental data.

$$q_e = \frac{(Q_{max} K_L C_{eq})}{(1 + K_L C_{eq})} \qquad (3)$$

where, q_e is the amount of As(III) adsorbed by the PFPF (mg g^{-1}), Q_{max} (mg g^{-1}) is the maximum monolayer adsorption capacity, and K_L (L mg^{-1}) is the Langmuir constant related to the affinity between the adsorption sites and the adsorbate.

The constant K_L was used to calculate the change in the free energy of adsorption ($\Delta_{ads}G^o$) for the adsorption of As(III) by the PFPF using Equation (4):

$$\Delta_{ads}G^o = -RT \ln K_a \tag{4}$$

where, R is the ideal gas constant (8.314 J K^{-1} mol^{-1}), T is the absolute temperature (K), and K_a is the thermodynamic equilibrium constant (dimensionless), which was calculated from the Langmuir constant, K_L, as discussed by Liu (2009).

The fitting of the Langmuir model was performed with error adjustment and statistical weighting provided by the *OriginPro 8.0* software. This version of Origin supports errors associated with the y-axis magnitude. For multiple data sets, it is possible to specify different weighting methods to calculate the y-values. The quality of the fit was evaluated using the following error functions: adjusted coefficient of determination (R_{adj}^2), reduced Chi-squared (χ^2_{red}), and residual sum of squares (RSS). The reduced Chi-squared function was calculated according to Equations (5)-(7). RSS was calculated using Equation (8).

$$\chi^2_{\mathrm{red}} = \frac{\chi^2}{\upsilon} \tag{5}$$

$$\chi^2_{\mathrm{red}} = \sum_{i=1}^{N} \omega_i \left(q_{\mathrm{e}} - \hat{q}_{\mathrm{e}}\right)^2 \tag{6}$$

$$\omega_i = \frac{1}{q_{\mathrm{e}}} \tag{7}$$

$$RSS = \sum_{i=1}^{N} \omega_i \left(\hat{q}_{\mathrm{e}} - q_{\mathrm{e}}\right)^2 \tag{8}$$

where, (χ^2_{red}) is the reduced chi-squared function, $\boldsymbol{\upsilon}$ is the number of degrees of freedom ($\upsilon = N - P$) where N is the number of experimental data points and P is the number of variables of the model), ω_i is the weighting coefficient, q_e is the point of the experimental data and $\hat{q}_{\mathrm{e}}$ is the point of the data estimated by the model.

2.5 Performance and reuse of PFPF in removal of As(III)

Evaluation was made of the performance of PFPF in the removal of As(III) from a wastewater produced during routine atomic absorption spectrometry analyses in the laboratory. This wastewater had an estimated As(III) concentration greater than 5.0 mg L^{-1}, together with an iron concentration of 2.3 ± 0.9 mg L^{-1}. Aliquots of 25.00 mL of the wastewater were added to (0.0200 ± 0.0001) g of PFPF in Erlenmeyer flasks, followed by stirring for 4 h at 150 rpm. The samples were then filtered through qualitative filter paper and the supernatants were analyzed to quantify the arsenic contents.

Desorption experiments were carried out as following. Aliquots of 25.00 mL of desorption solutions (0.1 mol L^{-1} KCl, 0.1 mol L^{-1} HCl, and 0.1 mol L^{-1} NaOH) were added to (0.0200 ± 0.0001) g amounts of PFPF loaded with As(III) at an initial concentration (C_0) of 46.33 mg L^{-1} (this point was chosen based on the isotherm saturation region). The systems were stirred for 4 h at 150 rpm and 25 °C, followed by filtering the samples through qualitative filter paper (Unifil) and analyzing the supernatants to quantify the arsenic contents. The percentage desorption (*%Des*) was calculated using Equation (9).

$$\%Des = \frac{\left(\frac{C_{\mathrm{eq,des}}}{m_{\mathrm{ads}}} V_{\mathrm{des}}\right)}{q_0} 100 \qquad (9)$$

