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Fabrication of method with nano-plates by dispersive solid-phase extraction of anionic dye from aqueous solution Eriochrome Black T (EBT)

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ABSTRACT: A UV-Vis spectrophotometric method for the determination of eriochrome black T (EBT) after adsorption of synthesis 2-aminopyridine/graphene oxide nano-plates has been developed. The nanocomposite was used to remove eriochrome black T (EBT) from the aqueous solution. The effects of pH, adsorption time, initial concentration of EBT, dose, and temperatures were studied. Applying a facile and accessible sample preparation method is highly important before the experimental analysis process. In the current study, a technique was introduced for preconcentration and analysis of trace amounts of EBT in water samples. The important parameters in the analytical procedure of EBT were optimized such as the pH of extraction, amount and type of elution solvent, time of extraction, and the effect of another ion. Analytical parameters such as the concentration factor, the limit of detection (LOD) of the technique, and relative standard deviation (RSD %) were achieved as 25, 15.0 μg L-1, and 2.7%, respectively.

Keywords: *Eriochrome black T (EBT), Graphene oxide nano-plates, Preconcentration of heavy metals, SPE.*

INTRODUCTION

The properties of nanomagneticparticlesresearch on their functionality as magnetic carrier [1, 2], alsoinmedicalimagingusessuchas magnetic resonanceimaging (MRI) It commonly, generated from industrial processes including electroplating, smelting, battery manufacturing, mining, metallurgy, and refining [2, 3]. Eriochrome Black T (Fig. 1) is an acidic anionic azo dye that is often and consistently used in textiles, laboratory studies, and other commercial products. In humans, the eyes, skin, mucous membranes, and respiratory organs will be affected as a result of extended contact with EBT. Therefore, it is necessary to remove the dye from the water. The usual methods for removing dyes from wastewater include: coagulation and flocculation [4, 5], oxidation [6], ozonation [7, 8] catalysis and photocatalysis [9, 10], membrane separation [11], and adsorption [12, 13]. Among these methods, adsorption is one of the methods that have been successfully applied to remove dyes from aqueous solution due to its effectiveness, simplicity, low cost, and feasibility in large-scale applications [14–17]. In recent years a new kind of SPE, magnetic solid-phase

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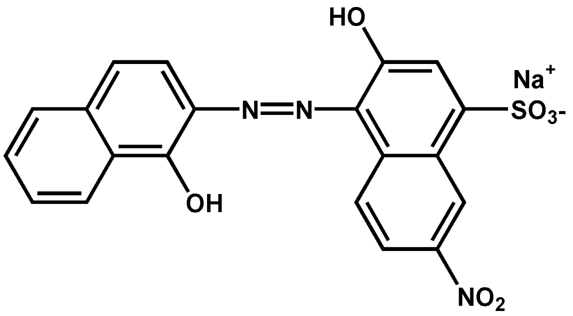

Fig. 1. Structure of Eriochrome black T (EBT).

extraction (MSPE), has attracted so much attention. The MSPE is based on magnetic materials as sorbent, which can be isolated from the matrix quickly by using a magnet. Compared with other isolation methods, MSPE can improve the extraction efficiency and simplify the process of preprocessing. In recent year, the application of nanomaterial's such as activated carbon [11], Different methods, co-extractant ligands has attracted considerable attention [15,16]. However, the use of classical extraction methods for this purpose is usually for the extraction and separation of EBT have been suggested including liquid chromatography [17] supercritical fluid extraction [18, 19], flotation [20], aggregate film formation [21], liquid membrane [22-34]. This is a multi-stage synthesis technique that includes the synthesis of Fe_3O_4 individually. Furthermore, no research has been done on the use of CM to remove EBT dyes from water.

Consequently, in the current investigation, the researchers focused on the first application of 2- aminopyridine/graphene oxide nano-plates as a novel adsorbent for dispersive solid-phase and extraction of eriochrome black T (EBT) wastewater samples before the UV-Vis spectrometry. The EBT removal feasibility of the materials was investigated. The batch method was used to investigate the effects of some major factors such as pH, adsorption time, initial EBT concentration, adsorbent dosage, and exteraction of EBT from aqueous solution.

EXPERIMENTAL

Instrumentation

The determination of eriochrome black T (EBT) by Varian UV-Vis spectrometer is equipped with D2 which was done according to the recommendations of the manufacturers. Accordingly, the pH measurements were used by Sartorius model PB-11.

