Effect of Aliphatic Diamine Length Functionalized Silica Coated Iron Magnetic Nanoparticles on Metal Capacity and Speed of Cu(II) Uptake from Aqueous Media

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Three solid phase extractors based on silica coated magnetic nanoparticles (Fe₃O₄–SiO₂) functionalized aliphatic diamines were synthesized. The magnetic core of Fe₃O₄ was synthesized first by the sol-gel method, then protected by a layer of silica using tetraethylorthosilicate (TEOS) followed by functionalization using three aliphatic diamines: 1,2-ethanediame (1,2-EDA), 1,5-pentanediame (1,5-PDA) and 1,8-octanediame (1,8-ODA). These steps for producing the targeted three adsorbents Fe₃O₄–SiO₂–1,2-EDA, Fe₃O₄–SiO₂–1,5-PDA and Fe₃O₄–SiO₂–1,8-ODA with different amines spacer arm were followed up using Fourier Transform Infrared (FTIR) spectra and scanning electron microscope (SEM). The effect of the spacer arm length of the diamines on selective binding and metal capacity values of Cu(II) ions was studied as a function of the time needed to attain equilibrium under optimized conditions of pH, mass of adsorbent and initial concentration of Cu(II) ions. The order of increasing metal capacity for copper ions using magnetic nano-adsorbents was Fe₃O₄–SiO₂–1,2-EDA < Fe₃O₄–SiO₂–1,5-PDA < Fe₃O₄–SiO₂–1,8-ODA at 5 s equilibrium time.

Keywords Magnetic nanoparticles, ethylenediamine, copper ions, kinetics, isotherm

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Introduction

Functionalization of various adsorbents for the removal of heavy metal ions from water or wastewater has attracted great research interest in recent years due to the advantages of achieving high capacity and good selectivity. Among the various studies, amine-functionalized adsorbents have been found to be the most common, arising from the strong binding properties of amine to transition metals. The mechanism for the amine functionalization process is mainly based on the use of aliphatic diamine (especially ethylenediamine) where one of the two amine groups is utilized for covalent binding to the desired adsorbent, while the other one could be easily available for coordination to the target analyte via its lone pair of valance electrons. For this reason, aliphatic diamines are widely used as analytical reagents for modification of different solid phases for purposes of selective removal, separation and/or determination of metal ions in an aqueous medium. Recently, applications of magnetic nanoparticles (MNPs) as adsorbing materials have been employed for removal of trace metal analytes from different samples. MNPs are particularly attractive due to their unique properties such as excellent magnetic response to external magnetic field, relatively large surface area and ease of surface modification, which enable them to have a wide range of potential applications in biological, environmental, food analysis, water treatment and analytical chemistry fields as solid phase extractors. However, these nanometer-size materials are not selective for extraction of metal ions in complicated matrices. So, it has been proven that the formation of inert coating materials such as silica on the surface of magnetic nanoparticles can realize their selectivity due to the presence of numerous hydroxyl groups on the surface of silica that can readily link to organic functional groups of metal chelates. Also, it can prevent aggregation of these particles in liquids and improves their chemical stability.

Due to the continuous need for shortening the time required to attain equilibrium along with improving selectivity and metal uptake capacity, the aim of this study was directed toward the synthesis of three new magnetic diamine adsorbents based on silica coated magnetic nanoparticles (Fe₃O₄–SiO₂) functionalized 1,2-ethanediame (1,2-EDA), 1,5-pentanediame (1,5-PDA) and 1,8-octanediame (1,8-ODA). This was performed to explore how the length of the diamine grafted adsorbents could affect the capacity and speed of Cu(II) uptake. So, the novel adsorbents combine the advantages of using nano materials and magnetic separation technique. This combination leads to high uptake capacity values and fast separation of target analytes. Moreover, we also sought to compare the obtained results with their analogues of non-magnetic character to assess the role played by the MNPs.