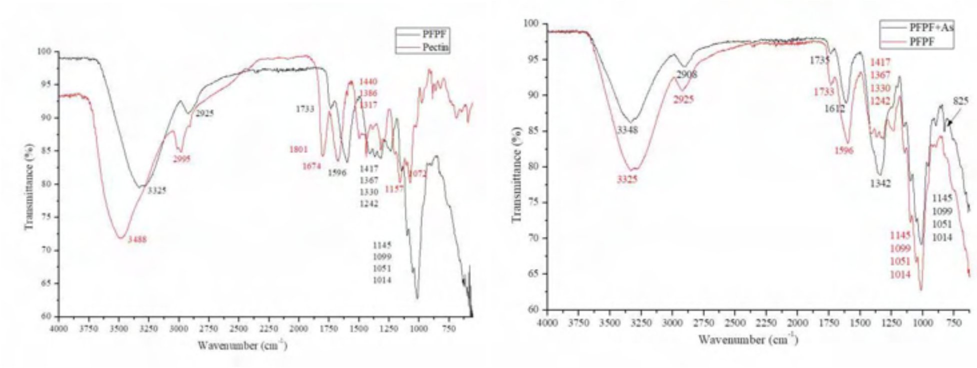
where, q_0 (mg g^{-1}) is the amount of adsorbed As(III) obtained from the adsorption experiment; $C_{\mathrm{eq,des}}$ is the equilibrium As(III) concentration (mg L^{-1}) in the desorption solution; V_{des} is the volume (L) of desorption solution; m_{ads} is the mass (g) of PFPF loaded with an initial concentration of 46.33 mg L^{-1} of As(III) from the adsorption experiment.

3 I RESULTS AND DISCUSSION

3.1 Characterization of the PFPF

3.1.1 Spectroscopic and surface characterization

The FTIR spectra of PFPF and pectin (Figure 1a, Table 1) showed the presence of similar functional groups, since pectin is an important component of PF. Both spectra presented a broad and strong band with a peak at around 3488-3325 cm^{-1} due to inter- and intramolecular hydrogen bonds. In the pectin spectrum, absorption in the -OH region was due to inter- and intramolecular hydrogen bonding of the galacturonic acid polymer (GNANASAMBANDAM; PROCTOR, 2000).



(a) (b)

Figure 1. FTIR spectra of (a) pectin flour and passion fruit peel flour (PFPF), and (b) passion fruit peel flour before (PFPF) and after (PFPF-As) arsenic adsorption

Sample	Wavenumber* (cm^{-1})	Attribution	Reference
Pectin, PFPF	3488-3325 (b,S)	v(OH) due to inter- and intramolecular hydrogen bonds	(GNANASAMBANDAM; PROCTOR, 2000)
	2995-2925	alkyl peaks	(GNANASAMBANDAM; PROCTOR, 2000; SCHIEWER; BALARIA, 2009)
	1801-1733	C=O carboxyl groups and their esters	
	1674-1596	v_{as}(C=O)	
	1500-1300	C, H, O, and N (various configurations)	(SCHIEWER; BALARIA, 2009)
	1440 (mi), 1300-1000	v_s(COO)	(GNANASAMBANDAM; PROCTOR, 2000)
PFPF-As	825	v(As-O)	(ARYAL; ZIAGOVA; LIAKOPOULOU-KYRIAKIDES, 2010; JIANG et al., 2019; MAITY et al., 2019)
	1342	interaction between As(III) and the oxygen from carboxyl groups	This study

*v_{as} = asymmetric stretching v_s = symmetric stretching, S = strong, b = broad, mi = moderately intense

Table 1. Peaks and bands from FTIR spectra of PFPF and PFPF-As.

The spectrum of PFPF-As (Figure 1b) showed a peak at 825 cm^{-1}, related to stretching of As-O, as reported elsewhere (ARYAL; ZIAGOVA; LIAKOPOULOU-KYRIAKIDES, 2010; JIANG et al., 2019; MAITY et al., 2019). There was a single peak at around 1342 cm^{-1}, while the spectrum of PFPF showed multiple peaks in this region. Since inorganic arsenite is an electrophile (SUMI, 2008), this peak could be explained by interaction between As(III) and the oxygen from carboxyl groups.

