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Alginate Chitosan Amine-Functionalized Silica-Coated as an Adsorbent for Magnetic Micro Solid-Phase Extraction of Bisphenol A from Canned Food Sample

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Abstract

A magnetic micro-solid phase extraction (M-μ-SPE) coupled with UV-visible spectrophotometry was developed to analyze Bisphenol A (BPA) in canned food. The method utilized alginate chitosan amine-functionalized silica-coated (alg/Cs-NH_2-SiO_2/Fe_3O_4) as an adsorbent. Optimized parameters, including sample pH, adsorbent mass, extraction time, and solvent desorption volume, were chosen to enhance separation and extraction efficiency. The maximum signal of BPA was achieved when extracted using 80 mg of adsorbent at sample pH 6, followed by desorption with 500 μL of ACN. The adsorption process was rapid and completed within 30 seconds, with UV detection at 275 nm. Calibration curves exhibited good linearity from 0.5 to 10 mg/L (R^2 = 0.9982). The method demonstrated an LOD {3.3 (S/N)} of 1.11 mg/L and LOQ {10 (S/N)} of 3.3 mg/L, with good repeatability (RSD < 8.7% for n = 3). Recoveries of spiked BPA (0.5-10 mg/L) ranged from 87.5% to 106.8%. Analysis of canned sardine (85% recovery) and canned lychee (93% recovery) samples showed promising results with RSD < 9%. This study indicates that M-μ-SPE coupled with UV-visible spectrophotometry was a rapid and reliable method for BPA analysis in canned food.

Keywords chitosan, adsorbent, micro solid-phase extraction, bisphenol A, alginate, magnetic, canned food, UV-visible spectrophotometry

1.0 INTRODUCTION

BPA is one of the chemicals used in food packaging, including in cans, plastic containers, and bottles, as usually used in manufacturing and other industries [1]. Packaging plays a crucial role in preserving food, as it helps maintain quality and safety by acting as a barrier against factors that cause chemical, physical, and microbiological degradation [2]. BPA is synthesized by combining bisphenol and diphenylmethane as major constituents, with two hydroxyphenyl groups attached to the carbon atom [3]. Polycarbonate plastics and epoxy resins gave essential building blocks for polymer plastics and coatings due to the use of BPA substances in the industry. Epoxy resins utilized as coatings on the inner surface of cans are components of can packaging. Studies showed that BPA seeps into food and drinks when containers made from the material are used. Small quantities of BPA inside foods cause adverse effects on human and animal health [2, 4]. A well-known endocrine disruptor, BPA, may have toxic effects on the immune, nervous, and reproductive systems [5, 6]. The substance was suspected of being an endocrine disruptor at low levels that could cause long-term exposure through migration to food from packaging materials. Other effects of BPA have been found to possess estrogenic properties, which can influence human anti-androgenic behaviour [7]. This substance also has been linked to cancer, obesity, behavioural changes, decreased fertility, and developmental issues, according to several studies [8]. According to the Food and Drug Administration (FDA), regulations prohibit the use of BPA in food contact applications, and infant formula packaging materials were prohibited in 2013 as a result. FDA published the margin of safety for other food contact applications as "NOAEL," which stands for "no observed adverse effect level". Approximately 5 mg/kg body weight per day was well above the estimated dietary intake for this substance. Nevertheless, exposure to BPA could be detected at a low concentration and may be hazardous to people. Hence, research on determining BPA in food packaging is essential for minimizing potential health concerns [9].

Therefore, optimized and developed methods for better analytical techniques become the top priority in any qualitative and quantitative research study. Sample preparation methods play an essential role in the pre-treatment of samples or pre-concentration of the target analyte in the analytical analysis, including food samples, biological samples, and environmental samples. Sample preparation could remove potential interferences, increase analyte concentrations, and introduce low-cost operation procedures by using extremely low or no solvent consumption [10]. A previous study extracted BPA from other matrices using several extraction methods, with or without large-size instruments. These methods pre-concentrate or isolate the analyte from food samples. Thus, it included solid-phase extraction (SPE) [11], stir bar sorptive extraction (SBSE) [12], solid-phase microextraction (SPME) [13], dispersive micro-solid phase extraction (D-µ-SPE) [14] or the basic LLE [10].