Experimental

Materials and instruments

Ferric chloride hexahydrate (FeCl₃·6H₂O) with 98% purity and ferrous sulphate (FeSO₄·7H₂O) with 98% purity were purchased from Oxford, India. Tetraethylorthosilicate (TEOS) was purchased from Alpha, India. Sodium hydroxide, 3-chloropropytrimethoxysilane with 97% purity, 1,2-EDA,
1,5-PDA and 1,8-ODA were purchased from BDH, UK. Copper salts, PAN used as indicator for complexometric EDTA titration, HCl and NH₄OH used for justifying the pH values were purchased from Aldrich Chemical Co., USA.

Fourier transform infrared (FTIR) spectra were measured in the range 4000 - 400 cm⁻¹ by spectrometer Perkin Elmer FTIR system Spectrum X (England) with spectral resolution of 1.0 cm⁻¹. Scanning electron microscope (SEM) analysis was obtained using JSM-5400 LV JEOL (Japan). 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 all pH measurements. Wrist Action mechanical shaker Model 75 (manufactured by Burrell Corp., Pittsburgh, PA) was used for the shaking process.

Synthesis of iron magnetic nano particles (Fe₃O₄-MNPs)
Iron magnetic nanoparticles (Fe₃O₄-MNPs) were prepared using the co-precipitation method, by adding 5.0 M NaOH solution into a mixed solution of 0.25 M ferrous sulphate and 0.5 M ferric chloride until obtaining pH 11 at room temperature. The slurry was washed repeatedly with doubly distilled water (DDW). The product was left to settle, then the supernatant was decanted and the nanoparticles were washed at least three times with DDW until obtaining pH 7.023 and then filtered and dried in an oven at 60°C. The final product obtained from this co-precipitation was dense, black and magnetic.

Synthesis of silica-amine iron magnetic nanoparticles
Silica coated iron magnetic nanoparticles (Fe₃O₄–SiO₂). To prepare silica coated iron magnetic nanoparticles, 1.0 g of Fe₃O₄-MNPs was suspended in 100.0 mL of ethanol and DDW (80:20 v/v, %) at 80°C. Then, 2.0 mL of TEOS solution was added drop wise to this suspension under vigorous stirring for 2 h. The pH of this mixture was adjusted at 6.0 and the reaction mixture was further stirred for 3 h. The product was then separated by decantation, washed with DDW, ethanol and finally dried in an oven at 50°C.

Fe₃O₄–SiO₂–Cl
Fe₃O₄–SiO₂–Cl was synthesized via surface reaction of Fe₃O₄–SiO₂ with 3-chloropropyltrimethoxysilane as silylating agent. A 2.0-g amount of Fe₃O₄–SiO₂ and 50.0 mL of toluene were mixed into a 250-mL round flask. A 4.0-mL volume of 3-chloropropyltrimethoxysilane was then added and the mixture was refluxed at 80°C with continuous stirring for 6 h. The resulting Fe₃O₄–SiO₂–Cl was collected and washed with ethanol and diethylether several times and dried in an oven at 50°C until reaching complete dryness.

Fe₃O₄–SiO₂-diamine adsorbents
We used 1,2-EDA, 1,5-PDA and 1,8-ODA to functionalize Fe₃O₄–SiO₂–Cl for the formation of Fe₃O₄–SiO₂–HN–(CH₂)n–NH₂, n = 2, 5 and 8 adsorbents according to the following procedure. First, 1.0 g of Fe₃O₄–SiO₂–Cl was added to 30.0 mL of toluene in a 100-mL round flask. Then, 2.0 mL each of 1,2-EDA and 1,5-PDA and 0.137 g of 1,8-ODA was added and the mixture was refluxed for 6 h at 80°C, decanted and washed by ethanol and diethylether several times and dried at 50°C to complete dryness. A diagram summarizing all the previous steps is given in Scheme 1.

Uptake of copper ions by the batch equilibrium technique
The batch equilibrium technique was used to study the affinity of the new adsorbents for uptake of copper ions. A variety of parameters, including effect of pH, amount of adsorbent, contact time and concentration of copper ions, were studied and optimized as illustrated in the following sections.

