Simple and facile synthesis of amino functionalized hollow core–mesoporous shell silica spheres using anionic surfactant for Pb(II), Cd(II), and Zn(II) adsorption and recovery

Ahmed Mohamed El-Toni, Mohamed A. Habila, Mohamed Abbas Ibrahim, Joselito Puzon Labis, Zeid A. ALOthman

HIGHLIGHTS

- Hollow core silica spheres were prepared by anionic surfactant and ultrasonic waves.
- Textural properties of hollow spheres are tuned by controlling synthesis conditions.
- Surfactant removal by solvent extraction resulted in amino-decorated nanoparticles.
- Coordination of amino group to metal ions is significant in heavy metal removal.

ABSTRACT

In this work, amino functionalized hollow core–mesoporous shell silica spheres (NH2-HCMSSs), which are expected to have a significant tendency for heavy metal removal, are synthesized by ultrasonic assisted soft-templating method using anionic surfactant. Ultrasonic waves, have produced bubbles on which the anionic surfactant micelles have assembled and thereafter the silica nuclei have precipitated to form hollow core structure. Co-structure directing agent, 3-aminopropyltrimethoxysilane (APMS), was used to assist the electrostatic interaction between the partially negatively charged silica particles and the negatively charged surfactant molecules through S’N’T pathway. Upon the surfactant removal by solvent extraction, amino groups of APMS have then functionalized the mesoporous shell of hollow core structure. Various synthesis parameters, such as sonication time, solvent type, and acid concentration, have been investigated to synthesize HCMSSs spheres with superior textural properties (e.g., total pore volume and surface area). Furthermore, the impact of these parameters on the removal of heavy metal cations from polluted water was evaluated accordingly. HCMSSs were characterized by low-angle X-ray diffraction (Lo-XRD), transmission electron microscopy (TEM), and N2 sorption analysis. In this study, the variation of synthetic parameters have led to a considerable increment of the surface area.
1. Introduction

The contamination of water with heavy metal ions is a worldwide environmental problem [1–3]. Many techniques have been used to remove heavy metals including chemical precipitation, electro-flotation, ion exchange, reverse osmosis, and adsorption [4–13]. Traditional adsorbent like chitosan/natural zeolites have been commonly used for the removal of copper ions [14]. Tirtom et al. [15] prepared cross linked chitosan–clay beads for lead ion removal but the low adsorption efficiency limits their applications. Nanomaterials, on the other hand, have been recently used as novel adsorbent to remove heavy metal ions from wastewater. Compared to the traditional ones, nanostructure based adsorbents have exhibited a much higher efficiency and faster rates in water treatment [16–19].

Mesoporous silica nanoparticles are unique versatile materials due to their chemical and thermal stabilities, low toxicity, tunable porosity, and compatibilities with other nanoparticles. The outstanding textural properties of mesoporous silica are good candidate for powerful platform in many applications [20]. Functionalized mesoporous silica nanoparticles with organic functional groups have been considered as the appropriate adsorbents for environmental pollutant removal because they possess high surface area, large adsorption capacity, and can be easily modified with other functional groups (i.e. amino functionalization) [21,22]. Hakami et al. [23] prepared thiol-functionalized silica-coated magnetite nanoparticles (TF-SCMNPs) for mercury removal and recovery. Emadi and Shams [24] functionalized magnetite/silica nanoparticles by immobilization with thiadiazole derivatives for heavy metal removal applications. Tang et al. [25] reported the preparation of amino-functionalized magnetic composite microspheres for the removal of Pb(II) and Cd(II).

Recently, core–shell structured microspheres have been extensively subjected to extensive research due to the combined functionalities of cores and shells with promising potential applications in various fields [26]. More recently attentions were directed for the design and synthesis of core–mesoporous shell based architectures that include hollow [27], solid [28], and rattle-type core–mesoporous shell [29], as well as their applications in drug delivery, catalysis, water-treatment, microwave absorption, protein separation, etc. [30]. Typically ordered mesoporous silica are synthesized using anionic surfactant and co-structure directing agent (CSDA) through a new S–N+I pathway [31], where S stands for surfactant, N stands for CSDA, and I stands for inorganic precursors. During the self-assembly process, the positively charged amine or ammonium sites of CSDA interacts electrostatically with the templating anionic surfactant micelles and the alkoxyalkoxysilane sites of CSDA co-condense with the inorganic precursors. The synthesis of mesoporous silica through the S–N+I pathway are considered more beneficial to the preparation of surface amino-functionalized mesoporous silica after single removal of the anionic surfactant by an acid extraction [32].