In the last two decades, SPE and LLE methods were not affordable and suitable for industries due to high solvent consumption and more steps than conventional methods [15]. Modifying SPE such as SPME, D-µ-SPE, and magnetic solid extraction (MSPE) were currently highly chosen in industries. A previous study on the determination of BPA in tap water using MSPE coupled with HPLC-DAD gave LOD = 0.031 mg/L [16]. However, SPME and D-µ-SPE need further centrifuges, filtration steps, and time-consuming [17]..Hence, a simple and rapid technique known as magnetic micro solid extraction (M-µ-SPE) was developed in this new application of analysis BPA. This method was expected to give efficiency, sensitivity, simplicity, and selectivity in determining target analytes. For instance, the lowest LOD obtained in previous work [9] which was 3.05 µg/L, utilizing M-µ-SPE coupled with HPLC-UV to determine BPA in milk. The M-µ-SPE method required using adsorbent as it is effective, whereas extracting analyte from sample solutions. Thus, the adsorbent was essential for developing the M-µ-SPE method, especially in real food samples. In the previous study, several development adsorbents have been used in M-µ-SPE, especially in BPA analysis. According to [11], they used the combination of graphene and magnetite (G-Fe_3O_4) as an adsorbent and prepared in magnetic dispersion SPE preparation (MDSPE). Additionally, this adsorbent provides a larger surface area for adsorption and better separation. However, the use of graphene is more toxic at high temperatures, expensive, and easy to oxidize in environments [18]. The popularity of chitosan has increased over the years. As a biocompatible, biodegradable, and low-toxic adsorbent, chitosan (CS) has natural additives that make it ideal for use as an adsorbent [19]. These materials are characterized by their high density of hydroxyl groups (-OH) and primary amines (-NH_2), which serve as active adsorption sites. Thus, the used alginate chitosan amine-functionalized silica-coated (alg/Cs-NH_2-SiO_2/Fe_3O_4) adsorbent in this method was expected to give higher absorptivity and efficiency in separation. The alg/Cs-NH_2-SiO_2/Fe_3O_4 adsorbent has reportedly been used to remove heavy metals utilizing the M-µ-SPE method for the first time, according to [19]. In this study, alg/Cs-NH_2-SiO_2/Fe_3O_4 extremely interesting to be examined as SPE materials for BPA extraction in food packaging because of its high surface area, capacity for π interactions, sensitivity, and stability [19]. As a result, it is initially suggested to use alg/Cs-NH_2-SiO_2/Fe_3O_4 as an adsorbent to remove BPA from food samples in canned packaging.

The main aim of this study is to apply the M-µ-SPE method by using alg/Cs-NH_2-SiO_2/Fe_3O_4 as an adsorbent for the adsorption and desorption of BPA in food. In recent studies, the M-µ-SPE method has gained attention in chromatography instruments for extraction such in the determination of BPA such as high-performance liquid chromatography UV-visible (HPLC-UV) [9], high-performance liquid chromatography (HPLC) [11] and liquid chromatography-tandem mass spectrometer (LC-MS-MS) [20]. In this study, a simple, fast, and affordable instrument and excellent separation for BPA detection are chosen. UV-vis spectrophotometry detected bisphenol in under one minute at 275 nm in a few research [21]. UV detection's linearity and ability to quickly quantify against a single standard made it preferred. The high molar absorptivity allowed quantitative analysis since no interfering compounds absorb at the same wavelength. Furthermore, UV-Vis spectrophotometry also was utilized for BPA and BPS detection in plastics, food cans and thermal receipt paper [21], cooperated with the MSPE method for pseudoephedrine detection in water and urine samples [22]. Therefore, UV-Vis spectrophotometry has been applied to assess this research. Here, a more advanced technique, magnetic micro solid extraction (M-µ-SPE), was proposed, combining with alg/Cs-NH_2-SiO_2/Fe_3O_4 acts as an adsorbent to achieve the highest absorptivity of BPA in food samples by using UV-Vis spectrophotometry.