Results and Discussion
Characterization of magnetic nano-adsorbents (FTIR spectra and scanning electron microscope)
The FTIR spectra of the parent iron magnetic nanoparticles (Fe₂O₃), silica coated iron magnetic nanoparticles (Fe₃O₄–SiO₂) and magnetic diamine adsorbents (Fe₃O₄–SiO₂–1,2-EDA, 1,5-PDA, 1,8-ODA) were measured in the range 4000 - 400 cm⁻¹ by spectrometer Perkin Elmer FTIR system Spectrum X (England) with spectral resolution of 1.0 cm⁻¹. Scanning electron microscope (SEM) analysis was obtained using JSM-5400 LV JEOL (Japan). 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 all pH measurements. Wrist Action mechanical shaker Model 75 (manufactured by Burrell Corp., Pittsburgh, PA) was used for the shaking process.

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Fe₃O₄–SiO₂–1,5-PDA and Fe₃O₄–SiO₂–1,8-ODA) are shown in Figs. 1(a) – 1(e). Fe₃O₄ spectra, Fig. 1(a), showed two stretching vibration bands at 581 and 631 cm⁻¹ due to Fe–O bond incorporated Fe₃O₄ in nano-scale dimensions, and they were located at higher wavenumbers than the characteristics Fe–O bond of bulk Fe₃O₄ at 570 and 375 cm⁻¹. This shift may be taken as a criteria to confirm the presence of Fe₃O₄ as nanoparticles. In addition, a characteristic peak ranged from 3408 - 3442 cm⁻¹ as shown in Figs. 1(a) – 1(e) due to the intramolecular hydrogen bonding in nano-materials. In the FTIR spectra of silica coated iron magnetic nanoparticles (Fe₃O₄–SiO₂), Fig. 1(b), the characteristic bands of the formed Fe-O-Si bond is mainly overlapped by the presence of the Fe-O bond vibration of magnetic Fe₃O₄. On the other hand, the
FTIR cannot distinguish between the position of Fe–O and O–Si bonding because they are both overlapped in the same frequency region (633 – 589 cm⁻¹) as previously described. The only identified absorption peak at 1027 cm⁻¹ is mainly due to the Si–OH bonding for Fe₃O₄–SiO₂, Fig. 1(b). The FTIR spectral bands of the three magnetic diamine adsorbents at 1632, 1467 and 1384 cm⁻¹ for Fe₃O₄–SiO₂–1,2-EDA; 1630 and 1459 cm⁻¹ for Fe₃O₄–SiO₂–1,5-PDA and 1630 and 1459 cm⁻¹ for Fe₃O₄–SiO₂–1,8-ODA correspond to the NH₂ bending of free NH₃. Figs. 1(c) – 1(e). The outlined results of the FTIR spectra refer to the formation of a silica layer shell on the MNPs core as well as surface functionalization with diamine derivatives, 1,2-EDA, 1,5-PDA and 1,8-ODA for the formation of Fe₃O₄–SiO₂–diamines adsorbents.

The surface morphology of Fe₃O₄-MNPs, Fe₃O₄–SiO₂, Fe₃O₄–SiO₂–1,2-EDA, Fe₃O₄–SiO₂–1,5-PDA and Fe₃O₄–SiO₂–1,8-ODA were analyzed using SEM at the same magnification values, Fig. 2. The microphotographs of Fe₃O₄-MNPs before coating with SiO₂ are characterized by a smooth surface with small particles as shown in Fig. 2(a). The image changed in shape after coating of SiO₂ to the surface of Fe₃O₄-MNPs, Fig. 2(b). On the other hand, Figs. 2(c) – 2(e) of Fe₃O₄–SiO₂–1,2-EDA, Fe₃O₄–SiO₂–1,5-PDA and Fe₃O₄–SiO₂–1,8-ODA, respectively, showed the presence of a more dense and more rough surface with large particles, thus confirming the modification process. Also, this is an important factor facilitating the mass transfer rate of metal ions toward the adsorbent surface and consequently improving its adsorption capacity.