Materials

In the current investigation, the following materials have been applied for the experiments; graphene oxide nano-plates, eriochrome black T (EBT), thio-

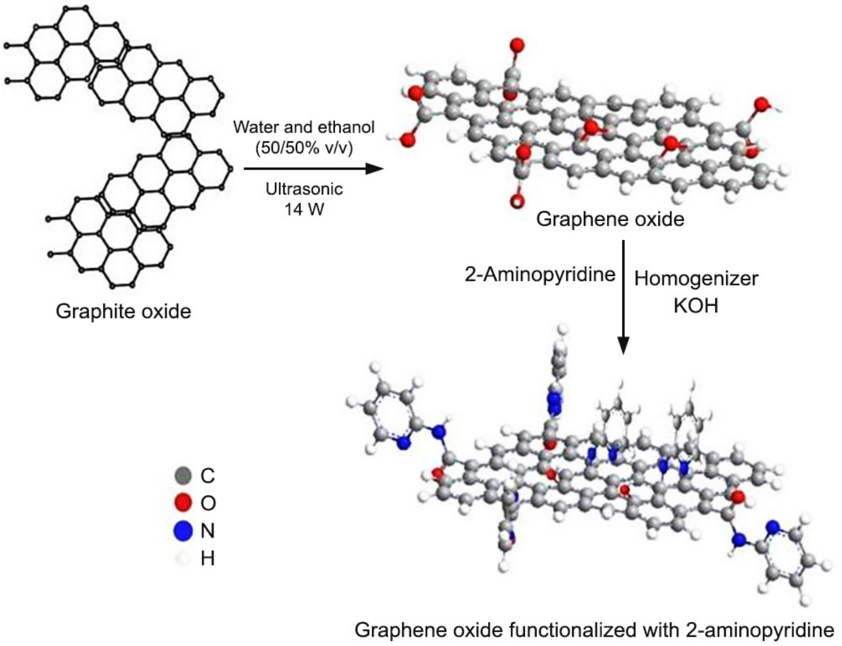

Fig. 2. Preparation of graphene oxide functionalized with 2-aminopyridine.

semi-carbazide ligand, buffer, and nitric acid. Additionally, ethylenediamine, thio-semi-carbazide ligand (CH_5N_3S) was prepared from Darmstadt, Germany of Merck.

Synthesis GrO

To prepare GrO, a certain amount of graphite oxide powder (0.1 g) was placed in 100 mL of water and ethanol solution (50/50%, v/v) under ultrasonic power of 140 W for 2 h. The resulted powder was dried in a vacuum desiccator [31].

GrO functionalized with 2-aminopyridine

The 0.1 g of GrO powder was poured in 200 mL of deionized water, then 0.2 g of 2 Ap was poured and the mixture was placed in a homogenizer for 30 min at 13000 rpm. Then, the 0.2 g KOH was added to the homogeneous mixture and was subjected to ultrasonic power of 140 W for 30 min. The precipitate was refluxed at 80°C and then washed with water and ethanol and dried at 25°C (Fig. 2) [32].

The initial experiment of eriochrome black T (EBT) extraction for determining the suitable adsorbent The procedure for extraction and recovery of eriochrome black T (EBT) by 2-aminopyridine/graphene oxide nano-plates is as follows; in the first step, 0.2 g of thiosemicarbazone ligand and 0.3 g of 2-aminopyridine/graphene oxide nano-plates and were dissolved in the little amount of acetone, and then it dried. Four 50 mL ballons were adopted, and then 0.05 g of 2-aminopyridine/graphene oxide nano-plates was poured into one of the balloons. Thereupon, a 1 ml buffer solution with a pH of 6.5 was added to balloons and a 2 ppm solution was prepared with an analyte. Four solutions were shaken at 25°C for 20 min, then these solutions for 20 min were centrifuged and the supernatant injected into an atomic absorption apparatus.

The effect of adsorbent amount for eriochrome black T (EBT) extraction

Seven 2.0 ppm solutions with 50 mL of eriochrome black T (EBT) were provided and poured into seven flasks. Seven solutions were adjusted at pH= 6.5 (optimum pH) and different amounts of the adsorbent (0.005, 0.01, 0.03, 0.05, 0.07, 0.12, and 0.15) added to flasks. The mixtures were shaken for 20 min, and then the mixtures were centrifuged and the top solution of the examine tube injected in UV-Vis spectrophotometry.

