ARTICLE



Chemometric Evaluation of a Biodegradable Tannic Acid-Polyurethane System for the Removal of Pb(II) and Hg(II) Ions from Water

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The industrialization has brought advances that have enabled a better quality of life for people and improved production stages and business models. However, some impacts still need to be resolved, such as water pollution. Industrial pollutants containing potentially toxic metal ions are expensive for the industry, so studying new materials and new processes has helped solve this problem. Adsorption processes using biodegradable adsorbent materials have been presented as relevant alternatives for reusing metallic ions from water bodies and sewage networks. In this perspective, tannic

acid (TA) immobilization in biodegradable polyurethane (PU) foams based on vegetable oil (castor oil) was used to remove metal ions Hg(II) and Pb(II) from water. The preliminary study was carried out in TA's immobilization in PUs, with a 2^k order factorial experimental design. The responses were obtained and evaluated by gravimetry and UV-Vis spectroscopy using Central Composite Design (CCD). The molar concentration of 0.1000 mol L⁻¹ by TA solution at pH equal to 7 and 19 hours of contact time was defined as optimal conditions for TA adsorption in the PU. The optimized PU-TA system was evaluated for removing

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Pb(II) and Hg(II) ions in aqueous solutions, and the tests showed that 59.93% and 51.48% were removed from water, respectively. The use of the PU-TA adsorbent system for removing metals in water can be widely valuable in industrial plants that need water treatment.

Keywords: tannic-polyurethane, Pb(II), Hg(II), adsorption, chemometrics.

INTRODUCTION

The growth of industrialization has brought benefits to humanity, but it has witnessed several environmental issues resolved. Numerous environmental tragedies are caused by changes in the physical, chemical, and biological properties of the environment. The contamination of ecosystems can come from the disposal of industrial and domestic effluents that threatens water resources integrity since they are constituted by metals considered toxic.^{1–4}

The allocation of industrial effluents in water bodies and sewage network without previous treatment can cause health and environmental problems.¹ Therefore, it is considered essential that the industries carry out a pre-treatment of the effluents before their discharge into sewers and rivers to remove the toxic metals.² Several techniques are used for physical removal of metallic ions, from which the most studied is the adsorption with adsorbent of natural origin like zeolites, clay, peat moss and agricultural wastes and modified materials like halloysite/chitosan and activated carbon.^{5–8} These methods are based on the immobilization of metallic ions, where they involve intermolecular interactions between the analyte and the adsorbent material.⁵ The adsorption with activated carbon, though, becomes often economically unviable for small industries, since it requires complexing agents, increasing treatment costs. In this way, alternative solutions have been studied for production of adsorbent systems, preferably of natural origin.^{1,7}

Some studies have evidenced the functionality of polyurethane (PU) foam with sulfonic acid groups for Pb(II) ions removal. This study indicated that the concentration of sulfonic acid and the reaction time are significant variables in removing Pb(II) ions.⁶ The great interest for studying the adsorbent system of PU is that, besides their petrochemical origin, they can also be obtained by polyols extracted from renewable sources, mainly polyols of natural oils. The advantage of PU foams of plant origin is related to the relative ease of biodegradation, fully integrating with nature.^{7,8}

Numerous methods in the literature investigate the behavior of PU foams to remove metal ions. However, solely the PU foam of castor origin is not efficient for ions removal. Thus, a complexing agent is required to increase this immobilization efficiency. Researchers have carried out a study comparing the use of activated carbon with and without Tannic Acid (TA) for adsorption of Cu(II), Cd(II), Zn(II), Mn(II) and Fe(III), varying different parameters, which evidenced that both activated carbons interact with metallic ions.⁹ However, the metals are adsorbed with a better efficacy on activated carbon with Tannic Acid. The TA is considered a natural antioxidant, besides possessing other properties, such as the capacity of interaction with proteins, polymers, complexing of metal ions Pb(II), Cu(II), Cd(II) e Zn(II) and ion reducer for the formation of metallic nanoparticles.^{9–17} The degree of the potentiality of the reducing characteristics and complexing by TA are dependent on some parameters such as pH variance, temperature, TA concentration, and others.^{13,18,19} The ability to interact with macromolecules and metal ions develops a toxicity factor. This factor may be linked to the higher weight and concentration of the molecule in the body.¹⁹

