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ENHANCING PRE-CONCENTRATION OF Pb(II) THROUGH SYNTHESIS OF TANNIN ACID-CHITOSAN (TAC) AS SOLID PHASE EXTRACTION ADSORBENT

(Penambahbaikkan Pra-pemekatan Pb(II) Melalui Sintesis Asid Tannin-Kitosan (TAC) Sebagai Penjerap Pengekstrakan Fasa Pepejal)

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Abstract

This study was conducted to incorporate tannin acid-chitosan (TAC) in solid phase method. The synthesized material was employed as an adsorbent to examine the effectiveness of solid phase extraction for preconcentration of Pb(II) in industrial wastewater. In addition, the parameters affecting extraction optimization were investigated and TAC was performed using a mass ratio of tannin acid and chitosan of 2:1 w/w. TAC absorbent was fully characterized using FTIR to detect functional groups and SEM-EDX to assess morphology and percentage of elements. The use of the optimal parameters for preconcentration on the performance of SPE method was obtained with adsorption, desorption, and enrichment factor at pH 5, a sample flow rate of 5 mL/min, Na_2EDTA eluent flow rate of 5 mL/min, a sample volume of 10 mL, Na_2EDTA eluent volume of 5 mL, sample concentration of 6 mg L^{-1} and Na_2EDTA concentration of 0.35 M. Furthermore, preconcentration application to Pb(II) wastewater at 0.05 mg L^{-1}, 0.06 mg L^{-1}, and 0.07 mg L^{-1} were concentrated 0.28 mg L^{-1}, 0.32 mg L^{-1}, and 0.38 mg L^{-1} with a factor of 5.6, 5.35, and 5.45 times. The result showed that the proposed method was effective for SPE with TAC adsorbent and Pb(II) preconcentration.

Keywords: solid phase extraction, preconcentration, Pb(II), tannin acid-chitosan

Abstrak

Penyelidikan ini menggabungkan asid tannin-kitosan (TAC) dalam kaedah fasa pepejal. Bahan tersintesis digunakan sebagai penjerap dan bertujuan untuk mengkaji keberkesanan pengekstrakan fasa pepejal untuk pra-pemekatan Pb(II) dalam air sisa industri. Di samping itu, parameter yang mempengaruhi pengoptimuman pengekstrakan telah disiasat. Asid tannin-kitosan (TAC) dilakukan menggunakan nisbah jisim asid tanin dan kitosan 2:1 b/b. Kemudian penyerap TAC dicirikan sepenuhnya menggunakan FTIR untuk mengesan kumpulan berfungsi dan SEM-EDX untuk menilai morfologi dan peratusan unsur yang terkandung di dalamnya. Menggunakan parameter optimum untuk pra-pemekatan pada prestasi kaedah pengekstrakan fasa pepejal diperolehi, dengan penjerapan, penyahjerapan, dan instrumen pengayaan pada pH 5 dengan kadar aliran sampel 5 mL/min, kadar alir eluen Na_2EDTA 5 mL/min, a isipadu sampel 10 mL, isipadu eluen Na_2EDTA 5 mL, kepekatan sampel 6 mg L^{-1} dan kepekatan Na_2EDTA 0.35 M. Penggunaan prapekatan pada air sisa Pb(II) pada kepekatan 0.05 mg L^{-1} boleh ditumpukan kepada 0.28 mg L^{-1} dengan faktor kepekatan 5.6 kali, pada kepekatan 0.06 mg L^{-1} boleh dipekatkan kepada 0.32 mg L^{-1} dengan faktor kepekatan 5.35 kali,

dan pada kepekatan 0.07 mg L^{-1} boleh ditumpukan kepada 0.38 mg L^{-1} dengan faktor kepekatan 5.45 kali. Nilai faktor kepekatan yang diperoleh sepadan dengan teori, 6 kali, masing-masing. Keputusan menunjukkan bahawa kaedah yang dicadangkan adalah berkesan untuk pengekstrakan fasa pepejal dengan penjerap TAC dan pra-pemekatan Pb(II).

Kata kunci: pengekstrakan fasa pepejal, pra-pemekatan, Pb(II), asid tannin-kitosan

Introduction

Wastewater generated from various industries, including garbage, metal plating, and leather industries, is known to pose a significant environmental risk by releasing harmful metal ions contaminating water [1]. Among these metal ions, lead (Pb) is particularly considered due to its toxicity, even at low concentrations, and can accumulate in living organisms, leading to long-term chronic exposure [2]. Typically, the concentrations in wastewater are measured by sampling at the site and then testing in the laboratory and the process often takes several days [3]. Determination of metal levels in water is commonly performed using techniques such as atomic absorption spectroscopy (AAS) instruments [4]. The accurate analysis becomes challenging when the metal ion concentration falls significantly below the detection limit of the instrument. Therefore, preconcentration step is necessary to enhance the detection capabilities of AAS instruments and solid phase extraction (SPE) has been widely recognized as an efficient method [5].

