New Trend for Acceleration Solid Phase Extraction Process Based on Using Magnetic Nano-adsorbents along with Surface Functionalization through Microwave Assisted Solvent-free Technique

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The use of a microwave assisted solvent-free technique for silica coating of iron magnetic nanoparticles (Fe_3O_4 -MNPs) and their functionalization with three aliphatic diamines: 1,2-ethylenediamine (1,2EDA), 1,5-pentanediamine (1,5PDA) and 1,8-octanediamine (1,8-ODA), were successfully achieved in a very short time. Only 60 min were needed for the nano-adsorbent modification as compared with more than 1000 min using conventional methods under reflux conditions. Their surface characteristics (observed by TEM, XRD and FT-IR), in addition to Cu(II) adsorption capacities (1.805, 1.928 and 2.116 mmol g^{-1}) and time of equilibration (5 s) were almost the same. Thus, the time required to accomplish the solid phase extraction process is greatly reduced. On the other hand, the phenomenon of the fast equilibration kinetics was successfully extended on using the functionalized aliphatic diamines magnetic nano-adsorbents as precursors for further microwave treatment. Three selective magnetic nano-adsorbents (Fe_3O_4 -MNPs- SiO_2 -1,2EDA-3FSA, Fe_3O_4 -MNPs- SiO_2 -1,5PDA-3FSA and Fe_3O_4 -MNPs- SiO_2 -1,8ODA-3FSA) were obtained *via* the reaction with 3-formyl salicylic acid (3FSA) as a selective reagent for Fe(III). At 5 s contact time, they exhibited maximum Fe(III) uptake equal to 4.512, 4.987 and 5.367 mmol g^{-1} , respectively. Furthermore, modeling of values of metal uptake capacity obtained at different shaking time intervals supports pseudo-second order kinetics.

Keywords Solid phase extraction, magnetic nano-adsorbents, microwave heating, 3-formyl salicylic acid

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Introduction

In analytical methodology, preparing a sample for analysis is an essential step. It must be achieved with due care especially when food, biological and environmental samples are concerned. Since the analyte present in these complex matrices as trace or ultra-trace concentrations, it is necessary to perform not only a selective separation, but also a potential enrichment for the targeted species before its quantification. In fact, solid phase extraction (SPE) is the most commonly used technique for isolation and preconcentration of analytes.¹⁻³ However, its use in its classical mode is now too limited. So, several modifications were explored in the last few years for miniaturization and automation of its various stages. Magnetic solid phase extraction (MSPE) is one of the newest approaches in this context, where, magnetic nanoparticles (MNPs) are used as alternatives to conventional SP-extractors.⁴ The use of magnetic nano-adsorbents in MSPE in comparison to conventional adsorbents introduce the following advantages: very large adsorptive surface area, low diffusion resistance, capability of efficient protection either by inorganic or organic coating, very short equilibrium time and unique advantage of fast separation from large volumes under an external magnetic field.⁵⁻⁷ In addition,

these magnetic nano-adsorbents were found to be cost effective, simple to use and environmentally sound. For instance, an iron oxide magnetic nanoparticle (Fe_3O_4 -MNPs) is the mostly commonly used magnetic adsorbent. This is because its coating by silica layer functions as an ideal shell composite to avoid leaching under acidic conditions and redox reaction as well.^{8,9} Moreover, SiO_2 coating introduces an abundance of surface hydroxyl groups available for reaction with a reagent of choice to obtain a well protective and a selective magnetic nano-adsorbent (Fe_3O_4 -MNPs- SiO_2 -reagent of choice) able to bind selectively with the aimed analyte. Unfortunately, both the coating and modification processes require multiple steps and are time consuming.^{10,11} To maximize the benefits of these magnetic nano materials, efforts should be directed to reduce the time required for achieving these two basic steps. In this respect, microwave assisted synthesis is expected to be promising. This technique has proven to be superior in terms of very short reaction time in comparison with conventional procedures using traditional heating techniques. Moreover, an environmentally benign dimension has been added to microwave heating protocols by performing reactions on solid supports such as silica and alumina under solvent-free conditions.^{12,13}

