



Research article

Chemically modified rice husk as an effective adsorbent for removal of palladium ions

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ABSTRACT

Bio-matrix of rice husk and Mobil Composition of Matter No. 41 (MCM-41) was modified with alizarin red S for preconcentration of Pd²⁺ prior flame atomic absorption spectrometric determination. The prepared bio-matrix (RH@MCM-41@ARS) was characterized by Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), transmission electron microscope (TEM), scanning electron microscope, energy dispersive X-ray spectrometer (SEM/EDX) and surface area studies. The impact of different parameters (solution pH, amount of sorbent, contact time, sample volume, initial Pd²⁺ concentration and diverse ions) on the uptake of Pd²⁺ were evaluated. The maximum adsorption capacity of Pd²⁺ onto RH@MCM-41@ARS was 198.2 mg g⁻¹ at optimum conditions. Applying the optimized procedure as a preconcentration step led to limit of detection of 0.13 µg L⁻¹ and dynamic analytical range up to 500 µg L⁻¹. The sorbent was regenerated by 0.5 mol L⁻¹ thiourea for at least 10 cycles without significant reduction of adsorption capacity. The method was applied for preconcentration of Pd²⁺ from real samples.

1. Introduction

Palladium (Pd) is an economic element of unique properties. It is used in combination with other metals for production of jewelry, dental alloys and catalytic converters for cars [1]. Exposure to Pd or its compounds may lead to toxic effects on skin, eyes, kidneys, liver and lungs depending on the route of exposure and the chemical form of Pd [2].

There are many methods for determination of Pd such as spectrophotometry [3], flame atomic absorption spectrometry (FAAS) [4], inductively coupled plasma-mass spectrometry (ICP-MS) [5] and inductively coupled plasma-optical emission spectrometry (ICP-OES) [6]. Most of these techniques are not suitable for direct analysis of real samples due to lack of sensitivity and presence of complex matrix with the analyte.

Preconcentration of Pd prior determination is an indispensable step to enhance sensitivity and selectivity. Different techniques based on physical, physico-chemical or chemical principles were used for this aim including high performance liquid chromatography [7], cloud point extraction [8], liquid-liquid extraction [9] and solid phase extraction [10].

Agriculture wastes have been employed with interest for preconcentration of metal ions [11] as they found in huge amounts, useless, reproducible and with low cost. Many researches have been done for removal of different metal ions using various types of agriculture wastes as wheat, corn, sugarcane and bajra agro [12], potato leaf [13], orange peel and groundnut shell [14].

Rice husk (RH) is continuously produced from rice industry. It is one of the low-value agricultural by-products which have been used as a biosorbent material due to its high chemical stability and mechanical strength and water insolubility [15]. The worldwide annual RH output is about 80 million tones [16]. Farmers often discharge RH by burning which liberates CO₂ into the environment. CO₂ is a well-known greenhouse gas so RH should be treated and modified to obtain useful materials [17]. RH is an organic agriculture waste which compose of about 50% cellulose and 15–20% silica so it can be used as starting material in synthesis of active biosorbents such as Mobil Composition of Matter No. 41 (MCM41) which is a mesoporous molecular sieve with hexagonal arrangement of pores [18]. The use of biosorbents possesses many advantages including the recycling of waste materials and overcome the

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input of expensive chemicals [19]. Non-modified RH has low adsorption capacity toward metal ions [20]. Modification of RH has received important attention of researched to enhance its adsorption properties [21]. Vyas et al prepared new sorbents based on modification of RH with succinic anhydride and different amines for removal of Pd^{2+} from aqueous solutions [20]. However, poor adsorption capacity was achieved (7.7–15.7 mg/g) and the adsorption process was relatively slow (3 h). Sun et al used magnetic rice husk biochar modified by KMnO_4 for adsorption of Cd^{2+} and Pb^{2+} with maximum adsorption capacities of 79 and 148 mg g^{-1} , respectively [22]. Other modification procedures of RH were presented to obtain better adsorption capacity [23].

The purpose of the present work is to prepare a bio-matrix of MCM-41 silica and RH modified with alizarin red S (RH@MCM-41@ARS) for separation and preconcentration of Pd^{2+} from different samples prior to its determination by FAAS. The main experimental parameters influencing the extraction were optimized to obtain sensitive and selective preconcentration procedure.

2. Experimental

2.1. Reagents and solutions

Double distilled water was through the study. Stock solution of Pd^{2+} (1000 mg L^{-1}) was prepared by dissolving proper amount of PdCl_2 in 100 mL double distilled water acidified with HCl. 3-aminopropyl trimethoxy silane, Cetyltri methylammonium-bromide (CTAB), alizarin red S (ARS), ethylenediaminetetraacetic acid (EDTA) and toluene were purchased from Sigma-Aldrich (St. Louis, MO, USA). Acetate buffer (pH 3.0–7.0) was used to control pH. Solution of 0.5 mol L^{-1} thiourea was prepared by dissolving 3.81 g of thiourea in 100 mL double distilled water and was used as eluent.

2.2. Instrumentation

A Buck Scientific atomic absorption spectrometer (model 210 VCP, East Norwalk, CT, USA) with an air–acetylene flame was used for determination Pd^{2+} (wavelength 244.8 nm and spectral bandwidth of 0.2 nm). Infrared spectrum was measured using KBr discs on Nicolet i10 FTIR spectrometer in the range of 4000 to 400 cm^{-1} . X-ray diffraction (XRD) analysis was carried out using a Philips PW 1390 X-ray diffractometer (Eindhoven, Netherlands). The size and morphology of the biosorbent were investigated by transmission electron microscopy (TEM; Model: JEM 2100, JEOL, Japan). The scanning electron microscopy (SEM) was carried out using JSM 6510LV scanning electron microscope (JEOL, Tokyo, Japan) operated at an accelerating voltage of 20 kV. Energy dispersive X-ray analysis (EDX) carried out by SEM model Quanta 250 FEG (Field Emission Gun). The BET surface area and pores radius were determined using adsorption-desorption isotherms of N_2 gas at 77 K using NOVAtouch™ gas sorption analyzer (Quantachrome Instruments, USA). The pores radius was determined using BJH method as the sample was degassed under vacuum at $200 \text{ }^\circ\text{C}$ for 4 h, using 0.1 g sample prior to surface area measurement [24].