Chemometric tools are widely used to evaluate several variables that influence a given system.^{10,20,21} A comparative study using different chemometric tools for Pb(II) ions adsorption onto tree leaves was realized. Firstly, a complete factorial design was carried out to identify the most significant variables and then the application of models for obtaining the response surfaces, such as the CCD (Central Compound Design), BBP (Box - Behnken Planning) and DM (Doehlert Matrix), which allowed analysis to optimize the adsorption process. From software help, numerous tests were used to adapt the mathematical model proposed, such as residue analysis, variance analysis (ANOVA), and coefficient of determination (R²).²²

The present study has the objective to determine optimal parameters for immobilization of TA in PU and then in-depth evaluation with the addition of a central point and a star point to estimate the optimum region;

also, to perform a comparative study of the analytical methods used to evaluate which one is efficient to quantify TA in PU. The chemometric tools used make it possible to study the possibility of removing Hg(II) and Pb(II) ions from industrial effluents.

MATERIALS AND METHODS

Reagents

The tannic acid solution (TA) was obtained by direct dissolution (Sigma-Aldrich, purity of 99%) in deionized water.

The aqueous buffer solutions used were prepared in the laboratory: acetic acid solution (QHEMIS) / sodium acetate (Synth 99%) 1 mol L⁻¹ (pH = 5); ammonium hydroxide (Vetec 99%) / ammonium hydrogen carbonate 1 mol L⁻¹ (pH = 8); citric acid (Ecibra 99%) / citrated sodium (Ecibra 99%) 1 mol L⁻¹ (pH 4); hydrogen phosphate (Synth 98%, of purity) / dihydrogen sodium phosphate 1 mol L⁻¹ (pH = 6.5), ammonium chloride (Vetec 99%) / ammonium hydroxide 1 mol L⁻¹ (pH = 9). Aqueous solutions of NaOH (Synth 97%) in concentrations of 1 and 2 mol L⁻¹ were also used. Polyol of vegetable origin (castor oil) and prepolymer (diphenylmethane-4,4-diisocyanate) were used for the preparation of polyurethane (PU).

Preparation of polyurethanes

PU were prepared by addition of polyol (PO) in the prepolymer (PP), following the bulk ratio of 1.0(PO):1.7(PP) (m/m), under manual agitation until homogenization of the materials. After formation, the PU's were cut into the standardized dimensions: length of 4.0 cm, width of 1.0 cm and thickness of 0.5 cm.²³ (Figure 1)



Figure 1. Scheme of preparation of cut PU foams.

Experimental design

The factorial design was performed using preliminary tests (see Table I). Firstly, to analyze the individual effects, as well as the interactions between the independent variables, the temperature (V1) of the TA immobilization process, the molar concentration of TA (V2), the pH value of TA solution (V3), the contact time of the TA with PU (V4) and the amount of PU (V5) were studied by applying a factorial design (2^k). The experimental range for (V2) was defined as of high concentrations from preliminary tests, by observing the mass varying of the floated product with experiments from low (0.0100 mol L⁻¹) to high concentrations (0.1000 mol L⁻¹). Although small, the change in mass only occurred for high concentrations.

The entire experimental data set was globally analyzed by multiple regression, measuring those variable effects, and fitting the data to an empirical model. The parameters with a significance level higher than 0.05 were considered insignificant.

Factors	Parameters	Higher level (+)	Lower level (-)
V1	Temperature / °C	60	30
V2	Molar concentration /mol L-1	0.1000	0.0100
V3	рН	8	5
V4	Contact time / hours	26	12
V5	Amount of PU / units	20	10

Table I. Experimenta	l variables ι	used for fac	torial design 2 ^t
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A second stage involved tests studied by applying a central composite design (CCD) with two center replicates, and with α equal to 1,68. To maintain rotatability, The CCD was obtained by fixing two variables (V4 and V5). The value of α was calculated by number of experimental runs in the factorial portion of the central composite design ($\alpha = [2^k]^{1/4}$). The experimental data obtained from the central composite design were statistically analyzed (Statistica[®] software) by measuring the effects of those variables.