The aim of this work is to speed up the overall SPE process for Cu(II) uptake by making the most of both the advantages of fast kinetics of MNPs and short reaction time characteristic for microwave heating for synthesizing silica coating MNPs and aliphatic diamines functionalized adsorbents. Comparing the

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results with the same adsorbents synthesized *via* conventional heating^{14,15} as a function of Cu(II) uptake capacities and time of equilibration is also planned to measure the success of the new trend. In fact, diamine functionalized adsorbents are widely used for further reactions with organic reagents to maximize selectivity properties and applications as well. So, it is important to explore if the phenomenon of fast kinetics can be extended. For this purpose the new adsorbents (Fe_3O_4 -MNPs- SiO_2 -1,2EDA-3FSA, Fe_3O_4 -MNPs- SiO_2 -1,5PDA-3FSA and Fe_3O_4 -MNPs- SiO_2 -1,8ODA-3FSA) incorporated of 3FSA as Fe(III) selective reagent¹⁶ were synthesized under microwave conditions. Characterization and their kinetic performance towards Fe(III) uptake is designed to be checked.

Experimental

Materials and methods

Analytical reagent grade ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), ferrous sulphate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and copper chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) were purchased from Aldrich Chemical Co., USA. Tetraethylorthosilicate (TEOS) was purchased from Sigma Alpha, India. Sodium hydroxide, hydrochloric acid, 3-chloropropyltrimethoxysilane (3-CPTMS), 1,2-ethylenediamine (1,2EDA), 1,5-pentanediamine (1,5PDA), 1,8-octanediamine (1,8ODA) were purchased from BDH, UK. Synthesis of 3-formylsalicylic acid (3FSA) was performed as previously described.¹⁶ HCl and NH_4OH used for justifying the pH values were purchased from Aldrich Chemical Co., USA.

Instrumentation

A Fisher Scientific Accumet pH-meter (Model 825, Germany), calibrated against two standard buffer solutions at pH 4.0 and 9.2, was used for pH measurements. A Wrist Action mechanical shaker Model 75 (manufactured by Burrell Corp., Pittsburgh, PA) was used for shaking. Microwave oven (KOR-131G, Korea) emitting 2.450 GHz microwave frequency, 200 – 240 V, 50 Hz, microwave input power: 1350 W, microwave energy output: 1000 W was used for silica coating and functionalization. Transmission electron microscopy (TEM) analysis was obtained using a JSM-5400 LV JEOL (Japan). X-ray diffraction (XRD) analysis was carried out using a Philips Co., PW 1370 X-ray diffractometer with Ni filtered $\text{CuK}\alpha$ radiation (1.5406 Å). Fourier transform infrared (FT-IR) analysis was measured by FT-IR system spectrometer (Perkin Elmer, England) in the range 4000 – 400 cm^{-1} .

Synthesis of iron magnetic nano-particles (Fe_3O_4 -MNPs)

Magnetic nano-particles (Fe_3O_4 -MNPs) were prepared by the co-precipitation method as described in the literature.¹⁷

Silica coating and functionalization of Fe_3O_4 -MNPs using microwave synthesis

Silica coated magnetic nanoparticles (Fe_3O_4 -MNPs- SiO_2). First, 2.0 mL volume of TEOS was mixed homogeneously with 1.0 g of Fe_3O_4 -MNPs. The mixture was irradiated in microwave for 30 min at 20 W power (as appears in the microwave oven scale refers to 20% of the value of the microwave output power). The resulting phase was then washed with hot water (60°C) to remove the residues and excess of TEOS and left to dry in an oven at 60°C to give a dark brown product.

Silica coated magnetic nanoparticles functionalized chloromethoxysilane (Fe_3O_4 -MNPs- SiO_2 -Cl). An amount of 2.0 mL of 3-chloropropyltrimethoxysilane was mixed well with 1.0 g of MNPs- SiO_2 . The mixture was irradiated with

Scheme 1 Synthetic route for microwave functionalized adsorbents.

microwave power of 20 W for 20 min. The resulting phase was then washed with hot water (60°C) to remove the residues and excess silylating agent and left to dry in an oven at 60°C to give a brown product.

