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NOVEL SOLID PHASE-EXTRACTOR BASED ON FUNCTIONALIZATION OF SILICA FUME WITH 8-HYDROXYQUINOLINE FOR DETERMINATION OF Pb(II) IN WATER SAMPLES BY SQUARE-WAVE ADSORPTIVE STRIPPING VOLTAMMETRY

Salwa AHMED[1], Ahmed ABDEL GABER[1], Asmaa ABDEL RAHIM[1,*]

[1]Chemistry Department, Faculty of Science, Minia University, Minia 61511, Egypt

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Abstract

A solid phase was developed by the fictionalization of silica fume with 8-hydroxyquinoline (SF-8HQ) through microwave-assisted solvent-free synthesis process for separation, removal and determination of Pb(II) in aqueous solutions. SF-8HQ was characterized by FTIR, XRD and SEM. The experimental conditions such as pH, shaking time, weight of sorbent and concentration of Pb(II) were optimized. It was found that SF-8HQ showed higher percentage of extraction (100.0 %) for Pb(II) and adsorption capacity value (171.55 mg g^{-1}). The sorption kinetic data of Pb(II) on SF-8HQ was fitted to pseudo-second-order ($r^2 = 1$). Moreover, the adsorption isotherm data for adsorption of Pb(II) was fitted to Langmuir and Freundlish isotherm models ($r^2 = 1$). Breakthrough curves were analyzed at different bed heights as well as flow rates using fixed bed column. The practical applicability of SF-8HQ was examined to determine a trace amounts of Pb(II) in environmental water samples with high recovery values.

Keywords*:* *Solid phase extraction, Silica fume, 8-hydroxyquinoline, Pb(II), microwave synthesis.*

Introduction

Lead as one of heavy metal ions is a toxic metal, generally identified as an element of high toxicity due to environmental accumulation and high mobility [1, 2] and can cause severe health problems for humans. Water is one of the main sources of lead contamination for the general public. Even though the lead quantity in these samples is low, its presenting in the daily diet may have significant physiological effects [3]. The determination of Pb(II) at trace levels in water samples requires the use of highly sensitive and reliable analytical techniques [4]. Solid phase extraction (SPE) has emerged as a powerful tool for enrichment/separation of metal ions because of its various advantages over other methods [5 – 9]. Various SP-extractors have been used for the separation and extraction of Pb(II) as its chelates, graphene [5], alumina-coated magnetite nanoparticles [7], multiwalled carbon nanotubes /poly(2-amino thiophenol) nanocomposites [9], SiO_2-nanoparticles [8, 10], silica-supported bis(diazoimine) ligand [11] and functionalized resin [12].

The nature of solid support whether organic [13, 14] or inorganic [15, 16] can control the stability, durability and mechanical properties. To increase its selectivity and loading capacity, there is a need to modify of its surface. In this context, silica fume (SF) was chosen as an ideal solid support for its advantages including; non-toxic, cheap and has specific high surface area [17]. SF could be modified with organic compounds to obtain a new SF-based material capable

Corresponding author: asmaa.ibrahim@mu.edu.eg

of chelating heavy metal ions. The selectivity of these materials mainly depends on the structure of the immobilized organic compounds and the position of the functional groups along the surface of the SF [18]. As a result of the success of the quinoline compounds to form stable complexes with different metal ions, 8-hydroxy quinoline (8HQ) was used as modifier on solid support in many applications. Its superiority in this field was attributed to the presence of the nitrogen atom in the heterocyclic ring and adjacent phenolic –OH group which are suitable for chelation with heavy metal ions [19].

Recently, microwave energy has been widely used in several fields of modifications and applications on research process [20] This microwave technique did not include the organic solvents, trying to minimize the use of hazardous chemicals and the treatment time can be considerably reduced. In particular, microwave heating arises from the direct interaction of matter with electromagnetic energy and it offers a number of potential advantages over conventional heating [21]. In the best of our knowledge, no reports have been published elsewhere to use SF as SP-extractor for the determination of Pb(II) and there are few of work in the use of modified SF for determination of other heavy metal ions. However, this modification was achieved by conventional methods [17, 22]. So, in the present work a new, simple and friendly method depending on microwave-assisted solvent-free synthesis was investigated for modification of SF with 8HQ. The new SP-extractor (SF-8HQ) was used for removal of Pb(II) from aqueous solutions. The influence of effective variables for selective extraction and determination of Pb(II) from different real water samples was also optimized.

Experimental

Materials

Silica fume (SF) was provided from the Ferrosilicon Company, Edfo, Egypt. Doubly distilled water (DDW) was used throughout all experiments. Lead acetate $Pb(CH_3COO)_2.3H_2O$, lead nitrate $Pb(NO_3)_2$, potassium nitrate KNO_3, sodium salt of ethylene diamine tetra acetic acid (Na_2EDTA) and 8-hydroxy quinoline (8HQ) were analytical grade from Merck. ACS reagent grade concentrated hydrochloric acid and sodium hydroxide were obtained from Aldrich and used for justifying the pH values. Samples of Nile River water (NRW), drinking tap-water (DTW), mineral drinking-water (MDW), ground water (GW) and firstly distilled water (DW) were collected from El-Minia City, Egypt.

Apparatus

Square-wave Adsorptive Anodic Stripping Voltammetric (SWAdSV) technique was carried out using AMEL 433 TRACE ANALYSER involving three electrodes system where mercury dropping electrode (HMDE), Ag/AgCl with saturated KCl and platinum wire were performed as working electrode, reference electrode and counter electrode, respectively. A magnetic stirrer and stirring bar provided the convective transport during the pre-concentration. The peak heights were automatically or manually measured using the 'tangent fit' capability of the instrument. The pH measurements were made with Accumet® model 825 pH meter (Germany). A Microwave oven of model: Sharp REM20 (Korea) having 2.450 MHz microwave frequency capacity was used in order to modify of SF. The infrared spectra of SF and its modified phases before and after modification were obtained using FT-IR model 410 JASCO (Japan). JEOL X-ray diffractometer model JSX-60 PA. SEM analysis was obtained using a JSM-5400 LV JEOL (Japan). Wrist Action mechanical shaker model 75 (manufactured by Burrell Corporation Pittsburgh. PA. U.S.A.) was used for equilibration experiments.

Modification of silica fume with 8-hydroxyquinoline using microwave technique

Silica fume has very fine amorphous silica particles with a surface area of about 20,000 m^2/kg. Before using SF as adsorbent, it was firstly washed with water then well dried in an oven at 70°C. Then, equal weight ratio of SF and 8HQ compound was irradiated at power 20.0 W for 5 min in a glass watch using a microwave oven. The product, SF loaded with 8HQ (SF-8HQ) was then washed with DDW to remove the residue of quinoline and left to dry (70°C) for use.

Batch adsorption experiments

The percentage extraction of Pb(II) using SF and its modified phase (SF-8HQ) were determined in triplicate under static conditions by the batch equilibrium technique. Definite weight of each phase (SF and SF-8HQ) was added to 50.0 mL of 1.0×10^{-3} M of $Pb(CH_3COO)_2.3H_2O$. Different additions of 1.0 M NaOH or 1.0 M HCl solutions were used for justifying the pH values at range 2.0 – 6.0 before adding the phase. This mixture was mechanically shaken for 30 min at room temperature to attain equilibrium. Then, the phase was separated by filtration and the unretained metal ion in the filtrate was determined by complexometric EDTA titration [23]. This method was implemented to examine the effect of shaking time, amount of adsorbent and metal ion concentration.