2.3. Preparation of the modified bio-matrix

2.3.1. Preparation of RH@MCM-41

Rice husk was washed several times by distilled water to remove dust and undesirable materials. The washed RH was rinsed with 3 mol L^{-1} HCl with stirring for 3 h at $100 \text{ }^\circ\text{C}$, the solution was filtered and washed several times with distilled water until the filtrate become neutral. The resulting RH was dried and ground to pass through 300 mesh sieve. Five grams of the treated RH was mixed with 2 g of CTAB, 50 mL distilled water and 35 mL ammonium solution and stirring for 10 min. The pH was adjusted to 10 using 5% (v/v) HCl. The mixture was sealed in Teflon vessels and heated at $120 \text{ }^\circ\text{C}$ in microwave oven for 3 h. The mixture was filtered and the separated solid was washed with ethanol and distilled

water then dried at $65 \text{ }^\circ\text{C}$ for 8 h, the solid ground gently using mortar to obtain homogenous particles of RH@MCM-41.

2.3.2. Preparation of RH@MCM-41@ARS

Five grams of RH@MCM-41 were added to 2 mL of 3-aminopropyltrimethoxy silane in 25 mL toluene. The mixture was heated in microwave oven at $120 \text{ }^\circ\text{C}$ in microwave oven for 3 h as described above. The separated solid phase was washed with ethanol and distilled water and heated again in the microwave oven ($120 \text{ }^\circ\text{C}$ for 3 h) with 3.0 g of ARS in 25 mL toluene. The obtained sorbent (RH@MCM-41@ARS, Scheme 1) was separated, washed, dried and characterized by FTIR, XRD, TEM, SEM, and EDX and BET surface area studies.

2.4. General adsorption process

Adsorption of Pd^{2+} onto RH@MCM-41@ARS was investigated by using batch procedure. Certain quantities of RH@MCM-41@ARS (10–100 mg) were added to 5 mL buffer solution (pH 3.0 to 7.0) in fixed volume (50–1200 mL) containing appropriate amount of Pd^{2+} . The mixture was stirred (5–60 min) and filtrated. The concentration of Pd^{2+} in the supernatant was determined by FAAS. The removal % of Pd^{2+} was calculated according to Eq. (1):

$$\% \text{Removal} = \frac{(C_i - C_e)}{C_i} \times 100 \quad \text{Eq. 1}$$

Where C_i and C_e are the initial and equilibrium concentrations of Pd^{2+} (mg L^{-1}).

2.5. Optimization of the adsorption process

To obtain the best adsorption conditions the procedure was optimized using uni-variant strategy as described in the experimental section.

2.5.1. Effect of pH

The effect pH on Pd^{2+} sorption onto RH@MCM-41@ARS was studied in order to obtain the optimum adsorption pH. Fifty mg of RH@MCM-41@ARS were mixed with 5 mL buffer solution (pH 3.0–7.0) and 10 mg L^{-1} Pd^{2+} in a conical flask, then the volume was completed to 100 mL using double distilled water. Mechanical stirring occurred for 20 min at room temperature ($25 \pm 1 \text{ }^\circ\text{C}$) then the solid material was separated from the solutions by filtration. The removal % was calculated according to Eq. (1).

2.5.2. Effect of amount of biosorbent

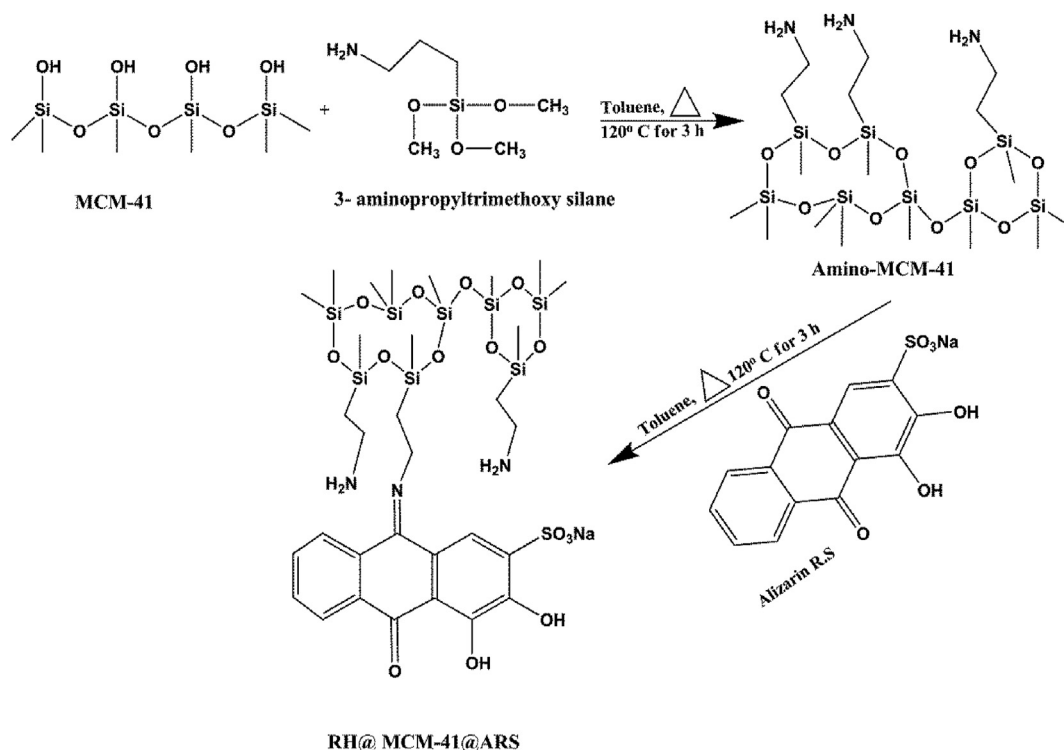
Different amounts of the RH@MCM-41@ARS (10–100 mg) were added in separated conical flasks. To each, 5 mL of buffer solution (pH 4.0) and appropriate amount of Pd^{2+} solution were mixed and the volume was marked to 100 mL using double distilled water. After stirring for 20 min, the solid phase was separated from the solutions by filtration and the removal % of Pd^{2+} was calculated as mentioned above.