Metal adsorption and uptake properties

Effect of solution pH. It is known that pH is an important factor affecting the removal of cations from aqueous solutions. The dependence of metal sorption on pH is related to both the metal chemistry in the solution and the ionization state of the functional groups of the adsorbent, which affects the availability of binding sites. First, 10.0 mg of the selected magnetic nano adsorbent was added to a mixture of 0.5 mL of 0.1 M of Cu(II) at pH from 1.0 to 8.0 (the pH was adjusted with 0.1 M HCl and 0.1 M NH₄OH solutions). The total volume was completed to 50 mL by DDW in 100 mL measuring flask. The mixed solution was shaken at room temperature by an automatic shaker for the equilibrium time. The combined magnetic nano-adsorbent with adsorbed metal ion was magnetically separated from the solution under an external magnetic field and the unsorbed metal ion solution was transferred to a conical flask and titrated against 0.01 M EDTA using the appropriate indicator.

The adsorption of amino magnetic nano-adsorbents for Cu(II) in the pH range 1.0 - 8.0 was studied at constant temperature and an equilibrium time of 60 min, Fig. 3. With pH from 1.0 to 8.0, it was found that the adsorption capacity increased with increasing solution pH. This revealed the coordination binding where no significant competitive adsorption of hydrogen ions at higher pH is expected. At pH > 8.0 Cu(II) ions precipitated as hydroxide, so no uptake experiments were conducted. To investigate the affinity of the three new adsorbents for copper ions, it could be noted that the sorbents had high adsorption capacities for these ions. The adsorption capacities of Fe₃O₄–SiO₂–1,2-EDA, Fe₃O₄–SiO₂–1,5-PDA and Fe₃O₄–SiO₂–1,8-ODA for Cu(II) at the optimum pH value (pH 7.0) were 1.85, 1.947 and 2.04 mmol g⁻¹, respectively. On the other hand, one could note that the adsorption capacity of copper ions was the highest using Fe₃O₄–SiO₂–1,8-ODA in comparison with the other two adsorbents. This may be explained based on effect of length of the diamine spacer arm. A reasonable explanation for this was that the longer spacer arm might increase the flexibility of the functional group, which would be beneficial for its coordination with metal ion.

Effect of the amount of adsorbent on Cu(II) uptake. The effect of the adsorbent dosage on the uptake of Cu(II) was studied by the batch equilibrium technique using various adsorbent masses (10.0 - 50.0 mg) and while keeping all the other experimental variables constant, viz., pH (7.0), initial concentration (0.001 M),
and contact time (60 min). Figure 3(b) presents the adsorbent weight profile versus Cu(II) adsorbed per unit mass. The adsorbents recorded with 10 mg metal uptake reached 1.852, 1.947 and 2.04 mmol g\(^{-1}\) using Fe\(_3\)O\(_4\)-SiO\(_2\)-1,2-EDA, Fe\(_3\)O\(_4\)-SiO\(_2\)-1,5-PDA and Fe\(_3\)O\(_4\)-SiO\(_2\)-1,8-ODA, respectively. However, it was observed that on increasing the adsorbent weight to 50.0 mg, the metal uptake capacity of Cu(II) at pH 7.0 decreased to 0.433, 0.586 and 0.612 mmol g\(^{-1}\) using Fe\(_3\)O\(_4\)-SiO\(_2\)-1,2-EDA, Fe\(_3\)O\(_4\)-SiO\(_2\)-1,5-PDA and Fe\(_3\)O\(_4\)-SiO\(_2\)-1,8-ODA, respectively. The deterioration in capacity upon increasing the amount of the adsorbent is in agreement with the following formula used for calculating metal uptake capacity:

\[
M_C = (X - Y)/Z
\]  

Where, \(M_C\) = metal capacity value in mmol g\(^{-1}\); \(X\) = initial concentration of metal ion in mmol; \(Y\) = concentration of the unadsorbed metal ion in the filtrate in mmol and \(Z\) = amount of the adsorbent in gram.