Fixed bed column adsorption experiments

1.0 g of SF-8HQ was taken to prepare a glass mini column of 30 cm length and 2 cm internal diameter. A small piece of cotton was placed at the bottom and above the known quantity of the phase. Pb(II) solution with initial concentration of 0.001 M were allowed to flow downward through the column at a specific flow rate. Samples were collected from the outlet of the column at different time intervals and analyzed for metal ion concentration. The experiment was terminated when the concentration of the metal ion at the outlet of the column equals the initial concentration of Pb(II).

Effect of temperature

To investigate the temperature effects, 200.0 mg of the phase was kept for 1 h at 50 to 200°C in an electric oven, then left to cool. To show the extent of decomposition of the modified SF phase, 50.0 mg of each medium and thermally treated phases along with untreated one took as standard were used to evaluate Pb(II) adsorption capacity under the same conditions previously described for batch experiments at optimum pH value. Then comparing the Pb(II) uptake values using treated phases with that of the standard untreated one (Ahmed 2011).

Determination of the surface coverage value of quinoline phases by the thermal desorption method

200.0 mg of SF-8HQ phase was weighed in a dry porcelain crucible and gradually heated in an oven up to 400°C to determine the concentration of quinoline derivatives loaded to SF surface. The sample was maintained at this temperature for 1 h to ensure the completion of the desorption process, then left to cool to room temperature. The weight loss due to quinoline desorption was evaluated by difference. Blank sample of dry unmodified SF was subjected to the same treatment for comparison.

Applications

Batch mode desorption and reusability studies

Desorption measurements were conducted in order to explore the feasibility of recovering the metal ion and the adsorbent. 1000.0 mg of SF-8HQ saturated with Pb(II) and 100.0 mL of 0.01 M Na_2EDTA solution were transferred into 250 mL measuring flask and were shaken for 1 h. The mixture has been left overnight, then filtrated and washed with DDW in order to remove the residues of Na_2EDTA. The treated phase was dried well to reuse for next experiment under the same conditions of batch method at the optimum pH value.

Study the effect of foreign ions and ionic strength

Different ions such as heavy metal ions (Cu(II) and Zn(II)), alkaline earth metal (Ca(II)) and alkali metal (K(I)) were used to determine the distribution coefficient values of Pb(II) on SF-8HQ.

50.0 mg of SF-8HQ was weighed and added to each solution containing an aliquot of Pb(II) and the other cation which were added with molar ratio (1:1, 1:2, 1:5, 1:10, 1:50 and 1:100), respectively. Then the volume was adjusted to 50.0 mL by DDW at the selected optimum pH of maximum uptake of Pb(II). The mixture was shaken for 30 min and was filtered. The concentration of Pb(II) in each filtrate was determined by SWAdSV through standard additions method. An aliquot of the filtrate was spiked in 10 mL of 0.1 M KNO_3 solution as supporting electrolyte including different standard additions of 0.01 M $Pb(NO_3)_2$ at $E_{acc.} = -0.7$ V and $t_{acc.} = 30$ s.

In order to investigate the effect of ionic strength on the extraction of Pb(II), the concentration of the working solution was varied from 0.0 to 1.0 M NaCl and the concentration of Pb(II) was determined also through SWAdSV with using the same pervious procedure.

Determination of Pb(II) in real water samples

Different real water samples were used such as Nile River water (NRW), drinking tap-water (DTW), ground water (GW), mineral drinking-water (MDW) and firstly distilled water (DW) were collected and stored in cleaned polyethylene bottles. NRW and GW were filtered before the analysis. 50.0 mg of SF-8HQ was conditioned with 50.0 mL of water sample spiked with 5.0 and 10.0 mg L^{-1} of Pb(II) after adjusting the pH samples to the optimum pH value and shaking for 30 min. 25.0 mL of each filtrate was taken and determined via SWAdSV by standard additions method.

Result and discussion

Microwave studies

The details of the modification conditions (power and time) on extraction are provided in Table 1a. According to the results, the microwave radiation synthesis gave a good percentage of extraction at a short reaction time. So, the optimum power and the time adequate for the microwave synthesis of SF-8HQ were 20.0W for 5 min. On the other hand, based on the results obtained on studying the effects of mass ratio of SF with 8HQ, 1.0 g SF: 1.0 g 8HQ as the optimum mass ratio for modification was selected (Table 1b).

Table 1a: The reaction conditions for the synthesis of SF-8HQ as a function of radiation power and time at fixed mass ratio, 1.0 g (SF): 1.0 g of (8HQ)

Power(Watt)	Time(min)	% Extraction
20	5	100.0
20	10	100.0
30	5	100.0
30	10	Solidification[a]

Table 1b: Effects of mass ratio of SF: 8HQ on extraction percentage of Pb(II)

Mass Ratio (g) SF:8HQ	Extraction%
1: 1	100.0
1: 0.5	29.57
1: 0.25	18.48
1:0.1	15.22