Herein, we report a facile and simple synthesis for hollow core–mesoporous shell silica spheres by ultrasonic assisted soft-templating method using anionic surfactant through S–N+I pathway. Upon surfactant removal by acid extraction, amino functionalized hollow core–mesoporous shell silica spheres are then obtained.

The impact of synthesis parameters such as sonication time, solvent type/concentration, acid concentration on formation and textural properties of hollow core–mesoporous shell silica spheres are then investigated. In addition, issues on optimization of adsorption parameters of Pb, Cd, and Zn on HCMSSs are addressed and kinetic and thermodynamic studies are also conducted.

2. Experimental

2.1. Chemicals

N-lauroylsarcosine sodium (Sar-Na), 3-aminopropyltrimethoxysilane (APMS), and tetraethoxysilane (TEOS) were purchased from Sigma–Aldrich. All chemicals were used without further purification.

2.2. Synthesis

2.2.1. Hollow core–mesoporous shell silica spheres (HCMSSs)

1.4667 g (1 mmol) of N-Lauroylsarcosine sodium was dissolved in 25 mL H2O then, 4 mL 0.1 M HCl was added with stirring for 1 h. Thereafter, 0.1 mL of 3-aminopropyltrimethoxysilane (CSDA) was added and stirred for 10 min and then 1.5 mL of TEOS was added to the reaction mixture and stirred for 10 min. The mixture was subjected to ultrasonic waves which are produced from ultrasonic homogenizer (sonic vibro cell, USA) for 4 min (750 W, 20 kHz). Thereafter, the mixture was left for 1 h to relax and finally it was heated at 80 °C for 18 h. The final solid product was recovered by centrifugation, washed with deionized water and dried in an oven at 60 °C for 12 h. The template removal was done by acid extraction to maintain the functionalization of hollow core–mesoporous shell silica spheres with amino groups.

2.2.2. Acid extraction of surfactant from HCMSSs

The surfactant was removed by an acid extraction and the detailed procedure was as follows: 1.0 g as-synthesized sample was stirred in a mixture solution of 100 mL acetonitrile and 10.42 g of 36–38 wt% HCl for 24 h at room temperature. The product was filtered, washed with deionized water and dried at 50 °C.

2.3. Characterization

Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2100F electron microscope (Japan) operated at 200 kV. Powder X-ray diffraction (XRD) patterns were recorded on a PANalytical X’Pert PRO MPD (Netherlands) with Ni-filtered Cu Kα radiation (45 kV, 40 mA). Nitrogen sorption isotherms were measured at 77 K with a Quantachrome NOVA 4200 analyzer (USA). Before measurements, the samples were degassed in a vacuum at 200 °C for at least 18 h. The Brunauer–Emmet–Teller (BET) method was utilized to calculate the specific surface area using adsorption data at the relative pressure range from 0.02 to 0.20. By using the Barrett–Joyner–Halenda (BJH) model, the pore volumes and size distributions were derived from the adsorption branches of isotherms and the total pore volumes (Vt) were estimated from the adsorbed amount at a relative pressure P/P0.
of 0.995. The Fourier transform infrared (FT-IR) spectra were recorded using the Bruker Vertex-80 spectrometer.

2.4. Adsorption of Pb(II), Cd(II) and Zn(II) on amino functionalized HCMSSs

Batch procedures were used to study the adsorption of Pb, Cd, and Zn on HCMSSs in terms of kinetic and thermodynamic as described in Refs. [34,35]. Stalk metals solution (200 ppm) were prepared from nitrate salts, then the other concentrations (100 ppm and 10 ppm) were prepared by dilution. 10 mL of mult-metal cation Pb, Cd, and Zn solution was mixed with 0.01 g of HCMSSs in Erlenmeyer flasks. The mixture was shaken at 150 rpm for a desired time in a thermostatic shaking water bath at 25 °C. By the end of adsorption test, the metal ion solutions were separated by centrifuge. Blank experiments without adding HCMSSs adsorbent were also performed at the same time. The metal ion concentrations were determined by Atomic Absorption Spectroscopy (AAS). The detection limit of AAS for Pb, Cd, Zn is 10, 1, 1.5 Ppb, respectively. However, all the measurements were conducted in the ppm range to ensure the good accuracy of the results. The above mentioned procedure was used also for studying the effect of pH of metal solution in the range from 2 to 6. On the other hand, pH 6 was chosen for the kinetic and thermodynamic studies. The pH of metal ion solution was adjusted by adding drops of very dilute HCl (0.001 M) and/or NaOH (1 × 10−4 M) solutions then monitor the pH change by pH meter till the targeted value is reached.

