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Silica Nanoparticles Modified by a Schiff Base Ligand; Preparation and Their Potential for Removal of Heavy Metal Ions from Water Samples

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***Abstract*— Bulk (silica gel) and nanometer silica, and their corresponding modified particles with a Schiff base binding moiety were prepared and their applications as adsorbents for Cu, Pb, Cd, Co, Ni and Zn ions were investigated. The Schiff base ionphore anchored on the silica particles was 3-methoxy salicylaldimine propyl triethoxy silane. The effect of parameters influencing the efficiencies of the studied adsorbents such as aqueous phase pH, shaking time, amount of sorbent, temperature and initial concentration of the investigated metal ions were assessed and discussed.**

It is shown that the modification affects significantly the adsorptive characteristics of the sorbent. The modified adsorbent shows to be selective adsorbent towards copper and lead ions. Comparison of the modified bulk silica gel and the corresponding nanoparticles reveals that, the later does not show a significant enhancement for uptaking the studied metal ions with respect to former. The advantage of applying the modified nanoparticles was that the more rapid kinetics with respect to the bulk modified sorbents. For the modified bulk and nanoparticles the graphical correlation of various adsorption isotherm models like, Langmuir, Freundlich and Tempkin have been carried out. The adsorption of these metal ions has been found endothermic. The kinetic studies suggest the process following pseudo second order kinetics.

***Keywords*— Modified silica nano-particles, Schiff base, removal, heavy metals.**

I. Introduction

The pollutions created by heavy metals are serious environmental problem in the world [1]. This provokes the removal of these ions from wastewater being the subject of extensive industrial research [2]. In addition, the recovery of some of heavy metals from secondary sources may be important from economical point of view [3].

Nowadays, nanometer materials play substantial role in metal ion separation studies owing to their special physical and chemical properties. The potential of these materials in removal of various biomolecules [4], organic [5] and inorganic [6] species is vastly investigated.

Schiff base ligands bearing nitrogen/oxygen donor atoms have been shown to exhibit interesting ionophoric properties, in particular towards heavy metal ions [7].

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Following to our investigations on the ionophore properties of Schiff base receptors [8] and studies on the application of modified silica nanoparticles [9], this report concerns on the application of bulk silica gel (MS) and silica nanoparticles (MNS) modified by a Schiff base ligand, named 3-methoxysalicylaldiminepropyltriethoxysilane (Fig. 1) for removal and separation of Cu, Pb, Co, Ni, Zn and Cd ions from aqueous solutions. The parameters affecting their adsorption properties have been investigated and discussed. The results were compared with those unmodified bulk silica gel and nanoparticles.

II. Experimental

A. *Materials*

All the chemical used and bulk silica gel particles (0.063-0.200 mm) were from Merck. Unmodified nanoparticles were purchased from the Iranian Nanomaterials pioneers Co., APS 20-30 nm. Modification of silica particles were realized according to the procedure reported in the literature [10]. Stock solutions of the metal ions (1000 ppm) were prepared by using corresponding nitrate salts. Working solutions were prepared by suitable dilution of the stock solutions with distilled water. Apparatus

B. *Apparatus*

FT-IR spectra were recorded on aUnicam (Matson 1000) spectrometer. Th pH adjustments were performed by a Metrohm (model 780) digital pH-meter equipped with a combined glass electrode. A Varian FAAS model 220 AA was used for ion measurements. Separation sorbent and aqueous solutions was assisted by high speed centrifuge (Sigma 3-30K). The SEM photograph was taken with Philips XL30 scanning microscope.

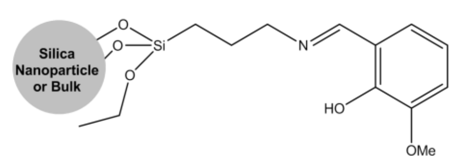

Figure 1. Structure of the modified adsorbents.