**Effect of equilibrium time (kinetic studies).** The importance of stirring time comes from the need for identification of the possible rapidness of binding and removal processes of the tested metal ion by the newly modified adsorbents and obtaining the optimum time for complete removal of the target metal ion. We mixed 10.0 mg of the selected nano-adsorbents with a solution of 0.5 mL of 0.1 M Cu(II) at optimum pH value (7.0). The total volume was completed to 50 mL by DDW in 100 mL measuring flask and automatically shaken for the selected time (5, 15, 30, 60, 300, 600, 1200, 1800 and 3600 s). The combined magnetic nano-adsorbent with adsorbed metal ion was magnetically separated from the solution under the effect of an external magnetic field and the free metal ion solution was transferred to a conical flask and titrated with 0.01 M EDTA by using the appropriate indicator.

It is well known that silica-immobilized organic chelates exhibit constant metal capacity values at short contact times in comparison to modified polymeric adsorbents. Silica was chosen because of its high stability under acidic conditions and inertness to redox reactions. Therefore, it is considered an ideal shell to protect the inner magnetic core. So, in case of using modified silica adsorbents, it is usually recommended to evaluate the uptake value of the target analyte at different time intervals starting from 5 to 60 min. The main goal of our study was to explore the effect of diamine length functionalized silica coated MNPs (Fe\(_3\)O\(_4\)-SiO\(_2\)-HN-(CH\(_2\))\(_n\)-NH\(_2\), \(n = 2, 5\) and 8) on fastness of Cu(II) uptake from an aqueous solution in comparison to their analogues of non-magnetic character (SiO\(_2\)-HN-(CH\(_2\))\(_n\)-NH\(_2\), \(n = 2, 5\) and 8). Thus, values of Cu(II) uptake capacity were determined at very short contact times: 5, 15, 30 and 60 s, in addition to 5, 10, 20, 30 and 60 min. The results of this study are shown in Figs. 4(a) (covering all time interval periods) and 4(b) (focusing on the short time intervals).

Generally, it is evident that Cu(II) uptake by any one of the three adsorbents incorporating MNPs was always higher than its analogue of adsorbents free of MNPs, along with shortening of equilibration time, Figs. 4(c) - 4(e). This may be attributed to the larger surface area of the adsorbents incorporating magnetic particles. Comparing the results as shown in Figs. 4(c) - 4(e) demonstrates the difference in behavior between magnetic and non-magnetic adsorbents. Thus, the three magnetic nano-adsorbents Fe\(_3\)O\(_4\)-SiO\(_2\)-1,2-EDA, Fe\(_3\)O\(_4\)-SiO\(_2\)-1,5-PDA and Fe\(_3\)O\(_4\)-SiO\(_2\)-1,8-ODA exhibit Cu(II) uptake capacity values equal to 1.805, 1.900 and 1.947 mmol g\(^{-1}\), respectively, at 5 s contact time and remain constant up to 60 s. However, very small changes in these values were recorded to be 1.852, 1.947 and 2.04 mmol g\(^{-1}\), respectively, after 300 s and remained constant after 3600 s of shaking. In fact, the percent changes in Cu(II) uptake capacity as a function of contact time from 5 to 3600 s were calculated for the three adsorbents as 2.60, 2.47 and 4.77%, respectively. This means that the time needed to attain equilibrium for uptake of Cu(II) ions using these magnetic nano-adsorbents is very short and 5 s is practically enough as the equilibration period.