Figure 2 shows SEM images of the PFPF (a and c) at 406x and 1,290x magnification and PFPF-As (b and d) at 318x and 1,500x magnification. The PFPF presented an amorphous structure, with large clusters of soft fibers (Figures 2a and 2b). Irregularity of the surface favors the physical adsorption process, because at an irregular surface, the adsorbed molecule can interact with several terrace atoms, instead of with a single atom, resulting in sufficiently strong interaction to trap the molecule (ATKINS; PAULA, 2009).

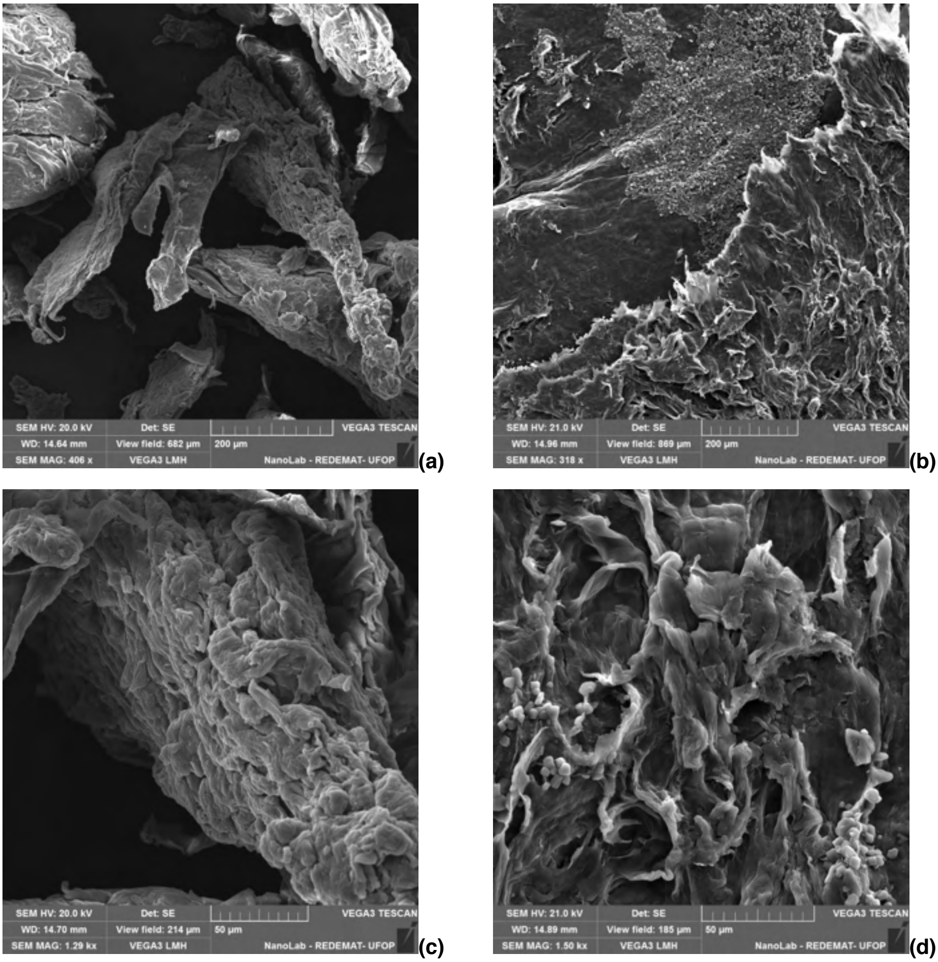


Figure 2. SEM images of PFPF (a and c) at 406x and 1,290x magnification, and PFPF-As (b and d) at 318x and 1,500x magnification.

EDS analysis (Figure 3) was employed to map the spatial distribution of the As(III) adsorbed by PFPF. Since arsenic was present at trace levels (due to the low initial arsenic concentration), the EDS technique was not able to precisely quantify the element. However, as shown in Figure 3, it was possible to detect its presence on the surface of the material, suggesting that adsorption had occurred.