[a] m.p.of 8HQ = 72-74°C

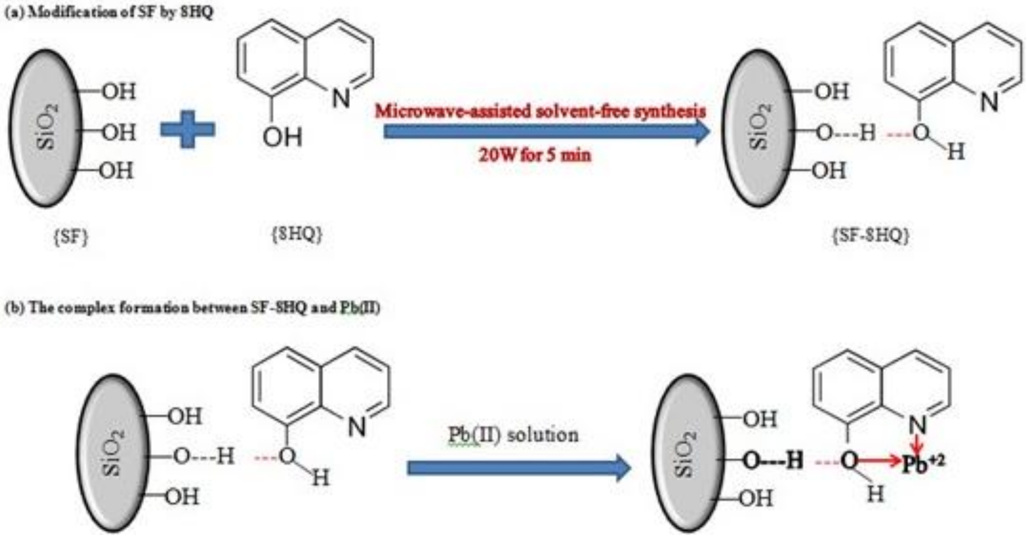
Characterization of SF-8HQ

FT-IR spectra

The infrared spectral analysis was carried out to understand the chemical bonding. Therefore, it provided useful information regarding the functional groups present in compound and described the change that occurred as a result of the modification process. The main bands in IR spectrum of silica fume (Fig. 1a) could be described as follows: the bands appeared at 1105, 799 and 475 cm^{-1} were attributed to asymmetric stretching frequency, symmetric stretching and the bending frequency of υ(O–Si–O), respectively. A broad and strong overlapped band at around 3443 cm^{-1} was due to υ(O–H) stretch [23]. The infrared spectrum of 8HQ (Fig. 1b) was as following: the presence of absorbance band at 3336 cm^{-1} was due to hydroxyl group vibrations of the system [24]. Also, FT-IR band observed at 1579 cm^{-1} was due to υ(C–O) stretching mode and the characteristic absorption of broad band near 3247 cm^{-1} was assigned to υ(C–H) stretching vibration. The very strong absorption bands of υ(C=C) stretching and υ(C–O) stretching were found at 1507 and 1279 cm^{-1}, respectively. The υ(C=N) stretching vibration was observed at 1624 cm^{-1} [25]. Fig. 1c, showed changes which occurred in spectra after modification of SF with 8HQ, where the band of SF attributed to υ(O–H) stretch decreased in intensity and shifted to 3535 cm^{-1}, also the band in 8HQ due to hydroxyl group vibrations was disappeared. The bands in 8HQ at 1579, 1507 and 1279 cm^{-1} were decreased in intensity. This was due to intra molecular hydrogen bond formed between SF and 8HQ (Scheme 1). The FT-IR spectrum of SF-8HQ after adsorption of Pb(II) (Fig. 1d) showed that the band at 1579 cm^{-1} due to υ(C–O) stretching mode in 8HQ was shifted to 1567 cm^{-1}. As well as, the υ(C=N) stretching vibration at 1624 cm^{-1} in 8HQ was shifted to 1635 cm^{-1}. These results supported the adsorption of Pb(II) onto SF-8HQ. This good adsorption can be attributed to the formation of penta-heterocycle chelating complex between Pb(II) and the 8HQ molecule as illustrated in Scheme 1. In addition to, an obvious color change was observed after Pb(II) adsorption by SF-8HQ which confirms metal binding as the color of the phase changed from grey to yellow.

Surface coverage of SF-8HQby the thermal desorption method

Moreover, the concentration of 8HQ onto SF surface (surface coverage, mg g^{-1}) was determined on the basis of the thermal desorption method [26]. This value was found to be 716.88 mg g^{-1} for the phase SF-8HQ. The higher surface coverage of the phase was in accordance with the increasing number of binding sites in 8HQ by its two additional amino and hydroxo groups.



Scheme 1. The complex formation between SF-8HQ and Pb(II)

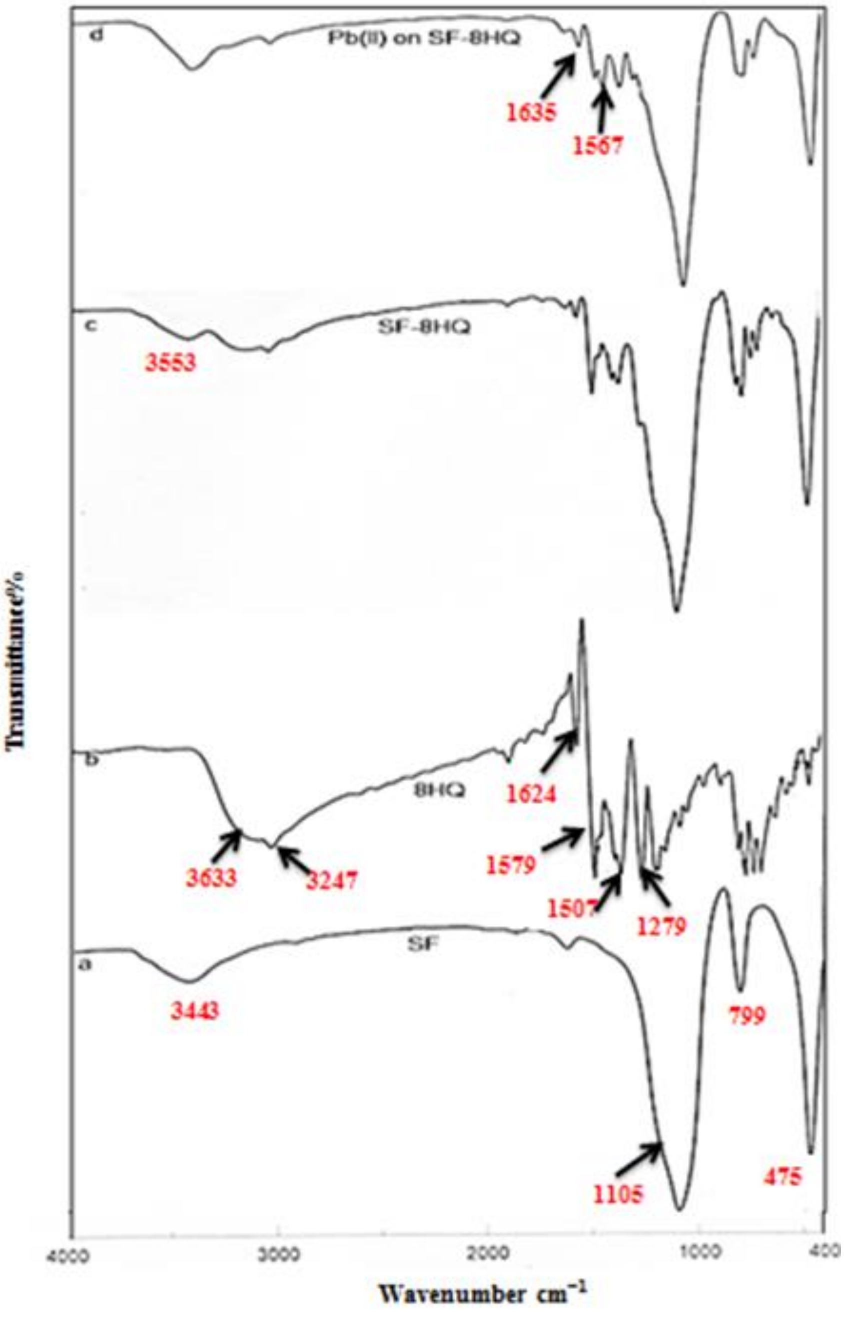


Fig. 1. FT-IR spectra of: (a) SF, (b) 8HQ, (c) SF-8HQ and (d) SF-8HQ after adsorption of Pb(II)

X-ray

The X-ray diffraction (XRD) pattern of SF showed a broad hump in the range between 10° to 30° (Fig. 2a). This indicates that SF is amorphous silica [23]. While the pattern in (Fig. 2b) showed sharp bands that elucidate 8HQ was found to cubic structure. After modification of SF with 8HQ (Fig. 2c), the broad band of SF converted into sharp bands with high intensities which support modification process. In (Fig. 2d), the intensities of bands decreased after adsorption of Pb(II) on SF-8HQ.

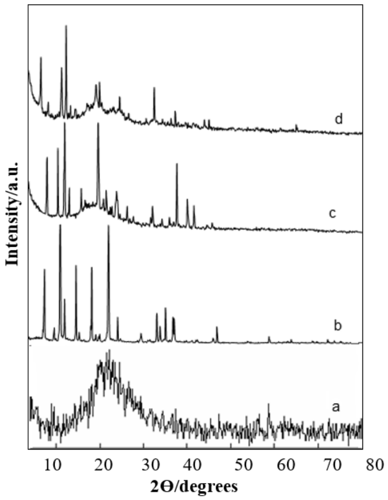


Fig. 2. X-ray diffraction spectra of (a) SF, (b) 8HQ, (c) SF-8HQ and (d) SF-8HQ after adsorption of Pb(II)

Scanning electron microscopy

The scanning electron microscopy (SEM) has been used for analysis of the surface morphology of SF and its modified phase before and after Pb(II) adsorption. The microphotograph (Fig. 3a) [scale: 1μm and magnification: 7500x] revealed that SF particles are in granular form and small in size. After modification with 8HQ, the particles became spherical in shape and larger in size (Fig .3b) [scale: 1μm and magnification: 5000x], while after adsorption of Pb(II), they changed to bacillary form which supports the highest adsorption of Pb(II) on SF-8HQ surface, Fig. 3c [scale: 1μm and magnification: 7500x]. These results supported the formation of penta-heterocycle chelating complex between Pb(II) and the 8HQ molecule as illustrated in Scheme 1.