SPE is a technique used to separate compounds in a solution based on their chemical and physical properties [6]. The process in the SPE method begins with a conditioning step in which the column is filled with an adsorbent, serving as an analyte holder, followed by a loading step passed through the column/matrix/tube. In the third step, the column/matrix/tube is washed with Aquabides recovered by passing the eluent through the column/matrix/tube to analyse the results [6, 7].

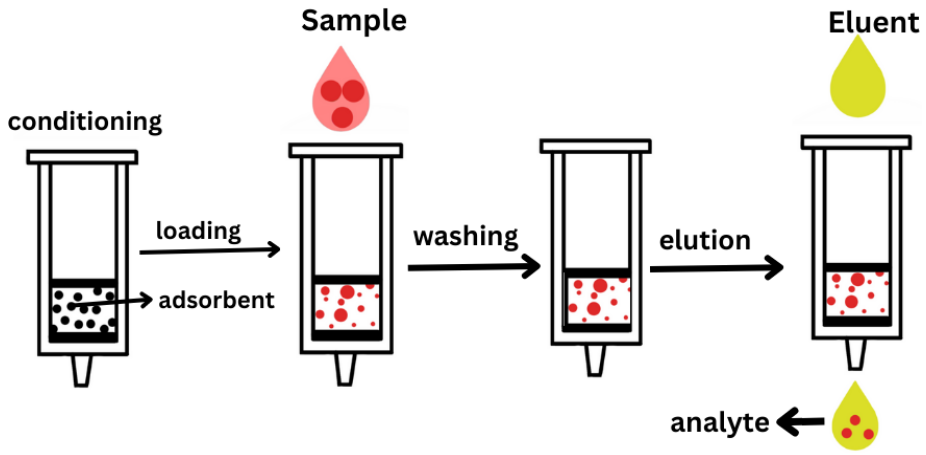

Figure 1. Main steps in solid phase extraction

Chitosan, a polymer found in crustaceans, fungal cell walls, and insect cuticles, is commonly employed as an adsorbent in SPE due to its hydroxyl and amino groups, acting as metal chelators and dye sorbents in solution [8]. Conversely, tannic acid possesses hydroxyl and carboxyl groups, making it suitable for adsorbing heavy metals. The high solubility in water necessitates immobilization with solid and porous materials, such as chitosan, to improve its applicability [9, 10]. Tannic acid and chitosan have been synthesized to obtain a new TAC adsorbent. It is more stable and effective for preconcentration/adsorption of metals riched in hydroxyl, carboxyl, and amino groups. A way to reduce metal analysis time is by combining the SPE method with TAC adsorbent.

The effectiveness of the SPE method can be evaluated based on the enrichment factor of the sample. The

enrichment factor, obtained from the performance of the SPE, reflects the increase in the absolute absorbance value, improving the validity of the concentration calculation beyond the detection limit on the linear curve [11]. In addition, optimization of parameters affecting SPE, such as solution pH, sample flow rate, eluent flow rate, sample concentration, and volume, can enhance the effectiveness of the method [12]. Previous studies also showed successful optimization of SPE parameters for preconcentrating Cd(II) and Pb(II), resulting in high concentration enrichment factors of 250 and recovery rates of 95% [13]. Similar efficiency and enrichment factor results have been achieved for Pb(II) using SPE in other studies [11, 14].

By combining the advantages of SPE with the use of TAC as an adsorbent, this study synthesizes and characterizes a novel adsorbent for preconcentration of Pb(II) from industrial wastewater. Additionally, the optimization of extraction parameters is explored to maximize the efficiency of preconcentration process. The results are expected to contribute to the development of sustainable and effective methods for preconcentration of heavy metal ions, specifically Pb(II), in industrial wastewater, facilitating the proper management and treatment of wastewater to mitigate the associated environmental and health risks.

Materials and Methods

Materials

The materials required are bi-distilled water and Merck's Pro-Analytical Quality (p.a.) chemicals, namely chitosan (%DD > 75%), tannic acid, $PbNO_3$, 25% glutaraldehyde, Na_2EDTA, filter paper, and universal pH paper.