Application on real samples

Once the extraction method was performed by the adsorbent, optimal conditions were achieved for it, and Multiple real aqueous samples were investigated. The real samples were as follows; well and drinking water in Pishva Town were collected with temperatures of 20 and 22°C, pH= 7.1, 7.3 in 23.8.95 at 9:45, 10:00, respectively. Finally, a fish farming sample was collected at, pH= 6.5. First, these suitable bottles were provided for the sampling of samples. The bottles were washed first with ordinary and distilled water. The bottles dried completely, and the ‘suitable’ label was attached to each bottle. To collecting of water samples, the used containers sample dried and cleaned and they had already been washed. For the analysis of the samples in the first stage, colloidal and suspended particles were removed. To this aim, the water samples passed through 0.22 µm filters. Next, the volume of 100 mL of samples was poured into the sample container. The pH of samples was adjusted at 10 and then, graphene oxide nano-plates and ligand were added to samples. They stirred for 20 min and the mixture was then centrifuged. Then, they were washed with HNO_3 0.1 M and were shaken again for 20 min. Finally, following the centrifugation of the mixture, absorption of eriochrome black T (EBT) was identified from the filtered solution by UV-Vis spectrophotometry. In the first step, the sample itself was injected into the apparatus without any eriochrome black T (EBT), wherein water samples, the device displayed no absorption. To identify certain amounts of EBT of the samples, the method of standard elevation was used. This stage was accomplished like the first step, the only discrepancy was that 0.5 mL of 200 ppm solution with eriochrome black T (EBT) added to the water samples. Finally, the absorption of EBT was identified from the filtered solution by UV-Vis spectrophotometry.

RESULT AND DISCUSSION

This section deals with the results of the research experiments. The results achieved in the experimental chapter, calibration curve, and the factors influencing the extraction (e.g. pH, temperature effect, time, etc.) of EBT by the 2-aminopyridine/graphene oxide nano-plates are discussed which are followed in the presentation of scientific justification and overall conclusion of the study.

Assessment of results of FT-IR spectrum of GrO and Gr2Ap

We synthesized Gr2Ap with the process of grafting of 2Ap on GrO. The recognition of the 2Ap group on the GrO surface via reaction of amination was demonstrated with the FT-IR test (Fig. 3c). Also seen, the spectrum of the GrO (Fig. 3a) shows two absorption bands in 1055 and 1401 cm^{-1} related to the C-O stretch bond from the carboxylic acid. Also, the band of tensile vibration bond of C–O–C was seen in the area of 1207 cm^{-1}. Moreover, a vibration band in 1629 cm^{-1} relating to the C=C bond belonging to unoxidized carbons. Finally, the strong band in 3443 cm^{-1} belongs to the O–H vibration [31]. In the FT-IR spectrum of 2Ap (Fig. 3b), the absorption band in 1630 cm^{-1} indexed to the C=N bond of the pyridine ring. The peak of 1558 cm^{-1} corresponds to the C=C of the aromatic ring. The peak of 1273 cm^{-1} ascribed to the C-N bond in the ring and also the peak of 3444 cm^{-1} related to N-H tensile vibrations [31]. Fig. 3c displays FT-IR spectra of Gr2Ap, this sample has an absorption band in 3448 cm^{-1} which originated from the group of OH from GrO. Two peaks at 2858 and 2923 cm^{-1} indicate asymmetric and symmetric vibrations of the CH2 group [35]. The weak peak in 1162 cm^{-1} is related to the grafting of the amine group to GrO. Also, the peak intensity of the C-O at 1074 cm^{-1} decreased compared to the spectra of GrO. The peak in 1629 cm^{-1} is related to the C=N bond of the pyridine ring on the GrO surface. The band of 1207 cm^{-1} indexed to the bond of C-N in the ring of pyridine on GrO. The results obtained from the FT-IR analysis confirm the functionalization of GrO.

Fig. 4 represents X-ray diffraction patterns of synthesized GrO and Gr2Ap. Regarding the results, GrO shows a drastic peak at 2θ= 11.6° demonstrating severe oxidation of graphite sheets and crystalline structure of GrO nano-plates (Fig. 4a) [35, 36]. After functionalization with 2Ap, a new broad peak has appeared at 2θ ranging from 23 to 37, and also was decreased the intensity of the main peak (Fig. 4b). These results are respectively related to the disordering of the regularity of GrO nanoplates due to the incorporation of 2Ap groups between them as well as concurrent reduction of its oxygenated groups.

