

RESEARCH ARTICLE

Open Access



# Insights into brewed tea waste as a green and low-priced adsorbent for solid-phase extraction of Cd(II) ions: isotherm, kinetic, and artificial neural network approach

Duygu Ozdes<sup>1</sup>, Nida Tilki<sup>2</sup>, Serdal Seker<sup>3</sup> and Celal Duran<sup>2\*</sup> 

## Abstract

In the present research, brewed tea waste (BTW) was utilized as a green, low-priced, and abundant adsorbent for separation/preconcentration of Cd(II) ions through solid-phase extraction method from water and foods for the first time. BTW was applied as a natural adsorbent, without using any chelating agent to bind Cd(II) ions or any chemical reagent for its modification. A three-layer artificial neural network model using backpropagation algorithm was utilized to explicate a prediction model for the extraction performance of Cd(II) ions by selecting the input parameters as solution pH, quantity of BTW, sample volume, eluent concentration and volume, and equilibrium time for desorption. The preconcentration factor, relative standard deviation, and detection limit were attained as 100, 3.03%, and  $0.56 \mu\text{g L}^{-1}$ , respectively. It was decided that the Langmuir isotherm model is acceptable to characterize the retention of Cd(II) ions on BTW. This result pointed out that the active binding sites on the BTW surface are homogeneously distributed. Adsorption capacity of BTW was achieved as  $41.5 \text{ mg g}^{-1}$  which is higher than several expensive and difficult-to-prepare adsorbents. Adsorption kinetics was elucidated by pseudo-second order kinetic model. After confirmed the accuracy of the method with spike/recovery studies, it was employed for Cd(II) determination in water (stream and sea water) and food (eggplant, lettuce, parsley, apple, and apricot) samples with high accuracy. The inferences of the study proved that the BTW offers a magnificent application prospect in the extraction of Cd(II) ions.

**Keywords:** Artificial neural network, Brewed tea waste, Cadmium, Heavy metal, Solid-phase extraction

## Introduction

With the continuous development in technology that improves people's living standards, industrial activities are accelerated, and in parallel, the necessity to control the environmental pollution is increasing day by day. Industrial wastewaters contain various organic and inorganic pollutants that can contaminate the food chain (Lin et al. 2022). Since heavy metals exist in many products used in daily life and are extensively utilized in numerous

industries including textiles, battery, mining, printing, etc., they are considered as one of the most important factors causing pollution (Amri et al. 2022; Kaur et al. 2020). Heavy metals, which are mostly exposed through eating, drinking, and breathing, are exceedingly poisonous and non-degradable pollutants that threaten human health. In order to maintain the metabolic activities, a number of heavy metals (Fe, Cu, Co, and Zn) at certain concentration levels must be taken into the living metabolism (Kilinc et al. 2022). On the other hand, some heavy metals such as Cd, Hg, and Pb have no benefit for living body and provoke detrimental effects even at trace levels. In addition to the intake of essential elements in the body at higher than tolerable levels, the body's exposure

\*Correspondence: [cduran@ktu.edu.tr](mailto:cduran@ktu.edu.tr)

<sup>2</sup> Faculty of Sciences, Department of Chemistry, Karadeniz Technical University, 61080 Trabzon, Turkey  
Full list of author information is available at the end of the article

to even trace amounts of non-essential heavy metals can cause damage to various organs and even cancer of the cells (Feist and Sitko 2018). Cadmium, among the quite hazardous heavy metals for humans and other living organisms, is a member of group I carcinogens and damages the body's kidney, liver, respiratory, gastrointestinal, and reproductive systems as a result of its accumulation in the organs (Bozyigit et al. 2022). Cd(II) is found in a variety of environmental sources such as water, air, and soil (Ofudje et al. 2020). It is mostly taken into the human body by drinking water and consuming vegetables and fruits grown in soils contaminated with cadmium. Maximum Cd(II) level in drinking water is allowed as  $3.0 \mu\text{g L}^{-1}$  by World Health Organization (Sahebi et al. 2022), and for vegetables its tolerable level is reported as  $0.05 \text{ mg kg}^{-1}$  wet weight (Altunay and Elik 2021). Thus, it is extremely substantial to ascertain Cd(II) and other heavy metal ions in typically consumed food and waters with accurate, credible, and sensitive methodologies.

Flame atomic absorption spectrometry (FAAS) is a low-priced and sensitive alternative that is commonly preferred for the quantitation of heavy metal ions' level (Roushani et al. 2017). Nevertheless, a separation and preconcentration method is generally indispensable before the analysis due to the existence of analyte ions at too low concentration levels to be precisely determined by modern instrumental methods and the complicated matrices that cause interferences during the analysis (Shahryari et al. 2022). Solid-phase extraction (SPE) method in which the analyte ions are extracted from the aqueous solution onto a solid adsorbent has a promising potential exhibiting a practical, facile, cost-effective, and reliable sample pretreatment process (Nguyen et al. 2022; Kocaoba 2022).

The environmentally friendly SPE method, which consumes less organic solvents, has great advantages over many other sample pretreatment techniques (Hashami et al. 2022). For efficient separation/preconcentration of analyte ions, it is indispensable to utilize a proper adsorbent that is low cost, selective, and exhibits a high adsorption capacity and a large specific surface area. Until now, both natural and modified materials have been used as adsorbent in the SPE method by different researchers. Özkalkan and Canlidinç used *Juglans regia* L. shells as an influential alternative to detect Cd(II) ions in a certified reference material (Özkalkan and Canlidinç 2021). Khodarahmi et al. (2018) assessed the usability of *Descurainia Sophia* seeds as a cheap and green adsorbent for analyzing Cd(II) levels in rice flour and water samples. Uçar et al. (2014) reported the utilization of an agricultural waste, natural sorghum, for the extraction of different metal ions in water and tea samples. Baki et al. (2013) evaluated the application of NaOH treated sawdust to

separate and preconcentrate the Cd(II), Co(II), and Pb(II) ions in fish, liver, lettuce, and water samples.

The present research aims to offer a new, environmentally friendly, and economical alternative for separation/preconcentration of Cd(II) ions by employing brewed tea waste (BTW) based SPE technique in fruit, vegetable, and waters. In previous researches, spent tea leaves were utilized for SPE of polycyclic aromatic hydrocarbons from water and foods before GC-FID detection (Nazir et al. 2020) and tea wastes were applied as an adsorbent for the extraction of Co(II) and Mn(II) ions from water samples (Khajeh et al. 2017). However, according to our literature survey, BTW was utilized for the first time for SPE of Cd(II) ions in the present study. Unlike other common adsorbents, the BTW was used directly without any chemical modification. Thus, there is no need to use expensive and toxic chemical reagents or organic solvents. In addition, BTW, which is an important domestic waste that emerges as millions of tons and is only thrown away, was also recycled with an important environmental application.

Artificial neural networks (ANNs), which are likened to the biological nervous system, have been employed as an extremely powerful alternative in modeling different processes in recent years (Khajeh et al. 2015; Taoufik et al. 2021). The present investigation describes a three-layer artificial neural network (ANN) model using backpropagation (BP) algorithm by a tangent sigmoid transfer function at hidden layer and a linear transfer function at output layer for modeling and estimating the Cd(II) extraction efficiency by BTW. The independent factors including solution pH, BTW amount, eluent concentration and volume, sample volume, and equilibrium time for desorption were preferred as input parameters, and a dependent variable, extraction percentage, was selected as the output layer. Experimental parameters on Cd(II) ions' extraction efficiency were assessed and the optimum conditions were determined. Eventually, the method was employed to analyze the Cd(II) ions in water (stream and sea water) and food samples (eggplant, lettuce, parsley, apple, and apricot).

## Materials and methods

### Reagents and instrumentation

Stock solution of Cd(II) ions at  $1000 \text{ mg L}^{-1}$  concentration was supplied from Merck (Darmstadt, Germany). It was diluted with distilled/deionized water to prepare the calibration standards and the solutions at required concentrations. All other chemical reagents used during the experimental studies are of analytical grade obtained from Sigma-Aldrich (Shanghai, China) and Merck.

Fourier transform infrared spectrometer (Perkin Elmer 1600 Series) was implemented to elucidate the functional

groups on BTW surface that may be responsible for Cd(II) adsorption. The morphological structure and element composition of BTW were interpreted by scanning electron microscope (ZIESS Evo Ls 10) equipped with energy-dispersive X-Ray spectrometry. Cd(II) ions determination was accomplished with PerkinElmer AAnalyst 400 model Flame Atomic Absorption Spectrometer with the aid of deuterium background system and air/acetylene burner at the wavelength of 228.80 nm. For pH adjustment/measurement, a Hanna pH-211 digital pH meter with glass electrode was utilized. BOECO S-8 model centrifuge device was applied for separation of the adsorbent from the aqueous solution. Mechanical shaker (Edmund Bühler GmbH) was performed for both batch adsorption and desorption experiments. Digestion of fruit and vegetable samples was achieved by a microwave device (Milestone Ethos D).

#### Preparation of adsorbent

Brewed tea waste (BTW), which is present in a large amount all around the world as a household waste, was employed as a costless adsorbent for the extraction of a hazardous heavy metal in some food and waters. Moreover, BTW was used naturally without any chemical pretreatment or modification. The BTW was collected, and washing of it was continued using distilled water until the filtrate becomes clear. Then, it was dried at 90 °C for 24 h using an oven. Prior to SPE experiments, the BTW was ground using a blender, and particles smaller than 0.20 mm were used as adsorbent.