Instrumentation

The equipment used includes laboratory glassware, stirrer, magnetic stirrer, analytical balance, oven, FTIR (Fourier Transform InfraRed, Thermo Nicolet Avatar 360), AAS (Atomic Absorption Spectrophotometer, Buck 205 Atomic Absorption Spectrophotometer), and SEM-EDX (Scanning Electron Microscope-Energy Dispersive X-ray).

Procedure: Synthesis of an adsorbent TAC

Tannic acid (up to 4g) was dissolved in 120 mL Aquabides by stirring until fully dissolved. Subsequently, 2g of chitosan was added to the solution and stirred for 6 hours using a stirrer. The stirring process was continued for 6 hours after adding 12 mL of 25% glutaraldehyde to crosslink the materials. The resulting precipitate was filtered and dried in an oven at 50 °C. The material was crushed using a mortar and pestle, followed by filtration to obtain the TAC adsorbent powder used in subsequent experiments [15].

Characterization of the TAC adsorbent

The TAC powder was subjected to characterization using an FTIR instrument (Thermo Nicolet Avatar 360) operating in the wave number range of 4000-400 cm^{-1}. This characterization aimed to identify the functional groups in the TAC powder analysed using an SEM-EDX instrument at a magnification of 1500-5000 times. The purpose of the analysis was to investigate the micro-scale properties of the material, including texture, morphology, composition, and surface characteristics.

Optimization of the SPE method

This study optimized SPE conditions by investigating different parameters. These parameters included the pH of the solution, the concentrations of the sample and eluent, the flow rates of the sample and eluent, the volumes of the sample and eluent, and the impact of eluent concentration on artificial wastewater.

Application of preconcentration to Pb(II)

The TAC adsorbent preconcentration process was applied to artificial wastewater samples containing Pb(II) ions. The experimental conditions included the pH, sample flow rate, eluent flow rate, sample volume, eluent volume, sample concentration, and optimal eluent concentration. The Pb(II) concentrations were set at 0.05, 0.06, and 0.07 mg L^{-1}, with a theoretical concentration factor of 6 times. Meanwhile, the resulting analyte concentrations were measured using an AAS instrument.

Results and Discussion

Characterization of the TAC adsorbent

The TAC adsorbent was subjected to characterization using FTIR to detect the functional groups present. The analysis results of the TAC adsorbent synthesis are presented in Figure 2, where peaks observed on the TAC adsorbent provide valuable information about the composition. Chitosan peak at 3442 cm^{-1} indicates the stretching vibrations of hydroxyl (O–H) and amino (N-H) groups. However, this peak shifts to 3434 cm^{-1} on the TAC adsorbent, suggesting the crosslinking of chitosan and glutaraldehyde [15]. Another peak shift is observed at 2932 cm^{-1} and 2955 cm^{-1}, which shifts to 2927 cm^{-1} on the TAC adsorbent, signifying the stretching vibrations of the (C–H) group [16]. Additionally, aldehyde stretching vibrations are indicated by a 2847 cm^{-1} peak on the TAC adsorbent [15]. The carboxyl group is confirmed by a peak at 1712 cm^{-1}, and the presence of the C–N group is indicated by 1341 cm^{-1} on the TAC adsorbent [16]. In chitosan, the carboxyl (C=O) stretching vibrations observed at 1642 cm^{-1} are shifted to 1627 cm^{-1}, suggesting the crosslinking of chitosan and tannic acid [15].

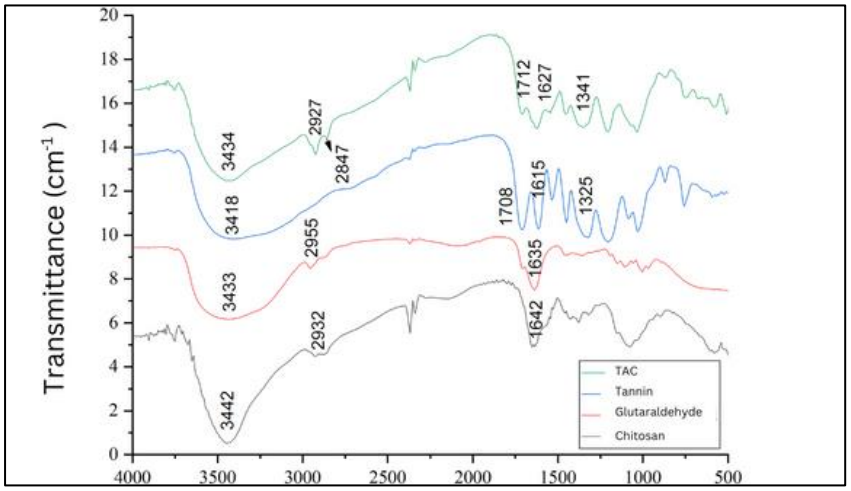

Figure 2. Spectra FTIR from tannin, acid, chitosan, glutaraldehyde, and TAC adsorbent