The immobilization results were determined by gravimetry and UV-Vis spectroscopy. The immobilization of each test was calculated using Equation 1.

$$%QTA = \frac{M_i - M_f}{M_i} x100$$
 Equation 1

where M_i represents the initial mass of tannic acid, M_i is the remaining tannic acid mass and Q is the amount of immobilized tannic acid.

Gravimetry and UV-Vis Spectroscopy obtained the responses of the experiments. Gravimetry method: the mass measures were realized using a Shimadzu model AX 200 analytical balance. The PU units cut into standardized dimensions (length of 4.0 cm, width of 1.0 cm and thickness of 0.5 cm) were grouped according to the experimental planning, and their masses were measured and recorded. After weighing, the PU's were placed in beakers containing 100.0 mL of the respective aqueous solutions of TA, according to experimental design. After the contact times, the PU's were removed and dried in an oven at 25 °C for 24 hours and kept in a desiccator until constant mass.

The maximum wavelength observed in the UV-Vis spectra was investigated by a Varian Cary 50 Scan Spectrophotometer. The spectra were obtained in a quartz cell with a 1 cm pathlength and the maximum wavelength was established at 374 nm. The analytical curves were performed using TA concentrations between 2.0 and 11.0 μ g mL⁻¹. The immobilization of TA in the PU's were obtained by absorbing TA's aqueous solutions before and after the PU's immersions.

Pb(II) and Hg(II) removal experiment in water

The 16 samples of PU-AT were used and determined by a central composite design (CCD). For the experiment, 52.0 mg L⁻¹ and 309.0 mg L⁻¹ of water solutions of Pb(II) and Hg(II) chlorides were prepared, respectively. The PU-TA system was immersed in the respective metal ion solutions, Hg(II) and Pb(II), for 24 h. The M-PU-TA (metal-polyurethane-TA) systems were dried, and their masses were measured and recorded.

The digestion of the M-PU-TA system was performed using an aqueous solution of HNO_3 (65%) and HCI (35%) in a microwave digester. Microwave treatment was performed using a sample system digester, Speedwave 4 model (Berghof), using 60 mL Teflon flasks. The irradiation power was set at 800 watts and the pressure was set at 40 bar.

After opening the samples, the systems were diluted, and the metal ions were analyzed using ICP-AES technique. The ICP-AES Spectroscopy was performed using an Atomic Emission Spectrometer of the iCAP7400 model, Duo Thermo Scientific. Detector operation: axial was used for quantitative analysis of the respective metal ions.

RESULTS AND DISCUSSION

Experimental design

In the preliminary stage of the experimental trials, the results were analyzed by mass measurement and electronic absorption. For both techniques, variables that significantly influence TA into PU's adsorption were evaluated at a level of confidence of 95% ($\alpha = 0.05$). To better evaluate the significance of the estimated effects and verify the possibility of a difference between the responses, null (Ho) and alternative (H1) hypothesis tests were used, comparing the p-value of the statistical test of the samples²⁴ with a significance level of $\alpha = 0.05$. Therefore, we considered the hypotheses H0: $\mu 1 = \mu 2 = \mu i j = 0$, so that interaction effects will not be significant when p > 0.05; and H1: $\mu i j \neq 0$, so that interaction effects will not be significant when p < 0.05.

The error was estimated with the exclusion of the effects of a high order. The effects of third and fourth order were presented closely to the error variability, indicating not to influence significantly. The 32 experiments were randomly performed.

Experimental design using UV-Vis spectrometry

The maximum wavelength obtained the responses at 374 nm observed in the UV-Vis spectra UV-Vis spectroscopy (Supplementary material) showed that in the experiments 17–26 and 29–32, the TA's immobilization was at least 92%. As indicated in Figure 2a, the variables that showed significant effects using the UV-Vis spectroscopic technique are indicated as (I) main interactions: amount of adsorbent (V5), pH (V3); and (II) second-order interactions (V3)*(V4); (V2)*(V4). The high order of interaction of the UV-Vis response variables belongs to a region close to the error variability, making its effects not significant.