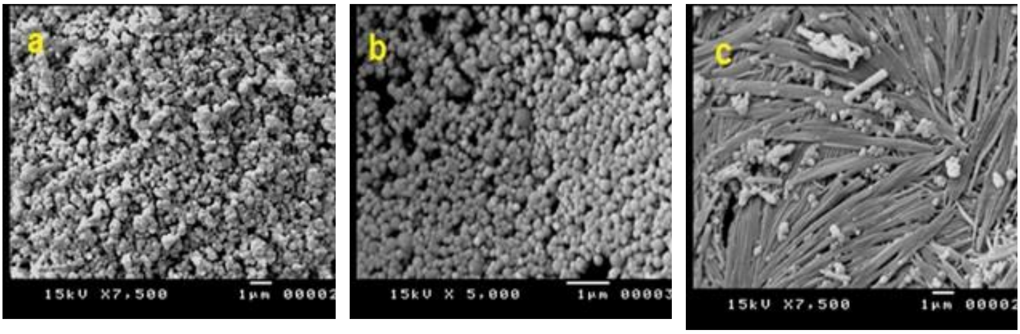


Fig. 3. SEM photographs of (a) SF, (b) SF-8HQ and (c) SF-8HQ after adsorption of Pb(II)

Extraction study using batch method

Effect of pH on metal extraction

Due to retain metal ions on a solid phase extractors as metal ion-chelates, the pH of the aqueous solution is an important parameter. Therefore, experiments were carried out in this section to follow-up the possible contribution of reaction medium on the determined metal adsorption capacity and extraction values. According to this, the effect of pH was investigated in the pH ranges 2.0 to 6.0 with the model solution, keeping other parameters constant. In the case of SF as shown in (Fig. 4a(i)), at low pHs (2.0 and 3.0) the adsorption capacity values of Pb(II) were low which equal 9.95 and 23.62 mg g^{-1}, respectively. With increasing pH up to 6.0, this value was also increased reaching to 29.84 mg g^{-1}. This can be explained as, at low pH values, the proton competes with Pb(II) for binding to SP-extractor which leads to a decrease in the extraction efficiency, while by increasing the pH up to 6.0, the extraction percentage increased (15 ± 0.005 %). On the other hand, in (Fig. 4a(ii)) was illustrated the efficiency of SF after modification with 8HQ towards Pb(II) adsorption. It was found that, the metal uptake and the extraction percentage were calculated to be 171.55 mg g^{-1} and 100.0 ± 0.001 %, respectively at all range of pH. In spite of, the concentration of the hydrogen ions is high at a very low solution pH, SF-8HQ has the ability to bind with Pb(II) more than hydrogen ions. This may be attributed to the strong penta-heterocycle chelating complex between Pb(II) and the 8HQ molecule which caused high extraction values in all pH range. This unique phenomena is suitable for extraction of Pb(II) from interfering ions in different matrices.

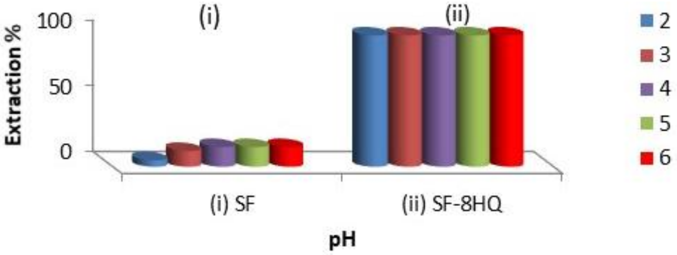


Fig. 4a. Effect of pH on Pb(II) extraction using SF and SF-8HQ

Effect of the amount of the SP-extractor

To study the effect of the amount of SP-extractor on the extraction efficiency, different amounts of this phase were added to the Pb(II) solution. The results in (Fig. 4b) showed that, the extraction percentage of Pb(II) did not affect by increasing the weight of SF up to 500 mg with adsorption capacity of 29.84 mg g^{-1}. But in the case of SF-8HQ, the extraction percentage increased with increasing the amounts of SF-8HQ up to 50 mg where adsorption capacity values ranged from 18.65 up to 171.55 mg g^{-1}. The extraction percentage increased with increasing the amount of SP-extractor as it provided greater surface area along with more adsorption sites for Pb(II). Therefore, 50 mg of SF-8HQ phase was selected for the further experiments.

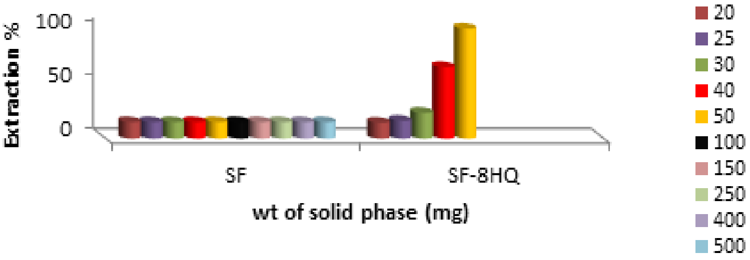


Fig. 4b. Effect of amount of SF and SF-8HQ on the Pb(II) extraction

Effect of the contact time

Modification of SF surface with organic complexing agent (8HQ) led to produce SP-extractor needed only few minutes to complete the Pb(II) extraction processes in comparison with other organic adsorbents and this represented one of the advantages of using SF as inorganic solid support for immobilization of chelating compounds. So, the effect of contact time on the Pb(II) adsorption process by SF and SF-8HQ was studied in presence of various time intervals (5 to 60 min) to determine the time needed to attain equilibrium. As represented in (Fig. 4c) SF was found to proceed via a gradual increase in the extraction percentage (15.0 to 28.3 %) and this required 30 to 60 min. On the other hand, Pb(II) uptake was found to obtained with a high extraction value of 100.0 ± 0.003 % after 5 min shaking time on SF-8HQ. It is, therefore, obvious that the extraction of Pb(II) on SF-8HQ was faster compare to SF.

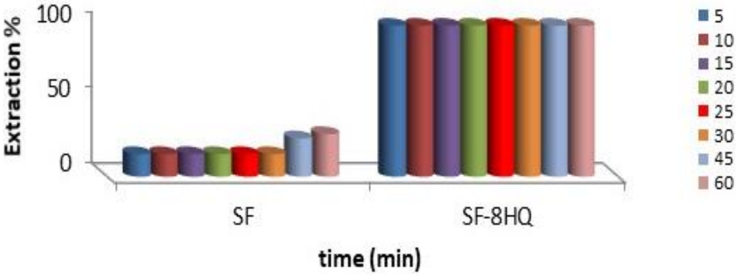


Fig. 4c. Effect of contact time of Pb(II) extraction onto SF and SF-8HQ

Adsorption kinetics

The kinetics of the adsorption process was investigated to study the effect of adsorption time of Pb(II) on the q_e value and the time required to achieve equilibrium between aqueous and solid phases. Two simple kinetic models, namely the pseudo-first-order and the pseudo-second-order, were the most often used to analyze the rate of adsorption. It was found that, Pb(II) was fast extracted on the new phase (SF-8HQ) and the values of extraction remained constant with changing time. So, the adsorption kinetic data of Pb(II) was analyzed in terms of pseudo-second-order sorption rather than pseudo-first-order. The pseudo-second-order equation [27] is shown below:

$$d q_e/dt = k_2\,(q_e - q_t)^2 \qquad (1)$$

where, k_2 (g mg^{-1} min^{-1}) is the rate constant of adsorption, q_e and q_t (mg g^{-1}) is the amount of metal ion sorbet on adsorbent surface at equilibrium and time t (min), respectively. Integration of Eq. (1) and application of the conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, give:

$$1/q_e - q_t = 1/q_e + k_2 t \qquad (2)$$

The following equation can be obtained by rearranging Eq. (2) into a linear form as follows:

$$t/q_t = 1/\upsilon_o + (1/q_e)\,t \qquad (3)$$

where, $\upsilon_o = k_2 q_e^2$ is the initial adsorption rate (mg g^{-1} min^{-1}), υ_o and q_e can be obtained from the intercept and slope of a plot of t/q_t versus t (Fig. 5a). The experimental values of υ_o = 2500, q_e = 170.94 mg g^{-1} and k_2 = 0.086 min^{-1}. The calculated q_e value (171.55 mg g^{-1}) was agreed very well with the experimental value (170.94 mg g^{-1}) with $r^2 = 1.0$. This explained that the model can be applied for the entire adsorption process and confirms the adsorption of Pb(II) onto the SF-8HQ phase.