2.5.3. Effect of stirring time

Fifty mg of RH@MCM-41@ARS were added to conical flasks containing 5 mL buffer solution (pH 4.0) and Pd^{2+} (10 mg L^{-1}) and the volume was completed to 100 mL using double distilled water. The mixture was stirred for (5–60 min) at room temperature then the biosorbent was separated by filtration. The removal % of Pd^{2+} by RH@MCM-41@ARS was estimated using Eq. (1).

2.5.4. Effect of sample volume

Certain amount of the biosorbent (50 mg), 5 mL of buffer (pH 4.0) and 10 mg L^{-1} Pd^{2+} were mixed in a conical flask and the volume was completed to a fixed volume (50–1200 mL). The content of the flask was stirred for 20 min and the experiment was continued and the removal % of Pd^{2+} as described above.



Scheme 1. Preparation of RH@MCM-41@ARS

2.5.5. Adsorption capacity

Five mL of citrate buffer solution (pH 4.0) was mixed with 50 mg of RH@MCM-41@ARS in a series of conical flasks. Different concentrations of Pd^{2+} (C_i) were added to each flask and the experiment was continued as mentioned above. For each flask the C_e was measured by FAAS and the adsorption capacity (q_e) was calculated from Eq. (2):

$$q_e = \frac{(C_i - C_e)V}{m} \quad \text{Eq. (2)}$$

Where V is volume of solution in L and m is the mass of the solid phase in grams.

2.5.6. Desorption and reusability studies

Fifty mg of RH@MCM-41@ARS were mixed with 5 mL of buffer solution (pH 4.0) and 10 mg L^{-1} of Pd^{2+} and the total volume was marked to 100 mL using double distilled water. The mixture was stirred for 20 min at room temperature. After separation of the solid phase by filtration, the biosorbent was washed three times by double distilled water to remove any excess Pd^{2+} . Desorption occur by shaking the biosorbent with 5 mL of different reagent (in separated experiments) for 5 min. EDTA and thiourea were studied as desorbing agents. The desorption efficiency (D) was determined from Eq. (3):

$$D(\%) = \frac{C_d V_d}{(C_i - C_e)V} \times 100 \quad \text{Eq. (3)}$$

Where:

- C_d : the concentration of Pd^{2+} in the eluate (mg L^{-1})
- V_d : the volume of the eluent (L)
- V : the volume of the solution (L).

To investigate the reusability of the biosorbent, 10 successive adsorption/desorption cycles were done. After each cycle, the biosorbent was rinsed with distilled water to outfit it for the following round. Eq. (1) was used to calculate the removal % after each cycle.

2.6. Application

Water samples were collected during January 2020 from Nile River approximately 1 m deep from the surface in acid-washed polypropylene containers and stored frozen at -20°C until analysis. All water samples were filtered before analysis. About 0.5–1.0 g of clay soil samples (Aswan, Egypt) was homogenized and digested in a TEFLON beaker by 2.0 mL HF and 2 mL HNO_3 . Near dryness, 10 mL of 10% boric acid was added to neutralize excess HF and the final volume was made up to 25.0 mL by distilled water.

3. Results and discussion

3.1. Characterization of modified bio-matrix MCM-41

The XRD pattern of RH, RH@MCM-41, RH@MCM-41@ARS and Pd^{2+} adsorbed on RH@MCM-41@ARS were shown in Figure 1. Intense peak at 23\AA due to presence of carbon and two peaks at 17\AA and 35\AA indicate the presence of SiO_2 . The peak at 2.55\AA in low angle XRD (Figure 1b) indicates the presence of (RH-MCM-41) [25].

Figure 2 shows FTIR spectra of RH and its modified materials. The bands in region between 1200 and 1000 cm^{-1} result from superposition of bond vibrations of C–OH and Si–O. The band at 3431 cm^{-1} is assigned for stretching of OH. Aliphatic C–H bond are located at $\approx 2855\text{ cm}^{-1}$ [26]. The band centered at 2922 cm^{-1} result from methyl group attributed to the presence of lignin [27]. After mobilization of 3-aminopropyltrimethoxy silane, a new band at 1546 cm^{-1} due to stretching C–N bond. Modification by alizarin R.S. leads to appearance of a band at 1655 cm^{-1} attributed to CO stretching vibration. The band at $(1600\text{--}1400)\text{ cm}^{-1}$ is attributed to C–C stretching vibrations in aromatic ring.

The EDX spectra in Figure 3 show intensive bands corresponding to C and Si which are the main components of RH and MCM-41. A new peak was found after adsorption of Pd^{2+} confirming successful uptake process.