The adsorption capacity of HCMSSs was evaluated using the following equation:

\[
q_e = (C_0 - C_e) \cdot V / M, \tag{1}
\]

where \(q_e\) is the adsorption capacity (mg/g), \(C_0\) is the initial concentration of metal ion solution, \(C_e\) is the equilibrium concentration of metal ion solution, \(V\) is the volume of the metal ion solution, and \(M\) is the mass of the adsorbent (g).

Optimization of adsorption test was done by studying process parameters such as pH, contact time, and metal cation concentration.

For the recovery of the adsorbed heavy metal ions, the HCMSSs/adsorbed metal ions were mixed with 5 mL of nitric acid (1–3 M) and shaken for 15 min. And finally the metal cation solutions were separated by centrifugation process.

3. Results and discussion

3.1. Synthesis of hollow core–mesoporous shell silica spheres (HCMSSs)

Hollow core–mesoporous shell silica spheres are prepared by ultrasonic assisted soft templating method using anionic surfactant. In this method, ultrasonic waves produced ultrasonic cavitation which in turn produced gas bubbles that acted as the template for the hollow particles [33]. These bubbles are stabilized by the surfactant at the gas–liquid interface as surfactant micelles are assembled around them. Finally the hollow structures are obtained upon electrostatic interaction between the partially positively charged silica particles and the negatively charged surfactant micelles through the assistance of CSDA. The impact of synthesis parameters on hollow core structure formation and its textural properties are then discussed in the next subsections.

3.1.1. Effect of type of solvent

Changing the type of solvent has shown a significant influence on the morphology and size of hollow core–mesoporous shell silica spheres [36]. With the addition of ethanol, hollow spheres were obtained with clear porous structure and thick shell as shown in Fig. 1a. The addition of propanol has caused the formation of mixture of hollow sphere together with mesoporous silica nanoparticles as by-product. It can be noticed also that the formed hollow spheres possessed large particle size ~600 nm with thin shell. Further increase in carbon chain of solvent, through addition of butanol, led to the mixture of hollow spheres and mesoporous silica nanoparticles. However, hollow spheres showed more porous character, smaller size and thicker shell. Finally, by addition of hexanol, the hollow core structure was lost and instead spherical silica lamellar interior was obtained as seen in Fig. 1d. Nitrogen adsorption/desorption isotherms measured at 77 K for hollow core–mesoporous shell silica spherical samples prepared at different solvent types are shown in Fig. 2A. The isotherms exhibited the type IV curves, which are characteristic of uniform mesoporous materials. Textural properties, BET surface area, and total pore volume, were 503.63 m² g⁻¹, 0.866 cc g⁻¹ and 635.84 m³ g⁻³, 1.082 cc g⁻¹ in case of ethanol and butanol addition, respectively as shown in Table 1. It can be seen that, these two solvents have promoted the porous character of HCMSSs, which is in agreement with the TEM results. On the other hand, addition of propanol and hexanol has led to successive reduction of surface area and pore volume of HCMSSs samples. The pore ordering was quite weak in all samples regardless the type of solvent used (Fig. 2B). All the samples have hexagonal pore ordering except sample prepared with hexanol that showed lamellar structure with main peak at 2θ = 2.7. Alteration of porous character and hollow sphere size and shell thickness can be attributed to the significant variation of solubility of TEOS with changing the type of alcohols due to their different carbon chain length and polarity that is expected to affect hydrolysis and condensation rate of silica source, and also influence the silica sphere mesostructure and morphology.