#### Model solutions

It is obvious that the Cd(II) ions' extraction performance depends on several essential variables including solution pH, BTW amount, equilibrium time for both adsorption and desorption, type and concentration of desorption solution, and sample volume. Adsorption technique was implemented in a batch system to reveal the influence of these parameters upon the quantitative recovery of Cd(II) ions. The optimization of the developed separation/preconcentration procedure was performed by model solutions as follows: 15 mL of aqueous solutions containing 5.0 µg of Cd(II) ions and 5.0 g L<sup>-1</sup> of BTW were placed in polyethylene centrifuge tubes. The solutions' pH values were arranged to 7.0 using dilute HNO<sub>3</sub> and NaOH solutions. The mixture was agitated for 15 min at 400 rpm in a mechanical shaker, and then, centrifugation was applied for 5 min at 3000 rpm. After the Cd(II) ions adsorbed BTW completely precipitated in the tube, the aqueous phase was discarded by decantation. To desorb the analyte ions, the BTW collected in the tube was treated with 5.0 mL of 0.5 M HNO<sub>3</sub> solution during 15 min. Afterward, the suspension was centrifuged again at 3000 rpm

for 5 min and the level of the analyte ions transferred to the solution was determined by FAAS analysis.

#### Preparation of real samples

The BTW was feathly utilized as an adsorbent for separation/preconcentration of Cd(II) ions by SPE method in waters (sea and stream water), vegetables (eggplant, lettuce, and parsley), and fruits (apple and apricot). The stream waters were collected from Değirmendere (Trabzon, Türkiye) and Harşit (Gümüşhane, Türkiye) while seawater was taken from Blacksea (Trabzon, Türkiye). The cellulose nitrate membrane was used to filter water samples. The pH values of water samples were adjusted to 7.0, and after the BTW was added at required quantity, the developed SPE method was applied to them. The vegetable and fruit samples were procured in a greengrocer. Before the digestion process, they were washed sequentially with tap water and distilled water and kept in an oven at 80 °C until dried. Afterward, they were thoroughly crushed in an agate mortar and kept in a desiccator. The closed vessel microwave system was utilized to digest the solid samples. For this aim, 0.750 g of eggplant, lettuce, parsley, apple, and apricot samples were weighed separately in Teflon vessels and digested with 6.0 mL of HNO<sub>3</sub> and 2.0 mL of H<sub>2</sub>O<sub>2</sub> according to microwave digestion program stated in literature (Bulut et al. 2009). The final volumes of the solutions were completed to 50 mL, and the developed SPE method was applied to these samples.

#### ANN modeling

Artificial neural networks, a biologically inspired simulation, are operated on the computer to execute a particular set of tasks such as clustering, classification, and pattern recognition. It consists of three main layers as input, hidden, and output layers (Yetilmezsoy and Demirel 2008). In the present research, Neural Network Toolbox in MATLAB R2017b mathematical software was utilized for the prediction of Cd(II) ions' recovery efficiency by selecting the solution pH, amount of BTW, eluent volume and concentration, sample volume, and equilibrium time for desorption as input factors and the percentage of extraction as output layer. In accordance with this purpose, three-layer backpropagation (BP) neural network model with a tangent sigmoid transfer function (tansig) at hidden layer and a linear transfer function (purelin) at output layer was employed. In order to decide the best BP algorithm with regression correlation coefficient ( $R^2$ ), various BP algorithms were assessed (Khajeh et al. 2015; Ghadirimoghaddam et al. 2021). It was noticed that Levenberg–Marquardt backpropagation (LMB) algorithm is the best to train the network. The training function updating the weight and bias values according to the

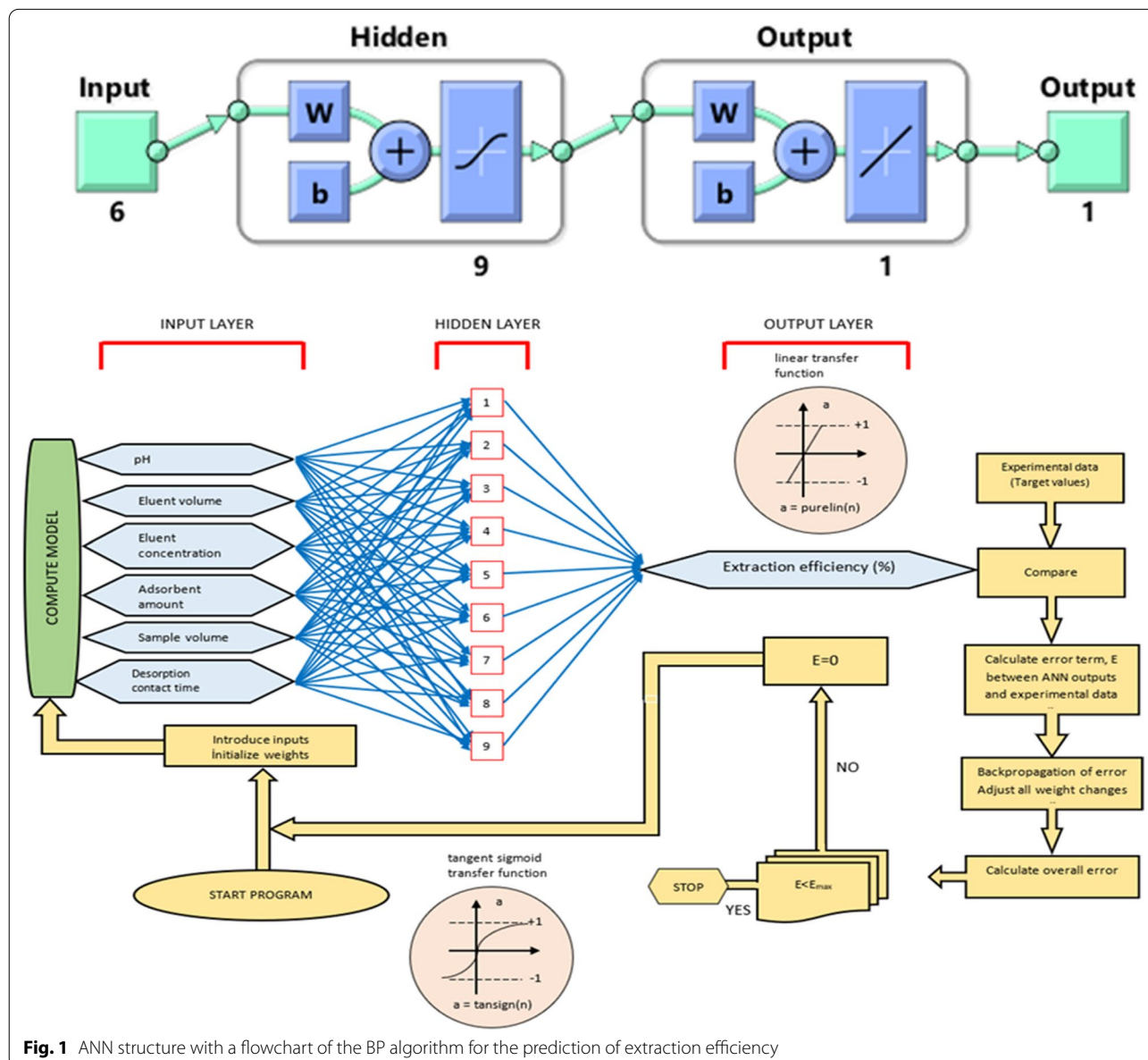
LMB algorithm was utilized to train the network. The network performance was measured by the  $R^2$  used as a function of the error. The optimum architecture of ANN model was constructed as 6-9-1 as given in Fig. 1.