C. *Adsorption procedure*

The absorption experiments were carried out in stoppered plastic vessels using appropriate amounts of the modified adsorbent in 20 ml of sample containing Cu, Pb, Co, Ni, Zn and Cd ions (20 mg/l) in 20°C. It is confirmed that the absorption equilibrium was reached after 50 min and 20 min magnetically stirring, in case of MS and MNS, respectively. After separation of the phases by centrifugation (at 20000 rpm), the concentration of cations remaining in the aqueous phase was measured using FAAS.

III. Results and discussion

Condensation of aminopropyltriethoxysilane and 2-hydroxy-3-methoxy benzaldehyde in methanol produced 3-methoxysalicylaldiminepropyltriethoxysilane $(EtO)_3SiCH_2CH_2CH_2N{=}C{-}C_6H_4(OH)(OCH_3)$. Refluxing this product with bulk (silica gel) and nanometer silica, in toluene results modified particles shown in Fig. 1. These products have been characterized by using their FT-IR spectra. The confirmation of the structure of the target adsorbent was realized by comparing of these data with those reported elsewhere [18]. The amount of grafted imine showed that the 3-methoxysalicylaldimine loading in modified nanoparticles was 0.34×10^{-3} mol imine/g of nanosilica and it was 0.57×10^{-3} mol imine/g of silica gel for modified silica gel. The SEM photograph was taken to examine the morphology and surface structure of the adsorbent at the required magnification at room temperature. It shows the modified nanoparticle have rough structure.:

A. *Effect of pH on the adsorption process*

Competitive adsorption of Cu, Pb, Co, Ni, Zn and Cd ions (initial concentration 20 mg/l) on bulk (silica gel) and nanometer silica, and their corresponding modified particles with the Schiff base binding moiety (MS and MNS, respectively) was studied at different pH values in the range 2-5.5. The results show the pH dependency of adsorption process with four adsorbents (Fig. 2). The modified adsorbents was selective to Cu(II) and lead ions.

It is noteworthy that whereas the modification of bulk (silica gel) and nanometer silica affects slightly the removal of other ions, a remarkable enhancement in uptake of Cu(II) and Pb(II) ions is presented by the modified bulk (silica gel) and nanometer silica particles. It is seen that the metal adsorption enhances with pH values and ensure the solubility of metal ions, experiments were carried out at pH<6. This can be described by considering the competition between H^+ ions and metal ions for adsorbing on the surface of adsorbent at low pH values.

With respect to the data of CHN analysis that showed modification of silica nanoparticles is less than (bulk) silica gel, lower uptake percentage in case of modified silica nanoparticle is acceptable.

A maximum value of Cu(II) ions uptake (~57%) was observed by using modified bulk silica particles at pH values higher than 5. Thus pH 5 was selected for further experiments.

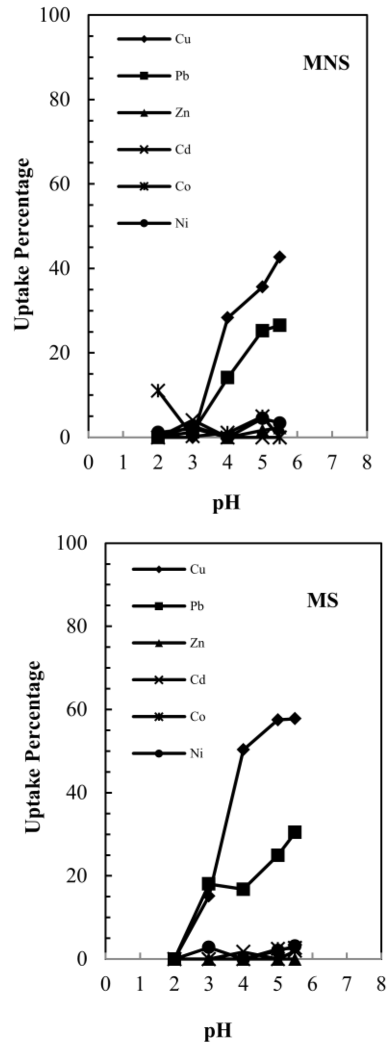

Figure 2. Effect of pH on the competitive sorption of the studied ions onto (a) modified bulk silica gel and (b) modified silica nanoparticles.