The formation of spherical silica with lamellar structure upon addition of hexanol can be attributed to the lowering of the charge density on the surface of surfactant micelles due to hexanol partitioning into the surfactant micelles. This changed the surfactant micelles packing manner with lower surface curvature, which contributes to the different packing parameters of the micelles and thus finally transformed the hexagonal mesostructure to the lamellar one in the product. Therefore, it could be suggested that hexanol has behaved as the co-surfactant to cause these structural transformations rather than as co-solvent [33].

3.1.2. Effect of ethanol concentration

Various concentrations of ethanol have been studied for their effect on the formation of hollow core–mesoporous shell silica spheres as shown in Fig. 3. In absence of ethanol (i.e., only water is present) a mixture of mesoporous silica nanoparticles and hollow core–mesoporous shell silica spheres were formed (Fig. 3a). It can be seen also that the mesoporous shell was thin and non-uniform. Further increase of ethanol amount from 0.01 to 0.21 g/ml led to the formation of hollow silica spheres and the disappearance of mesoporous silica nanoparticles as shown in Fig. 3b–d. Only at 0.09 g/mL ethanol, spherical hollow silica can be obtained. On the other hand, at 0.21 g/mL, the interior cavity of hollow silica spheres was reduced. It can be noticed also that the particle size of HCMSSs tended to increase with increasing ethanol concentrations up to 0.09 g/mL, then decreases thereafter. \(N_2\) sorption isotherms have been measured for all hollow core–mesoporous shell silica spheres prepared at different ethanol concentrations and were shown in Fig. 4A. The total pore volume was superior in sample prepared in the absence of ethanol due to the presence of a mixture of hollow spheres and mesoporous silica nanoparticles. Sudden loss of surface area and total pore volume was observed at 0.1 g/mL ethanol concentration due the
disappearance of mesoporous silica nanoparticle (by-product). Finally, a textural property was promoted at 0.09 g/mL and suppressed thereafter, which can be correlated to the decrement of the particle size. Low-angle X-ray diffraction patterns of the HCMSSs samples at different ethanol concentrations (as shown in Fig. 4B) displayed that the pore ordering of hollow silica spheres

![Fig. 1. TEM images of hollow core–mesoporous shell silica spheres prepared by anionic surfactant and ultrasonic waves at 0.01 g/mL of (a) ethanol, (b) propanol, (c) butanol and (d) hexanol.](image1)

![Fig. 2. (A) N₂ adsorption/desorption isotherms and (B) low-angle X-ray diffraction patterns of hollow core–mesoporous shell silica spheres prepared by anionic surfactant and at 0.01 g/mL of (a) ethanol, (b) propanol, (c) butanol and (d) hexanol.](image2)

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Solvent type</th>
<th>Solvent conc. (g/mL)</th>
<th>HCl conc. (g/mL)</th>
<th>BET S.A (m² g⁻¹)</th>
<th>Vₑ (cc g⁻¹)</th>
<th>Pore size (nm)</th>
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<tr>
<td>HCMSSs-1</td>
<td>Ethanol</td>
<td>0.01</td>
<td>0.11</td>
<td>613.84</td>
<td>1.190</td>
<td>3.65</td>
</tr>
<tr>
<td>HCMSSs-2</td>
<td>Propanol</td>
<td>0.01</td>
<td>0.11</td>
<td>484.84</td>
<td>0.886</td>
<td>3.87</td>
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<tr>
<td>HCMSSs-3</td>
<td>Butanol</td>
<td>0.01</td>
<td>0.11</td>
<td>635.84</td>
<td>1.082</td>
<td>3.85</td>
</tr>
<tr>
<td>HCMSSs-4</td>
<td>Hexanol</td>
<td>0.01</td>
<td>0.11</td>
<td>522.25</td>
<td>0.688</td>
<td>3.65, 10.00</td>
</tr>
<tr>
<td>HCMSSs-5</td>
<td>No solvent</td>
<td>0.00</td>
<td>0.11</td>
<td>503.63</td>
<td>0.866</td>
<td>3.65</td>
</tr>
<tr>
<td>HCMSSs-6</td>
<td>Ethanol</td>
<td>0.09</td>
<td>0.11</td>
<td>576.85</td>
<td>0.715</td>
<td>3.64</td>
</tr>
<tr>
<td>HCMSSs-7</td>
<td>Ethanol</td>
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<td>0.11</td>
<td>387.21</td>
<td>0.618</td>
<td>3.82</td>
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<tr>
<td>HCMSSs-8</td>
<td>Ethanol</td>
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<td>0.06</td>
<td>322.81</td>
<td>0.354</td>
<td>3.81</td>
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<tr>
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<td>Ethanol</td>
<td>0.09</td>
<td>0.16</td>
<td>450.58</td>
<td>0.847</td>
<td>3.80</td>
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was still weak as clarified from the appearance of only weak (100) peak characterizing the hexagonal mesophase and disappearance of other peaks such as (110) and (200). The formation of mesoporous silica nanoparticles in the absence of ethanol can be explained by the fact that the reduction of ethanol concentration causes the reaction medium to be more concentrated that in turn boost hydrolysis and condensation [37]. Consequently, uncontrolled fast hydrolysis resulted in the formation of non-ordered mesoporous silica nanoparticles with few HCMSS spheres. By addition of ethanol, reduction of hydrolysis and condensation rates allows the interaction of formed silica nuclei with micelles formed around air bubbles that finally produced only single mesophase (hollow core structure).