## Results and discussions

### Characterization of BTW

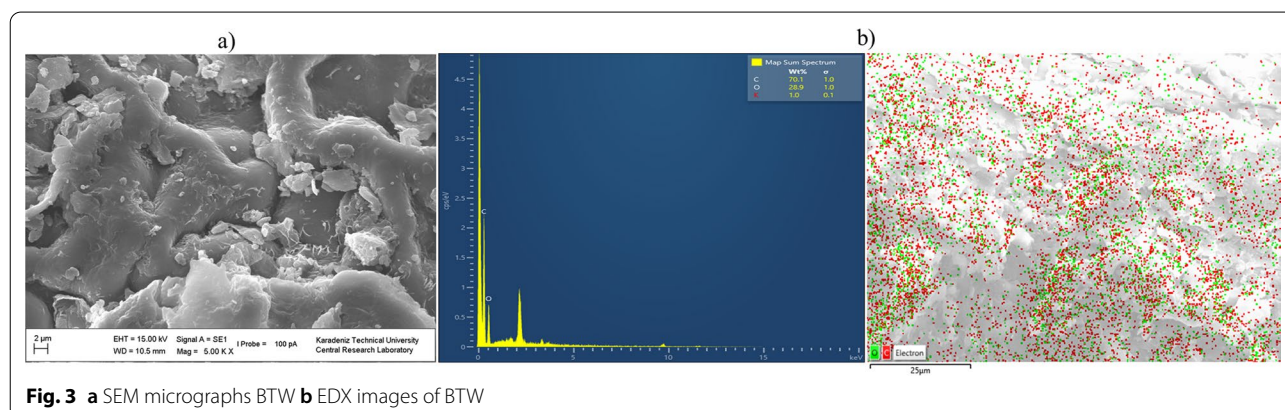
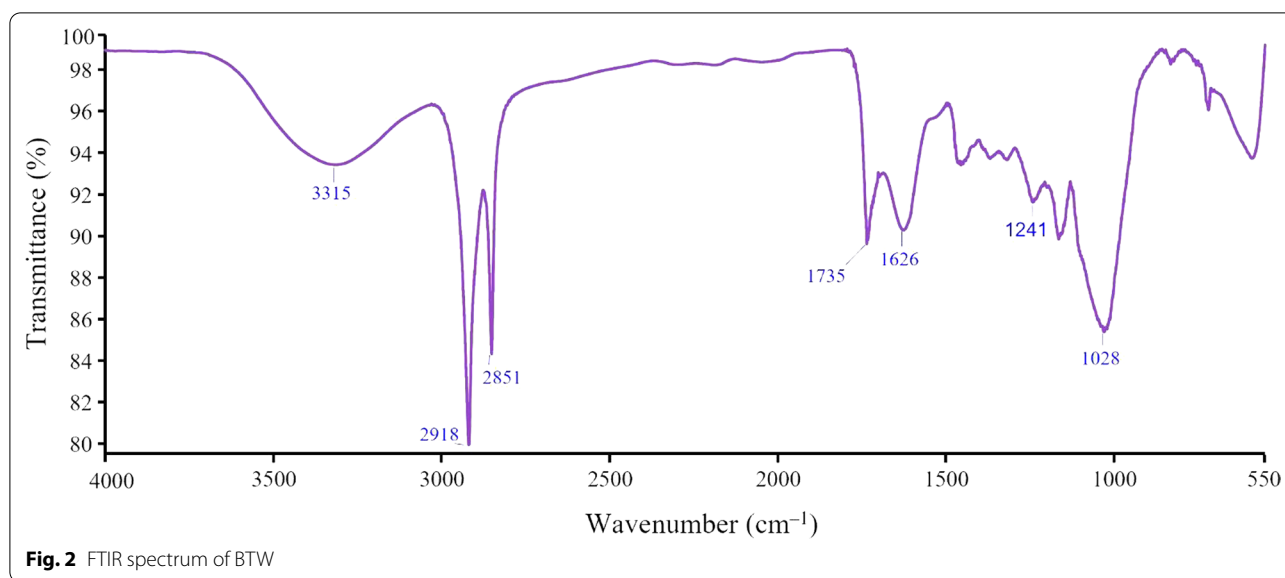
The FTIR spectrum of BTW was obtained between 4000 and 450  $\text{cm}^{-1}$  to identify the surface functional groups (Fig. 2). A band at 3332.1  $\text{cm}^{-1}$  is related to hydroxyl group ( $-\text{OH}$ ) due to the presence of alcoholic, phenolic, and carboxylic groups. The peaks at 2920  $\text{cm}^{-1}$  and 2851.6  $\text{cm}^{-1}$  are attributed to aliphatic

C–H stretching vibrations. The peaks at 1732.2  $\text{cm}^{-1}$  and 1625.1  $\text{cm}^{-1}$  indicate C=O bond of the carboxylic group and C=C stretching vibration, respectively. The C–O stretching vibration of the polysaccharides is observed at 1027.5  $\text{cm}^{-1}$  (Malook and Khan, 2020). The similar characteristics peaks were observed for spent tea leaves by different researchers (Nazir et al. 2020). The surface morphology and elemental composition of BTW were assessed by SEM–EDX analyses. SEM image displayed an irregular and heterogeneous surface structure providing more available adsorption sites for the retention of Cd(II) ions which enhances the extraction efficiency (Fig. 3a). It is worth noting



**Fig. 1** ANN structure with a flowchart of the BP algorithm for the prediction of extraction efficiency





that BTW consists of carbon and oxygen according to EDX spectrum (Fig. 3b).

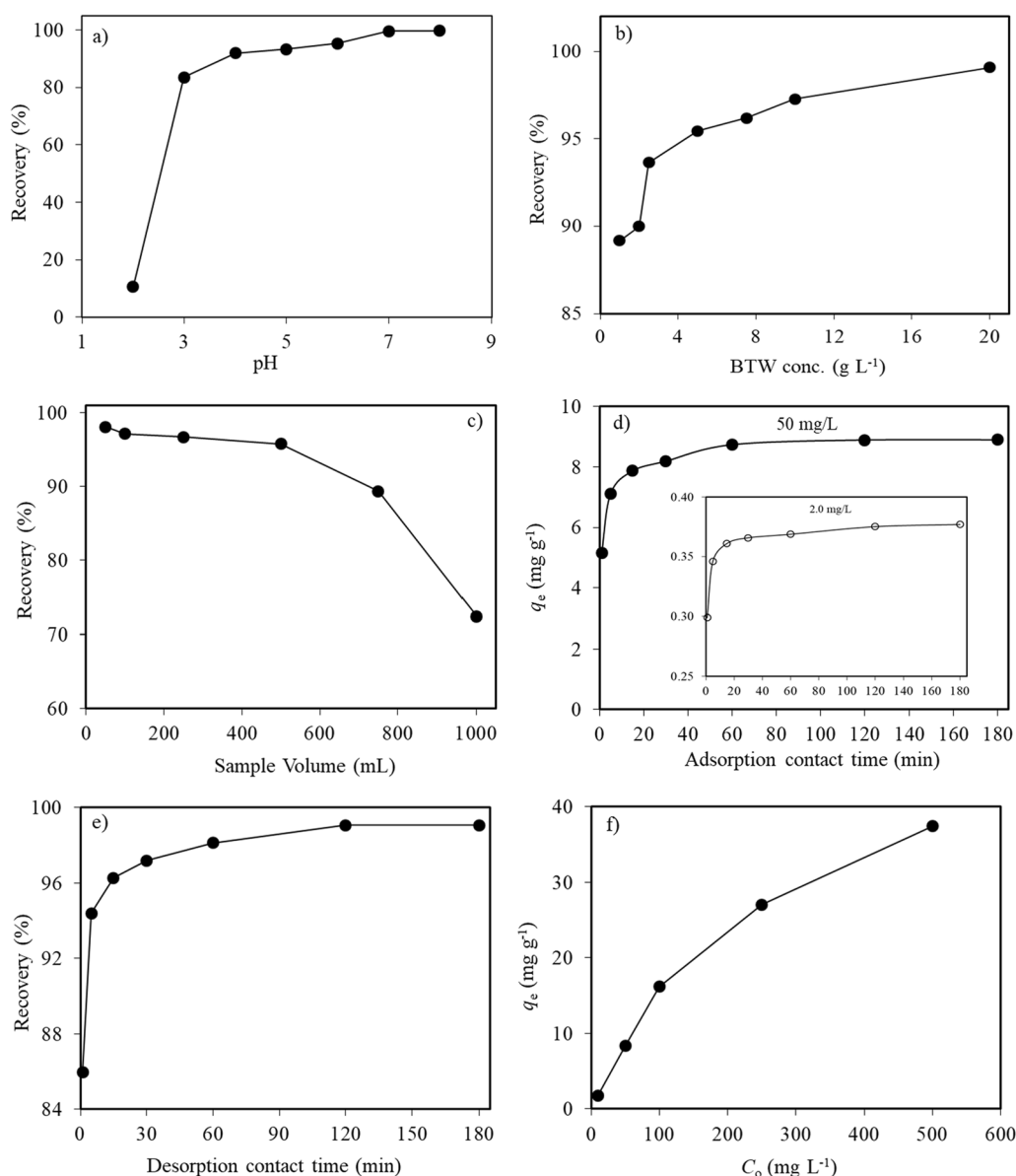
Boehm titration was carried out to quantitatively specify the amount of acidic groups (carboxylic, phenolic, and lactonic) on the BTW surface (Boehm, 1966). According to the results, the total amount of acidic groups was calculated as  $7.75 \text{ mmol g}^{-1}$ . The carboxylic, lactonic, and phenolic amounts of these acidic groups were found to be 2.50, 2.00 and  $3.25 \text{ mmol g}^{-1}$ , respectively. These results indicate the presence of significant amounts of acidic groups on the surface of the BTW. On the other hand, the point of zero charge ( $\text{pH}_{\text{pzc}}$ ) of BTW was ascertained as 6.1, indicating that the surface charge of BTW is positively charged when the pH is lower than 6.1 ( $\text{pH} < \text{pH}_{\text{pzc}}$ ) and negatively charged when the pH is higher than 6.1 ( $\text{pH} > \text{pH}_{\text{pzc}}$ ) (Oliveira et al. 2021).

### Optimization of the experimental parameters

The pH of the aqueous medium is a considerable analytical parameter which has a remarkable impact on the ionization level of an adsorbate and the surface charge of an adsorbent. Namely, at highly acidic conditions, active binding sites of the adsorbent may be protonated by  $\text{H}_3\text{O}^+$  ions and excess  $\text{H}_3\text{O}^+$  ions may also compete with the metal cations to adsorb the adsorbent surface. Both phenomena reduce the adsorption amount of metal ions and accordingly the extraction efficiency. Otherwise, at highly basic solutions, the metal ions may precipitate as their hydroxides (Rajabi and Razmpour 2016). Consequently, the pH of the aqueous solution must be optimized in adsorption based separation/preconcentration methods. Therefore, the pH effect on the quantitative extraction of Cd(II) ions by the developed SPE method was scrutinized in the pH range of 2.0–8.0. Recovery

of Cd(II) ions increases acutely as the solution pH is increased from 2.0 to 5.0 and then remains almost constant in the pH range of 5.0–8.0. Cd(II) recovery is 10.5% at pH 2.0, while it is higher than 95% in the pH between 6.0 and 8.0 (Fig. 4a). As expected, at acidic pH values, the competitive effect of  $\text{H}_3\text{O}^+$  with Cd(II) ions to bind the active adsorption sites on the BTW surface causes a decrease in recovery values. In other words, excess  $\text{H}_3\text{O}^+$  ions may occupy the surface of BTW that induced to a fewer available binding sites for Cd(II) ions (Sun et al. 2015). In addition, at low pH values, presumably the

protonation of BTW surface provokes a decrease in its metal binding capabilities, by virtue of the electrostatic repulsion between the BTW surface and Cd(II) cations. On the contrary, as the pH of the solution increases, the surface charge of BTW becomes negative due to the excess  $\text{OH}^-$  ions in the medium which lead to an increase in the adsorption amount and accordingly extraction efficiency. With these in mind, the influences of solution pH on the recovery of Cd(II) ions may also be interpreted by considering the  $\text{pH}_{\text{pzc}}$  value (6.1) of the BTW. The surface charge of BTW is positive when the pH of