B. *Amount of sorbents*

To test the effect of amount of adsorbent on the process, a series of experiments was performed by using 0.025-0.2 g of the modified adsorbents (Fig. 3). It was found that an amount of 0.1 g modified bulk (silica gel) and 0.15 g modified nanometer silica particles can quantitatively removed copper ions from the sample solutions. However, a quantity of 0.2 g of the modified bulk (silica gel) and nanometer silica particles adsorbent is able to uptake about 89 and 77 percent of lead ions, respectively.Avoid combining SI and CGS units, such as current in amperes and magnetic field in oersteds. This often leads to confusion because equations do not balance dimensionally. If you must use mixed units, clearly state the units for each quantity that you use in an equation.

C. *Shaking time*

The adsorption of metal ions from aqueous solutions, adjusted at pH 5, on the MS and MNS particles (0.075 g) was

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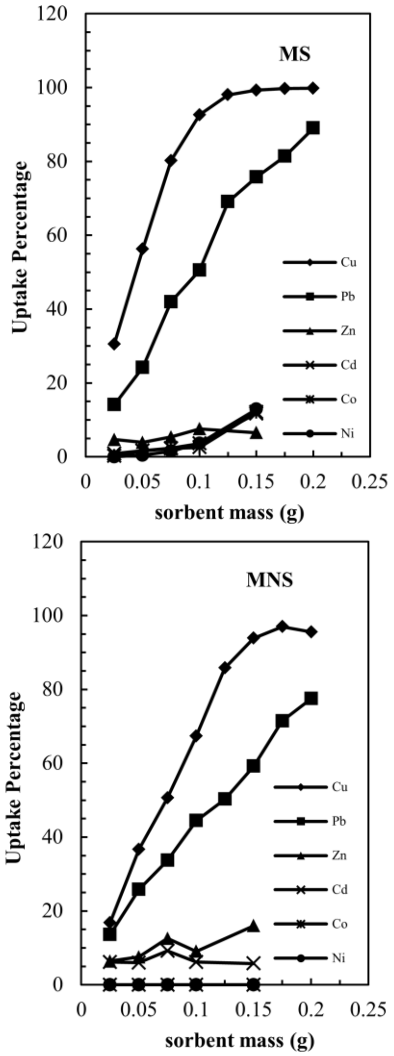

Figure 3. Effect of the amount of (a) modified bulk silica gel and (b) modified silica nanoparticles on sorption efficiency.

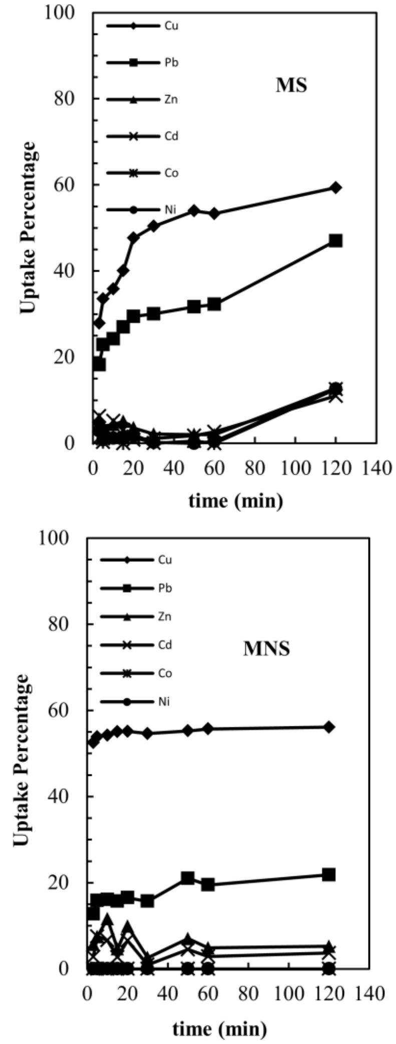

Figure 4. Time dependency of the adsorption process of a mixture of metal ions by the (a) modified bulk silica gel and (b) modified silica nanoparticles.