The morphology of GrO and Gr2Ap and the surface changes after functionalization was surveyed with SEM images. Fig. 5a is related to synthesized GrO through the improved Staudenmaier procedure. As is evident, the synthesized GrO has a finite number of layered structures with a flat surface. Fig. 5b1 implies that the GrO nano-plates retain their structure of layered while functionalizing process, but the structural regularity of the layers has been consider-

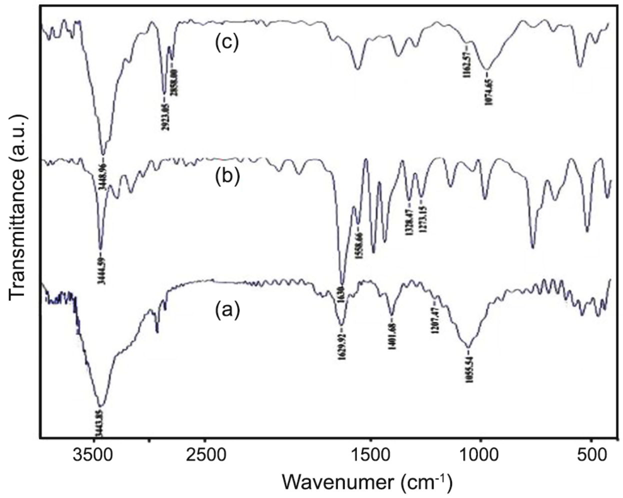

Fig. 3. FTIR spectra of GrO (a), 2Ap (b), and Gr2Ap (c).

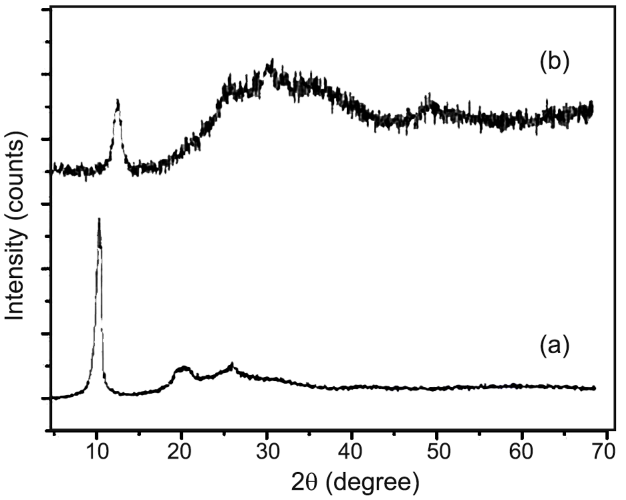

Fig. 4. XRD patterns of GrO (a) and Gr2Ap (b).

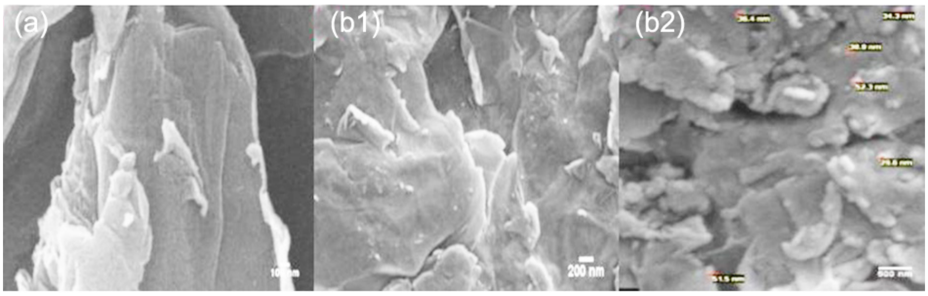

Fig. 5. SEM images of (a) GrO and (b1-2) Gr2Ap.

ably decreased. Moreover, the 2Ap functional group is seen as spherical shapes on the GrO surface in sizes of 29-53 nm (Fig. 5b2). The width of GrO pores was distributed in the range of 2-10 nm according to the synthesis method in the reference, which can be classified as mesoporous.