**Fig. 4** Influences of **a** pH, **b** BTW amount, **c** sample volume, **d** adsorption equilibrium time, **e** desorption contact time, **f** initial Cd(II) concentration on the adsorption and recovery of Cd(II) ions

the solution is lower than 6.1 ( $\text{pH} < \text{pH}_{\text{pzc}}$ ) and becomes negative above this value ( $\text{pH} > \text{pH}_{\text{pzc}}$ ). As noticed in Fig. 4a, the extraction efficiency of Cd(II) ions is lower at points where  $\text{pH} < \text{pH}_{\text{pzc}}$ . As the pH value approaches to the  $\text{pH}_{\text{pzc}}$  of the adsorbent, the recovery efficiency gradually increases, and at pH values higher than the  $\text{pH}_{\text{pzc}}$ , this increase continues steadily (Mohammadi et al. 2020). The optimum pH for subsequent experiments was determined as 7.0. Similar results were observed by Aliyari et al. in ultrasound-assisted dispersive magnetic SPE of Cd(II) ions by  $\beta$ -cyclodextrin-grafted magnetic graphene oxide nanocomposites (Aliyari et al. 2021).

Type and concentration of eluent are remarkable factors in the quantitative elution of heavy metal ions from the adsorbent surface in a short time. In this sense, the capability of mineral acids,  $\text{HNO}_3$  and  $\text{HCl}$  solutions which are low cost and ecofriendly, on the desorption of Cd(II) ions was scrutinized in the 0.01–3.0 M acid concentration range. Quantitative recovery values were achieved in the range of 0.1–1.0 M for both  $\text{HNO}_3$  and  $\text{HCl}$  concentrations (Table 1). It was observed that the recovery values decreased at lower and higher acid concentrations. The decrease in the recovery of Cd(II) ions when the eluent concentration is less than 0.1 M can be explicated by the inability of the acid for elution of the adsorbed analyte ions. At the same time, the decrease in recovery values at high acid concentrations ( $> 1.0$  M) may be related to the decomposition of the surface structure of BTW. When 0.5 M  $\text{HNO}_3$  and  $\text{HCl}$  were employed separately as the elution solution, the recovery values of Cd(II) ions were determined as 99.9% and 96.9%, respectively (Table 1). Quantitative recoveries were achieved with both acid solutions at 0.5 M concentration, and hence, 0.5 M  $\text{HNO}_3$  was preferred as desorption solution for further experiments.

The eluent volume was explored in the range of 2.5–10.0 mL of 0.5 M  $\text{HNO}_3$  solution. It was noticed that the extraction of Cd(II) ions was quantitative in the entire volume range studied. As a result, the volume of 0.5 M

$\text{HNO}_3$  solution was selected as 5.0 mL throughout the SPE experiments.

An appropriate amount of adsorbent is certainly required in SPE approaches to ensure the sufficient adsorbate-adsorbent interaction. Hence, different amounts of BTW were assessed within the range of 1.0–20.0 g  $\text{L}^{-1}$  in order to ascertain its optimum amount for quantitative Cd(II) extraction. The recovery efficiency of Cd(II) ions increased from 89.2 to 95.5% with an increase in BTW amount from 1.0 to 5.0 g  $\text{L}^{-1}$  (Fig. 4b). The increase in BTW amount resulted in an enhancement of the surface area and binding sites for the adsorption of Cd(II) ions, and in parallel with this increase, the recovery efficiency of Cd(II) ions increased. The Cd(II) recovery remains almost constant ( $> 95\%$ ) with further increase in BTW amount. For subsequent studies, the optimum amount of BTW was chosen as 5.0 g  $\text{L}^{-1}$ .

Sample volume is a critical parameter affecting the pre-concentration factor (PF) directly, which is a notable performance indicator of an analytical method developed. The high PF, which is observed by dividing the optimum sample volume by the eluent volume, is significant for accurate and reliable determination of low levels of analyte ions from different matrices. The effect of sample volume on the extraction of Cd(II) ions was assessed in the range of 50–1000 mL. As it is clear from Fig. 4c, the extraction efficiency of Cd(II) ions is quantitative in the sample volume range of 50–500 mL. As the volume is increased from 500 to 1000 mL, the recovery efficiency of Cd(II) ions decreases from 95.8 to 72.4%. Therefore, optimum sample volume was specified as 500 mL for the separation/preconcentration of Cd(II) ions with the developed SPE method, and the PF of 100 was achieved when 5.0 mL of eluent volume was used.

In order to assess the sufficient equilibration time and to minimize the time required for the retention of Cd(II) ions by BTW quantitatively, the experiments were performed at two different Cd(II) concentrations (2.0 and 50.0 mg  $\text{L}^{-1}$ ) using 5.0 g  $\text{L}^{-1}$  BTW suspensions at various contact times between 1 and 180 min. At the end of each specified time, the adsorbent-adsorbate mixture was separated from each other by centrifugation and the Cd(II) ions remained in the solution were analyzed by FAAS. The Cd(II) amounts ( $q_t$ ) adsorbed by 1 g of BTW at different equilibrium times were calculated using Eq. 1:

$$q_t = \frac{(C_o - C_e) \times V}{m} \quad (1)$$

$C_o$  (mg  $\text{L}^{-1}$ ); initial Cd(II) concentration,  $C_e$  (mg  $\text{L}^{-1}$ ); amount of Cd(II) remained in solution at equilibrium,  $V$  (mL); volume of solution, and  $m$  (g); amount of BTW. Time-dependent retention of Cd(II) ions on BTW at both

**Table 1** Type and concentration of desorption solution on the Cd(II) ions' extraction efficiency

Eluent (HCl) (M)	Recovery (%)	Eluent ( $\text{HNO}_3$ )	Recovery (%)
0.01	$85.0 \pm 2.7$	0.01	$82.6 \pm 2.2$
0.05	$93.5 \pm 3.9$	0.05	$89.4 \pm 3.4$
0.1	$102.6 \pm 0.8$	0.1	$98.9 \pm 4.0$
0.5	$96.9 \pm 2.9$	0.5	$99.9 \pm 3.3$
1.0	$101.4 \pm 4.1$	1.0	$101.8 \pm 3.6$
2.0	$92.5 \pm 2.7$	2.0	$91.5 \pm 0.4$
3.0	$85.5 \pm 2.3$	3.0	$87.3 \pm 2.1$

concentrations (2.0 and 50.0 mg L<sup>-1</sup>) demonstrated that the adsorption happens in three stages (Fig. 4d). In the first step, the process occurred expeditiously because of the empty sites on the BTW surface, while in the second step in which the adsorption rate tends to decrease, Cd(II) ions diffuse into the BTW pores. In the last stage, no considerable alteration was noticed in the adsorption rate because of the saturation of adsorption surfaces (Abatan et al. 2020). As a result, the equilibrium time for 2.0 and 50.0 mg L<sup>-1</sup> concentrations of Cd(II) ions was optimized as 15 and 60 min, respectively.

The sufficient time for the desorption of Cd(II) ions from the BTW surface was examined between 1 and 180 min of contact time. For this purpose, the solutions containing 5.0 µg of Cd(II) ions (at pH 7.0) were treated with 5.0 g L<sup>-1</sup> of BTW suspension for 15 min. At the end of the optimum equilibrium time required for adsorption, BTW was separated from the solution by centrifugation and treated with a 5.0 mL volume of 0.5 M HNO<sub>3</sub> solution for different periods of time between 1 and 180 min. At the end of each determined time, the mixture was centrifuged and the adsorbent was removed. Cd(II) levels in the eluent solutions were analyzed by FAAS. Recovery values of Cd(II) ions were calculated as 96.3% after 15 min of desorption contact time (Fig. 4e). Quantitative recoveries were obtained at all evaluated times in the range of 15–180 min. For subsequent studies, the time for desorption was determined as 15 min.

### Kinetics of Cd(II) adsorption

The data acquired by the equilibrium time experiments were fitted to pseudo-first-order (PFO), pseudo-second-order (PSO), and intraparticle diffusion models

to elucidate the rate and mechanism of the Cd(II) ions adsorption onto BTW (Lagergren 1898; Ho and McKay 1998; Weber and Morriss 1963). The kinetic model equations and the related constants of the models are given in Table 2. In order to estimate which kinetic model would be more convenient for specification of the adsorption rate and mechanism, the compatibility between the experimental  $q_e$  ( $q_{e,exp}$ ) and the theoretical  $q_e$  ( $q_{e,cal}$ ) obtained by applying the data to the models and the correlation coefficients ( $R^2$ ) were taken into consideration. Although the  $R^2$  values obtained from PFO model for initial Cd(II) concentrations of 2.0 and 50.0 mg L<sup>-1</sup> are higher than 0.90, there is no agreement between the  $q_{e,cal}$  values and the  $q_{e,exp}$  values. Nonetheless, the  $R^2$  values observed from the PSO model for both Cd(II) ions concentrations are 0.9999, and it is noticed that the  $q_{e,cal}$  values are quite close to the  $q_{e,exp}$  values (Table 3). Considering these outputs, it could be inferred that the adsorption behavior of Cd(II) ions onto BTW obeyed chemisorption that involves the electron exchange or sharing between the adsorbate ions and the adsorbent (Fawzy et al. 2022).