2.0 EXPERIMENTAL

2.1 Standard and reagents

The standard used was BPA, which was purchased from Sigma Aldrich. The adsorbent material was alginate chitosan amine-functionalised silica-coated, alg/Cs-NH_2-SiO_2/Fe_3O_4 which had previously been synthesized in [23]. All the solvents purchased from Merck (Darmstadt, Germany) were used: MeOH, ACN, and EtOH. Nitric acid (HNO_3) 65% purity were purchased from

Merck (Darmstadt, Germany). Sodium hydroxide (NaOH) and acid hydrochloric (0.1 and 2 M) were used for pH adjustment. Deionized water (DI) was produced from the Milli-Q water purification system (USA) and lastly, canned food packaging as samples was purchased from Target supermarket.

BPA was prepared as a 1000 mg/L stock solution dissolved in MeOH in a 100 mL volumetric flask. The series working standard mixture was prepared using MeOH solvent. All the stock solution and working standards were stored at 4°C and brought to room temperature before use. For cleaning purposes, all vessels were soaked in 10 % (v/v) of nitric acid for at least 24 hours and rinsed thoroughly with deionized water.

2.2 Apparatus and Instrument

Weighing balance, spatula, external magnet, 0.45 μm nylon filter syringe, 5 mL of the syringe, 5 mL of the centrifuge tube, and 4 mL of quartz cuvette were used in this research. The instrument used to determine BPA was UV-visible spectrophotometry (Perkin Elmer). The wavelength at the range 275 nm was selected for UV detection. A pH meter (Thermo Fisher Scientific) was used to adjust the pH of the sample and standard solution. A vortex mixture (VELP Scientific) was used to homogeneously mix the solution to extract the target analyte from the solution.

2.3 Magnetic-μ-SPE method

In this M-μ-SPE method (Figure 1), alg/Cs-NH_2-SiO_2/Fe_3O_4 adsorbent was synthesized in-house method by [23] and used as an adsorbent. Initially, 20 mL of 3 mg/L BPA was added to a 50 mL centrifuge tube. The solution was then adjusted to pH 6. Subsequently, 20 mg of adsorbents was added and poured into the sample solution. The extraction process was a crucial part due to the interaction between the adsorbent and absorbate that happened. The mixture was vortexed for 1 minute for the extraction process. After extraction, the adsorbent was isolated using an external magnet, and the supernatant was removed. Then, the adsorbed BPA was desorbed with 500 μL of MeOH by vortexing it for 1 minute. Another 3500 μL MeOH was added for UV-visible spectrophotometric analysis. Several parameters have been optimized to achieve optimum extraction conditions and improve the extraction method of BPA. In terms of the M-μ-SPE method, several parameters were optimized. First, study the effect of pH samples which were pH 5, pH 6, pH 7, and pH 10. Second, three different amounts of adsorbent were used: 40 mg, 60 mg, and 80 mg. Third, three desorption solvents were selected, including MeOH, ACN, and EtOH. In the final phase, the extraction time during analysis, which was 30 s, 1 minute, and 2 minutes, was optimized and evaluated. The results were validated using an external calibration graph, whereby the validation was based on the linearity of the graph, precision, LOD, LOQ, recovery, and repeatability.