Figure 2. Pareto graph of significant responses (a) UV-Vis spectroscopy (MS Residual = 151.3785) and (b) Gravimetry (MS Residual = 110.1887).

The main interaction of the variable, pH value, may indicate direct proportionality to TA's immobilization in PU. The system using a pH value equal to 8 showed immobilization of 55.42% TA in PU. This effect was probably favored by the lower interaction of phenolic groups present in the TA with water. The V5 effect became more pronounced when associated with the contact time effect (V4). Probably, in low contact times, the physicochemical equilibrium of the phenomena has not yet been carried out.

Some discrepancies can be explained. For example, when TA immobilization in PU was evaluated at a pH value of 5 and a contact time of 26 hours, TA adsorption was disadvantageous, probably due

to the microbial degradation of tannic acid, favored by the pH value. This observation was confirmed by visualization of fungi in the TA solutions after one week of storage.

The TA interaction effect with contact time showed a negative influence in the immobilization, and this effect is similar, both when associated with a high contact time and lower [TA], and vice versa (see Figure 2a).

The main interaction effect (E), adsorbent quantity (V5), significantly influenced the TA immobilization process in PU. We can observe in the complementary material (Table S1) that when the V5 level was increased, there was a more significant number of active sites in the PU.

The table of ANOVA (Table II) made it possible to evaluate the variance between the experimental data and if the determined effects have differences between them. F and p tests were considered.

The generated mathematical model can be observed in Equation 2. The correlation coefficient of the model presented value equal to 90.19%, which is considered acceptable.

$$Y = 56.431_{(\pm 2.047)} + 4.779 v_{3(\pm 2.174)} + 32.781 v_{5(\pm 2.174)} - 6.574 v_2 v_{4(\pm 2.174)} + 56.143 v_3 v_{4(\pm 2.174)}$$
Equation 2

Table II. Analysis of Variance (ANOVA) for UV-Vis spectroscopy and gravimetry								
	ANOVA							
		SSª	Df⁵	MS°	F	р	R² (%)	
	V3	730.94	1	730.94	4.83	0.03675		
	V5	34388.80	1	34388.80	227.17	0.00000		
UV-Vis	V2 * V4	1383.06	1	1383.06	9.14	0.0053	00.10	
Spectroscopy	V3 * V4	1065.36	1	1065.36	7.04	0.0132	90.19	
	Error	4087.22	27	151.38		0.0367		
	Total SS	41655.38	31					
		SS	Df	MS	F	р	R² (%)	
	V1	719.995	1	719.995	6.5340	0.0168		
	V2	1868.180	1	1868.180	16.9547	0.0003		
	V5	710.694	1	710.694	6.4497	0.0170		
Gravimetry	V1 * V 2	534.580	1	534.580	4.8550	0.0367	78.19	
	V2 * V 5	581.231	1	581.231	5.2749	0.0290		
	Error	2864.907	26	110.189				
	Total SS	7279.587	31					

^aSS represents Sum of squares; ^bDf represents Degrees of freedom; ^cMS represents Mean of squares.

Experimental design using gravimetry

In the responses obtained by gravimetry, the amount of adsorbent (V5), TA concentration (V2) and Temperature (V1) can be observed as variables that showed significant effects and second-order interactions (V1)*(V2); (V2)*(V5). However, the immobilization values did not exceed 60%, in addition to presenting low adsorption values.

V2 was the most significant (Figure 2b). This phenomenon can be explained by water interaction in PU, already reported in the literature.²³ The amount of adsorbent and temperature did not show as significant effects as [TA].

The interaction between variables (V1) and (V5) did not show a significant effect, but in the interaction of each of them, respectively, with [TA] effect, it can be observed that these second-order interactions are significant. These evaluations make [TA] effect a preponderant effect on the response obtained by gravimetry. Comparing the results of the effects determined by both techniques, it can be observed that the estimation of the most significant variables in the study region was different (Figure 2).