The results of TEM suggested that the as prepared bio-matrix is a nano-rod with average diameter of 35 nm as shown in Figure 4a. The rods consist of core-clade structure where RH represents the core surrounded

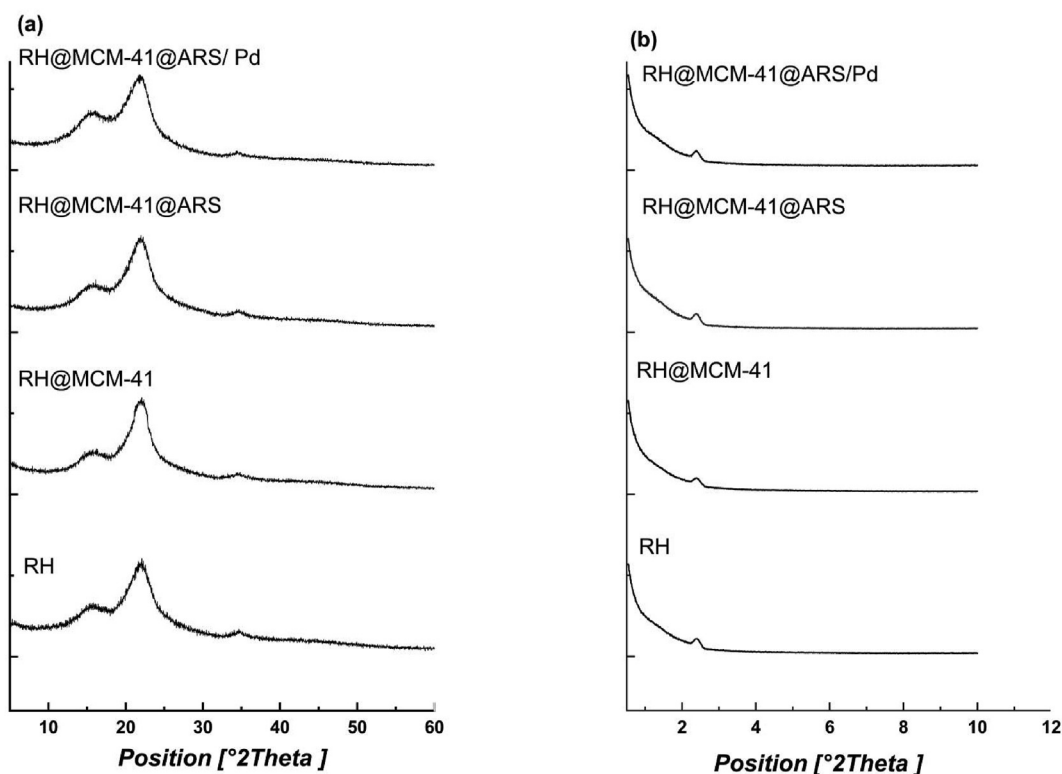


Figure 1. XRD pattern of RH, RH@MCM-41, RH@MCM-41@ARS and RH@MCM-41@ARS/Pd (a) high angle (b) low angle.

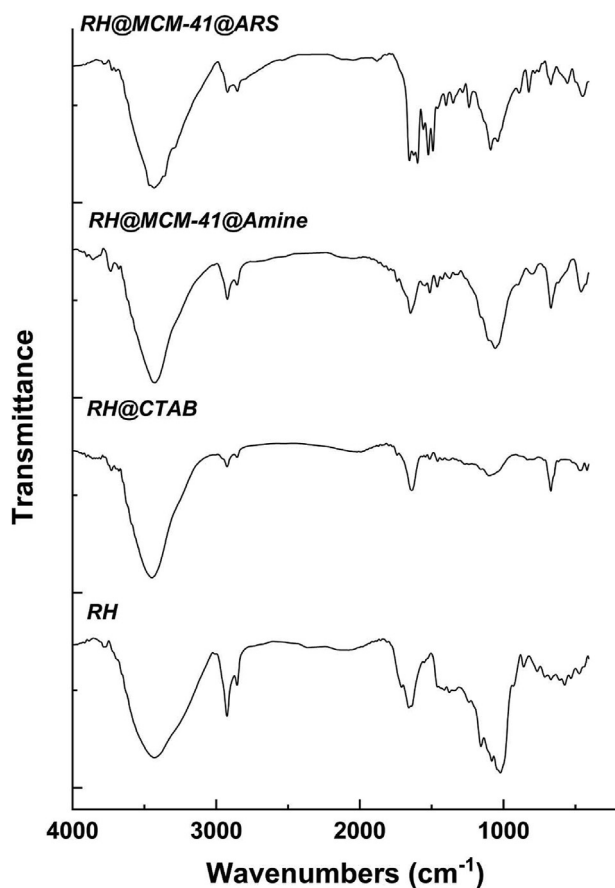


Figure 2. FTIR spectra of RH, RH@MCM-41, RH@MCM-41@Amine and RH@MCM-41@ARS.

by a layer of ARS as in Figure 4b. SEM images (Figure 5) revealed the porous and rough surface of RH@MCM-41@ARS. BET results indicated that the prepared sorbent is mesoporous in nature (average pore radius = 2.4 nm) with surface area of 32 m² g⁻¹.

3.2. Factors affecting the uptake of Pd²⁺ onto RH@MCM-41@ARS

3.2.1. Effect of pH

pH is a key factor for the adsorption of metal ions by SPE because it affect the activity of function groups on surface of the sorbent as well as speciation of the under-investigated ions in the solution [28, 29]. In order to detect the optimum pH at which maximum adsorption of Pd²⁺ occurred, the effect of pH was investigated in the range from 3.0 to 7.0. The results in Figure 6 indicate a strongly dependent relation between uptake of Pd²⁺ onto RH@MCM-41@ARS and pH of solution. The pH dependent adsorption manners of Pd²⁺ can be described easily based on the degree of protonation of active sites exist onto the surface of the adsorbent. The results proved that the extraction of Pd²⁺ increased as the pH increased reaching plateau at pH 4–5, then dropped beyond pH 5. This behavior can be due to the competitive adsorption between H⁺ and Pd²⁺ onto SO₃⁻ active groups and consequently reduced the removal of Pd²⁺ in strong acidic medium, while over pH 5, Pd²⁺ formed metal hydroxide. Simultaneous extractions of Pd²⁺ occurred at pH 4.0 for the next experiments.