Intraparticle diffusion model was also utilized to advanced interpretation of the adsorption kinetics. According to the model, the retention of Cd(II) ions on BTW consists of three steps. In the first stage (film diffusion), the Cd(II) ions are adsorbed on the surface of the BTW, while in the second step (intraparticle diffusion) adsorption occurs toward the interior of the BTW pores. The last stage, which eventuates expeditiously, is the equilibrium state and its impact on the mechanism is neglected. At equilibrium, an inappreciable amount of Cd(II) ions is adsorbed as a result of the saturation of the

**Table 2** Equations and variables of kinetics and isotherms models

Model	Equations	Variables	Graph	Slope	Intercept
<i>Kinetic models</i>					
PFO	$\ln(q_e - q_t) = \ln q_e - k_1 t$	$q_e$ (mg g <sup>-1</sup> ); Cd(II) ions adsorption at equilibrium, $q_t$ (mg g <sup>-1</sup> ); Cd(II) retention at any time $t$ , $k_1$ (min <sup>-1</sup> ); rate constant	$\ln(q_e - q_t)$ versus $t$	$k_1$	$q_e$
PSO	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	$k_2$ (g mg <sup>-1</sup> min <sup>-1</sup> ); rate constant	$t/q_t$ versus $t$	$q_e$	$k_2$
Intraparticle diffusion model	$q_t = k_{id} t^{1/2} + c$	$k_{id}$ (mg g <sup>-1</sup> min <sup>-1/2</sup> ); rate constant $C$ ; thickness of the boundary layer	$q_t$ versus $t^{1/2}$	$k_{id}$	$C$
<i>Isotherm models</i>					
Langmuir isotherm model	$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{b q_{max}}$	$C_e$ (mg L <sup>-1</sup> ); Cd(II) amount in solution at equilibrium, $q_e$ (mg g <sup>-1</sup> ); amount of Cd(II) uptake by BTW, $b$ (L mg <sup>-1</sup> ); Langmuir constant, $q_{max}$ (mg g <sup>-1</sup> ); maximum adsorption capacity	$C_e/q_e$ versus $C_e$	$q_{max}$	$b$
Freundlich isotherm model	$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e$	$K_f$ (mg g <sup>-1</sup> ) and $n$ ; Freundlich isotherm model constants	$\ln q_e$ versus $\ln C_e$	$n$	$K_f$
D-R isotherm model	$\ln q_e = \ln q_m - \beta \epsilon^2$	$q_m$ (mg g <sup>-1</sup> ); monolayer adsorption capacity, $\beta$ (kJ <sup>2</sup> mol <sup>-2</sup> ); activity coefficient, $\epsilon$ ; Polanyi potential	$\ln q_e$ versus $\epsilon^2$	$\beta$	$q_m$



**Table 3** Kinetics parameters for Cd(II) ions adsorption onto BTW

Cd(II) conc. (mg L <sup>-1</sup> )	PFO			$R^2$	PSO		$R^2$
	$q_{e\text{ exp}}$	$k_1$	$q_{e\text{ cal}}$		$k_2$	$q_{e\text{ cal}}$	
2.0	0.38	-0.028	0.046	0.902	3.09	0.38	0.9999
50.0	8.90	-0.051	2.920	0.990	0.07	8.98	0.9999
Cd(II) conc. (mg L <sup>-1</sup> )	Intraparticle diffusion model					$C$	
	$k_{id,1}$	$R^2$	$k_{id,2}$	$R^2$			
2.0	0.0204	0.999	0.0015	0.975		0.318	
50.0	0.9219	0.895	0.0828	0.748		6.278	

active adsorption sites on the BTW surface. The comparison of the rate constants belonging to film diffusion and intraparticle diffusion stages reflected that the calculated rate constants ( $k_{id,2}$ ) for intraparticle diffusion are lower for both Cd(II) ions levels. These results suggested that the intraparticle diffusion is sufficient to characterize the adsorption mechanism of Cd(II) ions. However, this assumption is valid if the line passes through the origin, that is, if the  $C$  constant is zero. According to the results obtained, the  $C$  constant was calculated as 0.318 and 6.278 for 2.0 and 50.0 mg L<sup>-1</sup> of initial Cd(II) concentration, respectively (Table 3). This result revealed that both film diffusion and intraparticle diffusion are effective on the adsorption of Cd(II) ions on BTW (Ozdes and Duran, 2021).

### Adsorption isotherms

Adsorption isotherm data that indicate the adsorbate amount, retained per unit mass of adsorbent at a constant temperature for different adsorbate concentrations in aqueous solution at equilibrium conditions, provide notable perspective for further assessment of adsorption mechanisms. In this respect, adsorption isotherms were evaluated by fitting the data to Langmuir (Langmuir 1918), Freundlich (Freundlich 1906), and Dubinin–Radushkevich (D–R) (Dubinin and Radushkevich 1947) isotherm models. For that purpose, the experiments were carried out by using different initial Cd(II) ions concentrations (10–500 mg L<sup>-1</sup>) at pH 7.0 by using 5.0 g L<sup>-1</sup> of BTW amount. According to the graph plotted by the  $q_e$  values versus initial Cd(II) ions concentration (Fig. 4f), it was noticed that the adsorption amount ( $q_e$ ) increased from 1.71 to 37.4 mg g<sup>-1</sup> as increasing the initial Cd(II) ions concentration from 10 to 500 mg L<sup>-1</sup>.

Langmuir model implies that the adsorbate species that do not interact with each other adsorb to a homogeneous adsorbent surface as monolayer, while Freundlich model assumes that the multilayer adsorption eventuates on heterogeneous adsorbent surface having different binding

energies. On the other hand, D–R model estimates that the adsorption is a physical or chemical process, considering the calculated adsorption energy ( $E$ ). The physical, ion exchange or chemical adsorption is supposed to be dominant on the mechanism when the  $E$  is less than 8 kJ mol<sup>-1</sup>, between 8 and 16 kJ mol<sup>-1</sup>, and higher than 16 kJ mol<sup>-1</sup>, respectively. The isotherm model equations and the related constants are given in Table 2.

A dimensionless parameter, separation factor ( $R_L$ ), that is utilized to speculate the favorability of the adsorption process is an outstanding feature of Langmuir isotherm model.  $R_L$  can be obtained by placing the initial adsorbate amount ( $C_o$  (mg/L)) and the Langmuir constant that expresses the adsorption enthalpy ( $b$  (L mg<sup>-1</sup>)) in Eq. 2;

$$R_L = \frac{1}{1 + bC_o} \quad (2)$$

The  $R_L$  value between 0 and 1 ( $0 < R_L < 1$ ) denotes the suitability of the developed process (Fakhar et al. 2021). In addition to this,  $n$  value obtained by the Freundlich model should be in the range of 1–10 for favorable adsorption under the studied conditions (Le et al. 2019).

The  $R^2$  values for the Langmuir and Freundlich isotherm models were observed as 0.9752 and 0.9396, respectively. Obviously, the Langmuir model is more convenient than the Freundlich model for specification of the Cd(II) adsorption onto BTW. In this sense, it is clear that the retention of Cd(II) ions occurs as monolayer on the homogeneous BTW surface. The maximum adsorption capacity of BTW was obtained as 41.5 mg g<sup>-1</sup> (Table 4). It is worth mentioning that BTW has relatively higher adsorption capacity for Cd(II) ions compared with most of the other reported adsorbents (Khodarahmi et al. 2018; Ozdes and Duran 2021; Bagherian et al. 2020; Sivrikaya et al. 2016; Altunay et al. 2021; Huang et al. 2020; Soylak et al. 2019; Lamaiphan et al. 2021; Mendil et al. 2019; Jamshidi et al. 2019; Daşbaşı et al. 2018; Gouda and Zordok, 2018) given in Table 5. Furthermore, the  $R_L$  has values in the range of 0.79–0.069 with the alteration of

**Table 4** Isotherm parameters for Cd(II) ions adsorption onto BTW

<i>Langmuir isotherm model</i>	
$q_{\max}$	41.5
$b$	0.027
$R^2$	0.9752
<i>Freundlich isotherm model</i>	
$K_f$	1.91
$n$	1.7
$R^2$	0.9396
<i>D-R isotherm model</i>	
$q_m$	12.6
$\beta$	-0.0056
$E$	9.45
$R^2$	0.9716

the initial Cd(II) level between 10 and 500 mg L<sup>-1</sup> demonstrating that the developed process is favorable. The fact that the  $n$  value obtained from the Freundlich isotherm model was 1.7 supported the suitability of the adsorption of Cd(II) ions onto BTW. The value of  $E$  for the adsorption of Cd(II) ions onto BTW was calculated as 9.45 kJ mol<sup>-1</sup> suggesting that the ion exchange mechanism is effective in the Cd(II) adsorption onto BTW (Thamilarasi et al. 2018).

#### ANN modeling of the extraction process of Cd(II) ions

The ANN model was evaluated by dividing thirty-eight experimental data randomly into three subgroups including training (70%), validation (15%), and testing (15%). Then, three-layer BP neural network model with tansig in the hidden layer and purelin in the output layer was evaluated by various neuron numbers to achieve the ideal number of neurons in the hidden layer. It performs best when nine neurons present in the hidden layer, and thus, nine neurons were selected for the hidden layer. After this stage, various training studies were conducted to find the best possible weights, errors, and correlations. The ANN regression plot for training, validation, testing, and the overall prediction set in the form of network output versus experimental extraction efficiency is given in Fig. 5. From the regression analysis, it is noticed that the network output values are close to the experimental extraction efficiency in all cases. The  $R^2$  for training, validation, and testing were obtained as 0.995, 0.997, and 0.996, respectively, while the overall prediction set was observed as 0.994. On the other hand, the compatibility between the recovery values obtained by applying the developed ANN model to the experimental data and the experimentally obtained values is shown in Fig. 6. The results indicated that the ANN model is suitable for prediction of Cd(II) extraction efficiency with reasonable accuracy.