studied at different shaking time in the range 3-120 min (Fig. 4). The results indicate that within 30 min. of shaking, ~50% and ~30% of Cu(II) and Pb(II) ions, respectively, were removed by MS from aqueous solution. In similar experimental conditions, 55% of Cu(II) and 16% of Pb(II) ions were removed after 10 min. of shaking by using MNS. This shows more rapid adsorption kinetics of copper and lead ions on MNS with respect to that of MS. A shaking time of 50 min. for MS and 20 min. for MNS was selected for following the experiments.

D. Initial concentration of metal ions

The capacity of the process can be monitored by the study of amount of maximum metal ions adsorbed by a given amount of the adsorbent. This variable was tested by removal of the studied metal ions from their mixture by 0.15 g of adsorbent at pH 5 (Fig. 5). The results show a decrease in the percentage removal of Cu(II) and Pb(II) ions for both sorbents.

This observation can be attributed to the relative decrease in adsorbing sites by increasing the amount of metal ions.

E. Temperature dependency of the process

Depends on the adsorption mechanism, the processes can be affected by temperature. To assess the effect of this parameter, the removal of Cu, Pb, Co, Ni, Zn and Cd ions from their mixture by the modified bulk SiO_2 and modified nanoparticles was examined in the range 20-70°C (Fig. 6). The process efficiency for MS is augmented by increasing temperature up to 70ºC except for Cu(II) ions which process efficiency approximately is constant. In the case of MNS sorbent, the process efficiency for all metal ions except Pb(II), by increasing temperature, is constant.

These observations can be explained by considering both chemical and physical adsorption mechanisms for the proposed process.

F. Desorption process

Four aqueous solutions (each 20 ml) containing mixture of Cu, Pb, Co, Ni, Zn and Cd ions (20 mg/l) were magnetically

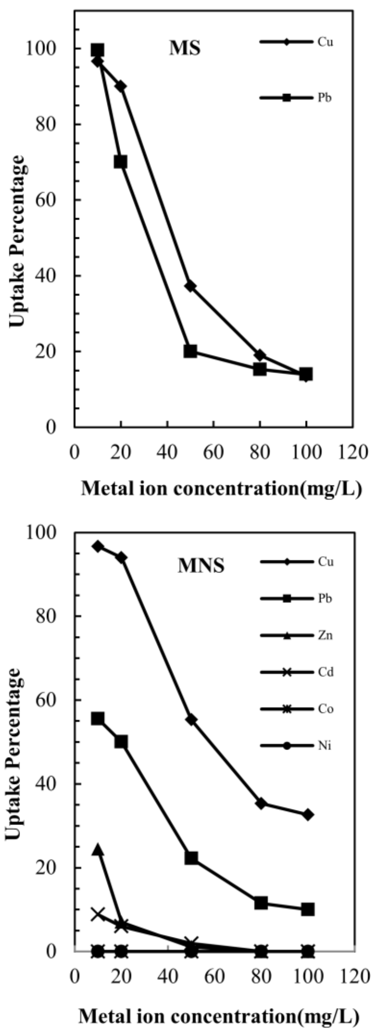

Figure 5. Effect of metal ion concentration on the adsorption of Cu(II) and Pb(II) ions onto (a) modified bulk silica gel and (b) modified silica nanoparticles.

stirred with 0.075 g of the MS and MNS, for 50 min. and 20 min., respectively, at room temperature (20°C). The loaded adsorbents were filtered-off and then were contacted with 5 ml of nitric, hydrochloric and sulfuric acids (0.1 M) and distilled water, separately. After that, nitric acid (0.1, 0.5 and 1 M) for MS sorbent and hydrochloric acid (0.05 and 0.1 M) for MNS sorbent was examined. It was found that the adsorbed ions can be quantitatively stripped by contacting the loaded adsorbents with 5 ml of nitric acid (0.1 M) and hydrochloric acid (0.1 M) in case of MS and MNS, respectively.