According to the results indicated by the experimental planning 2⁵, it was possible to determine by the two methods which variables could be considered significant, as indicated in the previous section. The mathematical model generated by gravimetric techniques can be observed in Equation 3. The correlation coefficient presented a value equal to 60.45%, showing a correlation inferior to that observed by spectroscopic technique.

 $Y = 9.237_{(\pm 1.85)} + 4.734V_{1(\pm 1.85)} - 7.607V_{2(\pm 1.85)} + 4.717V_{5(\pm 1.85)} - 4.087V_1V_{2(\pm 1.85)} - 4.219V_2V_{5(\pm 1.85)}$ Equation 3

Despite the quality of the linear gravimetric model, it was possible to estimate that the variables, temperature, [TA], and amount of adsorbent are significant.

Central Composite Designs

In UV-Vis spectroscopic technique, a significant variation rate was observed, explained by the indicated mathematical model. In this way, central and axial points were added to the significant variables (Figure 2) with these new points to obtain new experimental planning to carry out an in-depth study on the variables estimating the existence of a maximum condition in the region investigated.

The V4 and V5 were fixed during the planning to predict the surface response. Thus, the independent variables (Table III) were evaluated by central compound planning with axial points, at the temperature of 30 °C, with ten units of adsorbent and 50.00 mL of TA solution.

Table III. Experimental conditions of CCD, at constant temperature of 50°C							
Conditions: CCD Matrix							
		Levels					
Variables	-α (-1,681)	(-1)	0	(+1)	+α (+1,681)		
(V1) pH	3.97	5	6.5	8	9		
(V2) [AT]/mol L ⁻¹	0.0100	0.0300	0.0600	0.0800	0.1000		
(V3) Contact time/h	17	12	19	26	30		

Table III. Experimental conditions of CCD, at constant temperature of 30 °C

Central and star points were added in the independent variables determined as significant to estimate the optimal region of AT immobilization. In this way the new conditions were determined from the experimental coding, see Equations 4, 5 and 6.

$$V_{1} = \frac{[AT] - 0.055}{0.025}$$
Equation 4
$$V_{2} = \frac{pH - 6.5}{1.5}$$
Equation 5
$$V_{3} = \frac{Contact \ time - 19}{7}$$
Equation 6

The experimental matrix, completed with 16 experiments (Table S2), was performed using two analytical techniques. Two types of responses were again obtained, and their correlation coefficients and optimal conditions regions were determined. The errors were estimated by replicates at the central point.

The results of the analysis of variance for TA immobilization response, determined by the UV-vis spectroscopy, were described in Table S3. The results which presented percentages of explained variation are considered satisfactory (86.47%). The result obtained can be confirmed by the regression value of $F_{calculated}$ (6.572; 5%), because the value was higher than $F_{tabulated(7,8)}$ (3.505%), so that we can reject the null hypothesis (H₀), that is, the adjusted model can represent the experimental data and suggest inferences in the sample population. Based on the results, the CCD was found to be statistically significant for the responses.^{24,25}

The quadratic model with the highest rate of variation explained by the mathematical model was obtained by UV-Vis spectroscopic technique. Thus, the studied region of the adsorbent system can be represented by the mathematical expression (Equation 7). Residual analysis in regression showed an independent distribution and like the normal distribution, see Equation 7.

$$Y = 91.0982_{(\pm 1.569)} + 24.7343V_{1(\pm 0.602)} - 13.364V_{1(\pm 0.7314)}^{1} + 11.7895V_{2(\pm 0.7314)}$$

= 23.2812V₂² + 11.6459V₃³ + 13.1407V₁V_{3(\pm 0.787)} + 11.2589V₂V_{3(\pm 0.787)} Equation 7

The response surface corresponding to this mathematical expression is shown in Figure 3. The model generated, and the construction of the response surface permitted to obtain the optimal coded points. They could be determined for the variables V1, V2 and V3, and are of (1.073092), (0.224872) and (-0.272495), respectively. Then, the values were decoded, estimating optimal conditions of 0.1000 mol L⁻¹ by TA solution, at the pH of 7 and for 19 hours of contact time to obtain the maximum TA adsorption in the PU region of study.