Silica coated magnetic nanoparticles functionalized aliphatic diamines (Fe_3O_4 -MNPs- SiO_2 -NH-(CH_2)_n-NH₂, n = 2, 5 and 8). Again, 2.0 mL each of 1,2EDA, 1,5PDA and 0.173 g 1,8ODA was separately mixed well with 1.0 g of Fe_3O_4 -MNPs- SiO_2 -Cl. The mixture was irradiated with power of 20 W for 10 min. The resulting phase was then washed with hot water (60°C) to remove the residues and excess amine and left to dry in an oven at 60°C to give a brown product. The three adsorbents obtained were Fe_3O_4 -MNPs- SiO_2 -1,2EDA, Fe_3O_4 -MNPs- SiO_2 -1,5PDA and Fe_3O_4 -MNPs- SiO_2 -1,8ODA.

Incorporation of salicylic acid moiety via Schiff's base reaction with silica coated magnetic nanoparticles functionalized aliphatic diamine adsorbents (Fe_3O_4 -MNPs- SiO_2 -NH-(CH_2)_n-N-3FSA, n = 2, 5 and 8)

An amount of 1.0 g of Fe_3O_4 -MNPs- SiO_2 -1,2EDA was added to 1.0 g of 3-formylsalicylic acid (3FSA) and ground well, then irradiated with power of 20 W for 10 min. The resulting phase was then washed with hot water (60°C) and left to dry in an oven at 60°C to give a dark green product of the corresponding Schiff base. The same procedure was performed with 1,5PDA and 1,8ODA to form the other two Schiff's bases. They were named Fe_3O_4 -MNPs- SiO_2 -1,2EDA-3FSA, Fe_3O_4 -MNPs- SiO_2 -1,5PDA-3FSA and Fe_3O_4 -MNPs- SiO_2 -1,8ODA-3FSA. A suggested synthetic route for microwave functionalized magnetic nano-adsorbents is illustrated in Scheme 1.

Uptake of Cu(II) and Fe(III) by microwave functionalized adsorbents as a function of pH and shaking time

For uptake of Cu(II) and Fe(III) as a function of pH, 10.0 mg of the selected magnetic nano-adsorbent was equilibrated with

50 mL solution containing 0.5 mL of 0.1 M metal ion adjusted with 0.1 M HCl and 0.1 M NaOH at the pH values from 1.0 – 8.0 for Cu(II) and from 1.0 – 4.5 for Fe(III) in a 100 mL measuring flask. Then, the mixture was automatically shaken for 1 h (3600 s) at room temperature. The combined magnetic nano-adsorbent with adsorbed metal ion was magnetically separated from the solution under an external magnetic field and the metal ion-free solution was transferred to a conical flask. Cu(II) and Fe(III) concentrations were determined using complexometric EDTA titration. For studying the effect of contact time, the same protocol was conducted at optimum pH values for uptake of Cu(II) and Fe(III), and at the selected shaking time (5, 15, 30, 60, 300, 600, 1200, 1800 and 3600 s).

Results and Discussion

Silica coating and functionalization of Fe₃O₄-MNPs using microwave heating under solventless conditions

The use of microwave heating for silica coating and functionalization of Fe₃O₄-MNPs considerably reduced the reaction time compared to conventional heating as shown in Table 1. These results are consistent with the direct interaction

between microwave irradiation and reactants.¹⁸ In this respect, it is well known that in conventional thermal heating, energy is transferred to the sample or reactants through convection, conduction and radiation of heat. In contrast, in microwave heating, energy is directed to materials through molecular interaction with the electromagnetic field. Moreover, in heat

Table 1 Comparison of coating and functionalization processes of Fe₃O₄-MNPs using microwave and conventional heating in terms of reaction time

Type of reaction	Time needed in conventional method/min	Time needed in microwave method/min
Coating of Fe ₃ O ₄ -MNPs with silica	300	30
Functionalization of Fe ₃ O ₄ -MNPs coated silica with aliphatic diamines	720	30
Further functionalization of aliphatic diamines magnetic nano-adsorbents with 3FSA	120 ¹⁶	10
Total time	1140	70

Fig. 1 TEM images of (a) Fe₃O₄-MNPs, (b) Fe₃O₄-MNPs-SiO₂, (c) Fe₃O₄-MNPs-SiO₂-1,8ODA, (d) Fe₃O₄-MNPs-SiO₂-1,8ODA-3FSA.