3.2.2. Effect of adsorbent amount

The sorbent dose is a major factor that impacts the adsorption process. The quantitative separation of metal ions can't successfully be done when the sorbent dose is low [30]. Oppositely, using large amount of sorbent delays desorption of the retained metal ions by a small volume of eluent, in addition to the possible agglomeration of sorbent particles and the consequent reduction in its adsorption capacity [31]. The relation between amount of RH@MCM-41@ARS and removal % of Pd²⁺ ions was presented in Figure 7. The results showed that the recovery of Pd²⁺ adsorbed increased by increasing the amount of sorbent until reached a

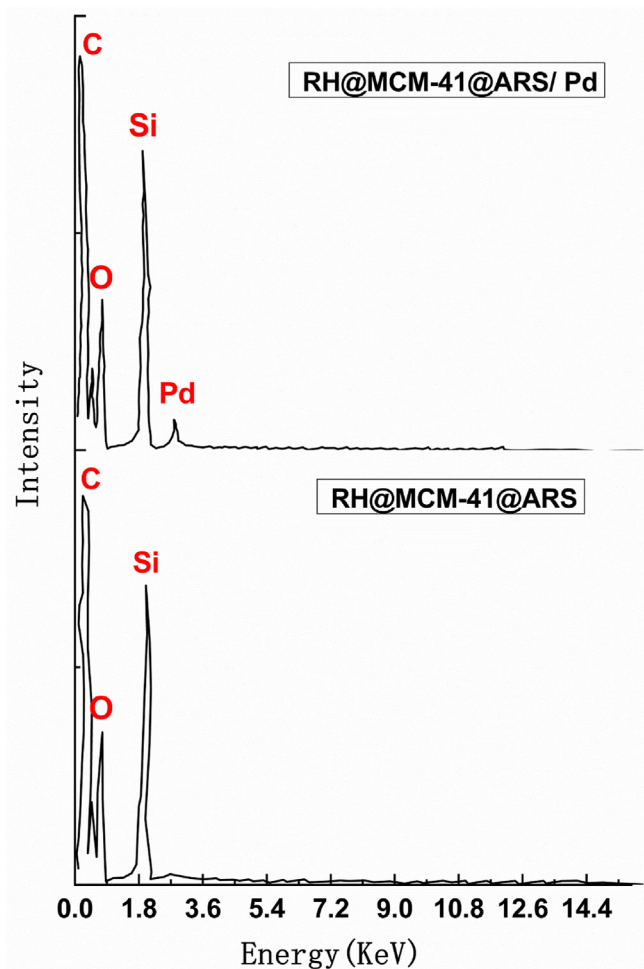


Figure 3. EDX spectra of RH@MCM-41@ARS and RH@MCM-41@ARS/Pd

platform at 50 mg. Over 50 mg of sorbent, non-significant increase in recovery of the metal ions adsorbed (become nearly constant) was observed which confirms almost adsorption of Pd^{2+} on the active sites of RH@MCM-41@ARS. Therefore 50 mg of RH@MCM-41@ARS was chosen for other adsorption process of Pd^{2+} .

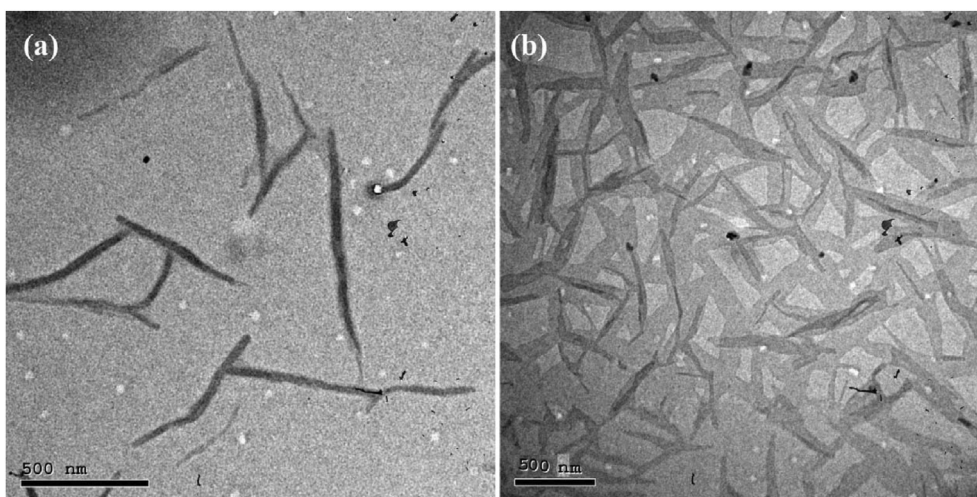


Figure 4. TEM of RH@MCM-41@ARS (a) the prepared bio-sorbent is rod-like shape with average diameter of 35 nm (b) the rods consist of core-clade structure where RH represents the core surrounded by a layer of ARS.