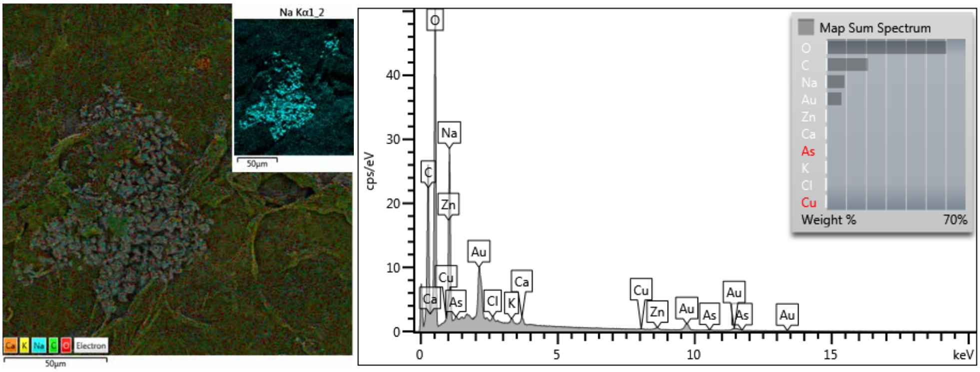


Figure 3. EDS analysis of PFPF-As.

The surface charge of biosorbents is determined by organic functional groups whose charge is pH dependent. The PZC for PFPF, pH at which the net charge on the surface is equal to zero, calculated using the convergence point ofthe three curves shown in Figure 4, was 4.95 ± 0.06. Therefore, for pH values lower than 4.95 ± 0.06, the net charge on the PFPF surface was positive, favoring anion adsorption, while for pH values above this value, the net charge on the PFPF surface was negative, favoring cation adsorption.

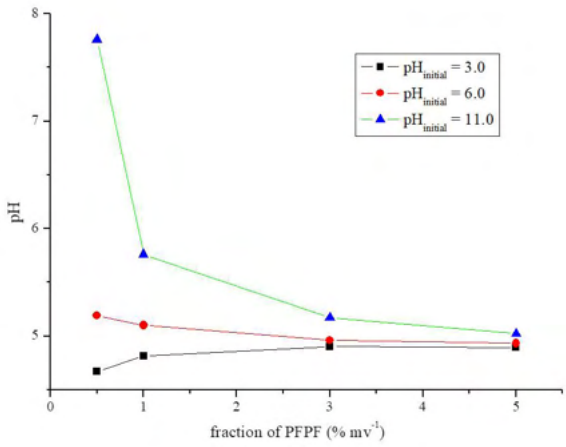
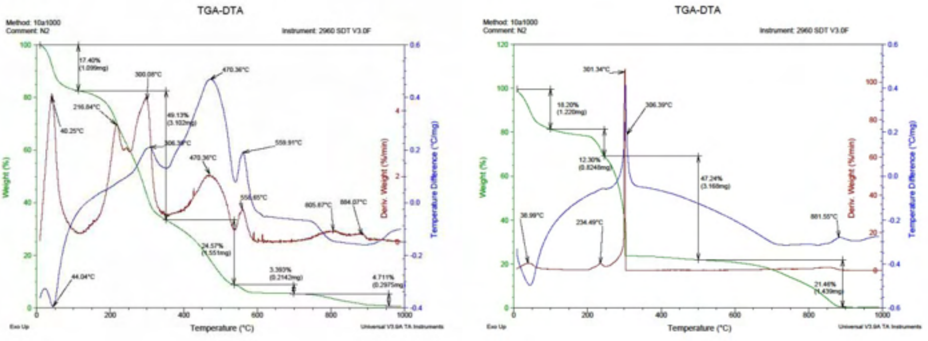


Figure 4. Curves for determination of the PZC of PFPF.

3.1.2 Thermal characterization

The TGA, DTG, and DTA curves for the thermal decomposition of PFPF and PFPF-As under a nitrogen atmosphere are shown in Figures 5a and 5b, respectively. The TGA curve for the PFPF showed three main stages of thermal decomposition (Figure 5a), while all the events shown by DTA were related to mass losses. The attributions of each mass loss are in Table 2.