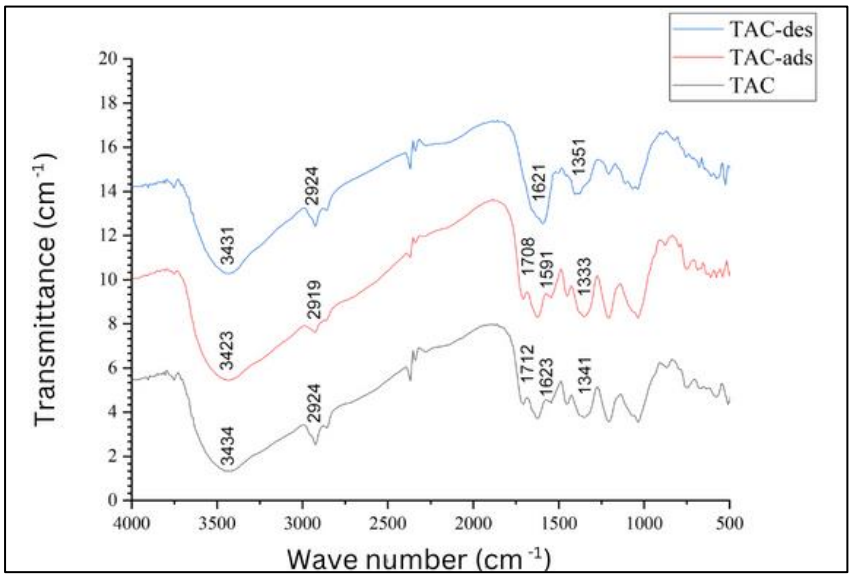

Figure 3. Spectra FTIR from TAC adsorbent, TAC-adsorption, and TAC-desorption

Characterization of the TAC adsorbent

The TAC adsorbent was analysed using Figure 3 to observe the peaks before and after adsorption and desorption. At the peak of 3434 cm^{-1}, there is a shift to 3423 cm^{-1}, indicating the narrowing of the stretching vibrations of the O–H and N–H groups. This shift suggests the interaction between the adsorbent and Pb(II) ions. In the desorbed TAC, the peak returns to 3431 cm^{-1}, indicating that Pb(II) absorbed in the adsorbent can be desorbed by the eluent. Another interaction can be observed at the 1623 cm–1 peak, which shifts to 1591 cm^{-1}, indicating C=O stretching vibration [15]. Moreover, the carboxyl and the C–N groups are visible at the peak of 1712 cm^{-1} and 1341 cm^{-1}, which shift to 1708 cm^{-1} and 1333 cm^{-1}, respectively. These shifts further confirm the interaction between the adsorbent and Pb(II) [17].

Based on the FTIR data described above, the interaction occurring in the TAC adsorbent with Pb can be estimated, as shown in Figure 4.

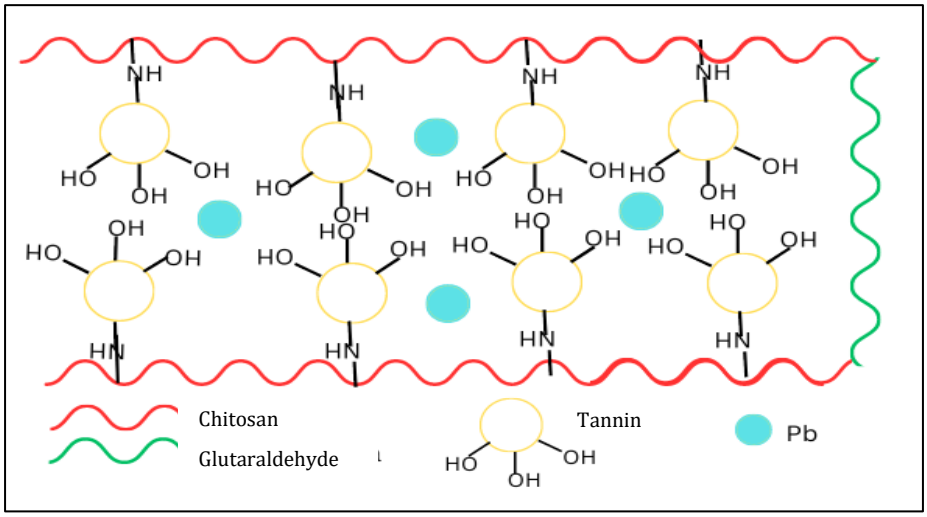

Figure 4. Estimation of the interaction between TAC adsorbent and Pb(II)