**Table 5** Method performance comparison with other studies on SPE of Cd(II) ions

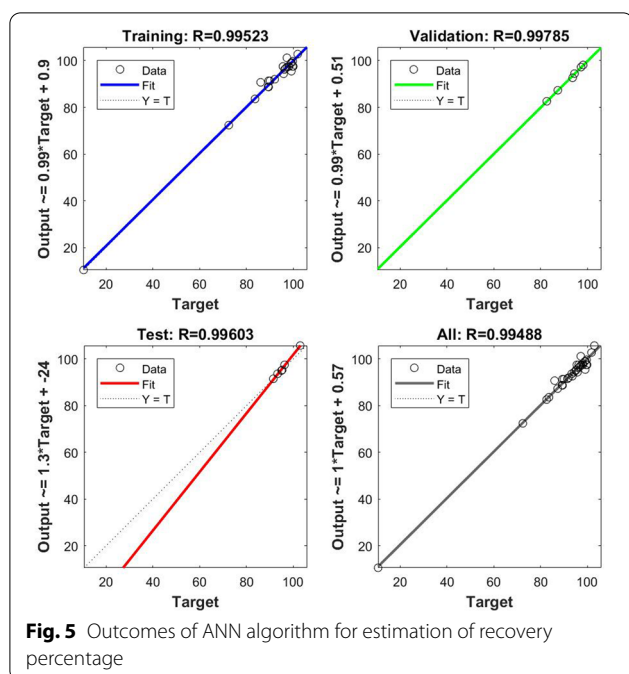
SPE Adsorbent	PF	LOD ( $\mu\text{g L}^{-1}$ )	RSD (%)	Ads. capacity ( $\text{mg g}^{-1}$ )	Ref
Polyvinyl chloride functionalized with 3-(2-thiazolylazo)-2,6-diaminopyridine	52.6	0.7	4.1	310	Bagherian et al. (2020)
2-[N,N'-bis(2,3-dihydroxybenzaldimin)] aminoethylamine-modified silica gel	12.3	0.65	—	41.1	Sivrikaya et al. (2016)
PHBvbNCI*	98	0.15	2.2	152.9	Altunay et al. (2021)
CS/MOF-SH**	25	0.008	4.1	109.9	Huang et al. (2020)
Watermelon biochar/CoFe <sub>2</sub> O <sub>4</sub>	50	1.82	4.19	8.75	Ozdes and Duran (2021)
Magnetic graphene oxide	10	2.3	<2.1	3.5	Soylak et al. (2019)
3-mercaptopropyl trimethoxysilane-functionalized graphene oxide-magnetic nanoparticles	19.3	0.9	5.04	—	Lamaiphan et al. (2021)
1-phenylthiosemicarbazide-modified silica gel	50	0.65	<5	6.4	Mendil et al. (2019)
Magnetic Mn <sub>2</sub> O <sub>3</sub> nanocomposite modified by N,N'-bis(salicylidene) ethylenediamine	33	320	1.1	—	Jamshidi et al. (2019)
<i>Descurainia Sophia</i> (DS) seeds	30	1.0	3.2	11.9	Khodarahmi et al. (2018)
PTMAAm-co-DVB-co-AMPS***	75	1.4	<2.0	11.4	Daşbaşı et al. (2018)
BCBATT****-modified multiwalled carbon nanotubes	100	0.2	3.2	8.0	Gouda and Zordok (2018)
Brewed tea waste	100	0.56	3.03	41.5	This study

\*Poly-3-hydroxy butyrate-polyvinyl triethyl ammonium chloride

\*\*Chitosan-/thiol-functionalized metal-organic framework composite

\*\*\*Poly[phenyl thiadiazole methacrylamide-co-divinylbenzene-co-2-acrylamido-2-methylpropane sulfonic acid]

\*\*\*\*5-benzyl-4-[chlororbenzylidene amine]-4H-1,2,4-triazole-3-thiol



### Influences of foreign ions

To speculate whether different anions and cations commonly found in environmental samples interfere during the extraction of analyte ions by BTW and quantification of analyte ions by FAAS, the procedure was performed by adding specific concentration of different ions in 15 mL of solution containing 5.0  $\mu\text{g}$  of Cd(II) ions (at pH 7.0) and 5.0 g L<sup>-1</sup> of BTW suspensions. It is obvious that the presence of several co-existing ions at high concentrations did not have a notable impact on the separation/preconcentration of Cd(II) ions by the proposed SPE method (Table 6). Therefore, it is concluded that the proposed method exhibited a sufficient tolerance to the matrix effect providing an opportunity

**Table 6** Different common ions effect on the Cd(II) extraction efficiency

Ions	Added as	Conc (mg L <sup>-1</sup> )	Recovery (%)
Na <sup>+</sup>	NaCl	5000	93.3 ± 0.7
K <sup>+</sup>	KCl	1000	99.6 ± 2.8
Ca <sup>2+</sup>	CaCl <sub>2</sub>	250	96.3 ± 3.0
Mg <sup>2+</sup>	Mg(NO <sub>3</sub> ) <sub>2</sub>	250	99.4 ± 1.1
SO <sub>4</sub> <sup>2-</sup>	Na <sub>2</sub> SO <sub>4</sub>	1000	97.9 ± 2.7
NO <sub>3</sub> <sup>-</sup>	NaNO <sub>3</sub>	1000	99.4 ± 3.4
PO <sub>4</sub> <sup>3-</sup>	Na <sub>3</sub> PO <sub>4</sub>	250	103.2 ± 1.9
NH <sub>4</sub> <sup>+</sup>	NH <sub>4</sub> NO <sub>3</sub>	250	94.5 ± 1.6
Cu(II), Ni(II), Pb(II), Mn(II)	*	25	102.1 ± 1.0
Mixed <sup>a</sup>			99.4 ± 3.1

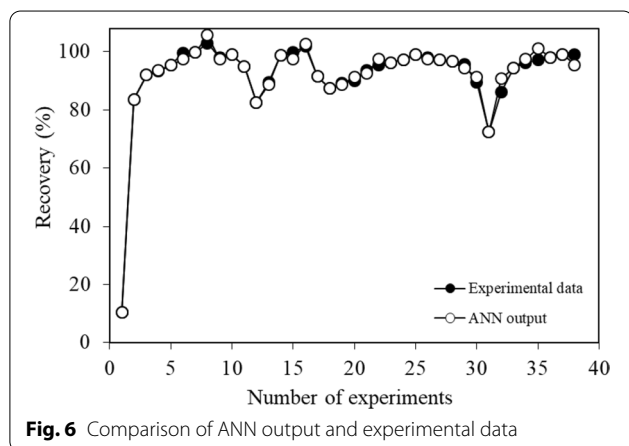
\*Their nitrate salts were added

<sup>a</sup> 268 mg L<sup>-1</sup> Na<sup>+</sup>, 692 mg L<sup>-1</sup> Cl<sup>-</sup>, 377 mg L<sup>-1</sup> NO<sub>3</sub><sup>-</sup>, 50 mg L<sup>-1</sup> K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, NH<sub>4</sub><sup>+</sup>, 10 mg L<sup>-1</sup> Cu(II), Mn(II), Ni(II), Pb(II)

to be applied with high selectivity to the complicated matrices.

### Analytical performance

The analytical features of the proposed methodology were characterized with respect to relative standard deviation (RSD%), limit of detection (LOD), and limit of quantification (LOQ) by performing the experiments under optimal conditions. The LOD and LOQ were calculated by considering three and nine times of the standard deviation of ten blank measurement signals, respectively, while RSD%, which is an indicator of method precision, is determined by applying the optimized procedure ten times using model solutions. The LOD, LOQ, and RSD% were observed as 0.56  $\mu\text{g L}^{-1}$ , 1.68  $\mu\text{g L}^{-1}$ , and 3.03%, respectively. A comparison in terms of analytical performance between the developed SPE method based



**Table 7** Addition/recovery data for water samples (sample volume: 50 mL)

Samples	Added ( $\mu\text{g}$ )	Found ( $\mu\text{g}$ )	Recovery (%)
Stream water (Değirmendere)	0	ND*	—
	6.0	5.67 ± 0.23	94.5
	12.0	11.9 ± 0.4	99.2
Stream water (Harşit)	0	ND*	—
	6.0	5.61 ± 0.13	93.5
	12.0	10.9 ± 0.6	90.8
Sea water	0	ND*	—
	6.0	5.55 ± 0.31	92.5
	12.0	11.4 ± 0.7	95.0

\*Not detected

**Table 8** Addition/recovery data for solid samples (vegetable and fruit quantities: 0.750 g)

Samples	Added ( $\mu\text{g}$ )	Found ( $\mu\text{g}$ )	Recovery (%)
Eggplant	0	$0.73 \pm 0.02$	–
	4.0	$4.37 \pm 0.15$	91.0
Lettuce	0	$0.28 \pm 0.01$	
	4.0	$4.29 \pm 0.11$	100.3
Parsley	0	$0.62 \pm 0.02$	
	4.0	$4.48 \pm 0.17$	96.5
Apple	0	$2.45 \pm 0.09$	
	4.0	$6.12 \pm 0.21$	91.8
Apricot	0	$0.19 \pm 0.01$	
	4.0	$3.93 \pm 0.09$	93.5

**Table 9** Cd(II) levels of real samples (eggplant, lettuce, parsley, apple, and apricot amount: 0.750 g, sea and stream water volume: 500 mL, final volume: 5.0 mL)

Water samples	Cd(II) conc. ( $\mu\text{g L}^{-1}$ )
Stream water (Değirmendere)	$1.76 \pm 0.28$
Stream water (Harşit)	$0.81 \pm 0.08$
Sea water	$0.37 \pm 0.04$
Solid samples	Cd(II) conc. ( $\mu\text{g g}^{-1}$ )
Eggplant	$0.97 \pm 0.03$
Lettuce	$0.37 \pm 0.01$
Parsley	$0.83 \pm 0.01$
Apple	$3.27 \pm 0.07$
Apricot	$0.25 \pm 0.02$

on BTW and some of the other reported SPE procedures is emphasized in Table 5. It is obvious that the obtained RSD% and LOD values are lower, while the PF is higher than most of the previous methods.