Adsorption isotherm

The equilibrium adsorption isotherms are one of the promising data to understand the mechanism of the adsorption. There are many isotherms models to describe adsorption process, however, we selected well known Langmuir and Freundlich isotherm models.

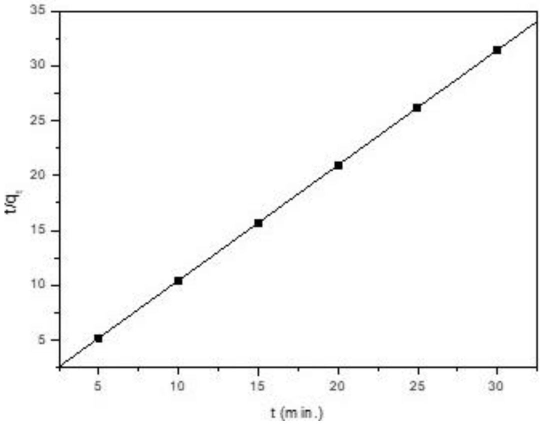


Fig. 5a. Pseudo-second-order kinetic plot for the adsorption of Pb(II) using SF-8HQ

Langmuir isotherm

The adsorption capacities for SF-8HQ increased, by increasing the Pb(II) concentration. Distribution of metal ions between liquid and solid phase could be described by Langmuir adsorption isotherm. The linearized Langmuir isotherm allows the calculation of adsorption capacities and the Langmuir constant. The model is described by the Eq. (4):

$$1/q_e = 1/q_{max.} + 1/q_{max.}\ K_L\ C_e \tag{4}$$

where q_e (mg g^{-1}) is the sorbed Pb(II), C_e (mg L^{-1}) is the solution equilibrium concentration of Pb(II), q_{max}. (mg g^{-1}) is the maximum amount of Pb(II) ion which is taken up by the adsorbent and K_L (L mg^{-1}) is Langmuir constant. K_L and $q_{max.}$ can be calculated from the intercept and slope of the linear plot (Fig. 5b), $1/q_e$ versus $1/C_e$ and their values were given in Table 2. Moreover, the essential characteristics of the Langmuir isotherm can also be expressed in terms of a dimensionless constant separation factor or equilibrium parameter R_L. The value of R_L indicates if the type of Langmuir isotherm is irreversible ($R_L = 0$), favorable ($0 < R_L < 1$) or unfavorable ($R_L > 1$) (Ikram ul Hoque et al., 2015). The factor is defined as:

$$R_L = \frac{1}{1 + K_L C_o} \tag{5}$$

where K_L is the Langmuir constant (indicates the nature of sorption and the shape of the isotherm accordingly); C_o the initial concentration of the analyte. The correlation coefficient ($r^2 = 1.0$) for the adsorption of Pb(II) on SF-8HQ showed that the Langmuir model fitted the results better.

Freundlich isotherm

The basic assumption of Freundlich isotherm is that if the concentration of the solute in the solution at equilibrium, C_e was raised to the power 1/n, the amount of solute sorbet being q_e, then $C_e^{1/n}$ q_e was a constant at a given temperature. This model is more widely used but provides no information on the monolayer biosorption capacity and it assumes neither homogeneous site energies nor limited levels of sorption. The non-linear form of Freundlich equation expressed as follows:

$$q_e = K_f\, C_e^{1/n}, \text{(non-linear form)} \qquad (6)$$

Here, K_f and $1/n$ are Freundlich constants (indicators of the adsorption capacity and intensity, respectively). Taking logs and rearranging of Eq. (5), it can give the linear form of Freundlich model which expressed as:

$$\log q_e = \log K_f + 1/\,n \log C_e, \text{(linear form)} \qquad (7)$$

The constants K_f and $1/n$ can be calculated from the intercept and slope of this linear equation, respectively. The illustration of log q_e vs. log C_e (Fig. 5b) for the evaluated SF-8HQ was found to produce straight lines suggesting that the adsorption process of Pb(II) obeyed Freundlich isotherm over the entire range of the studied Pb(II)´s concentrations. From Table 2, it was clearly found that the identified K_f and n values were 0.583 and 1.126, respectively. For SF-8HQ, r^2= 1 indicate that the Freundlich isotherm model also fitted the results well.

Table 2. Isotherm parameters for Pb(II) adsorption onto SF-8HQ at room temperature

Langmuir constants				Freundlich constants		
K_L	$q_{max}{}^a$	r^2	R_L	K_f	1/n	r^2
210.16	324.56	1.0	0.8	0.583	0.888	1.0

^{a} mg g^{-1}

Both isotherms showed a sharp initial slope indicating that the adsorbent operators at high efficiency at low metal ion concentration. The correlation coefficients indicate that adsorption on SF-8HQ was fitted by the two models. The maximum adsorption capacity ($q_{max.}$) was determined as 324.56 mg $g^{-1}$for Pb(II) on SF-8HQ. This high value of adsorption capacity may be due to the physico-chemical properties of Pb(II) with the higher atomic weight, greater electro-negativity and ionic radius. The Freundlich constant "n" represents the measure of both the relative magnitude and diversity of energies associated with Pb(II) adsorption onto SF-8HQ and the numerical value of 1/n for the metal ion that lie at less than unity, indicating that the marginal adsorption energy decreases with increasing surface concentration and that the Pb(II) is favorably adsorbed by SF-8HQ [28].

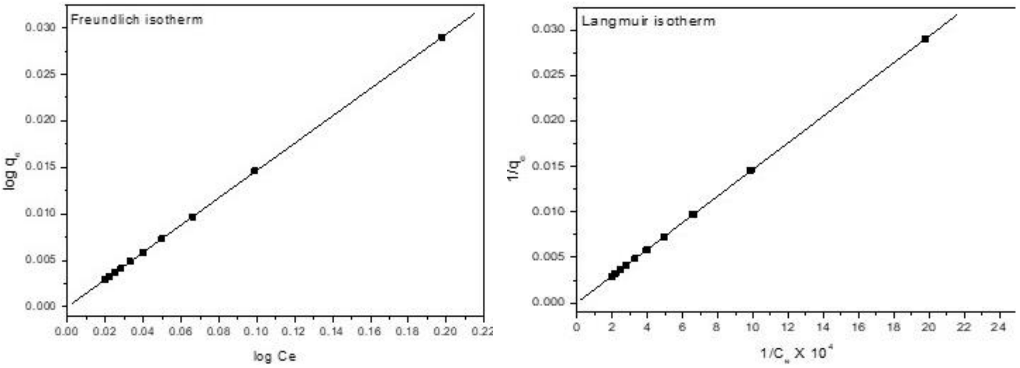


Fig. 5b. Langmuir and Freundlich isotherm plots for the adsorption of Pb(II) using SF-8HQ