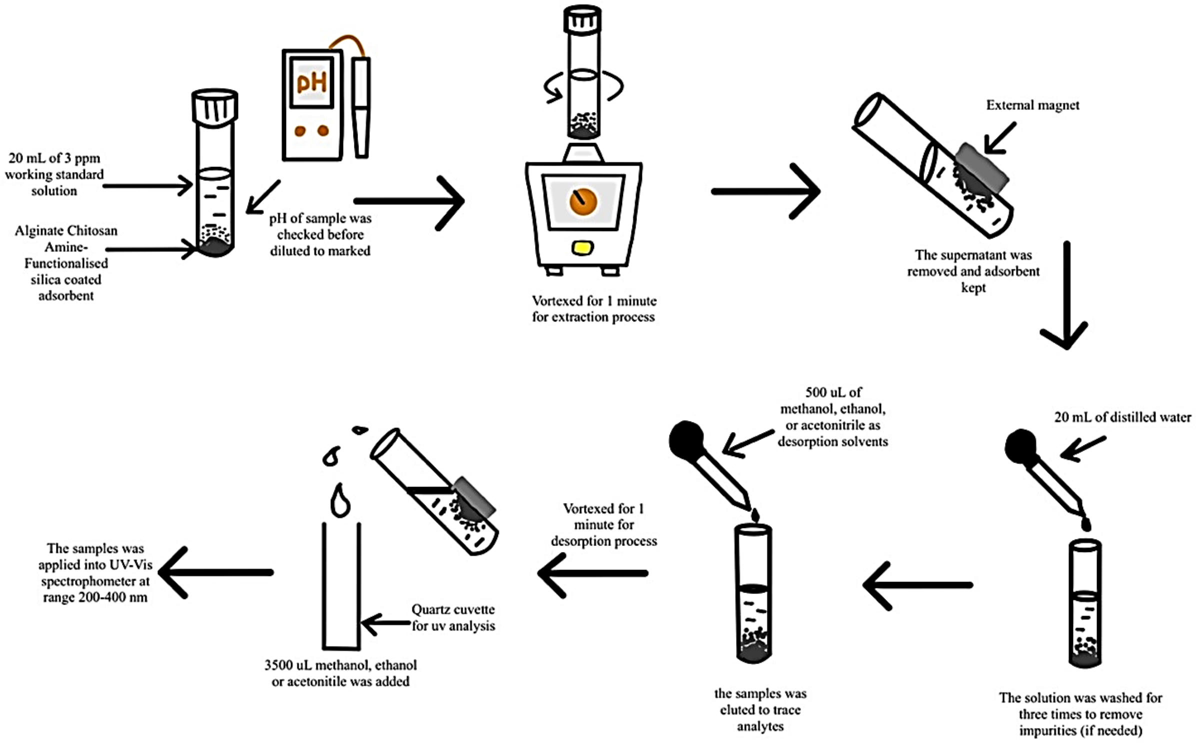

Figure 1 M-μ-SPE procedure utilizing the alginate chitosan amine-functionalised silica-coated adsorbent.

2.4 Real Sample Analysis

The developed M-μ-SPE method was applied to two types of canned food: sardine and lychee. The samples were purchased from a Target supermarket in Benut (Johor, Malaysia). Sealed samples were stored at room temperature (± 20°C), protected from light, and opened only during the analysis. Prior to analysis, each solid sample was homogenized with solvents, centrifuged, and filtered several times using 0.45 μm nylon filter syringes. Then, the resulting solid-liquid extracts were further extracted with the optimized M-μ-SPE method and analyzed as usual. To investigate the applicability of the developed method for real sample analysis and better calculate the recovery of analytes, the same canned food samples were spiked with 3 mg/L of standard BPA and subjected to M-μ-SPE method.

3.0 RESULTS AND DISCUSSION

3.1 UV-Vis Determination and Standard Calibration for BPA

UV-Vis determination of the BPA analytes was carried out using MeOH as the blank reference at ambient temperature using a 4 mL cuvette. The UV-VIS Spectrophotometer performance was tested in the standard calibration study because its capabilities could be degraded with time. As a result, it can make the measurement output less reliable. According to the data gathered, it was carried out using MeOH spiked with BPA analytes to obtain a series of working standard solutions of 1-5 mg/L. For the BPA analyte, a signal versus concentration graph was created. Using the least squares method, trend lines were applied to create the linear equation. With R^2 = 0.9991, the BPA analyte result demonstrated good linearity from 1-5 mg/L.