Figure 3. Response surface design for TA adsorption on PU.

The TA percentage (%) determined by the technique using the analytical balance, showed a low explained variation of the experimental data (Table S4), unable to determine the lack of adjustment. Therefore, this model was unsatisfactory to infer the population sample in the region studied, an inappropriate model for predictive purposes. The gravimetric technique was unsatisfactory, probably due to the higher affinity of water with the PU's. The drying process of the PU-TA system may have influenced the evaluation of this technique.

CCD in metal ion removal

The instrumental technique ICP OES obtained the response of the experimental matrix. Therefore, the quantification of metal ions was performed by two types of the data treatment: the intensity of the analytical signal and recovery (%) of metal ions.

Metal ions were quantified as a function of the sum of the element intensity ratios by their maximum diagnosed intensity at a specific wavelength, which can be represented by Equation 8.

$$RM = (I_{Pb}/I_{max.Pb}) + (I_{Hg}/I_{max.Hg})$$
Equation 8

The significance of the experimental data indicated through ANOVA and applying the hypothesis test, was considered as follows:

- I) $H_0 = \mu_1 = \mu_2 = \mu_{ij} = 0$: the interaction effects are not significant when p > 0.05; the model is inadequate to represent the experimental data;
- II) $H_1 = \mu_{ij} \neq 0$, the interaction effects are not significant when p < 0.05). The mathematical model is adequate to represent the experimental data.

The validation of the hypotheses can be determined by Fisher's test, which assesses the reason for the variation within or between the variables analyzed by the experimental design. This test evaluates the difference in the samples, depending on the size of the variation within each sample, making it possible to estimate from the comparison of tabulated values with the data obtained experimentally.

The null hypothesis (H₀) was considered to analyze the responses obtained by the digester since the $F_{calculated}$ values were lower than $f_{tabulated(6.9)}5\% = 3.37$, as it can be seen in the ANOVA table (Table S5). Considering that the variation explained is low, the regression model generated was inadequate for representing the data sets.

The values obtained for the response of the remaining solution are represented in the normal probability graph, see Figure 4, observing that they are close to the error variability. These values do not represent any physical significance and may represent random errors during the process. Thus, the effects of the variables determined by the remaining solution's response do not statistically influence the adsorption process of metals.



Figure 4. Plot of normal probability to metal adsorption by remaining TA solution.

With the recovery response of the metal by the adsorbent, the significant effects and significance of the model obtained by the Analysis of Variance (ANOVA) were determined, considering the same hypotheses described above. The variance of the experimental data analyzed by the ANOVA table of "recovery /%" (Table S6) obtained a variation of 55.17%, considered a low variation. Also, the lack of adjustment showed significance, that is, the value of $f_{calculated} = 331.334$, was higher than the $f_{tabulated(1.1)}5\% = 161.4$, showing that the linear model does not describe the experimental data well.

The variable response of the remaining solution for metal recovery showed effects that are not significant for the metal adsorption process, as the results tend to be linear around zero, where the error variability is located (Figure 5). The evaluation of the amount of adsorbed metal by analyzing the remaining solution containing M-PU-TA and the digestion method, evaluated by different types of responses, presented unsatisfactory models to represent the experimental data. The variation in the metal adsorption data showed a low quadratic correlation coefficient. Thus, it was not possible to estimate the optimized condition for the metal's behavior with statistical reliability. Despite the inexistence of the optimum point in the region investigated by the experimental planning, it is possible to carry out a qualitative assessment of the analyzes. Thus, the amount of Pb(II) and Hg(II) removed from water by the adsorbent system was investigated and compared proportionally with the amount of metal detected by analytical techniques. The values of the analysis were summarized and evaluated graphically. (Figures 6 and 7)



Figure 5. Plot of normal probability to metal adsorption after the M-TA system goes through microwave digester.



Figure 6. Evaluation of the Hg(II) ion content in the adsorption study.



Figure 7. Evaluation of the Pb(II) ion content in the adsorption study.