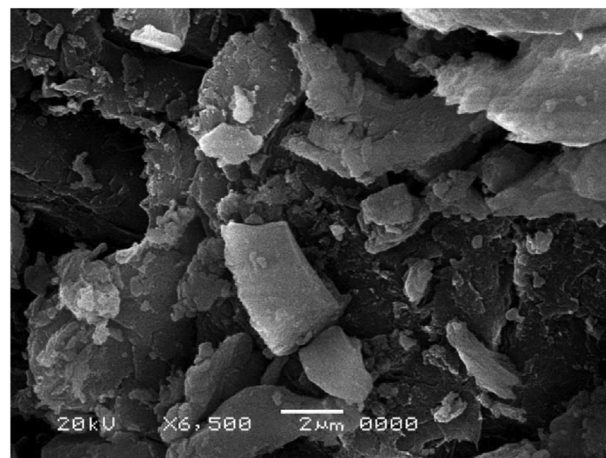


Figure 5. SEM of RH@MCM-41@ARS

3.2.3. Effect of stirring time

Stirring time is a very important factor in the adsorption process as it shows the rapidness of complete adsorption of metal ions onto the surface of biosorbents. Originally, the adsorption is rapid because the active groups on the surface of biosorbent are available for the target metal ions. By time these active groups become occupied by the adsorbed metal ions and the adsorption kinetic turn out to be slow. Accordingly, the effect of stirring time on adsorption of Pd^{2+} onto RH@MCM-41@ARS in the range of 5–60 min at room temperature and pH 4.0. The results pointed out that there was an increase in the adsorption of Pd^{2+} while increasing the stirring time. The adsorption amounts reached equilibrium within 20 min (Figure 8). After that, the increase in extraction of Pd^{2+} was negligible. This value is indicative of rapid kinetics of RH@MCM-41@ARS towards Pd^{2+} compared to other sorbents. Maximum adsorption efficiency of Pd^{2+} was attained after 45 min on a biomass of fungi and yeast [32], 180 min on silk fibroin fiber [33], 30 min onto a montmorillonite derivative [34], 240 min on bayberry tannin immobilized collagen fiber [35] and 120 min on glycine modified crosslinked chitosan resin [36]. According to the obtained results, 20 min has been set as the optimum stirring time for the next experiments.

3.2.4. Desorption studies and effect of sample volume

Different eluents (EDTA and thiourea) were tested for desorption of Pd^{2+} from RH@MCM-41@ARS under the previously stated optimum

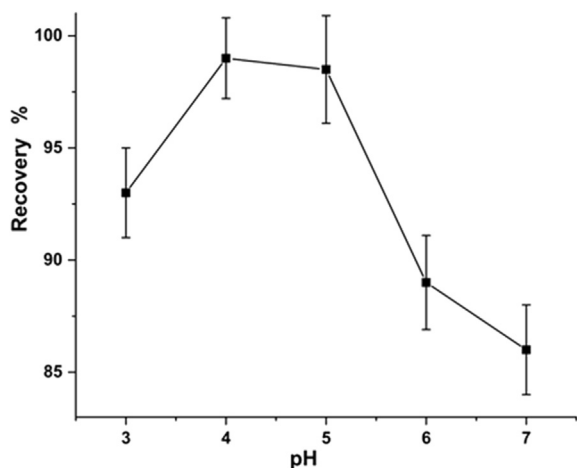


Figure 6. Effect of pH on the adsorption of Pd²⁺ onto RH@MCM-41@ARS (100 mL sample, 50 mg of sorbent, 10 mg L⁻¹ Pd²⁺, stirring for 20 min).

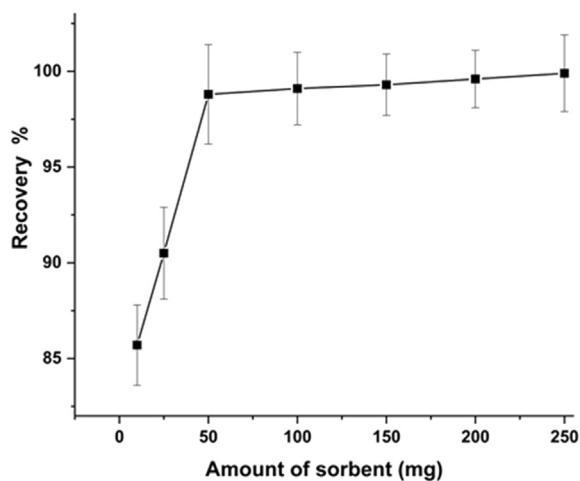


Figure 7. Effect of amount of sorbent (100 mL sample, pH 4.0, 10 mg L⁻¹ Pd²⁺, stirring for 20 min).

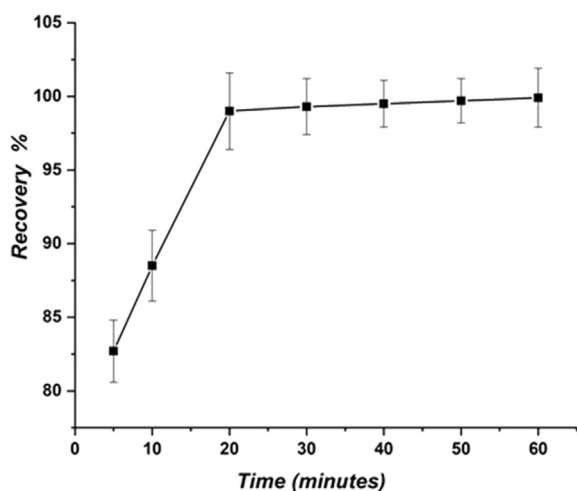


Figure 8. Effect stirring time (100 mL sample, pH 4.0, 50 mg of sorbent, 10 mg L⁻¹ Pd²⁺).

Table 1. Effect of different eluents on desorption of Pd²⁺ from RH@MCM-41@ARS

Eluent	Concentration of the eluent (mol L ⁻¹)	Volume of the eluent (mL)	Recovery (%)
EDTA	0.1	2.5	69.5 ± 4.3
	0.1	5	77.0 ± 3.9
	0.5	2.5	84.9 ± 3.4
Thiourea	0.5	5	93.6 ± 4.0
	0.1	2.5	73.4 ± 3.8
	0.1	5	85.8 ± 4.3
	0.5	2.5	91.5 ± 3.5
	0.5	5	98.6 ± 3.3

conditions. The results in Table (1) show that 0.5 mol L⁻¹ thiourea has the maximum ability to desorb Pd²⁺ from RH@MCM-41@ARS. We avoided the use of acids due to its denaturation effects on the sorbent which can decrease its reusability [37]. Therefore, 0.5 mol L⁻¹ thiourea was used as eluent through the study.