3.2 Optimization of M-μ-SPE Method

3.2.1 Effect of Sample pH

In this study, a method for the optimization used was OVAT (one variable at a time). The first aspect to be optimized was the sample pH of the BPA solution. The pH of the solution affects how the analyte and alg/Cs-NH_2-SiO_2/Fe_3O_4 adsorbent was adsorbing [24]. Temporarily, there were strong interactions, and intermolecular forces occurred between the carbon atoms of the analytes and the adsorbent [25] Van der Waals forces or London dispersion interaction are other names for it [24]. Initially, the technique was carried out using 20 mL of 3 mg/L working standard applied to the M-μ-SPE procedure under the conditions of 60 mg adsorbent, 1 minute of extraction time, and 500 μL MeOH as the desorption solvent. These experimental setups were created to examine how sample pH varied from pH 5 to pH 10 or vice versa. According to Figure 2a, pH 6 represented the maximum capacity absorption, demonstrating that the neutral environment was more favourable to the extraction of BPA's neural structure. This was due to alg/Cs-NH_2-SiO_2/Fe_3O_4, through electrostatic attraction, π-stacking, and hydrophobic interaction aids in increasing contact with the benzene rings in the BPA structure. Aside from improving the adsorption of BPA into the porous adsorbent, the large surface area and pore volume of alg/Cs-NH_2-SiO_2/Fe_3O_4 also give rise to more active sites for BPA adsorption. The adsorption capacity of alg/Cs-NH_2-SiO_2/Fe_3O_4 gave greater signal, where the maximum adsorption capacity was observed at pH = 6 and reduced at acidic (pH = 5) and alkaline (pH = 10) environments, respectively. Low adsorption capacities were observed at low and high pH values due to the competitive adsorption between H^+, OH^- ions, and BPA molecules. At low pH, the protons (H^+) was integrated with the amine groups NH^{2-} of the alg/Cs-NH_2-SiO_2/Fe_3O_4, hindering the π-stacking, and hydrophobic interactions between the alg/Cs-NH_2-$SiO_2/Fe_3O_4$and BPA. In addition, this was likely caused by iron oxide leaching, which may have a tendency to reduce attraction towards both analyte and adsorbent.

3.2.2 Effect of Adsorbent Mass

Effect of alg/Cs-NH_2-SiO_2/Fe_3O_4 nanocomposite mass was investigated because the amount of adsorbent used in M-μ-SPE is directly proportional to the sample volume that could be passed through the adsorbent before the analyte breakthrough. This information makes it possible to calculate the adsorbent's capacity for a specific initial concentration of adsorbate. To adsorb BPA from the solution, more adsorption sites were available as the adsorbent surface area increased with increasing adsorbent mass [25]. In order to extract BPA molecules from the working samples and achieve a good recovery, different mass adsorbents were used, ranging from 60 to 80 mg. As the amount of adsorbent was increased, the findings showed that the signal value slightly increased. The higher amount of adsorbent offered more adsorption sites for analytes to be adsorbed on the surface alg/Cs-NH_2-SiO_2/Fe_3O_4. Hence, 80 mg was chosen as the higher adsorption capacity towards analytes, as shown in Figure 2b.

.3.2.3 Effect of Extraction Time

In this study, equilibrium was achieved largely throughout the extraction process as a result of the extraction time. The effect time was optimized in this experiment by increasing vortex time, which was from 30 s, 1 min to 2 min (Figure 2c). The outcome showed that the signal produces stronger signals for BPA analytes at an extraction time of 30 s. The sudden decrement in signal that occurs with increasing time (1 and 2 min) happened. This was caused by the back-extraction of analytes from the adsorbent into the sample solution. This could occur because of hydrophobic interactions, where transient intermolecular tensions and reversible reactions occur. As a result, the 30 s was determined to be the optimal extraction period and was used in subsequent research.

3.2.4 Effect of Desorption solvents

Desorption of BPA from alg/Cs-NH_2-SiO_2/Fe_3O_4 adsorbent following extraction was investigated using three different organic solvents of varied polarity (MeOH, EtOH, and ACN (Figure 2d) to determine the best desorption solvents. The solvent ACN produced the maximum desorption efficiency. The polarity of the target analyte and the desorption solvent could be used to explain this. A relatively polar substance is BPA. Since ACN was more polar than MeOH and EtOH, it was shown to be the most effective method for removing BPA from the alg/Cs-NH_2-SiO_2/Fe_3O_4 adsorbent. ACN was typically considered more polar than MeOH and EtOH in terms of polarity. The carbon-nitrogen triple bond (C≡N), which results in a greater electronegativity differential between the carbon and nitrogen atoms, gives ACN its higher polarity. Although ACN and MeOH include polar hydroxyl groups (OH^-), ACN has a larger dipole moment due to the carbon-nitrogen triple bond.