On the other hand, under the same experimental conditions the behavior of non-magnetic adsorbents (SiO\(_2\)-1,2-EDA, SiO\(_2\)-1,5-PDA, and SiO\(_2\)-1,8-ODA) was significantly different. There is a gradual increase in Cu(II) capacity along the short time interval periods from 5 to 60 s. At 5 s these values were recorded for SiO\(_2\)-1,2-EDA, SiO\(_2\)-1,5-PDA, and SiO\(_2\)-1,8-ODA to 1.567, 1.662 and 1.731 mmol g\(^{-1}\), respectively. These values increased to 1.710, 1.805 and 1.852 mmol g\(^{-1}\) at 60 s and reached a constant value equal to 1.805 mmol g\(^{-1}\) for SiO\(_2\)-1,2-EDA at 30 min, 1.900 mmol g\(^{-1}\) for SiO\(_2\)-1,5-PDA and 1.947 mmol g\(^{-1}\) for SiO\(_2\)-1,8-ODA at 20 min. Regarding the efficiency of adsorbents under investigation for Cu(II) binding as given from mmol/g values of their Cu(II) uptake as a function of the incorporated diamine length along with equilibrium time, one can concluded that the order of increasing metal capacity for copper ions using magnetic nano-adsorbents is Fe\(_3\)O\(_4\)-SiO\(_2\)-1,2-EDA < Fe\(_3\)O\(_4\)-SiO\(_2\)-1,5-PDA < Fe\(_3\)O\(_4\)-SiO\(_2\)-1,8-ODA.
ODA at 5 s equilibrium time. This order also holds true for non-magnetic adsorbents. The results obtained clearly indicate the role played by the diamine length on values of copper capacities. Furthermore, the effect of the diamine spacer arm on the fastness of Cu(II) uptake was not detectable for magnetic nano-adsorbents compared to non-magnetic ones. However, this effect may occur at time intervals less than 5 s. Unfortunately, we are not able to record this time reliably.

Treating the previous data kinetically is useful in predicting the adsorption rate, which can be used as important information in designing and modeling of the adsorption process. Several adsorption kinetic models have been established to understand the adsorption kinetics and rate-limiting step. The pseudo-second-order rate model is the most well-liked model to study the adsorption kinetics of heavy metals and quantify the extent of uptake. In the present work, adsorption rate of Cu(II) has been analyzed by using pseudo-second-order equations, proposed by Ho and McKay.37,38 The sorption kinetic data of Cu(II) measured on magnetic and non-magnetic adsorbents were analyzed in terms of pseudo-second-order sorption equation. This model is based on the assumption that the adsorption rate is linearly related to the square of the number of unoccupied sites, and thus the kinetic rate law can be written as follows:

\[ \frac{t}{q_t} = \frac{1}{\nu_o} + \left(\frac{1}{q_e}\right)t \]  

(2)

Here, \( \nu_o = k_2 q_e^2 \) is the initial adsorption rate/mmol g\(^{-1}\) s\(^{-1}\), \( k_2/\text{mmol}^{-1} \text{s}^{-1} \) the rate constant of adsorption, \( q_e/\text{mmol g}^{-1} \) the amount of metal ion sorbed at equilibrium, and \( q_t/\text{mmol g}^{-1} \) the amount of metal ion on the surface of the adsorbent at any time \( t/s \). The values of \( \nu_o \) and \( q_e \) can be obtained from the intercept and slope of plotting \( t/q_t \) vs. \( t \) as shown in Figs. 5(a) - 5(f), respectively. The kinetic adsorption data can be processed to understand the dynamics of the adsorption reaction in terms of the order of the rate constant.

As a summary of the kinetic studies of the amine magnetic and non-magnetic nano-adsorbents calculated in Table 1, it was found that the equilibrium adsorption capacity values calculated by the pseudo-second-order model (\( q_e \), calculated) were 1.805, 1.905 and 1.992 for SiO\(_2\)-1,2-EDA, SiO\(_2\)-1,5-PDA and SiO\(_2\)-1,8-ODA, respectively, and 1.85, 1.949 and 2.045 mmol g\(^{-1}\) for Fe\(_3\)O\(_4\)-SiO\(_2\)-1,2-EDA, Fe\(_3\)O\(_4\)-SiO\(_2\)-1,5-PDA and Fe\(_3\)O\(_4\)-SiO\(_2\)-1,8-ODA, respectively. These values were in very good agreement with those obtained from experiments (\( q_e \), experimental), which were 1.805, 1.900 and 1.998 for the non-magnetic adsorbents and 1.852, 1.947 and 2.040 mmol g\(^{-1}\) for the magnetic ones. These data along with the obtained \( r^2 \) values in the range of 0.999 - 1.0 confirm that this kinetic behavior was better fitted with the pseudo-second-order kinetic model.