G. ***Applications***

According to the obtained data, the removal efficiency of the proposed method from different water samples is tested. A given amount of metal ions (each 20 mg/l) was added to tap water, mineral water and molten snow samples. The pH of these solutions was adjusted to 5 and 0.2 g of modified adsorbents was added. These mixtures were magnetically stirred for 20 and 50 minutes in case of MNS and MS, respectively. The analysis of the solution showed the

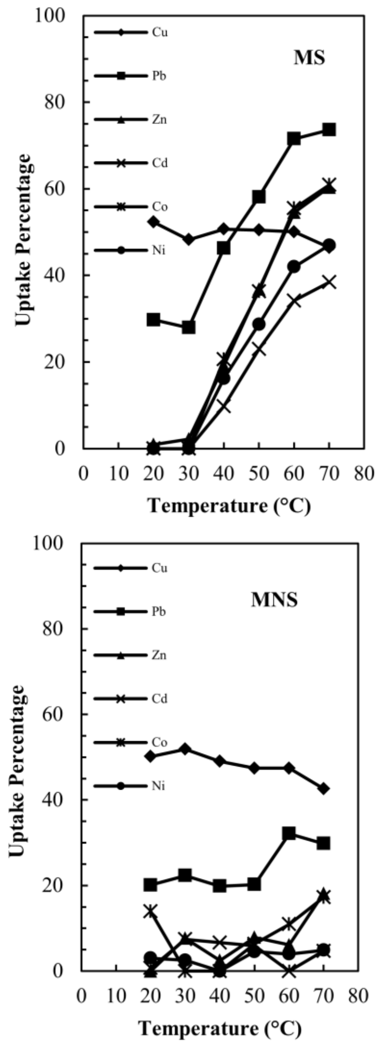

Figure 6. Effect of temperature on sorption efficiency of metal ions onto (a) modified bulk silica gel and (b) modified silica nanoparticles.

quantitatively removal of copper and lead ions. This reveals that the matrix of the selected sample does not affect the process efficiency.

H. ***Kinetics and isotherms of the adsorption processes***

In order to investigate the mechanism controlling the adsorption processes, pseudo first-order, pseudo second-order, power function and simple Elovich kinetic models [11] were examined. Considering the evaluated values of correlation coefficients, the experimental results were well described by the pseudo second-order kinetic model. This model provided an impressive and comparable correlation for the adsorption of ions with respect to the other models.

In order to specify the models characterizing the sorption isotherm three conventional model i.e. Langmuir, Freundlich and Temkin models [12] were used and applied to the experimental data.

Comparison of the R^2 values results selecting the appropriate adsorption isotherm model describing the adsorption process of the studied ions by the modified adsorbents. This comparison reveals the adsorption process isotherms of copper and lead ions to be more suitably described by the Langmuir model for MS, and the adsorption process of these ions on MNS is better described by Langmuir and Temkin models, respectively. In addition the evaluated R_L, in the Langmuir model, confirm the favorable uptake of metal ions by the examined sorbents.

IV. CONCLUSIONS

Both of the modified sorbents, MS and MNS, show better ability especially towards Cu and Pb ions with respect to the unmodified bulk silica gel and silica nanoparticles.

The adsorption kinetics on modified nanoparticles was faster than that of bulk modified ones. Although the adsorption efficiency of both of the modified adsorbents was comparable.

The modified sorbents show different kinetic and thermodynamic behavior.

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