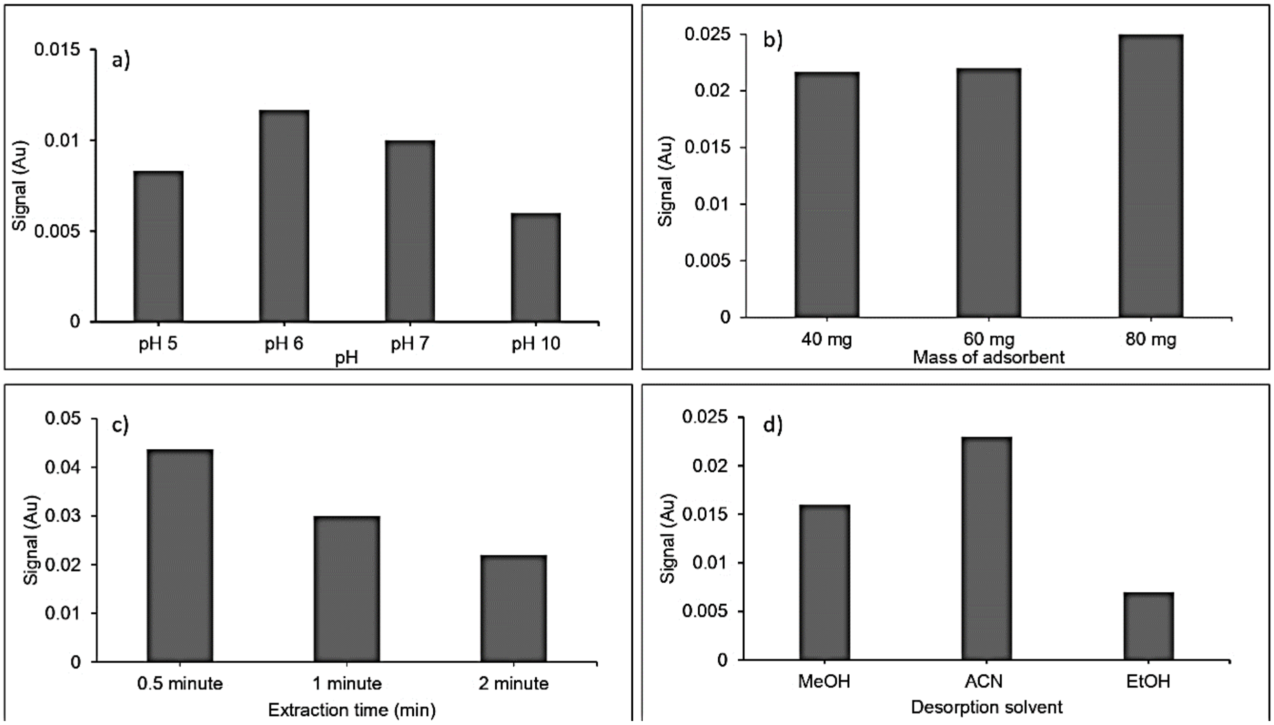

Figure 2 (a-d) Bar chart of M-µ-SPE optimization results for a) different pH, optimal condition: adsorbent amount: 60 mg, extraction time: 1 min, desorption solvent 500 µL methanol, b) various mass of adsorbent, optimal condition: sample pH 6, 1 min extraction time, 500 µL methanol as desorption solvent, c) various extraction time, optimal condition: sample pH 6, 80 mg mass of absorbent, 500 µL methanol as desorption solvent and d) different desorption solvent, optimal condition: sample pH 6, 30s extraction time, 80 mg mass of absorbent Concentration of spiked; BPA = 3.00 mg/L. M-µ-SPE parameters optimized were based on one variable at a time (OVAT).