Effect of concentration of copper ions (adsorption isotherms, maximum metal uptake capacities and binding constants of the new adsorbents).

The relationship between the amount of a substance adsorbed per unit mass of adsorbent at constant temperature and its concentration in the equilibrium solution is called the adsorption isotherm. Adsorption isotherm is important to describe how solutes interact with the adsorbent. Developing an appropriate isotherm model for adsorption is essential to the design and optimization of adsorption processes. Several isotherm models have been developed for evaluating the equilibrium adsorption of compounds from solutions. The more common models used to investigate the adsorption isotherm are Freundlich and Langmuir equations; the experimental results of this study were fitted with these two models.32,39 The sorption isotherms for the uptake of the copper ions under investigation with the new adsorbents were determined by the batch technique at the pH of maximum uptake. Thus, solutions of copper ions in the concentration range \( 2.0 \times 10^{-4} - 2.0 \times 10^{-3} \text{M} \) were...
shaken for 5.0 s with a constant weight of 10.0 mg of the sorbent at optimum pH (7.0). The analysis of the isotherm data is important in order to develop an equation that accurately represents the results. The widely used empirical Freundlich model is based on sorption on a heterogeneous surface and the linear form of this model can be expressed as:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e,$$

(3)

where, $C_e$ and $q_e$ are the equilibrium concentrations of adsorbate in the liquid and adsorbent in mmol mL$^{-1}$ and mmol g$^{-1}$, respectively. $K_f$ and $1/n$ are Freundlich constants (indicators of sorption capacity and intensity, respectively). The constants ($K_f$) and ($1/n$) can be calculated from the intercept and slope of this linear equation, respectively (Table 2). It is clearly indicated that the data is fitted well to the Freundlich model with high correlation factor $\geq 0.95$.

On the other hand, the Langmuir equation is given by the following equation:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{K_{ads}}{q_{max}}.$$

(4)

Here, $q_{max}$ is related to maximum Cu(II) adsorption capacity/mmol g$^{-1}$ and $K_{ads}$ is the Langmuir constant related to the affinity of binding sites/mL mmol$^{-1}$, respectively, and can be calculated from the intercept ($K_{ads}/q_{max}$) and slope ($1/q_{max}$) of the linear plot, $C_e/q_e$ vs. $C_e$. The correlation coefficient showed that the Langmuir model also fitted well with correlation factor $\geq 0.99$, Table 2. Moreover, the essential characteristics of the Langmuir isotherm can also be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, $R_L (0.999)$, which is defined as:

$$R_L = 1/(1 + bC_o),$$

(5)

where, $b = 1/K_{ads}$ is the affinity parameter related to binding energy (indicates the nature of sorption and the shape of the isotherm accordingly) and $C_o$ the initial concentration of analyte. $R_L$ values between 0 and 1 indicate favorable adsorption, while $R_L > 1$, $R_L = 1$, and $R_L = 0$ indicate unfavorable, linear, and irreversible adsorption isotherms, respectively. Generally, the very high binding constants support the adsorption of metal ion from the solution by the solid phase extractor via strong binding with N donor sites. Also, the higher correlation factors indicate that both Freundlich and Langmuir give a better fit to the experimental data and so the nature of adsorption of copper ions.

Table 1 Parameters of pseudo-second-order kinetic constants for binding of Cu(II) using magnetic diamine adsorbents at room temperature

| Adsorbent       | $q_e$ | $K^b$  | $v_o$ | $r^2$ |
|-----------------|-------|--------|-------|-------|
| SiO$_2$-1,2-EDA | 1.805 | 0.057  | 0.186 | 0.999 |
| SiO$_2$-1,5-PDA | 1.905 | 0.049  | 0.180 | 0.999 |
| SiO$_2$-1,8-ODA | 1.992 | 0.039  | 0.156 | 0.999 |
| MNP-SiO$_2$-1,2-EDA | 1.855 | 1.113  | 3.831 | 1.000 |
| MNP-SiO$_2$-1,5-PDA | 1.949 | 1.115  | 4.237 | 1.000 |
| MNP-SiO$_2$-1,8-ODA | 2.045 | 0.133  | 0.556 | 0.999 |

a. mmol g$^{-1}$, b. min$^{-1}$.