Investigation of the influential factors on EBT extraction

Study the effect of pH on EBT extraction

The results of this study As the results indicate, at pH= 6.5, EBT adsorption was maximized, while at lowest and highest pHs, the extent of adsorption declines, inferring that at pH<6 adsorptions of EBT cannot occur completely. As revealed, to determine the amount of 2-aminopyridine/graphene oxide nano-plates required for effective removal of EBT, different amounts of the 2-aminopyridine/graphene oxide nano-plates (50 mg) for modification of 2-aminopyridine/graphene oxide nano-plates with fixes amount (3 mg) and its effect for the removal of EBT from 20 mL solutions of EBT (50 µg/L) were investigated.

Investigation of the effect of time on EBT extraction

Based on the results, the extent of absorption increases, and the EBT present in the solution find more chance to be adsorbed in the adsorbent’s sites. Therefore, the quantitative extraction of EBT is possible for a period of longer than 20 min, and within durations longer than 20 min and more, the reaction happens completely.

Survey of the effect of type of various desorption solvent for recovery of EBT

Based on the results (Table 1), NaOH cannot be used as appropriate desorption and these bases do not possess a complete detergence power. Therefore, mineral acids with determined concentrations, H_2SO_4, and HNO_3 were applied. As shown in Table 1, the results of this table offer that all acids contain a good detergence power for EBT, but the recovery percentage of HNO_3 is higher than that of other acids. In an acidic environment, the possible deposits dissolved and recovery of these ions increased. However, the results obtained from nitric acid were better than H_2SO_4, in

Table 1. Selection of the appropriate desorption for recovery of EBT

Solvent	Recovery (%)
HNO_3 0.1M	90.80(2.5) [a]
HNO_3 0.01M	92.52(2.6)
HNO_3 0.03M	79.55(2.7)
H_2SO_4 0.1M	71.64(2.7)
H_2SO_4 0.03M	60.70(2.8)
NaOH .0.01 M	56.46(2.9)

a) measurement RSD after three replications

Table 2. The optimum volume of the desorption solvent.

Solvent volume (mL)	Recovery (%)
5	50.20(2.5) [a]
6	69.67(2.2)
7	79.96(2.4)
10	98.75(2.2)
14	89.15(2.2)
16	89.96(2.0)
20	89.99(2.5)

a) Measurement RSD following three replications that 0.01 M of solution washed 92.52% of the EBT adsorbent. So, for the rest of the experiments, nitric acid 0.10 M was used as the desorption solution.

Survey of optimization of the volume effect of desorption solvent for EBT recovery

After the investigation and choice of optimal desorption, the volume of solvent was investigated, with the results which are shown in Table 2. The volume of 12 mL for HNO_3 was selected as the optimal volume for washing.

Investigation the effect of breakthrough volume

Following the optimization of the pH of the desorption solvent and sample solution, etc., to elute the EBT in the adsorbents, the maximum volume of the aqueous solution containing EBT should be measured. If the volume of the test solution to be less than the breakthrough volume, and passaging of that volume, all analytes are kept in the solid phase. The results in (Table 3) verify that up to 250 mL of ions are adsorbed by the nano adsorbents and if the sample volume is greater than this value, some of the EBT is not kept on the adsorbent and pass over the adsorbent with no inhibition. Also with definition by the concept of breakthrough volume, it can be reported that the breakthrough volume in the current study is 250 mL and if the sample solution volumes which includes EBT is over 250 mL, adsorption does not occur completely and hence if 250 mL of sample volume is passed over the adsorbent and then with 12 ml of the desorption solvent washed, the concentration factor could not be achieved as 30. This concept that the concentration of EBT in 7 mL of desorption solvent which was passed over the adsorbent grows by 20 times. Based on the related results (Table 3), the breakthrough volume calculations are as follows:

Concentration factor = breakthrough volume/the desorption solvent volume=250/10=25

Table 3. Investigations of the effect of solution volume in the sample

V (mL)	Recovery (%)
50	89.7(2.3) [a]
100	85.2(2.3)
150	84.5(2.7)
250	81.0(2.6)
350	71.4(2.7)
500	30.9(2.6)

a) Measurement RSD following three replications

Determination of the blank standard deviation (S_b)

The accuracy or replicability of any method is the main factor to recognize its validity and reliability. To inquire about the method's replicability, the results data of the study of four blank solutions (deionized water) deposited in Table 4.