The values obtained for the remaining solution response is represented in the normal probability graph, see Figure 3, observing that they are close to the error variability. These values do not represent any physical significance and may represent random errors during the process 21. Thus, the effects of the variables determined by the remaining solution response do not statistically influence the adsorption process of metals.

When analyzing experimental condition 13, were observed 52.07% of Hg(II) and 44.30% Pb(II) in the remaining solution. Theoretically, the rest of the metals that were not evaluated in the remaining solution should be adsorbed on the adsorbent 47.94% and 55.70%, respectively. When evaluated by the digestion process, 21.98% and 9.797% of Hg(II) and Pb(II) metals were, respectively determined, showing that the digestion process was not completely efficient, as the material was probably deposited in the digestion block during the process, so that the complete evaluation was not allowed. With the absence of reliability of the digestion method, the amount of metals in the remaining solution becomes more reliable, indicating that the adsorbent system adsorbed on average 59.93% and 51.48% of Hg(II) and Pb(II) metals, respectively, making it an efficient adsorbent system for ions removal.

The PU-AT system is formed by natural materials, cheap, and showed to be a promising adsorbent. In addition, it is metal absorbing capacity indicated to be greater than other toxic metal adsorbents.^{26,27}

CONCLUSIONS

For the quantification of TA, the method that used UV-Vis spectroscopy proved to be more suitable for both estimation of the significant variables, as well as to obtain the response surface and the generation of optimal points. Thus, the experimental planning contributed to analyze the influences of several variables in the adsorbent system, in an agile way, contributing to future analyzes, as well as to understand the behavior of the adsorbent system. The molar concentration 0.1000 mol L⁻¹ of the AT solution, pH value equal to 7, and contact time equal to 19 hours were determined as the optimal condition for the adsorption of AT on PU.

For the process of determining Hg(II) and Pb(II) metals, the most appropriate was the analysis of the remaining solution, which was more reliable than the determination by digestion. Despite the results of the metals, an optimal region was not found, and significant variables, the PU-AT system evaluated showed to be a good metal ion scavenger, even in the coexistence of different ions and in different amounts. The optimized PU-TA system removed 59.93% of Pb(II) and 51.48% Hg(II) ions in aqueous solutions.

Therefore, the maximum control of external influences of the system is ideal, making the analytical instrumental techniques adequate and efficient for detecting toxic ions, enabling better conclusions about the behavior of metals, and assisting in real future studies of metal retention present in industrial systems.

Conflicts of interest

The authors declare that there is no conflict of interest/competing interest (financial or not) for this study.

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SUPLEMMENTARY MATERIAL

Table S1. Experimental matrix 2⁵ and the respective responses using spectroscopic absorption UV-Vis and gravimetry

Experiment	V ₁	V ₂	V ₃	V ₄	V ₅	% AT UV-Vis	% AT Gravimetry
1	-1	-1	-1	-1	-1	9.506 ₃	0.697 ₉
2	1	-1	-1	-1	-1	32.871 ₇	6.809 ₇
3	-1	1	-1	-1	-1	40.545 ₃	0.3672
4	1	1	-1	-1	-1	25.417 ₆	0.3472
5	-1	-1	1	-1	-1	10.760 ₂	0.5427
6	1	-1	1	-1	-1	19.834 ₈	15.902 ₁
7	-1	1	1	-1	-1	10.674 ₄	0.662 ₉
8	1	1	1	-1	-1	46.214 ₆	2.316 ₈
9	-1	-1	-1	1	-1	10.201 ₇	1.645 ₅
10	1	-1	-1	1	-1	21.616 ₇	25.865 ₃
11	-1	1	-1	1	-1	8.9700 ₀	0.2601
12	1	1	-1	1	-1	14.799 ₀	3.198 ₁
13	-1	-1	1	1	-1	36.755 ₄	7.721 ₆
14	1	-1	1	1	-1	55.036 ₀	4.0415 ₄
15	-1	1	1	1	-1	24.536 ₆	1.261 ₆
16	1	1	1	1	-1	10.368 ₂	0.7507 ₂
17	-1	-1	-1	-1	1	92.8500 ₄	10.268 ₈
18	1	-1	-1	-1	1	95.3302 ₀	39.747 ₃
19	-1	1	-1	-1	1	93.560 ₀	0.5084
20	1	1	-1	-1	1	95.013 ₈	6.618 ₈
21	-1	-1	1	-1	1	95.661 ₇	13.241 ₈
22	1	-1	1	-1	1	95.476 ₃	60.769 ₀
23	-1	1	1	-1	1	94.683 ₅	1.691 ₁