(a) (b)

Figure 5. TGA, DTG, and DTA curves for (a) PFPF and (b) PFPF-As

Temperature (ºC)	**Mass loss (%)**	**Thermal event** (ABURTO et al., 2015; SESLIJA et al., 2018)
<100	17.4	Release of water
100-350	49.1	Pyrolytic decomposition of PFPF - primary decarboxylation
350-550	24.6	Pyrolitic decomposition of PFPF - secondary decarboxylation
>550	8.10	Gasification of the ash

Table 2. Attributions of PFPF thermal decomposition from TGA and DTA curves.

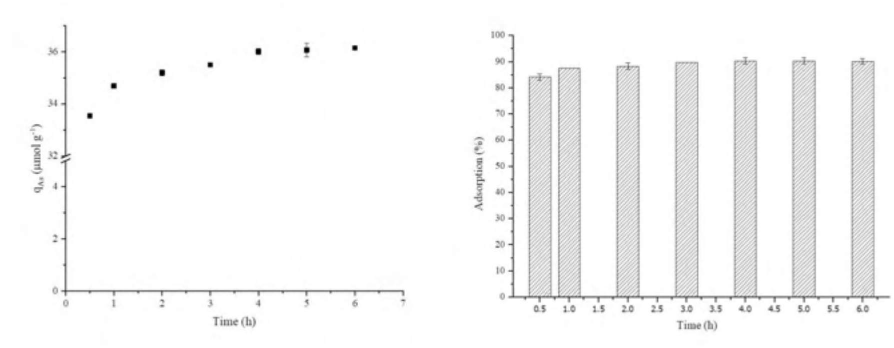
The TGA curve for PFPF-As (Figure 5b) showed four main mass loss events. The first mass loss (18.2%) below 100 ºC was due to the loss of H_2O, as observed for PFPF. The second and third mass losses (12.3 and 47.3%) between 200 and 600 ºC could be attributed to decarboxylation. The DTA curve for PFPF-As was significantly different from the curve for PFPF, with a narrow exothermic peak at around 300 ºC. The changes in the profile of the DTA curve suggested alteration of the thermal decomposition reactions of PFPF, which could have been related to desorption of arsenic oxide or the fusion of arsenic oxides (since As_2O_3 and As_2O_5 have melting temperatures of 313 and 315 ºC, respectively). A similar TGA curve was reported previously for As_2O_3 (FARIAS, 2000).

The narrow peaks in the TGA and DTA curves were indicative of an abrupt loss of mass, suggesting that the arsenic was adsorbed by fairly weak interactions, such as physisorption.

3.2 Adsorption experiments

The kinetic curve for the adsorption of As(III) by PFPF (Figure 6a) showed a slight initial increase in the amount of adsorbed As(III). It could be concluded that saturation was reached in the first hour, since the amount of As(III) only varied slightly between 30 min and 6 h (from 2.512 ± 0.005 to 2.71 ± 0.02 mg g^{-1}). Nonetheless, the adsorption experiments were performed for 4 h of contact between the adsorbent and the adsorbate.

The PFPF adsorbed (84 ± 1)% of total As(III) in the first 30 min, with an increase to (90 ± 1)% at saturation, after 4 h (Figure 6b). It could be concluded that an adsorbent dose of 0.8 g L^{-1} provided sufficient adsorption sites for 90% adsorption, under the experimental conditions employed (2.42 mg L^{-1} As(III) solution at 25 ºC). Therefore, the PFPF presented excellent performance in the adsorption of As(III). This was especially important considering that the experimental concentration was many orders of magnitude higher than typical arsenic concentrations found in groundwater. For example, the ranges of concentrations reported for groundwater were 0.2-326.4 µg L^{-1} in Quebec (Canada) (BONDU et al., 2017), 1.3-104.7 µg L^{-1} of total arsenic in Bihar (India) (KUMAR et al., 2016), <0.25-185 µg L^{-1} in Xinjiang (China) (ZHOU et al., 2017) and >50 µg L^{-1} in Paraiba do Sul (Brazil) (MIRLEAN; BAISCH; DINIZ, 2014). Therefore, it is reasonable to conclude that PFPF can reduce groundwater arsenic concentrations to levels acceptable for drinking water (10 µg L^{-1}, according to the World Health Organization) (WHO, 2018).