Based on the results achieved in Table 4, the blank standard deviation was obtained as follows; S_b= 0.0005

Determination of the accuracy and RSD% of the method

This parameter was used to investigate the accuracy and proximity of the examined data. As shown in 2.4% standard deviation has been calculated for three tests and the relative standard deviation (RSD) achieved for three replications.

The linear range and a calibration curve of the method

To assess the linear range in the analysis method, a calibration curve should be plotted. This curve is not linear across all concentrations and different factors cause the calibration curve to the situation in the linear range and follow from Beyer Law. the calibration curve of the method is as conform and the line equation is y= 0.012x+0.061 and R2= 0.9998.

Determining the method's limit of detection

The lowest EBT concentration or weight in a sample

Table 4. measurement RSD following three replications

Sample	Device response
1	0.013(4.8) [a]
2	0.014(4.6)
3	0.013(4.6)
4	0.014(4.3)

a) Measurement RSD following three replications

Table 5. Determination of EBT in the real sample

Recovery	R.S.D.% (n =5)	This method (μg.g $^{-1}$)*	Reference method (μg.l $^{-1}$)*	Samples
98.3	2.5	20.3	21.7	Tap water
97.0	2.7	26.07	25. 0	Pure water
98.2	2.6	29.5	28.5	Industrial wastewater *Average of five determinations.

*Average of five determinations.

that could be determined with a certain confidence level is called the limit of detection (LOD), which is defined as follows. The LOD of a method is a concentration of an analysis sample where the device response to concentration (which is significantly different from the response of the control sample) is defined as follows; the limit of detection is the lowest amount of EBT +, where the presented method can detect it. Based on the presented definition, LOD can be calculated by the following relation;

$$\mathrm{LOD} = \frac{3S_b}{m} \tag{1}$$

where S_b and m are the standard deviations of the blank signal and the slope of the calibration curve, respectively. Based on the experimented, S_b= 0.0011 and the slope of the calibration curve is 0.0002. Therefore, LOD can be calculated at 15.0 ppb.

Investigation of the obtained results on real sample

The proposed method has been successfully applied to the determination of EBT in three real drinking water samples (tap water of tehran, pure water and industrial wastewater sample of Charmshar Varamin. The results were shown in Table 5, together with results of a recovery test by added known amounts of silver in water sample. The results of this analysis are shown in Table 5, the level of EBT was measured across different water and biological samples at 250 mL. As can be seen, in the water samples, in the Tap water sample of Tehran, on 10 oct 2022, and industrial wastewater sample of Charmshar Varamin on 10 oct 2022, there is a larger amount of EBT than in the experimented water samples. Although, in other samples, there is less EBT. Based on this, the performance and power of preconcentration and EBT measurement could be deduced.

A comparison between the current method and other methods

A comparison of this method with other methods verified that the current method is more accurate, easiest, and faster as it had smaller relative standard deviation values in comparison with other methods [36-47]. The current method is one of the foremost systems for determining the very trace amounts of heavy metal ions including EBT in aqueous samples. Another point in the usage of graphene oxide nano-plates adsorbent is that instead of using the proposed ligand, one can put other ligands on the adsorbent which to adsorb mineral ions, thereby measuring trace amounts of metal ions. A wide variety of ligands can be used given their properties, which act selective towards one or several ions and applying this set, preconcentration, and determination of cations can be carried out. Using UV-Vis and solid drop microextraction, single-drop liquid-liquid extraction, and homogeneous liquid-liquid extraction with other devices, one can determine trace amounts of EBT by this adsorbent and achieve a smaller limit of detection value.

CONCLUSIONS

In comparison with other procedures reported for measurement of EBT, this method has considerable advantages that are easy and inexpensive and can be applied quickly for environmental aqueous samples. Furthermore, it minimizes the utilization of organic, toxic, and costly solvents. Moreover, the design and development of this procedure for separation, measurement, and preconcentration of EBT are essential considering its importance in various industries and the little concentration of EBT in most samples. Therefore, this research aims to present an effective, selective, cost-effective, and simple method for measurement of the level of EBT across different environmental aqueous samples (in this research, the limit of detection, the value of breakthrough volume, and RSD has been obtained). This research indicated that the measurement of EBT occurs at an appropriate level without the interference of any other interfering factor and thus the current method can be applied easily in the measurement of the quantity of EBT in aqueous samples.

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