Column method

Effect of bed height

Fixed bed column studies were conducted using column with SF-8HQ for three different bed heights of 0.2, 0.4 and 0.7 cm at a constant flow rate of 1 ml/min and influent concentration of 1.0×10^{-3} M Pb(II) solution. The breakthrough curves at different bed heights for studied ion were showed in (Fig. 6a). In all curves, when adsorption was continued beyond the breakthrough point, the C/C$_0$ would rise rapidly to about 6.5. For Pb(II) the breakthrough and the exhaust times were found to be increased with increasing the bed height from 0.2 to 0.7 cm, which resulted in a higher removal percentage of Pb(II) in the column due to the greater number of binding sites existing for adsorption and also because the transfer zone needs more time to reach the column end for Pb(II) to has more time to be in contact with adsorbent [28]. Consequently, the breakthrough curves will be rather gradual with increasing the bed height. As revealed by (Fig. 6a), Pb(II) has a higher binding affinity for making bonds with nitrogen atom of heterocyclic ring and adjacent phenolic –OH group on the surface of the SF-8HQ which required the shortest time period to reach the exhaustion time.

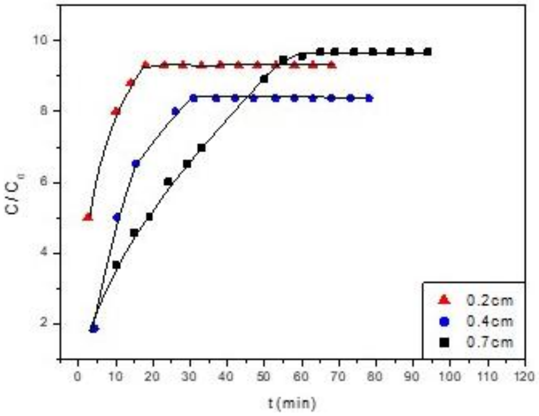


Fig. 6a. Effect of bed height on the uptake of Pb(II) using SF-8HQ at flow rate 1.0 mL/min

Effect of flow rate

The breakthrough curves for Pb(II) at various flow rates of 1.0, 3.0 and 5.0 mL/min through a 0.4 and 0.7 cm bed height columns and influent concentration of 1.0 × 10^{-3} M Pb(II) were shown in (Fig. 6b), The results showed that with increasing the flow rate from 1.0 to 5.0 mL/min the breakthrough curves shift towards a lower time scale and the breakthrough and exhaustion time decrease because if the flow rate increases, Pb(II) could not get enough time to penetrate from the solution to the SF-8HQ pores and bind with its functional groups. This consequently results in a lower removal percentage of Pb(II) in the column.

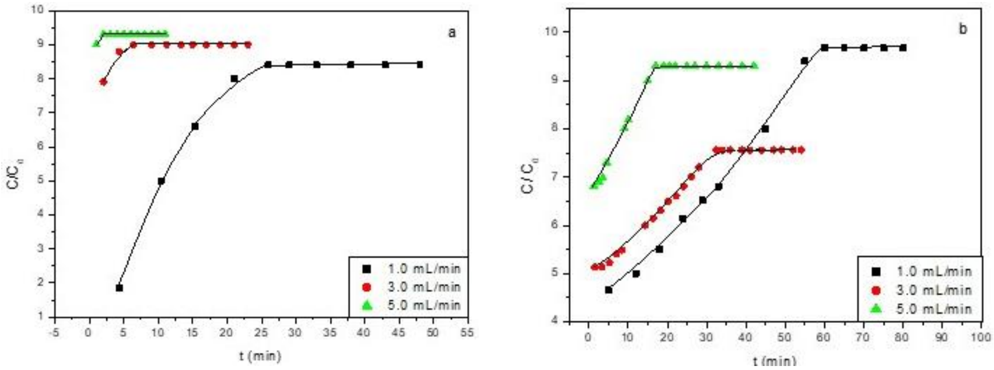


Fig. 6b. Effect of flow rate on the uptake of Pb(II) by SF-8HQ: with bed heights (a) 0.4 cm and (b) 0.7 cm

Thermal stability of the SF-8HQ phase

SF-8HQ phase showed thermal stability judging from values of extraction percentage determined by batch method for uptake of Pb(II) after thermal treatment of the phase for 1 h at elevated temperatures (50–200°C). It was cleared that SF-8HQ exhibited pronounced thermal stability where no loss in their efficiency for Pb(II) uptake was observed till 110°C (compared with their standard values at room temperature without thermal treatment) and a low percentage of decreasing efficiency for Pb(II) uptake which was evaluated to be 4.77 % ± 0.01 from 120 to 200°C. Based on the data obtained, decreasing bulkiness of the chelating 8HQ covalently bonded to SF surface, leading to thermal instability, followed by decomposition and decreasing efficiency of Pb(II) adsorption.

Applications

Desorption and regeneration

Studies of desorption is important in order to regenerate the phase and recover the metal ions. In fact, regeneration using acid or base treatment as ion-exchangers is not adequate for SF modified organic complexing agents, because acid or base treatment may increase the chance of hydrolysis of the bound complexing agent [29]. It was selected to use another strong complexing agent such as EDTA to back extract of Pb(II) from the metal chelate formed modified SF phase in the regeneration process. It was observed that, the result of extraction percentage determined after the second extraction was similar to extraction percentage found in the first one. The efficiency of phase regeneration (E.R.) was obtained using the following Eq. (8):

$$E.R. = \frac{total\ adsorption\ capacity\ in\ the\ second\ run}{total\ adsorption\ capacity\ in\ the\ first\ run} \times 100 \qquad (8)$$

Generally, the E.R. % using 0.01M Na_2EDTA reached to 100.0 ± 0.001 % for SF-8HQ. From desorption studies it was concluded that treatment of SF-8HQ with Na_2EDTA solution could not alter the surface sites of the phase where these results show promising regeneration potential of SF-8HQ.

Distribution coefficient values of interfering ions

Effect of interfering ions on the distribution coefficient of Pb(II) was investigated. The tolerance limits were less than 95.0 % for the ions causing recoveries of the examined elements. The result showed that in excess of 100-fold K(I), Ca(II), Cu(II) or Zn(II) with respect to Pb(II); has no significant interferences in the determination of Pb(II).

The distribution coefficient value, K_d (mL g^{-1}) was calculated according to the following Eq. (8).

$$K_d = C_{i,\,ex} / C_{i,\,sol} \qquad (9)$$

where, $C_{i,\,ex}$ and $C_{i,\,sol}$ are the concentration values of surface-bound metal ion (µg g^{-1}) and solution-free metal ion (µg mL^{-1}), respectively. From this research, it is evident that surface modification of SF with 8HQ as an organic chelating modifier has led to change the chemical properties of SF and therefore, SF-8HQ exhibited its strong affinity towards binding and extraction of Pb(II). So, The contribution of 8HQ is considered as the key factor in the extraction processes of low Pb(II) concentration levels leading to such high selectivity of its extraction based on its high determined distribution coefficient values.

The separation factor is another important value for describing the selectivity characters of SF-8HQ phase. The separation factor ($\alpha_{a/b}$) of any two cations a and b is calculated from the following Eq. (10).

$$\alpha_{a/b} = K_d(a) / K_d(b) \qquad (10)$$

where $K_d(a)$ and $K_d(b)$ are the distribution coefficients of Pb(II) and the interfering ions, respectively. The high value separation factor for Pb(II) versus other tested ions by SF-8HQ were calculated and represented in (Fig. 7).