(a) (b)

Figure 6. (a) Amount and (b) percentage of arsenic adsorbed by PFPF, based on the contact time (note: at the scales used, the error bars can be seen for some points of both graphs)

The As(III) standard solutions presented Eh values between 100 and 150 mV. The Pourbaix diagram indicates that for these Eh values and pH 5.0, the H_3AsO_3 molecular species is almost the only species present in the solution, as shown by the distribution diagram of As(III) species (AKTER et al., 2005). Considering the PZC calculated previously (4.95 ± 0.06), the net surface charge of the PFPF in aqueous solution at pH 5 was zero. At the pH value of the PCZ, the H_3AsO_3 molecular As(III) form is the main species present (for H_3AsO_3, $pk_{a1} = 9.22$, $pk_{a2} = 12.13$, and $pk_{a3} = 13.40$), representing almost 100% of the As(III) species. Therefore, the adsorbed arsenic was a neutral species, rather than an ionic form. Therefore, the interaction between the adsorbate (molecular H_3AsO_3) and the adsorbent (PFPF) was probably due to physisorption, since both components were neutral. Consequently, despite the high adsorption capacity, under these experimental conditions there was only weak interaction between the adsorbent and the adsorbate, which could be attributed to van der Waals interactions.

Figure 7 shows the isotherm for As(III) adsorption by the PFPF. Sorption isotherms describe the relation between the initial concentration of the adsorbate in the fluid phase and the concentration of the adsorbate on the adsorbent. The Langmuir model provides a representation of the adsorption process, in the form of a simple mathematical expression, which can be used to estimate the maximum adsorption capacity of the adsorbent and the intensity of the adsorbent-adsorbate interaction.

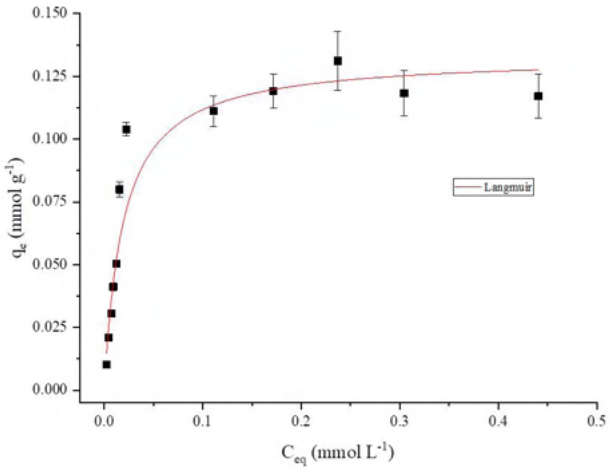


Figure 7. Isotherm curve for the adsorption of As(III) by the PFPF at 25 ºC.

The experimental adsorption data could be satisfactorily fitted using the Langmuir model, with a high value of R_{adj}^2 (0.9545) and low values of X_{red}^2 (0.1554) and RSS (1.7099). According to the Langmuir model, Q_{max} was 10.2 ± 0.6 mg g^{-1} (0.133 ± 0.009 mmol g^{-1}) and K_L was 0.7 ± 0.1 L mg^{-1} (52 ± 9 L $mmol^{-1}$). Table 3 shows the maximum adsorption capacities of other biomaterials for As(III). Although some of the values reported (ARYAL; ZIAGOVA; LIAKOPOULOU-KYRIAKIDES, 2010; PHOLOSI; NAIDOO; OFOMAJA, 2019; PODDER; MAJUMDER, 2016; SALIH et al., 2019; SIGDEL et al., 2016) were higher than found here, they were obtained using modified biomasses. The unmodified biosorbents employed previously (CHOWDHURY; MULLIGAN, 2011; KAZI et al., 2018; SARI; ULUOZLÜ; TÜZEN, 2011; SHAKOOR et al., 2019) generally showed lower maximum adsorption capacities for As(III), compared to PFPF. On the other hand, PFPF showed lower K_L values than most of the unmodified biomasses (Table 3), indicating that As(III) had lower affinity for the PFPF adsorption sites.