(continues on the next page)

Table S1. Experimental matrix 2⁵ and the respective responses using spectroscopic absorptio	n UV-Vis and
gravimetry (Continuation)	

Experiment	V ₁	V ₂	$V_{_3}$	V_4	V_{5}	% AT UV-Vis	% AT Gravimetry
24	1	1	1	-1	1	95.938 ₇	0.575 ₇
25	-1	-1	-1	1	1	95.112 ₆	0.371 ₂
26	1	-1	-1	1	1	94.825 ₀	3.3034
27	-1	1	-1	1	1	41.233 ₁	0.419 ₆
28	1	1	-1	1	1	54.296 ₅	1.598 ₉
29	-1	-1	1	1	1	96.170 ₅	29.887 ₉
30	1	-1	1	1	1	96.040 ₃	49.229 ₃
31	-1	1	1	1	1	94.502 ₈	2.350 ₉
32	1	1	1	1	1	96.433 ₁	2.614,

Table S2. Full CCD Experimental Matrix

	2**(3) CCD. nc=8 n	Rej	olies		
Samples	V ₁	V ₂	V ₃	% AT (UV-Vis)	% AT Gravimetry
12	0	1.68179	0	27.6235	22.2419
13	0	0	-1.68179	13.3489	8.7266
6	1	-1	1	12.8734	8.6495
11	0	-1.68179	0	11.9208	6.1108
3	-1	1	-1	28.4276	5.5913
16 (C)	0	0	0	93.6122	2.5356
8	1	1	1	86.6779	12.7864
5	1	-1	-1	91.2938	7.00568
9	-1.68179	0	0	4.140998	22.5061
10	1.68179	0	0	91.5031	16.2081
4	-1	1	1	47.6055	17.0565
2	-1	-1	1	9.0748	7.0353
7	1	1	-1	91.3084	9.2204
1	-1	-1	-1	6.1781	5.9338
14	0	0	1.68179	92.0140	0.31838
15 (C)	0	0	0	90.4636	17.2019

ANOVA							
	SS	Df	MS	F	р		
Regression	19566.95	7	3947.333	6.572	0.032504		
Waste	4804.75	8	600.594				
Lack of adjustment	4799.79	7	685.685	138.326	0.065378		
Error	4.96	1	4.957				
Total SS	22625.42	15					

Variation explained 86.47%

Explainable maximum variation: 99.98%

	Table S4. Analysis of variance for CCD using Gravimetry						
		A	NOVA				
Variables	SS	df	MS	F	р		
(2)Var2 (L)	136.3969	1	136.3969	4.827875	0.046734		
Var3 (Q)	167.7112	1	167.7112	5.936271	0.029966		
Error	367.2753	13	28.2519				
Total SS	671.3834	15					

Variation explained 45.30%

Table S5. Analysis of the signal intensity obtained from ICP OES by ANOVA

		ANOVA		
	SS	Df	MS	F
Regression analysis	2.5157	9	0.2795	1.433
Residual error	1.077	6	0.1795	
Lack-of-fit	0.9525	5	0.1905	1.5
Error	0.1245	1	0.1245	
Total SS	3.6219	15		

Variation explained 69.458%

ANOVA						
	SS	Df	MS	F		
Regression analysis	3.104	3	1.034	0.7950		
Residual error	2.601	2	1.3005			
Lack-of-fit	2.601	1	2.601	331.334		
Error	0.000785	1	0.000785			
Total SS	5.803511	15				

Table S6 $\Lambda NOVA$ for adsorption of metals using microwave digester

Variation explained 55.17% Explainable maximum variation 99.99%