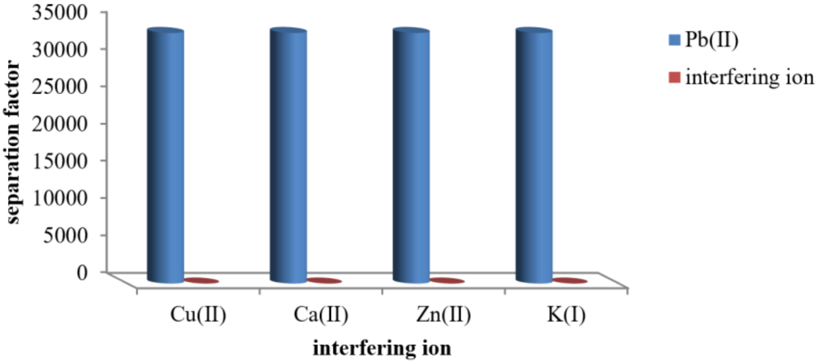


Fig. 7. Separation factors of Pb(II) versus other interfering ions using SF-8HQ

The effect of ionic strength

The effect of ionic strength on the extraction percentage of Pb(II) using SF-8HQ was studied. The results in Table 3a confirmed that, salt addition had no significant effect up to 0.2 M of NaCl on the extraction of Pb(II) by SF-8HQ. But by increasing the concentration of NaCl (0.5 M), the percentage of extraction decreased (79.25 % ± 0.001). This could be attributed to the competition between Na(I) and Pb(II) for the active donor centers incorporated onto the surface of SF-8HQ. Therefore, these observation suggested the applicability of the method for the separation of Pb(II) from saline solutions.

Table 3a. The effect of ionic strength on the extraction percentages of Pb(II) using SF-8HQ

Concentration of NaCl, M	Molar ratio of Pb(II) (1×10^{-3} M): NaCl	Percentage of metal extracted (%)
0.0	1:0	100.0
0.02×10^{-2}	1:0.2	100.0
0.2×10^{-2}	1:2	100.0
1.0×10^{-2}	1:10	100.0
5.0×10^{-2}	1:50	100.0
10.0×10^{-2}	1:100	100.0
20.0×10^{-2}	1:200	100.0
50.0×10^{-2}	1:500	79.25
100.0×10^{-2}	1:1000	79.25

Determination of Pb(II) in water samples

The method validation should be investigated in order to check the accuracy and precision of the new proposed extraction method. In order to estimate the accuracy of the procedure, different amounts (5.0 and 10.0 mg L^{-1}) of Pb(II) were spiked in different water samples. The technique SWAdSV tested using standard additions method was used for the determination of Pb(II) in all water samples. The results exhibited fairly good analytical performance as expressed by the acceptable accuracy, repeatability and sensitivity. Table 3b showed the obtained results which demonstrated the validity of the used SP-extractor for determination of the spiked ultra-trace amount of Pb(II) with no matrix effect. As can be seen, recoveries between 99.4 % to 100.0 % were obtained which confirmed the accuracy of the method.

Table 3b. Results obtained for Pb(II) determination in various water samples after extraction by SF-8HQ phase

Water sample	Spiked Pb(II) (mg/L)	Mass of the phase (mg)	Recovery[a] (%)	*t*-statistic[b]	*F*-statistic[c]	Reference method
	5	50	100.0 ± 0.1	2.276	0.0026	
DW	10	50	100.0 ± 0.1	2.276	0.0026	[11]
				Theoretical value = 2.306	Theoretical value = 6.39	
GW	5	50	99.8 ± 0.05	12.695	0.004	
	10	50	99.4 ± 0.01	11.552	1.5×10^{-4}	[21]
				Theoretical value = 2.306	Theoretical value = 6.39	
NRW	5	50	100.0 ± 0.1	– 0.797	0.0016	
	10	50	100.0 ± 0.5	– 0.773	0.0393	[11]
				Theoretical value = 2.306	Theoretical value = 6.39	
DTW	5	50	100.0 ±	– 0.417	9.6×10^{-6}	
	10	50	0.01	– 0.579	9.6×10^{-6}	[11]
			99.4 ± 0.01	Theoretical value = 2.306	Theoretical value = 6.39	
MDW	5	50	100.0 ± 0.1	− 0.5	0.01	
	10	50	100.0 ±	− 0.5	0.0025	[18]
			0.05	Theoretical value = 2.447	Theoretical value = 19.25	

[a] average of five determination ± standard deviation (S.D.)
[b] theoretical *t*-value at 95 % confidence level
[c] theoretical *F*-value at 95 % confidence level

Comparison with other solid-phase extractors

The proposed methodology was compared to a variety of SP-extractors reported recently in the references. The distinct features were summarized in Table 3c. From the table, it is obvious that, SF-8HQ had high affinity and selectivity towards Pb(II). Furthermore, the direct mode of separation and the simplicity of SF-8HQ synthesis compare with the other SP-extractors.

Table 3c. Comparison of SF-8HQ with some recent SP-extractors used for determination of Pb(II)

The phase used	pH	Adsorption capacity (mg/g)	Weight of the phase (mg)	Equilibrating time (min)	Simplicity of sorbent synthesis		reference
					Synthesis steps	Time needed for synthesis	
MWCNTs modified with 8HQ	7.0	0.076	250.0	10	Multistep	>24 h	[30]
Graphene	6.0	16.6	30.0	50	Multistep	>24 h	[7]
HNT-PSA	5.0	23.58	30.0	20	Multistep	>24 h	[8]
SF-8HQ	2.0–6.0	171.55	40.0	5	One step	10 min	present work

Conclusion

The present study reported new selective solid phase extractor (SF-8HQ) for effective extraction and determination of Pb(II) from aqueous solutions in batch and fixed bed column. The strong binding between SF and 8HQ made this new phase which rendered high extraction efficiency (100.0 %) and capacity (171.55 mg g^{-1}) for Pb(II). Both Langmuir and Freundlich isotherm were fitted with the equilibrium data along with higher correlation coefficients ($r^2 = 1$). The adsorption kinetics of Pb(II) on SF-8HQ revealed that these ions were adsorbed satisfactorily according to the pseudo-second-order equation ($r^2 = 1$). Regeneration experiments showed the good potential of SF-8HQ for reuse. The batch method was applied for determination of Pb(II) from natural water samples with high recovering values (≈100.0 %), good precision and no matrix interferences.

References

[1] M.E. Mahmoud, M.M. Osman, O.F. Hafez, A.H. Hegazi, E. Elmelegy, *Removal and preconcentration of lead (II) and other heavy metals from water by alumina adsorbents developed by surface-adsorbed-dithizone*, **Desalination, 251**, 2010, pp.123–130.

[2] A.S. Özcan, O. Gök, A. Özcan, *Adsorption of lead(II) ions onto 8-hydroxy quinoline-immobilized bentonite*, **J. Hazard. Mater.**, **161**, 2009,pp. 499−509.

[3] Z. Es'haghi, M. Khalili, A. Khazaeifar, G.H. Rounaghi, *Simultaneous extraction and determination of lead, cadmium and copper in rice samples by a new pre-concentration technique: Hollow fiber solid phase microextraction combined with differential pulse anodic stripping voltammetry*, **Electrochimica Acta**, **56**, 2011, pp. 3139–3146.

[4] M. Rajabi, B. Mohammadi, A. Asghari, B. Barfi, M. Behzad, *Nano-alumina coated with SDS and modified with salicylaldehyde-5-sulfonate for extraction of heavy metals and their determination by anodic stripping voltammetry,* **Journal of Industrial and Engineering Chemistry**, **20**, 2014, pp. 3737−3743.