Since the adsorbate was a neutral species (molecular H_3AsO_3), Equation (8) was converted to Equation (10) (LIU, 2009)changes in free energy (?G°:

$$\Delta_{ads}G^{o} = -RT\ln K_{L} \qquad (10)$$

Using Equation (10), $\Delta_{ads}G^{o}$ for the adsorption of As(III) by PFPF was -27 ± 5 kJ mol^{1}, where the negative value indicated that the adsorption process was spontaneous. Table 4 shows some $\Delta_{ads}G^{o}$ values for the adsorption of As(III) by other sorbents. Similar values were reported for As(III) adsorption by inorganic materials (AREMU; LAY; GLASGOW, 2019; HE et al., 2019) and modified biomass (PODDER; MAJUMDER, 2016). Nevertheless, the process of As(III) adsorption by PFPF showed higher $\Delta_{ads}G^{o}$, compared to other unmodified biomasses (BAIG et al., 2010; BRAHMAN et al., 2016; SARI; ULUOZLÜ; TÜZEN, 2011).

The use of 0.1 mol L^{-1} HCl and 0.1 mol L^{-1} KCl solutions did not lead to As(III) desorption. The HCl solution extracted some of the pectin from the PFPF, resulting in gelification at the surface of the material. The use of 0.1 mol L^{-1} NaOH desorbed (17 ± 4)% of the As(III) from the PFPF-As. Above pH 9, negative species of As(III) predominate in aqueous systems, while above pH 5, the net surface charge of the PFPF was also negative. Therefore, coulombic repulsion caused the desorption of As(III) when 0.1 mol L^{-1} NaOH was used as the desorption solution. Although NaOH solution has been reported to provide efficient desorption of As(III) (SIGDEL et al., 2016), here it removed only 17% of the adsorbate, which could be explained by the high value of $\Delta_{ads}G^{o}$ for As(III) desorption from the PFPF.

Material	**Q_{max} (mg g^{-1})**	**K_L (L mg^{-1})**	**Reference**
Passion fruit peel flour	10.2 ± 0.6	0.7 ± 0.1	This work
Alginate (modified with hydrous iron oxide)	47.8	0.0152	(SIGDEL et al., 2016)
Chitosan-coated diatomaceous earth (composite)	87.81	0.149	(SALIH et al., 2019)
Staphylococcus xylosus biomass (pretreated with Fe(III))	54.35	0.031	(ARYAL; ZIAGOVA; LIAKOPOULOU-KYRIAKIDES, 2010)
Magnetic pine cone biomass	14.83-22.33	0.1025-0.8745	(PHOLOSI; NAIDOO; OFOMAJA, 2019)
Chitosan-magnetic graphene oxide nanocomposite	2.340	0.021	(SHERLALA et al., 2019)
Anaerobic biomass	0.164	3.97	(CHOWDHURY; MULLIGAN, 2011)
Acidithiobacillus ferrooxidans BY-3	0.293	5.4	(YAN et al., 2010)
Algae biomass (*Maugeotia genuflexa*)	57.48	0.025	(SARI; ULUOZLÜ; TÜZEN, 2011)
Bacillus arsenicus biofilms supported on a Neem leaves/$MnFe_2O_4$ composite	53.175*	-	(PODDER; MAJUMDER, 2016)
Perilla leaf-derived biochars prepared at 300 °C	4.71	1.40	(NIAZI et al., 2018)
Perilla leaf-derived biochars prepared at 700 °C	11.01	3.25	

Cucumis pubescens	0.0267	7.116×10^{-5}	(KAZI et al., 2018)
Corn cob	4.33	0.79	(SHAKOOR et al., 2019)
Water chestnut shell	9.61	2.12	
Java plum seed	4.63	1.13	
Tea waste	7.36	2.32	
Egg shell	11.69	4.03	
Pomegranate peel	5.57	1.73	

*Equivalent biosorption capacity obtained from the fractal-like pseudo-second order kinetic model.