#### Method accuracy and application to real samples

The applicability and accuracy of the method were assessed by applying it to spike samples of waters (Table 7), vegetables, and fruits (Table 8). As seen, the recovery values for Cd(II) ions were in the range of 90.8–99.2% and 91.0–100.3% for water and solid samples, respectively. The obtained results for spike/recovery tests indicated that the proposed method is independent from the interferences of different components contained in real samples. Eventually, the recommended method was employed successfully to determine the Cd(II) levels of water (stream and sea water) and food (eggplant, lettuce, parsley, apple, and apricot) samples (Table 9).

## Conclusions

A new, low-cost, sensitive, and ecofriendly SPE procedure based on utilization of brewed tea waste was reported as a practical approach to determine Cd(II) ions in water and food samples. The application of BTW as a natural adsorbent, without any chemical pretreatment and modification, is considered as an important advantage of the study. Considering that millions of tons of tea is produced annually worldwide, it can be estimated that a large amount of BTW will also be formed. The utilization of such a material, which is generated as millions of tons as domestic waste, for significant analytical and environmental applications, indicates the importance of the study. Compared to other reported high-priced adsorbents in the literature, the BTW exhibited higher preconcentration factor (100) and adsorption capacity ( $41.5 \text{ mg g}^{-1}$ ) and lower detection limit ( $0.56 \mu\text{g L}^{-1}$ ) with fast adsorption kinetic (15 min). The three-layer backpropagation (BP) neural network model was utilized for the estimation of Cd(II) ions extraction efficiency by BTW. The ANN model demonstrated a satisfactory estimation of the experimental data with  $R^2$  of 0.995, 0.997, 0.996, and 0.994 for training, validation, testing, and all data, respectively. In brief, the obtained results demonstrated that BTW is a promising alternative for the accurate analysis of Cd(II) ions without any significant matrix interference in various environmental samples with high precisions ( $\text{RSD} < 3.1\%$ ).

#### Abbreviations

BTW: Brewed tea waste; SPE: Solid-phase extraction; ANN: Artificial neural network; FAAS: Flame atomic absorption spectrometry; BP: Backpropagation; LMB: Levenberg–Marquardt back propagation; FTIR: Fourier transform infrared spectrometer; SEM–EDX: Scanning electron microscope equipped with energy-dispersive X-ray spectrometry;  $\text{pH}_{\text{pzc}}$ : Point of zero charge; PFO: Pseudo-first order; PSO: Pseudo-second order; RSD: Relative standard deviation; LOD: Limit of detection; LOQ: Limit of quantification.

#### Acknowledgements

Not applicable

#### Author contributions

All authors contributed to the study conception and design. CD designed and carried out the research and improved the manuscript. NT, SS, and DO carried out the experiments. DO and CD analyzed the data and wrote the manuscript. The authors read and approved the final manuscript.

#### Funding

Not applicable.

#### Availability of data and materials

All data generated or analyzed during this study are included in this published article.

#### Declarations

#### Competing interests

The authors declare that they have no competing interest.

## Author details

<sup>1</sup>Chemistry and Chemical Processing Technologies Department, Gumushane Vocational School, Gumushane University, 29100 Gumushane, Turkey. <sup>2</sup>Faculty of Sciences, Department of Chemistry, Karadeniz Technical University, 61080 Trabzon, Turkey. <sup>3</sup>Department of Chemistry, Graduate School of Education, Gumushane University, 29100 Gumushane, Turkey.

Received: 10 October 2022 Accepted: 20 November 2022

Published online: 16 December 2022

## References

- Abatan OG, Alaba PA, Oni BA, Akpojevwe K, Efeovbokhan V, Abnisa F. Performance of eggshells powder as an adsorbent for adsorption of hexavalent chromium and cadmium from wastewater. *SN Appl Sci*. 2020;2:1996.
- Aliyari E, Fathi AA, Alvand M, Jamshidi P, Shemirani F, Mozaffari S, Neyestani MR.  $\beta$ -cyclodextrin-grafted magnetic graphene oxide nanocomposites in ultrasound-assisted dispersive magnetic solid-phase extraction for simultaneous preconcentration of lead and cadmium ions. *Res Chem Intermed*. 2021;47:1905–18.
- Altunay N, Elik A. Ultrasound-assisted alkanol-based nanostructured supramolecular solvent for extraction and determination of cadmium in food and environmental samples: experimental design methodology. *Microchem J*. 2021;164:105958.
- Altunay N, Hazer B, Tuzen M, Elik A. A new analytical approach for preconcentration, separation and determination of Pb(II) and Cd(II) in real samples using a new adsorbent: synthesis, characterization and application. *Food Chem*. 2021;359:129923.
- Amri ELA, Bensalah J, Essaadaoui Y, Lebki I, Abbou B, Zarrouk A, Rifi EH, Lebki A. Elaboration, characterization and performance evaluation of a new environmentally friendly adsorbent material based on the reed filter (*Typha Latifolia*): kinetic and thermodynamic studies and application in the adsorption of Cd (II) ion. *Chem Data Collect*. 2022;39:100849.
- Bagherian G, Pourbahramian A, Bahramian B, Chajangali MA, Ashrafi M. Evaluation of polyvinyl chloride functionalized with 3-(2-Thiazolylazo)-2,6-diaminopyridine as a new chelating resin for on-line pre-concentration and determination of traces of cadmium in real samples by flame atomic absorption spectrometry. *Anal Bioanal Chem Res*. 2020;8(1):39–53.
- Baki MH, Shemirani F, Khani R. Potential of Sawdust as a green and economical sorbent for simultaneous preconcentration of trace amounts of cadmium, cobalt, and lead from water, biological, food, and herbal samples. *J Food Sci*. 2013;78(5):1797–804.
- Boehm HP. Chemical identification of surface groups. *Adv Catal*. 1966;16:179–274.
- Bozyigit GD, Kilinc Y, Zaman BT, Chormey DS, Bakirdere S. Polystyrene-coated magnetic nanoparticles based dispersive solid phase extraction for the determination of cadmium in cigarette ash prior to slotted quartz tube flame atomic absorption spectrometry system. *Anal Sci*. 2022;38:843–9.
- Bulut VN, Ozdes D, Bekircan O, Gundogdu A, Duran C, Soyлак M. Carrier element-free coprecipitation (CEFC) method for the separation, preconcentration and speciation of chromium using an isatin derivative. *Anal Chim Acta*. 2009;632:35–41.
- Daşbaşı T, Muğlu H, Soykan C, Ülgen A. SPE and determination by FAAS of heavy metals using a new synthesized polymer resin in various water and dried vegetables samples. *J Macromol Sci A*. 2018;55(3):288–95.
- Dubinina MM, Radushkevich LV. Equation of the characteristic curve of activated charcoal. *Proc Acad Sci USSR Phys Chem Sect*. 1947;55:331–3.
- Fakhar N, Khan SA, Siddiqi WA, Khan TA. Ziziphus jujube waste-derived biomass as cost-effective adsorbent for the sequestration of Cd<sup>2+</sup> from aqueous solution: isotherm and kinetics studies. *Environ Nanotechnol Monit Manag*. 2021;16:100570.
- Fawzy MA, Al-Yasi HM, Galal TM, Hamza RZ, Abdelkader TG, Ali EF, Hassan SHA. Statistical optimization, kinetic, equilibrium isotherm and thermodynamic studies of copper biosorption onto *Rosa damascena* leaves as a low-cost biosorbent. *Sci Rep*. 2022;12:8583.
- Feist B, Sitko R. Method for the determination of Pb, Cd, Zn, Mn and Fe in rice samples using carbon nanotubes and cationic complexes of batophenanthroline. *Food Chem*. 2018;249:38–44.
- Freundlich HMF. Über die adsorption in lösungen. *Z Phys Chem*. 1906;57:385–470.
- Ghadirimoghaddam D, Gheibi M, Eftekhari M. Graphene oxide-cyanuric acid nanocomposite as a novel adsorbent for highly efficient solid phase extraction of Pb<sup>2+</sup> followed by electrothermal atomic absorption spectrometry; statistical, soft computing and mechanistic efforts. *Int J Environ Anal Chem*. 2021. <https://doi.org/10.1080/03067319.2020.1861260>.
- Gouda AA, Zordok WA. Solid-phase extraction method for preconcentration of cadmium and lead in environmental samples using multiwalled carbon nanotubes. *Turk J Chem*. 2018;42:1018–31.
- Hashami ZS, Taheri A, Alikarami M. Synthesis of a magnetic SBA-15-NH<sub>2</sub>@ dual-template imprinted polymer for solid phase extraction and determination of Pb and Cd in vegetables. *Box Behnken Des Anal Chim Acta*. 2022;1204:339262.
- Ho YS, McKay G. Kinetic models for the sorption of dye from aqueous solution by wood. *J Environ Sci Health Part B: Process Saf Environ Protect*. 1998;76:183–91.
- Huang L, Huang W, Shen R, Shuai Q. Chitosan/thiol functionalized metal-organic framework composite for the simultaneous determination of lead and cadmium ions in food samples. *Food Chem*. 2020;330:127212.
- Jamshidi P, Alvand M, Shemirani F. Magnetic Mn<sub>2</sub>O<sub>3</sub> nanocomposite covered with N, N'-bis(salicylidene) ethylenediamine for selective preconcentration of cadmium(II) prior to its quantification by FAAS. *Microchim Acta*. 2019;186:487.
- Kaur S, Kaur K, Kaur A, Aulakh JS. SiO<sub>2</sub>@Fe<sub>3</sub>O<sub>4</sub>-SB nano-hybrids as nanosorbent for preconcentration of cadmium ions from environmental water samples. *J Environ Chem Eng*. 2020;8(2):103448.
- Khajeh M, Moosavi-Movahedi AA, Shakeri M, Zadeh FM, Khajeh A, Bohlouli M. Dispersive solid phase extraction combined with dispersive liquid-liquid extraction for the determination of BTEX in soil samples: ant colony optimization-artificial neural network. *J Chemom*. 2015;29:245–52.
- Khajeh M, Sarafraz-Yazdi A, Moghadam AF. Modeling of solid-phase tea waste extraction for the removal of manganese and cobalt from water samples by using PSO-artificial neural network and response surface methodology. *Arab J Chem*. 2017;10:51663–73.
- Khodarahmi M, Eftekhari M, Gheibi M, Chamsaz M. Preconcentration of trace levels of cadmium (II) ion using *Descurainia Sophia* seeds as a green adsorbent for solid phase extraction followed by its determination by flame atomic absorption spectrometry. *J Food Meas Charact*. 2018;12:1485–92.
- Kilinc E, Ozdemir S, Poli A, Niolaus B, Romano I, Bekmezci M, Sen F. A novel bio-solid phase extractor for preconcentrations of Hg and Sn in food samples. *Environ Res*. 2022;207:112231.
- Kocaoba S. Determination of some heavy metals from aqueous solutions using modified Amberlite XAD-4 resin by selective solid-phase extraction. *J Anal Sci Technol*. 2022;13:15.
- Lagergren S. About the theory of so-called adsorption of soluble substance. *Kungl Svenska Vetenskapsakad Handl*. 1898;24:1–39.
- Lamaiphan N, Sakaew C, Sricharoen P, Nuengmatcha P, Chanthai S, Limchoowong N. Highly efficient ultrasonic-assisted preconcentration of trace amounts of Ag(I), Pb(II), and Cd(II) ions using 3-mercaptopropyl trimethoxysilane-functionalized graphene oxide-magnetic nanoparticles. *J Korean Ceram Soc*. 2021;58:314–29.
- Langmuir I. The adsorption of gases on plane surfaces of glass, mica and platinum. *J Am Chem Soc*. 1918;40:1361–403.
- Le VT, Tran TKN, Tran DL, Le HS, Doan VD, Bui QD, Nguyen HT. One-pot synthesis of a novel magnetic activated carbon/clay composite for removal of heavy metals from aqueous solution. *J Dispers Sci Technol*. 2019;40(12):1761–76.
- Lin H, Wang Z, Liu C, Dong Y. Technologies for removing heavy metal from contaminated soils on farmland: a review. *Chemosphere*. 2022;305:135457.
- Malook K, Khan H. Removal of Cd(II) from water using zero valent iron/copper functionalized spent tea. *Water Sci Technol*. 2020;82(11):2552–61.
- Mendil D, Uluzlu OD, Tuzen M, Soyлак M. Multi-element determination in some foods and beverages using silica gel modified with 1-phenylthiosemicarbazide. *Food Addit Contam Part A*. 2019;36(11):1667–76.
- Mohammadi SZ, Mofidinasab N, Karimi MA, Beheshti A. Removal of methylene blue and Cd(II) by magnetic activated carbon-cobalt nanoparticles and its application to wastewater purification. *Int J Environ Sci Technol*. 2020;17:4815–28.