The morphology and percentage of elements present in the TAC adsorbent were assessed using SEM-EDX analysis. Figure 5 shows the morphology of the TAC adsorbent before and after adsorption and after desorption. Each sample was analysed at magnifications of 1000 and 5000 times to provide a detailed view of the surface morphology of TAC adsorbent during the different adsorption and desorption stages.

Figure 5 provides valuable insights into the structure and elemental composition of the TAC adsorbent. The adsorbent exhibits a complex and loose structure favorable for molecular diffusion and provides sufficient free space for Pb(II) molecules. In Figure 5b, the TAC adsorbent appears denser due to Pb(II) molecules filling the spaces. However, in Figure 5c, the TAC adsorbent returns to a looser structure, similar to the initial state, due to the desorption treatment. The analysis of the elements in the TAC adsorbent is presented in Table 1, displaying the mass percentage of elements in the TAC.

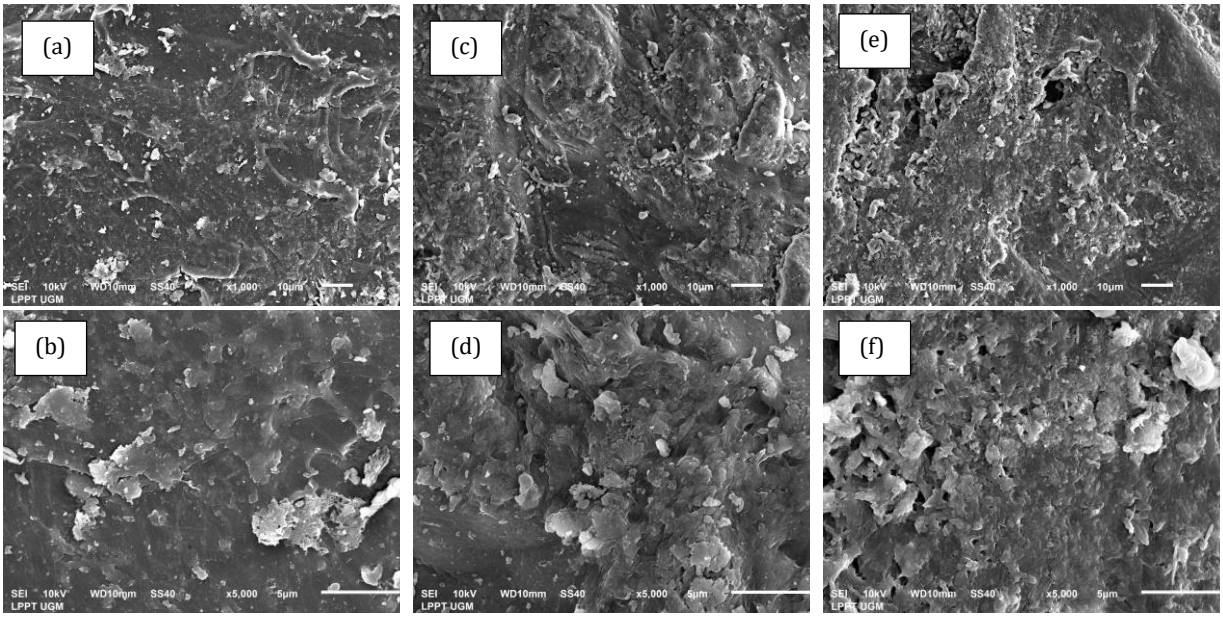

Figure 5. SEM images (a) TAC 1000x, (b) TAC 1500x, (c) TAC-adsorption 1000x, (d) TAC-adsorption 1500x, (e)TAC-desorption 1000x, and (f) TAC-desorption 1500x.