3.1.3. Effect of acid catalyst concentration

The anionic surfactant, N-lauroylsarcosine sodium salt, should be converted to the corresponding carboxylic form in order to fabricate mesoporous silica shell. The concentration of acid affected the degree of transformation of surfactant that in turn affects the mesophases formation. At 0.06 g/mL HCl, small hollow silica spheres (<100 nm) having irregular shapes were formed (Fig. 5a). At 0.11 g/mL HCl, round and larger size (>100 nm) hollow silica spheres were produced. No hollow silica spheres were obtained after further increment of HCl, but mesoporous silica spheres with radially oriented mesochannels were obtained instead (Fig. S1, see Supplementary information). The N2 sorption analysis (Fig. 6A) showed significant change in textural properties of hollow silica spheres with varying HCl concentration. At 0.06 g/mL HCl, low surface area and porosity of the formed hollow silica spheres indicated a weak porous character of this sample. With acid addition of 0.11 g/mL, the textural properties have been promoted due to the increase of hollow spheres particle size as indicated in the TEM images. Finally, excess acid caused the suppression of textural properties due to the loss of hollow spheres.
structure and formation of radially oriented mesoporous silica spheres. Low-angle X-ray diffraction patterns measured for HCMSSs samples prepared at different acid concentrations are shown in Fig. 6B. Sample with 0.06 g/mL showed no peak in low-angle range confirming the lack of porous character. At 0.11 g/mL HCl concentration, the weak (100) peak appears suggesting the formation of hexagonal mesophase, but with defects since other reflections were absent. After adding 0.16 g/mL HCl, the strong (100) peak clearly appeared which then confirms the hexagonal mesophase formation.

In the synthesis, part of the anionic surfactant can be protonized, and the carboxyl head group will be negatively charged through the neutralization reaction with the amino group of CSDA. The amount of electrostatic interaction sites between the anionic surfactant and APMS plays an important role to control the mesostructure of the silica spheres. At lower pH, more anionic surfactants are neutralized by protons to yield Sar-H, which can interact with APMS. This results in a larger amount of interaction sites of the anionic surfactant and APMS, giving rise to well-ordered mesostructure. In contrast, disordered mesostructure is formed at higher pH [38].

3.2. Evaluation of adsorption capacities of the produced hollow core–mesoporous shell silica spheres (HCMSSs)

The adsorption capacities of some HCMSSs samples (HCMSSs 1–6) for Pb(II), Cd(II) and Zn(II) metal cations were evaluated and adsorption parameters were optimized as well. As shown in Fig. 7, it is clear that all selected samples (HCMSSs 1–6) had a small difference in their adsorption capacities for Pb, Cd, Zn metal cations despite of the variation in their textural properties (their surface area and total pore volume varied from 387.217 m² g⁻¹, 0.818 cc g⁻¹ to 613.84 m² g⁻¹, 1.190 cc g⁻¹). This can be attributed to the fact that amino group (Fig. S2) content, in all tested samples, was almost closer since the APMS content was kept constant during the all synthesis experiment. However, our results are in agreement with the findings of Hao et al. [21] and Najafi et al. [22], indicating that amino groups play an important role in facilitating the adsorption of Pb, Cd and Zn from their aqueous solutions. Since amino groups are concentrated in the mesoporous shell [39] therefore it is expect that the adsorption sites that work effectively are in mesoporous shell. However, the inner cavity and outer surface of hollow spheres to less
extent will also function as adsorption sites due to existence of some amino groups at these sites.