Fig. 2 X-ray diffraction of (a) Fe_3O_4 -MNPs and (b) Fe_3O_4 -MNPs- SiO_2 .

transfer, energy is transferred due to thermal gradients, but microwave heating is the transfer of electromagnetic energy to thermal energy, rather than heat transfer.¹⁸ So, one can conclude that specific thermal microwave heating is responsible for a speeding up of chemical reactions, consequently reducing reaction time.

Characterization studies (TEM, X-ray and FT-IR spectral analyses)

In order to characterize the morphology and structure of magnetic nanoparticles (Fe_3O_4 -MNPs), silica coated magnetic nanoparticles (Fe_3O_4 -MNPs- SiO_2), aliphatic diamines adsorbents (Fe_3O_4 -MNPs- SiO_2 - $\text{NH}(\text{CH}_2)_n\text{NH}_2$, $n = 2, 5$ and 8) and Schiff's base adsorbents (Fe_3O_4 -MNPs- SiO_2 - $\text{NH}(\text{CH}_2)_n\text{-N-3FSA}$, $n = 2, 5$ and 8), different techniques such as TEM, XRD and FT-IR analyses were used. Figure 1(a) shows the TEM analysis of Fe_3O_4 -MNPs reveals that their nanoparticles have sizes ≤ 14.3 nm (actual size range $9.83 - 14.3$ nm). The condensation of silica on the surfaces of the magnetic cores resulted in a fairly core-shell like structure with range $11.3 - 14.3$ nm (Fig. 1(b)). Figure 1(c) illustrates that the particle size of Fe_3O_4 -MNPs- SiO_2 -1,8ODA was within the range $10.5 -$

15.8 nm.¹⁹ Finally, the particle size of Fe_3O_4 - SiO_2 -1,8ODA-3FSA was within the range $11.4 - 14.7$ nm (Fig. 1(d)). Keeping in mind the advantages of MNPs as previously introduced,⁵⁻⁷ it is important to note that both the adsorbents, aliphatic diamines and its Schiff's bases still retain particles in the nano-size as the parent Fe_3O_4 nanoparticles.

To affirm the Fe_3O_4 and Fe_3O_4 -MNPs- SiO_2 structure, X-ray diffraction patterns (XRD) were employed. As shown in Figs. 2(a) and 2(b), the powder XRD pattern of the synthesized magnetic nanoparticles was close to the pattern for crystalline magnetite Fe_3O_4 .²⁰ Using the most intense peak in Fe_3O_4 nanoparticles XRD pattern, the particle sizes of approximately $9.8 - 18.8$ nm was estimated by the Debye-Scherrer formula,²¹ which was consistent with the results obtained from the TEM image. The characteristic peaks of pure Fe_3O_4 -MNPs nanoparticles at $2\theta/\text{deg.} = 30.1, 35.4, 43.9, 53.4, 57.0$ and 62.6 were also observed for Fe_3O_4 -MNPs- SiO_2 , confirming the presence of the crystalline structure of the magnetite. Moreover, the intensity of the peaks decreases and becomes slightly wide, indicating the occurrence of coating of non-magnetic and amorphous silica shell onto the surface of Fe_3O_4 .

Furthermore, the successful coating of Fe_3O_4 surface by

Fig. 3 FT-IR spectra of (a) Fe_3O_4 -MNPs, (b) Fe_3O_4 -MNPs- SiO_2 , (c) Fe_3O_4 -MNPs- SiO_2 -1,2EDA, (d) Fe_3O_4 -MNPs- SiO_2 -1,5PDA, (e) Fe_3O_4 -MNPs- SiO_2 -1,8ODA, (f) 3FSA, (g) Fe_3O_4 -MNPs- SiO_2 -1,2EDA-3FSA, (h) Fe_3O_4 -MNPs- SiO_2 -1,5PDA-3FSA, (i) Fe_3O_4 -MNPs- SiO_2 -1,8ODA-3FSA.