Table 2 Parameters of Freundlich and Langmuir isotherm constants for binding of Cu(II) using magnetic diamine adsorbents at room temperature

| Adsorbent       | Freundlich constants | Langmuir constants |
|-----------------|----------------------|--------------------|
|                 | $K_f$ | 1/$n$ | $q_{max}$ | $K_{ads}$ | $R_L$ | $r^2$ |
| MNP-SiO$_2$-1,2-EDA | 16.181 | 0.314 | 0.956 | 2.833 | 5.048 | 0.999 | 0.994 |
| MNP-SiO$_2$-1,5-PDA | 19.055 | 0.318 | 0.952 | 3.155 | 4.596 | 0.999 | 0.995 |
| MNP-SiO$_2$-1,8-ODA | 54.200 | 0.462 | 0.985 | 3.831 | 4.697 | 0.991 | 0.991 |

a. mmol/g.

Fig. 5 Pseudo-second-order kinetic plot for the sorption of Cu(II) on (a) SiO$_2$-1,2-EDA, (b) SiO$_2$-1,5-PDA, (c) SiO$_2$-1,8-ODA, (d) Fe$_3$O$_4$-SiO$_2$-1,2-EDA, (e) Fe$_3$O$_4$-SiO$_2$-1,5-PDA and (f) Fe$_3$O$_4$-SiO$_2$-1,8-ODA.
on the adsorbents is more compatible with these models.

Comparison of the time of equilibrium and uptake capacities of heavy metal ions using the new magnetic diamine adsorbents with other magnetic ones

The proposed magnetic nano-adsorbents were compared to a variety of recent adsorbents reported in literature for the determination of Cu(II). The distinct features are summarized in Table 3. The new modified magnetic adsorbents described in this work showed high equilibrium binding capacity of Cu(II) and reduced time to reach the equilibrium (5 s) compared to the other adsorbents mentioned in this Table. This may be argued to the nature of the amine used, its structure and its concentration on the surface. In this context, aliphatic diamine used to functionalize silica coated magnetic nanoparticles with different spacer arm length are flexible enough for uptake of Cu(II) freely from a solution with no steric hindrance. This may lead in part to high copper uptake capacity along with fast kinetics.40 Moreover, the nature of the parent solid phase with the synergistic effect of their own functional groups should not be neglected.40

Conclusions

In this study, the surface of nano-magnetic iron oxide was successfully modified by silica, and then functionalized by covalent binding to three aliphatic diamines. The produced magnetic nano-adsorbents with the general formula Fe3O4-SiO2-\(\text{HN-(-(CH}_2\text{)}_n\text{-NH}_2\), \(n = 2, 5 \text{ and } 8\), were characterized by FTIR and SEM analyses, certain incorporated selectivity properties and good metal adsorption behaviors. The experimental controlling parameters affecting the Cu(II) ions uptake were studied and optimized and the results confirmed the heavy dependence on reaction pH, adsorbent dosage, contact time and Cu(II) ions concentrations. The percent changes in Cu(II) uptake capacity as a function of contact time from 5 to 3600 s were calculated for the three magnetic nano-adsorbents Fe3O4-SiO2-1,2-EDA, Fe3O4-SiO2-1,5-PDA and Fe3O4-SiO2-1,8-ODA to be 2.60, 2.47 and 4.77%, respectively. This means that the time needed to attain equilibrium for uptake of Cu(II) ions using these magnetic nano-adsorbents is very short and 5 s is practically enough as the equilibration period. Also, it was concluded that Cu(II) uptake capacity values by the three magnetic nano-adsorbents were always higher than their analogous non-magnetic ones, along with shortening of equilibration time. The results obtained depicted the rule played by MNPs. It is recommended on studying the effect of contact time on the uptake of metal analytes using magnetic nano-adsorbents to start at time intervals less than 60 s.

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