It is also clear from Fig. 7 that same HCMSSs sample showed different adsorption capacities for different metal cations. Hao et al. [40] have reported that the differences of the adsorption capacity for metal ion could be related to the interaction strength between the metal ions and the amino groups in the adsorbent. The radius of Pb²⁺ is much larger than that of Cu²⁺, and the larger the metal ion radius, the greater the polarization. Probably, the interaction strength between the metal ions and the amino groups in the adsorbent is proportional to the metal ion polarization, implying a greater bonding strength with the amino groups for Pb²⁺. This may result in a higher utilization of the amino groups in the adsorbent for Pb²⁺ adsorption, leading to its larger saturation adsorption capacity.

3.3. Adsorption studies

3.3.1. Effect of pH

The influence of pH of adsorption process for Pb(II), Cd(II) and Zn(II) metal cations on HCMSSs samples was examined by varying the solution pH values from 2 to 6. As shown in Fig. S3, the maximum adsorption capacities of HCMSSs-6 for Pb(II), Cd(II) and Zn(II) metal cations were obtained at pH 6. This may be due the presence of highly electronegative atoms, such as nitrogen in amino functional group as well as oxygen, in the OH group in the structure of HCMSSs-6, where the competition is expected between H⁺ and heavy metal ions. Therefore the adsorption capacities are higher in the weak acid medium. This was in agreement with Sakkayar-wong et al. [41], who reported that the pH of the aqueous solution is an important factor that controls the surface charge of the adsorbent and the degree of ionization of the adsorbate in the solution.

3.3.2. Effect of contact time and initial heavy metal ion concentrations

The amount of Pb, Cd and Zn ions adsorbed onto HCMSSs were studied as a function of the contact time. As shown in Fig. 8, it is clear that the adsorbed amount of Pb, Cd, and Zn increases with increasing contact time. The adsorption was rapid in the early stages and then gradually become constant after equilibrium. At this point, the amount of heavy metal cation desorbed from the HCMSSs is in a state of dynamic equilibrium with the amount of the heavy metal cations being adsorbed. The amount of heavy metal cation adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent. The adsorption capacity of Pb, Cd, and Zn was found to be dependent on the initial concentration; it increased for Pb, Cd, and Zn from 6.8 to 194.3, 6.5 to 190.3, and 7.8 to 193 mg/g, respectively by increasing the initial concentration from 10 to 200 ppm. The mass transfer driving force becomes larger as the initial concentration increases and hence resulting in higher capacity of the adsorbate. At low concentrations, the ratio of available surface to initial Pb, Cd, and Zn concentration is large, so the removal becomes independent on the initial concentration. However, in the case of higher metal cation concentrations, this ratio becomes lower and the removal percentage depends upon the initial concentration [42,43].

3.3.3. Kinetic studies

Prediction of the adsorption rate provides important information for designing batch adsorption systems. Information on the kinetics of solute uptake is required to select optimal operating conditions for full-scale batch process.

Different kinetic equations have been implemented to reach the one that fits with our results and expresses how the adsorption process is controlled. Firstly, the pseudo-first-order equation of Lagergren [44] was applied to our results. The equation is generally expressed as following equation:

\[ \frac{dq_t}{dt} = k_1(q_e - q_t), \]  

where \( q_e \) and \( q_t \) are the sorption capacities at equilibrium and at time \( t \), respectively, and \( k_1 \) is the rate constant of pseudo-first-order sorption \( \text{min}^{-1} \). After integration and applying the boundary
conditions, \( q_t = 0 \) to \( q_t = q_e \), at \( t = 0 \) to \( t = t \), the integrated form of Eq. (2) becomes

\[
\log(q_e - q_t) = \log q_e - k_1 t / 2.303.
\]

The pseudo-first-order rate constant, \( k_1 \), can be obtained from the slope of the graph of \( \log(q_e - q) \) versus time \( t \) (Fig. 9). The calculated \( k_1 \) values and corresponding linear regression correlation coefficient values are shown in Table 2. It is clear that the linear regression correlation coefficient value \( R_1^2 \) ranged between 0.87 and 0.96 and the calculated \( q_e \) for Pb, Cd, and Zn uptake is significantly different from the experimental \( q_e \) in the case of all tested initial heavy metal ion concentrations. The results indicate that this model cannot be applied to predict the adsorption kinetics.