Table 1. Elemental composition in TAC before and after preconcentration

Sample	Elemental Composition (%)				
	C	N	O	Na	Pb
TAC	45.17	16.56	38.27	-	
TAC-adsorption	45.35	16.53	37.93	0.02	0.17
TAC-desorption	38.64	13.25	40.67	7.38	0.06

The TAC adsorbent contains 0.17% of the Pb element, decreasing to 0.06% after desorption. This significant decrease shows the successful desorption of Pb(II) using the Na_2EDTA eluent. The reduction in the Pb element can be attributed to the interaction between Pb(II) and the ligand of Na_2EDTA, confirming the effectiveness of the desorption process [18].

Optimization of SPE methods: pH optimization

The optimal pH of the solution plays a crucial role in the sorption of Pb(II) ions using the TAC adsorbent and the study tested pH 4, 5, 6, and 7. Figure 6(a) shows the varying percentage of Pb(II) sorption at different pH levels. The sorption capacity at low pH values (pH >4) is reduced due to the competition between hydrogen ions and Pb(II) ions for adsorption sites on the TAC adsorbent [19]. Additionally, the protonation of functional groups at lower pH values hampers the optimal adsorption of Pb(II) ions. At a higher pH (pH 5), the competition for protons decreases, leading to enhanced adsorption of Pb(II) ions on the TAC adsorbent [20]. However, at higher pH levels (pH 6-7), a decrease in adsorption is observed due to the precipitation of lead ions [19]. The optimal pH for the SPE process with Pb(II) samples is determined to be pH 5, aligning with previous results [20]. Furthermore, it is essential to consider the effect of solution pH on Pb(II) analysis and the changes in metal speciation for an effective SPE process [21].

Sample flow rate optimization

The flow rate of the sample is another influential factor in the SPE method. The study tested different sample flow rates, namely 5, 10, 15, and 20 mL/min to

determine the optimal flow rate, yielding high adsorption, desorption, and concentration factor. The results depicted in Figure 6(b) showed that the optimal sample flow rate was 5 mL/min. A low flow rate can positively affect adsorption due to selective interaction between the adsorbent and the lead metal [12]. However, at higher flow rates (10-20 mL/min), the limited contact time between the adsorbent and the metal decreases the percentage of adsorption [22]. This result aligns with previous studies, where higher flow rates result in insufficient absorption of lead metal by the adsorbent due to reduced contact time [23].

Eluent flow rate optimization

The flow rate of the eluent used for desorption significantly influences the desorption percentage and concentration factor of the SPE method. The study conducted tests with 5, 10, 15, and 20 mL/min variations for the eluent flow rate. The results in Figure 6(c), indicate that the optimal flow rate is 5 mL/min, since it provides a higher enrichment factor than other flow rates. Besides the higher enrichment factor, selecting an eluent flow rate of 5 mL/min helps avoid excessive duration [7]. This result was consistent with previous studies, where eluent flow rates in the 2-5 mL/min range were considered high for optimal SPE methods [24]. Conversely, higher flow rates (10-20 mL/min) resulted in decreased desorption and lower enrichment factors, possibly due to reduced contact between Na_2EDTA and the TAC adsorbent, which led to a decreased amount of desorbed Pb(II) analyte [25].

Sample volume optimization

The sample volume employed in the SPE method affects both the desorption percentage and the concentration factor. This study tested the optimal sample volume with 5, 10, 15, and 20 mL variations. The results in Figure 6 (d) show that the optimal sample volume is 10 mL and larger sample volumes increase the likelihood of a higher enrichment factor [26]. However, excessively large sample volumes can also reduce enrichment [12] and the obtained enrichment is low at lower volumes (5 mL) due to limited interaction between the analyte and the adsorbent [27]. In this study, the optimal results were obtained with a sample volume of 10 mL, and at higher volumes (15-20 mL), the active sites become saturated, leading to suboptimal absorption and decreased enrichment values [12]. These results are consistent with previous studies by Jiménez-Soto et al. [28] and Sanagi et al. [27], which found 10 mL to be the optimal sample volume for the SPE method.

Eluent volume optimization

The volume of eluent used for desorption affected the desorption percentage and the concentration factor in the SPE method. The study conducted tests of 5-, 10-, 15-, and 20-mL variations for the eluent volume, and the results in Figure 6(e), indicated that the optimal eluent volume was 5 mL. At higher volumes, there was a decrease in desorption due to excessive eluent volume, which had a limited effect after the analyte was sufficiently eluted. This result was consistent with the studies conducted by Sanagi et al. [27] and Maranata et al. [12], which determined the optimal eluent volume in the range of 3 to 6 mL for the SPE method.