Fig. 4 Effect of pH on uptake of (a) Cu(II) and (b) Fe(III) by magnetic nano-adsorbents.

TEOS, aliphatic diamines functionalization and Schiff's base formation could also be proven by analysis of their FT-IR spectra, Figs. 3(a) – 3(i). As shown in Fig. 3(a), two stretching vibration bands were located at 581 and 631 cm^{-1} due to Fe-O bond incorporated Fe_3O_4 in nano-scale dimensions.²² They appeared at higher wavenumbers than the characteristic Fe-O bond of bulk Fe_3O_4 at 570 and 375 cm^{-1} .^{22,23} This may be taken as criteria to confirm the presence of Fe_3O_4 as nanoparticles.^{24,25} Figure 3(b) shows the bands of Fe_3O_4 - SiO_2 located at 1157, 1027 and 633 – 589 cm^{-1} corresponding to the stretching vibration of $\nu(\text{Si-O-Si})$, $\nu(\text{Si-OH})$ and $\nu(\text{Si-O-Fe})$, respectively.²⁶⁻²⁹ In the FT-IR spectra, the stretching bands are located at 1639, 1628 and 1641 cm^{-1} for Fe_3O_4 -MNPs- SiO_2 -1,2EDA, Fe_3O_4 -MNPs- SiO_2 -1,5PDA and Fe_3O_4 -MNPs- SiO_2 -1,8ODA, respectively, and these are corresponding to the NH_2 bending of free NH_2 . Moreover, the new additional peaks located in the range of 1563.84 – 1292.04 cm^{-1} were attributed to the aliphatic hydrocarbon chain incorporated amine moiety

$\nu(\text{N-(CH}_2)_n\text{-N})$ stretching vibration,³⁰ Figs. 3(c) – 3(e).

On the other hand, FT-IR spectral analysis for the adsorbents (Fe_3O_4 -MNPs- SiO_2 -NH-(CH_2) $_n$ -N-3FSA) as shown in Figs. 3(f) – 3(i) ensure Schiff's base formation *via* microwave condensation reaction between amino and aldehyde groups.³¹ This is based on: a) the appearance of new bands located around 1580 cm^{-1} due to $\nu(\text{C=N})$ stretching vibration and b) the disappearing of FT-IR band characteristics for free amino group.¹⁶

Performance of microwave functionalized adsorbents for Cu(II) and Fe(III) uptake

Effect of pH. The pH value played a key role in the SPE technique. An appropriate pH value can improve the adsorption efficiency, and also reduce interference from the matrix. Solution pH would change the charge property of the adsorbent and the ionized targets thus influence the adsorption of adsorbent to targets. In this context, the results of uptake of Cu(II) by magnetic nano-adsorbents (Fe_3O_4 -MNPs- SiO_2 -1,2EDA, Fe_3O_4 -

MNPs-SiO₂-1,5PDA and Fe₃O₄-MNPs-SiO₂-1,8ODA) synthesized by microwave assisted solvent-free approach in the pH range 1.0 – 8.0 showed that the adsorption capacity increased with increasing solution pH in accordance with decreasing competition with hydrogen ion concentration, Fig. 4(a). At optimum pH value (pH 7.0), values of Cu(II) uptake were evaluated to be 1.862, 1.995 and 2.190 mmol g⁻¹ using Fe₃O₄-MNPs-SiO₂-1,2EDA, Fe₃O₄-MNPs-SiO₂-1,5PDA and Fe₃O₄-MNPs-SiO₂-1,8ODA, respectively. These values were comparable with the values (1.852, 1.947 and 2.040 mmol g⁻¹) obtained using the same adsorbents synthesized by the conventional approach, respectively.¹⁷ On the other hand, the previous diamines adsorbents act as precursor for Schiff's base formation with the chosen 3FSA as selective for Fe(III). So, the uptake of Fe(III) by Fe₃O₄-MNPs-SiO₂-1,2EDA-3FSA, Fe₃O₄-MNPs-SiO₂-1,5PDA-3FSA and Fe₃O₄-MNPs-SiO₂-1,8ODA-3FSA as a function of pH (Fig. 4(b)) was also investigated. The results showed maximum uptake capacities at pH 3.5 evaluated to be 4.512, 4.987 and 5.367 mmol g⁻¹ for the above adsorbents, respectively.