3.3 Validation of M-µ-SPE Method

The magnetite adsorbent M-μ-SPE method for the BPA analyte was validated after all the optimum parameters were obtained. The optimum M-μ-SPE protocol was applied to solid food samples in cans where the solid samples were prepared to be small size and clean before the method was applied. The validation parameters such as linearity, LOD, LOQ, precision, and extraction recovery were assessed under the optimized conditions, sample solution of pH 6, 80 mg of adsorbent, 30s of extraction time, and 500 μL of ACN as the desorption solvent, to confirm the capability of the method applied to real food sample. The linearity of the developed method was checked by constructing the calibration curves at concentration levels in the range of 0.5 to 10 mg/L. Construction of method calibration curves for BPA involved plotting the signal against the concentration of the spiked standard in MeOH within the showed concentration range. Linear regression analysis was used to determine the coefficient of determination (R^2), slope, and intercept. The correlation found was linear for the analyte studied over the concentration range with R^2 = 0.9982 which was near 1. The lowest concentration or amount of an analyte that can be accurately identified and quantified using this M-μ-SPE method is referred to as the LOD and LOQ, respectively. To ensure the analytical methodology is appropriate for the intended purpose, such as identifying trace levels of contaminants or quantifying analytes in low-concentration samples, defined LOD and LOQ values were significant in developing and validating the M-μ-SPE method. Equation (3.1) was used to calculate the LOD:

$$LOD = 3.3\left(\frac{S}{N}\right)$$

where S is the standard deviation of the response of the curve, and m is the slope of the calibration curve. Equation (3.2) was used to compute the LOQ:

$$LOQ = 10\left(\frac{S}{N}\right)$$

where S is the standard deviation of the response of the curve, and m is the slope of the calibration curve.

The LOD was found to be 1.11 mg/L, whereas the LOQ for the BPA analyte was 3.3 mg/L. Repeatability refers to precision as used standard deviation expression for determining the mean value of percentage (% RSD). Three replications of each concentration range (with intra-day precision) were performed. An analysis of standard solution at a certain concentration within a day (n = 3) is used to determine the intra-day precision, which is a study of repeatability. As a result, the relative standard deviation, which at some concentrations provides values of 8.6 %, indicated high precision. By examining spiked blank matrices, accuracy was examined and provided as a percent relative recovery. The percent relative recovery was expressed by contrasting the measured concentration as determined by the calibration lines with the spiked concentration. The findings indicated that the range of 87.5–106.8 % represented the percentage recovery and % RSD < 8.7 for BPA spiked at a concentration of 0.5–10 mg/L.

3.4 Application M-μ-SPE to Canned Food Samples

The study found no detectable levels of BPA in the canned food samples under investigation. However, additional experiments were conducted to further evaluate the method's applicability and ascertain the recovery rates of analytes. The canned food samples were spiked with a standard concentration of BPA (3 mg/L) and subjected to the M-μ-SPE method. The results demonstrated promising outcomes, particularly in terms of analyte recovery. The sardine sample exhibited a recovery of 85%, while the lychee sample showed a higher recovery of 93%. Moreover, both samples demonstrated low RSD %, with values below 9%. This indicates good precision and reproducibility of the developed method across different types of canned food.

4.0 CONCLUSION

The new extraction, which was the combination between M-μ-SPE with the alg/Cs-NH_2 SiO_2/Fe_3O_4 coupled to an ultraviolet-visible (UV-Vis) spectrophotometry equipment has been developed as a new technique for analyzing BPA in food container samples. M-μ-SPE method provides simple and rapid analysis time (30s for extraction), minute organic solvent consumption, and reduced cost analysis. Under optimal condition parameters, sample solution at pH 6, 30s extraction time, ACN acted as desorption solvent and 80 mg amount of adsorbent was chosen as the higher absorption efficiency between analyte and adsorbent. Optimizing the extraction parameters for the quantitative assessment of the BPA in canned food samples demonstrated good LOD (1.1 mg/L) and LOQ (3.3 mg/L) extraction efficiency. All the parameters' validation results demonstrated good linearity (0.5–10 mg/L), precision (% RSD < 9), and accuracy (average relative recovery ranged from 87–110 %). The canned food samples with applied 3 mg/L of BPA analyte had a good recovery of about 85 %, while lychee gave a recovery of 93 % for the second sample. Both give RSD % < 9, which was good. Hence, according to the results, due to its simplicity, speed, environmental friendliness, and minimal equipment needs, this methodology qualifies as the most straightforward and suitable sample preparation method for both off-site and on-site testing of BPA in food.

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