Sample concentration optimization

The sample concentration influenced the desorption percentage and the concentration factor of the SPE method. This study tested the optimal sample concentration with 5, 6, 7, and 8 mg/L variations, and the results are shown in Figure 6(f), where the optimal result is 6 mg/L. Petrović et al. [20] stated that higher concentrations resulted in higher adsorption values as the availability of Pb(II) metal ions increased, leading to increased adsorption [29]. However, a significant decrease in adsorption occurred at higher concentrations (8 mg/L), impacting the enrichment value. This decrease was due to the saturation of active sites on the adsorbent caused by a more significant number, rendering the adsorbent suboptimal for adsorbing Pb(II) metal ions [30].

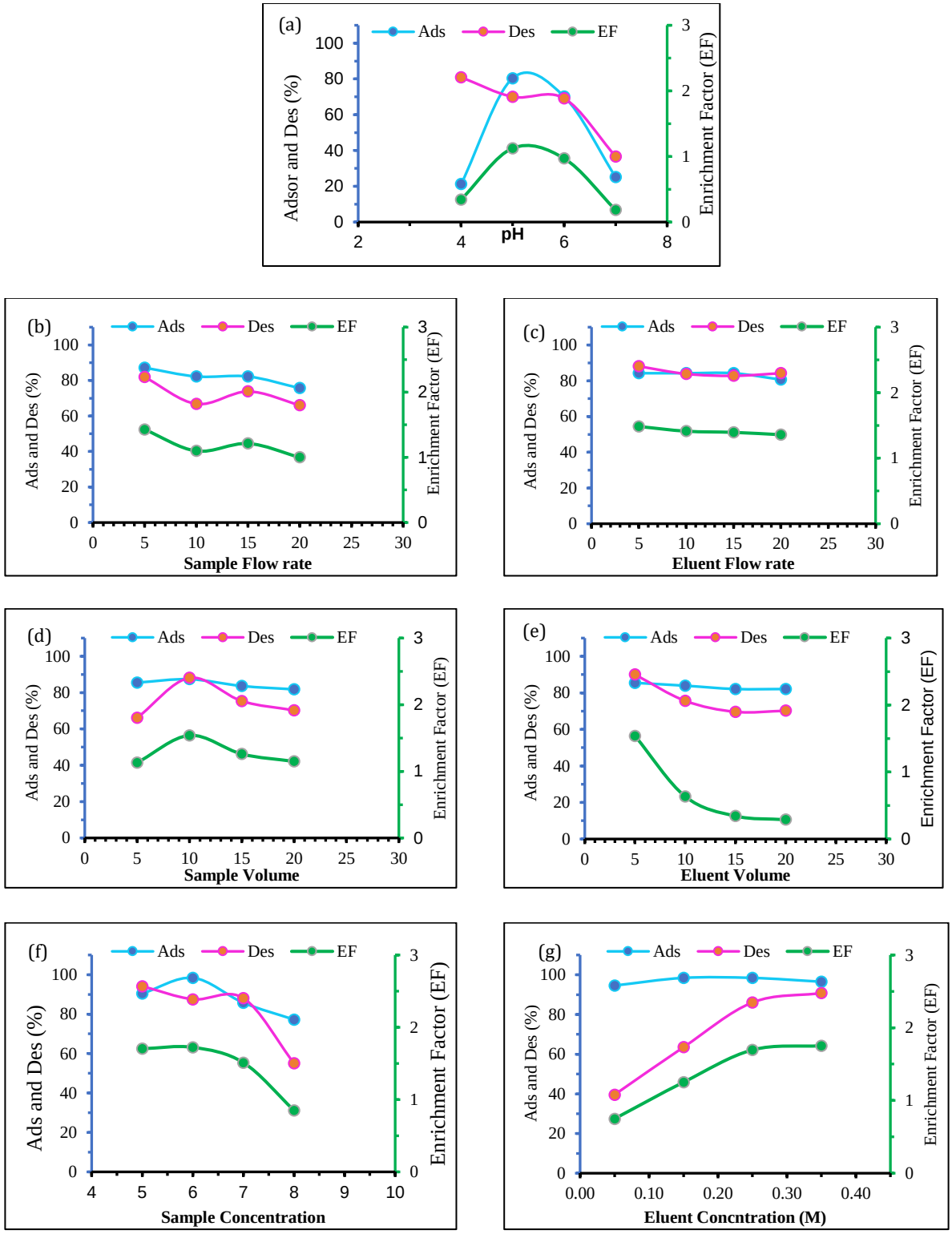

Figure 6. Effect of (a) pH (b) sample flow rate (c) eluent flow rate (d) volume sample (e) volume eluent (f) sample concentration (g) eluent concentration. (Ads is Adsorption, Des is Desorption, EF is Enrichment Factor)