Secondly, the pseudo-second-order kinetic rate equation has been applied to the obtained adsorption capacities to seek its fittingness. The equation is expressed in Eq. (4) [45]:

\[
dq_t/dt = k_2 (q_e - q_t)^2,
\]

where \( q_e \) and \( q_t \) are the sorption capacities at equilibrium and at time \( t \), respectively, and \( k_2 \) is the rate constant of pseudo-second-order sorption \( (g/(mg \text{ min})) \). After integration and applying the boundary conditions, \( q_t = 0 \) to \( q_t = q_t \) at \( t = 0 \) to \( t = t \), the integrated form of Eq. (4) becomes:

\[
t/q_t = 1/K_2 q_t^2 + 1/q_e \cdot t,
\]

where \( t \) is the contact time (min), and \( q_e \) (mg/g) and \( q_t^2 \) (mg/g)^2 are the amount of solute adsorbed at equilibrium. Fig. 10 shows the linear relationship of the graph plot of \( t/q_t \) versus \( t \), from which \( q_t \) and \( k_2 \) can be determined from the slope and intercept, respectively.

The calculated \( k_2 \) values and corresponding linear regression correlation coefficient values are shown in Table 2. The results showed that the calculated \( q_t \) for Pb, Cd, and Zn uptake is in agreement with the experimental \( q_e \) and model fittingness was much better than that in case of pseudo first order model. In the view of these results, it can be argued that the pseudo second order kinetic model provided a good correlation for the description of the mechanism of sorption of Pb, Cd, and Zn onto HCMAFs. However, it is reported in the early studies by Mohan et al. [46] and Rostamian et al. [22] that in the case of the pseudo-second order kinetic equation, there are 3 consecutive steps taking place in the sorption of an adsorbate by a porous adsorbent namely: (1) the migration of the metal ions from solution to the surface of the adsorbent; (2) the migration of the metal ions into the pores of the adsorbent; and (3) the adsorption of the metal ions on the interior surface of the adsorbent. And they have concluded that the rate of the reaction is mainly controlled by the first two steps.

Langmuir isotherm was applied for the adsorption results of heavy metal ions onto HCMSSs as shown in Fig. S4 (supplementary information). The adsorption data for our system is well fitted by Langmuir isotherm, the correlation coefficients \( R^2 \) values were 0.96, 0.95 and 0.98 for Pb, Cd, and Zn, respectively. These results confirm the monolayer coverage of adsorbate molecules onto the adsorbent surface, and indicate that the energy of adsorption is constant and there is no transmigration of adsorbate to the plane surface [41].

### 3.3.4. Thermodynamic study

In order to determine whether the adsorption of Pb, Cd, and Zn(II) onto HCMAFs is spontaneous or non-spontaneous process, and also whether it was physical or chemical in nature, thermodynamic parameters, such as change in Gibbs free energy \( (\Delta G^\circ) \), enthalpy \( (\Delta H^\circ) \) and entropy \( (\Delta S^\circ) \), were evaluated using following equations:

\[
\log K_d = \Delta S^\circ / 2.303R - \Delta H^\circ / 2.303RT.
\]

\[
\Delta G^\circ = -RT \ln K_d.
\]

Fig. 9. Lagergren first-order plot for (A) Pb, (B) Cd, (C) Zn adsorption onto HCMAFs (0.01 g) at pH 6.
where $K_d$ is the equilibrium partition constant calculated as the ratio between sorption capacity ($q_e$) and equilibrium concentration ($C_e$), $R$ is the gas constant (8.314 J/mol K) and $T$ is the temperature in Kelvin (K). From Eq. (6), by plotting Log $K_d$ versus $1/T$ (Fig. S5) $D_\text{H}/C_\text{176}$ and $D_\text{S}/C_\text{176}$ values can be obtained.