Table 3. Comparison of biosorbents used for the removal of As(III) at 298 K.

Material	**$\Delta_{ads}G^o$ (kJ mol^{-1})**	**Reference**
Passion fruit peel flour	-27 ± 5	This work
Silica-based catalytic media	-36.4 to -38.5	(AREMU; LAY; GLASGOW, 2019)
Zirconium metal-organic frameworks	-26.0	(HE et al., 2019)
A. nilotica biomass	-2.04	(BAIG et al., 2010)
Tecomella undulata	16.0	(BRAHMAN et al., 2016)
Acidithiobacillus ferrooxidans BY-3	-0.01	(YAN et al., 2010)
Algae biomass (*Maugeotia genuflexa*)	-18.4	(SARI; ULUOZLÜ; TÜZEN, 2011)
Bacillus arsenicus biofilms supported on a Neem leaves/ $MnFe_2O_4$ composite	-22.6	(PODDER; MAJUMDER, 2016)

Table 4. Free energy of adsorption ($\Delta_{ads}G^o$) for the adsorption of As(III) by various sorbents.

4 I CONCLUSIONS

Passion fruit peel flour (PFPF) can be employed as an efficient low cost biosorbent for the removal of As(III) from water. It has an amorphous structure, with large clusters of soft fibers that should favor physical adsorption. Under the experimental conditions employed, the PFPF presented an As(III) adsorption capacity of 10.2 ± 0.6 mg g^{-1}, with performance of about 90% for As(III) removal. The adsorption of As(III) by the PFPF was a spontaneous process. The adsorption capacity and $\Delta_{ads}G^o$ values for the adsorption of As(III) by PFPF were higher than the values reported previously for other unmodified biomasses.

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SOBRE O ORGANIZADOR

CLEISEANO EMANUEL DA SILVA PANIAGUA - Técnico em química pelo Colégio Profissional de Uberlândia (2008), Bacharel em Química pela Universidade Federal de Uberlândia (2010), Licenciado em Química pela Universidade de Uberaba (2011). Especialista em Metodologia do Ensino de Química e em Docência do Ensino Superior pela Faculdade JK Serrana em Brasília (2012). Mestre em Química pela Universidade Federal de Uberlândia (2015), com ênfase em desenvolvimento de bioadsorvente para remoção dos íons metálicos As(V), Sb (III) e Se (IV) em diferentes matrizes aquáticas. Doutor em Química pela Universidade Federal de Uberlândia (2018), com ênfase em Processos Oxidativos Avançados [fotocatálise heterogênea (TiO_2/UV-A e TiO_2/Solar, H_2O_2/UV-C) para remoção de contaminantes de interesse emergente (CIE) em diferentes matrizes aquáticas. Atualmente realiza Pós-doutorado (maio de 2020 a maio de 2022) na Universidade Federal de Uberlândia com ênfase em aplicação de novos agentes oxidantes empregando radiação solar para remoção de CIE em efluentes provenientes de estação de tratamento de esgoto. Possui 11 anos de experiência como técnico em química no Instituto Federal de Goiás, tendo atuado como responsável por análises de parâmetros físico-químicos e biológicos de águas e efluentes provenientes de estação de tratamento de esgoto. Atualmente, vem atuando nas seguintes linhas de pesquisa: (*i*) Desenvolvimento de novas metodologias para tratamento e recuperação de resíduos químicos gerados em laboratórios de instituições de ensino e pesquisa; (*ii*) Estudos de monitoramento de CIE; *(iii*) Desenvolvimento de novas tecnologias avançadas para remoção de CIE em diferentes matrizes aquáticas; (*iv*) Aplicação de processos oxidativos avançados (H_2O_2/UV-C, TiO_2/UV-A e foto-Fenton e outros) para remoção de CIE em efluentes provenientes de estação de tratamento de esgoto para fins de reutilização; (*v*) Estudo e desenvolvimento de novos bioadsorventes para remediação ambiental de CIE em diferentes matrizes aquáticas e (*vi*) Educação Ambiental.

ÍNDICE REMISSIVO

O ensino e a pesquisa em QUÍMICA

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