Eluent concentration optimization

The eluent concentration used for desorption affected the desorption value and the factor in the SPE method. In this study, Na_2EDTA was used as the eluent because of its effectiveness compared to other solvents [31]. The optimal eluent concentration was tested with 0.05, 0.15, 0.25, and 0.35 M variations. Figure 6(g) showed that higher eluent concentrations resulted in higher desorption values and enrichment factors. The optimal eluent concentration was 0.35 M since higher concentrations fostered more interactions between the Na_2EDTA ligand and the TAC adsorbent, leading to a more effective desorption process [32]. The approximate interaction between the Na_2EDTA ligand and Pb(II) was shown in Figure 7.

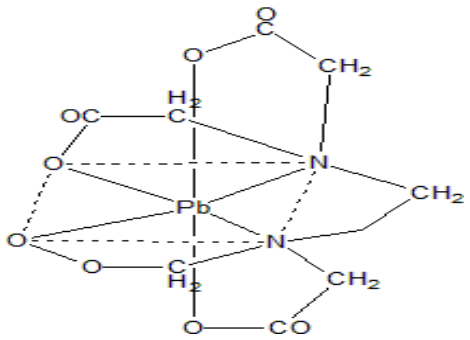

Figure 7. Approximate interaction between Na_2EDTA ligand and Pb(II)

Pre-concentration application to Pb(II)

Pre-concentration test was conducted to assess the effectiveness of SPE method with TAC adsorbent for pre-concentrating Pb(II) waste below the detection limit of the available AAS instrument (with a detection limit of 0.1 mg/L). Synthetic Pb(II) waste solutions were prepared with concentrations of 0.05 mg/L, 0.06 mg/L, and 0.07 mg/L, and were subjected to SPE using the TAC adsorbent under optimal conditions. Subsequently, desorption was performed using 5 mL of 0.035 M Na_2EDTA eluent, and the resulting samples were analysed using AAS.

Preconcentration test on Pb(II) waste showed the successful application of SPE method with TAC adsorbent. Table 2 shows the difference between the synthetic waste samples' initial and Pb(II) concentrations. The concentration was undetectable below the detection limit of the instrument but after preconcentration, Pb(II) was successfully detected. For the 0.05 mg/L, 0.06 mg/L, and 0.07 mg/L Pb(II) waste solution, the concentration was concentrated to 0.23 mg/L, 0.32 mg/L, and 0.038 mg/L with a factor of 5.6, 5.35, and 5.45, respectively. These concentration factor values obtained from the three waste variations closely approximate the theoretical factor of 6 times. Therefore, SPE method with TAC adsorbent is well-suited for preconcentration of Pb(II) metals. Preconcentration test results affirm the proposed method's efficacy and its potential for effectively concentrating Pb(II) below the detection limit of the AAS instrument.

Table 1. The result of TAC application on artificial wastewater

Wastewater Concentration (mg/L)	Wastewater Concentration (mg/L)		Enrichment Factors
	Initial	Final	
0.05	-	0.28	5.60
0.06	-	0.32	5.35
0.07	-	0.38	5.45

Conclusion

The synthesis of TAC as an adsorbent for pre-concentration using SPE method was successfully showed. The synthesized TAC adsorbent possessed active groups, including hydroxyl (–OH), amino (–NH_2), and carboxyl, which acted as effective metal chelators. By optimizing various parameters, the performance of the SPE method for pre-concentration had been significantly improved. The optimal parameters for pre-concentration using the SPE method were determined as follows pH 5, the sample flow rate of 5 mL/min, Na_2EDTA eluent flow rate of 5 mL/min, a sample volume of 10 mL, Na_2EDTA eluent volume of 5 mL, sample concentration of 6 mg/L, and Na_2EDTA concentration of 0.35 M. These parameters resulted in successful preconcentration of Pb(II) wastewater. For initial concentrations of 0.05 mg/L, 0.06 mg/L, and 0.07 mg/L, the concentrations were 0.28 mg/L, 0.32 mg/L, and 0.38 mg/L, with corresponding factors of 5.6, 5.35, and 5.45 times. Therefore, these concentration factors aligned with the theoretical value of 6 times. The results showed the effectiveness of the proposed SPE method using the TAC adsorbent for preconcentration of Pb(II). The technique offered a reliable and efficient method for preconcentration, allowing for the analysis of Pb(II) at concentrations below the detection limit of analytical instruments.

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