Sample volume ranged from 50 to 1200 mL was tested to determine the maximum volume of sample which gives both high preconcentration factor and recovery. As shown in Figure 9 the maximum sample volume that leads to quantitative extraction (>95%) of Pd²⁺ is 1000 mL and the subsequent preconcentration factor is 200 when 5.0 mL of eluent was applied. By using larger volumes significant decline in the extraction efficiency was noticed.

3.3. Adsorption capacity of the solid phase

Figure 10 displays the adsorption equilibrium isotherms gained from adsorbing Pd²⁺ onto RH@MCM-41@ARS. It is clear that, the sorption capacities toward Pd²⁺ increased rapidly in the beginning, then increased slowly, and attained saturation by the end of the experiment. Langmuir adsorption model was used to represent the data obtained [38]. Langmuir adsorption isotherm model suggests the formation of an ideal, homogeneous monolayer adsorption. The general form of the Langmuir isotherm is:

$$C_e/q_e = C_e/q_m + 1/bq_m \quad \text{Eq. (4)}$$

Where C_e is the equilibrium concentration of Pd²⁺, q_e is the amount Pd²⁺ adsorbed (mg/g), q_m is the maximum adsorption capacity of Pd²⁺ (mg/g), and b is the adsorption constant (L mg⁻¹) that is related to bonding-energy between the adsorbate and the sorbent. By plotting a relation between C_e/q_e against C_e , a straight line was obtained with a slope equals to $1/q_m$ and an intercept equals to $1/bq_m$. The q_m of Pd²⁺ equals 198.2 mg g⁻¹ which is

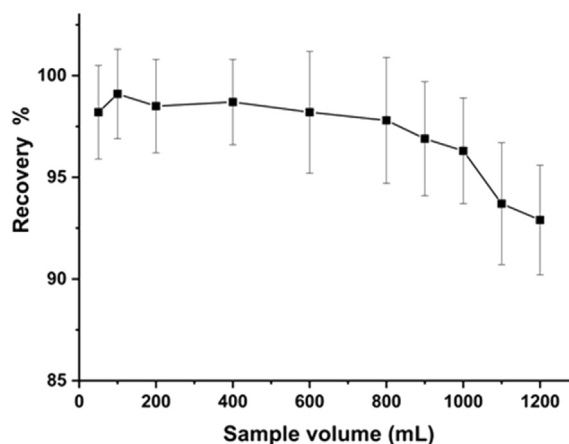


Figure 9. Effect of sample volume (pH 4.0, 50 mg of sorbent, 10 mg L⁻¹ Pd²⁺, stirring for 20 min).

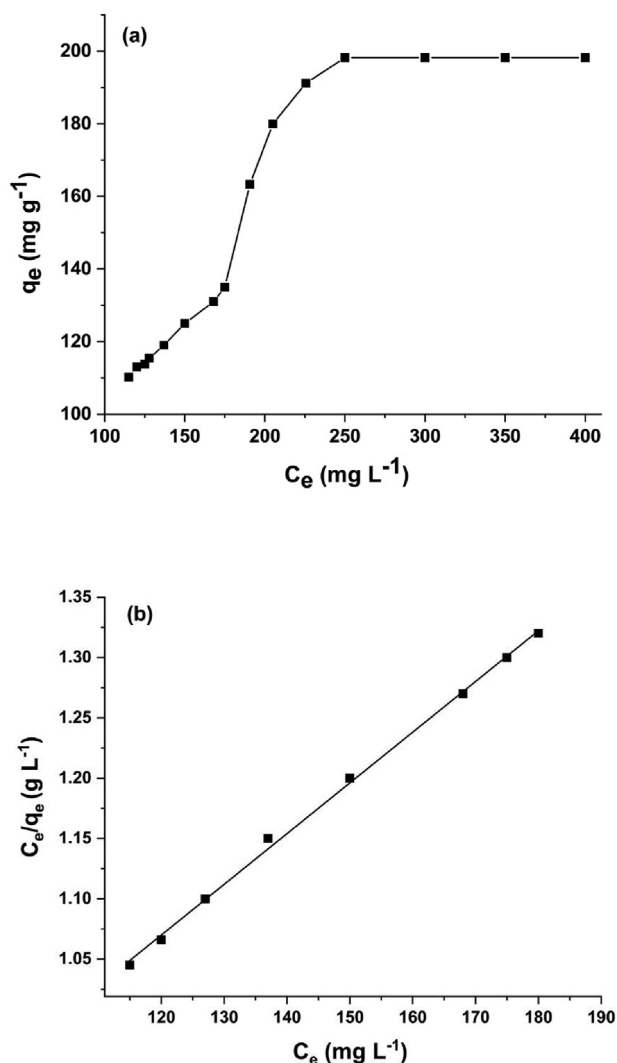


Figure 10. (a) Adsorption isotherm (b) linear Langmuir plots of Pd²⁺ onto RH@MCM-41@ARS

higher than that achieved by other sorbents [10, 39, 40, 41] as shown in Table (2). The results also showed that RH@MCM-41@ARS had greater q_m compared to that of RH@MCM-41 and RH (16.1 and 13.3 mg g⁻¹, respectively). Langmuir adsorption equilibrium constant b equal to 0.0074 mL mg⁻¹ and the correlation coefficient for the adsorption R^2 is 0.998. The Langmuir isotherm can also expressed in term of separation factor or equilibrium parameter, R_L which is defined as:

$$R_L = 1 / (1 + b C_i) \quad \text{Eq. (5)}$$

where C_i is the initial metal concentration. The value of R_L indicates the type of isotherm to be favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear

Table 3. Tolerance limits of potentially interfering ions in determination of 100 $\mu\text{g L}^{-1}$ Pd²⁺.