As shown in Table 3, $D_\text{G}/C_\text{176}$ was in the range from 7.0 to 12.1 kJ/mol while $D_\text{H}/C_\text{176}$ and $D_\text{S}/C_\text{176}$ values were in the range of 9.6–11.7 kJ mol$^{-1}$ and 61.2–75.7 J mol$^{-1}$ K$^{-1}$, respectively. The negative value of $D_\text{G}/C_\text{176}$ indicates the spontaneous nature of Pb, Cd, and Zn adsorption onto HCMSSs. The value of $D_\text{G}/C_\text{176}$, in the range of 0 and –20 kJ/mol, is consistent with electrostatic interaction between adsorption sites and the adsorbing ions (physical adsorption), while a more negative $D_\text{G}/C_\text{176}$ value ranging from –80 to –400 kJ/mol indicates that the adsorption involves charge sharing or transferring from the adsorbent surface to the adsorbing ions to form a coordinate bond (i.e., chemisorptions) [47–49]. $D_\text{H}/C_\text{176}$ (–7.0 to –12.1 kJ/mol) value indicates a typical physical process. On the other hand, the positive value of $D_\text{H}/C_\text{176}$ suggests an endothermic nature of adsorption while the positive values of $D_\text{S}/C_\text{176}$ indicates an increase in the degree of freedom (or disorder) of the adsorbed species. The positive values of $S_0$ show the increased randomness at the solid/solution interface during the adsorption process. The adsorbed water molecules, which are displaced by the adsorbate species, gain more translational energy than is lost by the adsorbate ions, thus allowing the prevalence of randomness in the system. The enhancement of adsorption at higher temperatures may be attributed to the enlargement of pore size and/or activation of the adsorbent surface [50,51].

### 3.3.5. Regeneration and reusability of HCMSSs

The reusability of HCMSSs is crucial in practical applications. Regeneration of HCMSSs was done by desorption of Pb, Cd, and Zn cations from HCMSSs porous structure. The impact of different concentrations of nitric acid was investigated on recovery of Pb, Cd and Zn cation from HCMSSs. As shown in Table 4, it can be seen that 98–99% of Pb, Cd and Zn can be recovered from HCMSSs by using 3 M nitric acid. However, both adsorption capacity (Fig. S6)
with superior textural properties. It was found that ethanol was
been prepared by soft templating method using anionic surfactant
as compared to other adsorbents from other literatures (Table 5).
Comparing HCMSSs adsorption capacity with other studies.
determination by AAS.
concluded that the prepared HCMSSs could be applied for the
shell silica spheres under acidic conditions. Therefore, it can be
pressed after adsorbent usage for 4 times. This can be attributed
and metal cations quantitative recovery% (Table 4) were not sup-
pressed after adsorbent usage for 4 times. This can be attributed
to the stability of amino-functionlized hollow core–mesoporous
shell silica spheres under acidic conditions. Therefore, it can be
concluded that the prepared HCMSSs could be applied for the
separation and preconcentration of Pb, Cd and Zn before their
determination by AAS.
In addition, the prepared HCMSSs showed high adsorption
capacity for the removal of Pb, Cd, and Zn from aqueous solutions
as compared to other adsorbents from other literatures (Table 5).

4. Conclusion

Hollow core–mesoporous shell silica spheres (HMCSSs) have
been prepared by soft templating method using anionic surfactant
and ultrasonic waves. Different synthetic parameters, such as effect
of solvent type and concentration as well as acid concentration,
have been investigated to tailor and modify hollow core structure
with superior textural properties. It was found that ethanol was
appropriate solvent to construct hollow core structure. At 0.09 g/mL ethanol, spherical hollow silica can be obtained with clear
porous structure and thick shell. The concentration of acid affected
the degree of neutralization of surfactant that, in turn, affects the
formation of hollow core structure. The amino functionalized
HCMSSs showed high efficiency in adsorption of Pb(II), Cd(II)
and Zn(II) metal cations due to the coordination of amino group to metal ions which is much superior to physical adsorption due to
textural properties (surface area and total pore volume). The maximum
adsorption capacity was obtained at pH 6 and at contact time of
150 min. Adsorption kinetics was analyzed by pseudo first- and sec-
ond-order equations and the results showed that Pb, Cd and Zn
adsorption onto HCMSSs followed second-order kinetics model.
Thermodynamic parameters; \( \Delta G^0, \Delta H^0 \) and \( \Delta S^0 \) indicated that the
sorption process was spontaneous and endothermic in nature. Effective recovery of Pb, Cd and Zn was obtained with 3 M nitric acid
and the prepared HCMSSs showed reasonable reusability.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in
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