- Nazir NAM, Raoov M, Mohamad S. Spent tea leaves as an adsorbent for micro-solid-phase extraction of polycyclic aromatic hydrocarbons (PAHs) from water and food samples prior to GC-FID analysis. *Microchem J.* 2020;159:105581.
- Nguyen TT, Nguyen THD, Huynh TTT, Dang MHD, Nguyen LHT, Doan TLH, Nguyen TP, Nguyen MA, Tran PH. Ionic liquid-immobilized silica gel as a new sorbent for solid-phase extraction of heavy metal ions in water samples. *RSC Adv.* 2022;12:19741.
- Ofudje EA, Adeogun IA, Idowu MA, Kareem SO, Ndukwe NA. Simultaneous removals of cadmium(II) ions and reactive yellow 4 dye from aqueous solution by bone meal-derived apatite: kinetics, equilibrium and thermodynamic evaluations. *J Anal Sci Technol.* 2020;1:7.
- Oliveira MRF, do ValeAbreu K, Romão ALE, Davi DMB, de Carvalho Magalhães CE, Carrilho ENVM, Alves CR. Carnauba (*Copernicia prunifera*) palm tree biomass as adsorbent for Pb(II) and Cd(II) from water medium. *Environ Sci Pollut Res.* 2021;28:18941–52.
- Ozdes D, Duran C. Preparation of melon peel biochar/CoFe<sub>2</sub>O<sub>4</sub> as a new adsorbent for the separation and preconcentration of Cu(II), Cd(II), and Pb(II) ions by solid-phase extraction in water and vegetable samples. *Environ Monit Assess.* 2021;193(10):642.
- Özkalkan H, Canlidinç RS. Investigation of the conditions for preconcentration of cadmium ions by solid phase extraction method using modified *Juglans regia* L. Shells. *J AOAC Int.* 2021;104(5):1246–54.
- Rajabi HR, Razmpour S. Synthesis, characterization and application of ion imprinted polymeric nanobeads for highly selective preconcentration and spectrophotometric determination of Ni<sup>2+</sup> ion in water samples. *Spectrochim Acta A Mol Biomol Spectrosc.* 2016;153:45–52.
- Roushani M, Baghelani YM, Abbasi S, Mavai M, Mohammadi SZ. Flame atomic absorption spectrometric determination of cadmium in vegetable and water samples after preconcentration Using magnetic solid-phase extraction. *Int J Veg Sci.* 2017;23(4):304–20.
- Sahebi H, Fard SMB, Rahimi F, Jannat B, Sadeghi N. Ultrasound-assisted dispersive magnetic solid-phase extraction of cadmium, lead and copper ions from water and fruit juice samples using DABCO-based poly (ionic liquid) functionalized magnetic nanoparticles. *Food Chem.* 2022;396:133637.
- Shahryari T, Singh P, Raizada P, Davidyants A, Thangavelu L, Sivamani S, Naseri A, Vahidipour F, Ivanets A, Bandegharaei AH. Adsorption properties of Danthron-impregnated carbon nanotubes and their usage for solid phase extraction of heavy metal ions. *Colloids Surf A: Physicochem Eng Asp.* 2022;641:128528.
- Sivrikaya S, Imamoglu M, Yildiz SZ, Kara D. Novel functionalized silica gel for on-line preconcentration of Cadmium(II), Copper(II), and Cobalt(II) with determination by flame atomic absorption spectrometry. *Anal Lett.* 2016;49:957–943.
- Soylak M, Acar D, Yilmaz E, El-Khodary SA, Morsy M, Ibrahim M. Magnetic graphene oxide as an efficient adsorbent for the separation and preconcentration of Cu(II), Pb(II), and Cd(II) from environmental samples. *J AOAC Int.* 2019;100:1544–50.
- Sun J, Liang Q, Han Q, Zhang X, Ding M. One-step synthesis of magnetic graphene oxide nanocomposite and its application in magnetic solid phase extraction of heavy metal ions from biological samples. *Talanta.* 2015;132:557–63.
- Taoufik N, Elmchaouri A, El Mahmoudi S, Korili SA, Gil A. Comparative analysis study by response surface methodology and artificial neural network on salicylic acid adsorption optimization using activated carbon. *Environ Nanotechnol Monit Manag.* 2021;15:100448.
- Thamilarasi MJV, Anilkumar P, Theivarasu C, Sureshkumar MV. Removal of vanadium from wastewater using surface-modified lignocellulosic material. *Environ Sci Pollut Res.* 2018;25:26182–91.
- Uçar G, Bakircioglu D, Kurtulus YB. Determination of metal ions in water and tea samples by flame AAS after preconcentration using sorghum in nature form and chemically activated. *J Anal Chem.* 2014;69(5):420–5.
- Weber WJ Jr, Morriss JC. Kinetics of adsorption on carbon from solution. *J Sanit Eng Div Proc Am Soc Civ Eng.* 1963;89:31–60.
- Yetilmeysoy K, Demirel S. Artificial neural network (ANN) approach for modeling of Pb(II) adsorption from aqueous solution by Antep pistachio (*Pistacia Vera* L.) shells. *J Hazard Mater.* 2008;153:1288–300.

## Publisher's Note

Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

**Submit your manuscript to a SpringerOpen<sup>®</sup> journal and benefit from:**

- Convenient online submission
- Rigorous peer review
- Open access: articles freely available online
- High visibility within the field
- Retaining the copyright to your article

Submit your next manuscript at ► [springeropen.com](https://www.springeropen.com)