Interfering ions	Tolerated limit (mg L ⁻¹)
Na ⁺ , Mg ²⁺ , Ni ²⁺ , K ⁺ , SO ₄ ²⁻ ,	4000
Co ²⁺ , Cr ³⁺ , Br ⁻ , SCN ⁻ , HCO ₃ ⁻ , Cd ²⁺	1000
Ba ²⁺ , Pb ²⁺	500
Cu ²⁺ , Fe ³⁺	250
Rh ³⁺	50
Pt ⁴⁺	10

($R_L = 1$), or irreversible ($R_L = 0$) [42]. From our study, R_L value was 0.473 so the adsorption process is favorable.

3.4. Effect of potential interfering ions

The extraction efficiency of Pd²⁺ by RH@MCM-41@ARS was studied under optimum conditions in presence of various concentrations of different ions. The ions considered as an interfering species when it changes the absorbance value of Pd²⁺ by $\pm 5\%$. The results displayed in Table (3) show that most tested ions did not interfere even at high concentrations. So the method described is applicable for the analysis of Pd²⁺ in different samples.

3.5. Reusability of the sorbent

In order to estimate the reusability of RH@MCM-41@ARS, adsorption and desorption cycles were run for 10 consecutive times. The results in Table (4) indicate that the q_m value remains almost constant after the 10 cycles. Therefore; RH@MCM-41@ARS maintained its metal removal efficiency with only $\sim 5\%$ reduction in its efficiency as compared to 20% reduction in the efficiency of oil palm frond biosorbent after four cycles [43] and barley straw biosorbent after three cycles [44]. Also the efficiency of Dalbergia sissoo pods biosorbent reduced by nearly 10% after 10 cycles [45]. These results suggest the better reusability and recoverability potentials, and consequently approving the advantages of using RH@MCM-41@ARS as biosorbent.

3.6. Analytical features and application

The optimized procedure has dynamic linear range from 0.4 to 500 $\mu\text{g L}^{-1}$ and limit of detection (LOD = 3 s/S) of 0.13 $\mu\text{g L}^{-1}$ where s and S are standard deviation of 10 blank determinations and slope of calibration curve, respectively. The precision was determined as relative standard deviation (RSD). The between and within run RSD were 1.9–2.6%. Good recoveries of Pd²⁺ were obtained from analysis of spiked samples indicating accurate procedure as shown in Table (5). Comparison with other SPE procedure [46, 47, 48, 49, 50] for preconcentration of Pd²⁺ in Table (6) revealed that our procedure is superior as it possesses lower LOD and larger q_m .

Table 2. Comparison between maximum adsorption capacity of RH@MCM-41@ARS and other biosorbents.

Method	q_m (mg g ⁻¹)	Ref.
Polyethyleneimine-Functionalized Alumina Nanopowder	97.7	[39]
Poly (N-phenylethanolamine) modified MWCNTs	101	[40]
Cellulose filter paper grafted with polymer chains bearing thiocarbamate moieties	37	[41]
Modified activated carbon	92	[10]
RH@MCM-41@ARS	198.2	Our work

Table 4. Reusability of RH@MCM-41@ARS in adsorption of Pd²⁺.

Cycle no.	1	2	3	4	5	6	7	8	9	10
q _m	198.2	198.0	196.9	196.2	195.1	193.9	192.8	191.5	190.2	189.3

Table 5. Determination of Pd²⁺ in spiked samples after separation and preconcentration using RH@MCM-41@ARS

	Added	Found	Recovery
Sea water (μg L ⁻¹)	0	BDL	-
	2.5	2.45	98.0
	5.0	4.93	98.6
Nile water (μg L ⁻¹)	0	BDL	-
	2.5	2.48	99.2
	5.0	4.98	99.6
Waste water (μg L ⁻¹)	0	BDL	-
	2.5	2.40	96.0
	5.0	4.91	98.2
Clay (μg g ⁻¹)	0	0.026	-
	0.5	0.523	99.4
	1.0	1.019	99.3

BDL = below detection limit.

Table 6. Comparison with other procedure for preconcentration of Pd²⁺.

Adsorbent	Analytical technique	LOD (μg L ⁻¹)	Maximum adsorption capacity (mg g ⁻¹)	Preconcentration factor	Reference
Multi-walled carbon nanotubes modified with 8-aminoquinoline	ICP-OES	10	7.09	Not provided	[46]
Mesoporous silica modified with ammonium (4-chloro-2-mercaptophenyl) carbamodithioate	ICP-AES	1.17	157.2	Not provided	[47]
Glutaraldehyde cross-linked magnetic chitosan nanoparticles (GMCNs)	FAAS	2.8	Not provided	Not provided	[48]
Amberlite XAD-1180 resin	FAAS	0.19	2.4	250	[49]
Thiophene-2-carbaldehyde-modified mesoporous silica	ICP-AES	0.2	5.0	100	[50]
RH@MCM-41@ARS	FAAS	0.13	198.2	200	Our study

4. Conclusion

One of the benefits of this study is the recycling of rice husk to obtain an effective adsorbent that can be used for removal and enrichment of Pd²⁺ from aqueous solution. The prepared solid phase (RH@MCM-41@ARS) exhibits excellent adsorption properties towards Pd²⁺. It processes good adsorption capacity (198.2 mg g⁻¹) as well as is low cost. Quantitative extraction of Pd²⁺ occurred at pH 4.0 using 50 mg of the biosorbent. The present procedure gave accurate and precise results with higher preconcentration factor (200) when compared to other procedures. The biosorbent was recycled easily using 0.5 mol L⁻¹ thiourea and retain its adsorption capacity after 10 adsorption/desorption cycles.

Declarations

Author contribution statement

K. Nabieh: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

W. Mortada, Y. Abou El-Reash: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

T. Helmy, I. Kenawy: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

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Data availability statement

Data will be made available on request.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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