Equilibration time for Cu(II) uptake using (Fe₃O₄-MNPs-SiO₂-NH-(CH₂)_n-NH₂) and Fe(III) uptake using (Fe₃O₄-MNPs-SiO₂-NH-(CH₂)_n-N-3FSA, n = 2, 5 and 8)

The importance of contact time comes from the need to determine the time required to attain equilibrium and consequently the speed of extraction of the target metal ion.

Cu(II) uptake

The results of Cu(II) uptake (mmol g⁻¹) as a function of shaking time (s) using the three magnetic nano-adsorbents produced *via* microwave synthesis are illustrated in Figs. 5(a) and 5(b). Focusing on mmol g⁻¹ values obtained at four sequential stages including (start, middle and end) of the examined time intervals for Cu(II) uptake using the adsorbents: Fe₃O₄-MNPs-SiO₂-1,2EDA, Fe₃O₄-MNPs-SiO₂-1,5PDA and Fe₃O₄-MNPs-SiO₂-1,8ODA indicate, respectively, the following: 1.805, 1.928 and 2.116 mmol g⁻¹ at 5 s; 1.852, 1.947 and 2.137 mmol g⁻¹ at 300 s (5 min); 1.852, 1.995 and 2.190 at 1800 s (30 min) and 1.862, 1.995 and 2.190 mmol g⁻¹ at 3600 s (60 min). These results clearly indicate that equilibration is very fast and 5 s is quite enough for quantitative uptake. Their percentage increases do not exceed 3.06, 3.36 and 3.38%, respectively, on performing shaking time at 3600 s in comparison to only 5 s. On the other hand, these values are too close or better regarding the same adsorbents produced *via* conventional synthesis recorded to be 1.805, 1.900 and 1.947 mmol g⁻¹, respectively, at 5 s.¹⁷

Fe(III) uptake

Values of Fe(III) uptake as a function of shaking time using the new magnetic nano-adsorbents (Fe₃O₄-MNPs-SiO₂-1,2EDA-3FSA, Fe₃O₄-MNPs-SiO₂-1,5PDA-3FSA and Fe₃O₄-MNPs-SiO₂-1,8ODA-3FSA) are represented as shown in Figs. 5(c) and 5(d). Surprising results were observed, where fixed Fe(III) uptake values (4.512, 4.987 and 5.367 mmol g⁻¹, respectively) were obtained irrespective to the studied time intervals. The above values were recorded at 5 s and continued to 3600 s. This behavior emphasizes that, the very fast equilibrium phenomenon is not only realized but also extended. These new adsorbents were produced after further functionalization of their parent diamines. In addition, the order of Fe(III) uptake values found to be in agreement with increasing aliphatic diamine length Fe₃O₄-MNPs-SiO₂-1,2EDA-3FSA < Fe₃O₄-MNPs-SiO₂-1,5PDA-3FSA < Fe₃O₄-MNPs-SiO₂-1,8ODA-3FSA denote to a significant

Fig. 5 Effect of time (5 – 3600 s) and (5 – 60 s) on uptake of (a, b) Cu(II) and (c, d) Fe(III) by magnetic nano-adsorbents.

space arm effect. However, the absence of this influence with respect to time needed to attain equilibrium can refer to the possibility of its occurrence below 5 s or fraction of a second.

Kinetics of Cu(II) and Fe(III) uptake

The adsorption kinetic data of Cu(II) and Fe(III) measured on magnetic nano-adsorbents were employed in terms of pseudo-second order adsorption equation.^{32–34} Based on this model, the kinetic rate law can be written as follows:

$$t/q_t = 1/k_2 q_e^2 + (1/q_e)t$$

where $k_2 q_e^2$ is the initial adsorption rate/mmole g⁻¹ s⁻¹, k_2/g mmole⁻¹ s⁻¹ is the rate constant of adsorption, q_e /mmole g⁻¹ is the amount of metal ion sorbed at equilibrium, and q /mmole g⁻¹ the amount of metal ion on the surface of the sorbent at any time t /s. The values of $k_2 q_e^2$ and q_e can be obtained from the intercept and slope of plotting t/q_t vs. t as shown in Figs. 6(a) and 6(b), respectively. For Cu(II) uptake, it was found that the theoretical q_e values 1.862, 1.996 and 2.193 mmol g⁻¹ were too close to the experimental values 1.852, 1.947 and 2.137 mmol g⁻¹ recorded at 300 s on using the adsorbents Fe₃O₄-MNPs-SiO₂-1,2EDA, Fe₃O₄-MNPs-SiO₂-1,5PDA and Fe₃O₄-MNPs-SiO₂-1,8ODA, respectively. Regarding shaking time at 300 s, the percentage increase of Cu(II) uptake in comparison to only 5 s (1.805, 1.928 and 2.116 mmol g⁻¹) did not exceed 2.54, 0.97 and 0.98%,

Fig. 6 Pseudo-second-order kinetic plot for the adsorption of (a) Cu(II) and (b) Fe(III) on magnetic nano-adsorbents.

respectively. This confirmed again that 5 s is still quite enough for quantitative uptake. With respect to Fe(III) uptake using the adsorbents $\text{Fe}_3\text{O}_4\text{-MNPs-SiO}_2\text{-1,2EDA-3FSA}$, $\text{Fe}_3\text{O}_4\text{-MNPs-SiO}_2\text{-1,5PDA-3FSA}$ and $\text{Fe}_3\text{O}_4\text{-MNPs-SiO}_2\text{-1,8ODA-3FSA}$, the theoretical q_e values 4.504, 5.000, and 5.376 mmol g^{-1} were in good agreement with the experimental values 4.512, 4.987 and 5.367 mmol g^{-1} recorded at 5 s, respectively. Finally, these results along with r^2 values (0.999 – 1.0) seem to be in harmony with a pseudo-second-order kinetic model.

Conclusions

Due to the increasing need for accelerating the SPE process as a whole, a new trend has been introduced. Its main features can be outlined in the following two concepts:

- 1- Reduction of the time required for surface functionalization of $\text{Fe}_3\text{O}_4\text{-MNPs}$ to act as a parent adsorbent core by utilizing a microwave solvent-less technique.
- 2- Shortening the equilibration time for uptake of the target analyte by adapting functionalized $\text{Fe}_3\text{O}_4\text{-MNPs}$. In addition, making use of their unique characteristics for separation under the influence of an external magnetic field.

By applying the above two concepts, the following were achieved:

- a) A drastic reduction of time from many hours to a few minutes for performing silica coating and functionalization for $\text{Fe}_3\text{O}_4\text{-MNPs}$ using a microwave solvent-free synthesis technique. Moreover, the essential property regarding the nano size of Fe_3O_4 particles (9.83 – 14.3 nm) was still maintained after modification either by aliphatic diamine (10.5 – 15.8 nm) or formyl salicylic acid (11.4 – 14.7 nm) as proven by TEM analysis.
- b) Only 5 seconds were recorded for Cu(II) uptake using the diamine adsorbents ($\text{Fe}_3\text{O}_4\text{-MNPs-SiO}_2\text{-NH-(CH}_2\text{)}_n\text{-NH}_2$, $n = 2, 5$ and 8) demonstrating very fast equilibration.
- c) Continuation of the phenomenon of fast equilibration time on using the adsorbents $\text{Fe}_3\text{O}_4\text{-MNPs-SiO}_2\text{-NH-(CH}_2\text{)}_n\text{-N-3FSA}$, ($n = 2, 5$ and 8) produced via further functionalization of the parent diamines, for Fe(III) uptake.

In view of this mode of fast kinetics and regarding values of nano-size particles of the used adsorbents, one can satisfactorily assume that on using selective magnetic nano-adsorbents with particle size < 15 nm, the studies concerning the effect of contact time intervals of less than 60 s is quite adequate for assessment of the equilibration time required for uptake of the target analyte. In other words, equilibration time ≤ 5 s can be taken as a criteria for a nano-particle size adsorbent < 15 nm.

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