[5] Y. Wang, S. Gao, X. Zang, J. Li, J. Ma, *Graphene-based solid –phase extraction combined with flame atomic absorption spectrometry for a sensitive determination of trace amounts of lead in environmental water and vegetable samples,* **Anal. Chim. Acta**, **716**, 2012, pp. 112−118.

[6] Q. He, D. Yang, X. Deng, Q. Wu, R. Li, Y., Zhai, L. Zhang, *Preparation, characterization and application of N-2-Pyridylsuccinamic acid-functionalized halloysite nanotubes for solid-phase extraction of Pb(II),* **Water Research**, **47**, 2013, pp. 3976−3983.

[7] H. Tavallali, *Determination of Pb (II) in some real samples based on alumina-coated magnetite nanoparticles solid phase extraction method*. **Int. J. of Chem. Tech. Research**, **3**, 2011, pp. 1641−1646.

[8] M.E. Mahmoud, A.A. Yakout, H. Abdel-Aal, M.M. Osman, *High performance SiO2-nanoparticles-immobilized-penicillium funiculosum for bioaccumulation and solid phase extraction of lead,* **Bioresource technology, 106**, 2012, pp.125−132.

[9] M.R. Nabid, R. Sedghi, A. Bagheri, M. Behbahani, M. Taghizadeh, H. Abdi Oskooie, et al. *Preparation and application of poly(2-amino thiophenol)/MWCNTs nanocomposite for adsorption and separation of cadmium and lead ions via solid phase extraction,* **J. Hazard. Mater.**, **203-204**, 2012, pp. 93−100.

[10] A.E. Karatapanis, Y. Fiamegos, C.D. Stalikas, *Silica-modified magnetic nanoparticles functionalized with cetylpyridinium bromide for the preconcentration of metals after complexation with 8-hydroxyquinoline,* **Talanta, 84**, 2011, pp. 834−839.

[11] S. Uruş, S. Purtaş, G. Ceyhan, F. Tümer, *Solid phase extraction of Pb(II), Cu(II), Cd(II) and Cr(III) with syringe technique using novel silica-supported bis(diazoimine) ligands,* **Chemical Engineering Journal**, **220**, 2013, pp. 420−430.

[12] S. Khazaeli, N. Nezamabadi, M. Rabani, H.A. Panahi, *A new functionalized resin and its application in flame atomic absorption spectrophometric determination of trace amounts of heavy metal ions after solid phase extraction in water samples,* **Microchemical Journal**, **106**, 2013, pp. 147−153.

[13] V. Gurnani, A.K. Singh, B. Venkataramani, *Cellulose based macromolecular chelator having pyrocatechol as an anchored ligand: synthesis and applications as metal extractant prior to their determination by flame atomic absorption spectrometry,* **Talanta**, **61**, 2003, pp. 889–903.

[14] Y. Guo, B. Din, Y. Liu, X. Chang, S. Meng, J. Liu, *Preconcentration and determination of trace elements with 2-aminoacetylthiophenol functionalized Amberlite XAD-2 by inductively coupled plasma-atomic emission spectrometry,* **Talanta**, **62**, 2004, pp. 207−2013.

[15] S.A. Ahmed, *Alumina physically loaded by thiosemicarbazide for selective preconcentration of mercury(II) ion from natural water samples,* **J. Hazard. Mater.**, **156**, 2008, pp. 521−529.

[16] E.M. Soliman, M.B. Saleh, S.A. Ahmed, *New solid phase extractors for selective separation and preconcentration of mercury(II) based on silica gel immobilized aliphatic amines 2-thiophenecarboxaldehyde Schiff's bases*, **Anal. Chim. Acta**, **523**, 2004, pp. 133−140.
[17] Y. Li, T. Li, Z. Jin, *Stabilization of Fe^0 nanoparticles with silica fume for enhanced transport and remediation of hexavalent chromium in water and soil,* **Journal of Environmental Sciences**, **23**, 2011, pp. 1211–1218.
[18] D. Perez-Quintanilla, A. Sanchez, I. del Hierro, M. Fajardo, I. Sierra, *Solid phase extraction of Pb(II) in water samples using a new hybrid inorganic-organic mesoporous silica prior to its determination by FAAS,* **Microchim Acta**, **165**, 2009, pp. 291−298.
[19] R.K. Kumbasar, *Selective extraction of nickel from ammoniacal solutions containing nickel and cobalt by emulsion liquid membrane using 5,7-dibromo-8-hydroxyquinoline (DBHQ) as extractant*, **Minerals Engineering**, **22**, 2009, pp. 530–536.
[20] S.A. Ahmed, E.M. Soliman, *Novel route for silylation of silica gel and aliphatic amines immobilization based on microwave-assisted solvent free synthesis and their applications for Cu(II) and Fe(III) removal from natural water samples,* **J. Environ. Sci. Health A**, **48**, 2013, pp. 817–828.
[21] F.K. Yuen, B.H. Hameed, *Recent developments in the preparation and regeneration of activated carbons by microwaves,* **Adv. Colloid Interf. Sci.**, **149**, 2009, pp. 19−27.
[22] Y. Zhou, S. Wang, K. Xie, *Functionalized silica fume for chromium (VI) removal from wastewater*, **Material Science Forum**, **675-677**, 2011, pp. 95−98.
[23] S.A. Ahmed, A.A. Abdel Gaber, A.M. Abdel Rahim, *Application of silica fume as a new SP-extractor for trace determination of Zn(II) and Cd(II) in pharmaceutical and environmental samples by square-wave anodic stripping voltammetry,* **Appl Water Sci**, **7**, 2015, pp. 677–688.
[24] R. Silverstein, G.C. Basseler, T.C. Morrill, *Spectroscopic identification of organic compounds*, 5th edn., **John Wiley and Sons**, New York, 1991, p 430.
[25] M. Rajasekaran, P. Anbusrinivasan, S.C. Mojumdar, *Growth, spectral and thermal characterization of 8-hydroxyquinoline,* **Journal of Thermal Analysis and Calorimetry**, **100**, 2010, pp. 827–830.
[26] M.A. Hafez, I.M. Kenawy, M.A. Akl, R.R. Lashein, *Preconcentration and separation of total mercury in environmental samples using chemically modified chloromethylated polystyrene-PAN (ion-exchanger) and its determination by cold vapour atomic absorption spectrometry,* **Talanta**, **53**, 2001, pp.749−760.
[27] Z. Reddad, C. Gerente, Y. Andres, *Ni(II) and Cu(II) binding properties of native and modified sugar beet pulp,* **Carbohydrate Polymers**, **49**, 2002, pp. 23–31.
[28] A. Shahbazi, H. Younesi, A. Badiei, *Functionalized SBA-15 mesoporous silica by melamine-based dendrimer amines for adsorptive characteristics of Pb(II), Cu(II) and Cd(II) heavy metal ions in batch and fixed bed column,* **Chemical Engineering Journal**, **168**, 2011, pp. 505−518.
[29] S.A. Ahmed, *Batch and fixed-bed column techniques for removal of Cu(II) and Fe(III) using carbohydrate natural polymer modified complexing agents,* **Carbohydrate Polymers**, **83**, 2011, pp. 1470–1478.
[30] S.A. Kosa, G. Al-Zhrani , M. Abdel Salam, *Removal of heavy metals from aqueous solutions by multi-walled carbon nanotubes modified with 8-hydroxyquinoline,* **Chemical Engineering Journal**, **181-182**, 2012, pp. 159−168.

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