Simultaneous removal of heavy metals from wastewater using
modified sodium montmorillonite nanoclay

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Abstract

In this paper, sodium montmorillonite nanoclay particles were modified by 3-
aminopropyltrimethoxysilane using physical vapor deposition method and applied for
simultaneous removal of Cd, Zn, Pb and Ni heavy metals from wastewater samples. Experiments
were performed in both batch and column systems. Several parameters influencing removal
efficiency such as pH, contact time, amount of adsorbent, interfering ions, flow rate of sample
passage and eluent solvent were evaluated and optimized. Results showed that the adsorption
isotherms obeyed from Langmuir isotherm for all heavy metals. Also, interfering ions does not
influenced the removal efficiency. Finally, modified nano clay was successfully could remove all
heavy metals from real wastewater sample to near completeness.

Keywords: Nano clay; Heavy metals; Wastewater treatment; Adsorption

INTRODUCTION

Today, pollution of wastewater with chemical contaminants such as heavy metals
(HMs) and radioactive materials is one of most important raised concerns. Development
of industries, population growth and inadequate wastewater disposal caused more heavy
metals enter into the environmental aquatic media.1 Heavy metals in environmental
aquatics cause serious problems with human health. They may correspond to adverse
health effects include Hepatorenal necrosis, Bone marrow Suppression, Pulmonary
Edema, impair production of red and white blood cells, cardiac depression, increase
cancer risk, LoQTS, painful neuropathy. These ions can be removed from aqueous
samples using several techniques such as precipitation,2 ion exchange,3 membrane
filters,4 electrochemical deposition5 and adsorption.6 Adsorption methods are widely
applied for treatment of water and wastewater that contaminated with heavy metal ions
because of simplicity, low cost, high removal efficiency, flexibility, easy operation and maintenance, regeneration and reusing properties.  

For this purpose, many researchers are focused on finding new adsorbents with high surface area and low cost preparation. Nano material adsorbents have unique properties such as good mechanical, thermal and electrical properties. Also, they contain very large surface area with tunable pore dimensions and topologies which facilities their physicochemical properties for adsorption studies. The porous structure of nano materials can create well adsorptive sites to adsorb pollutants such as heavy metals. In recent years, different types of nano materials such as carbon nanotubes, nano-alumina, sodium titanate nanofibers, polymer-modified magnetic nanoparticles and other nano sorbents were applied for adsorption and removal of heavy metals from real aqueous samples. Natural clays are belonging to low cost adsorptive substances that have high adsorption capacity; among them, sodium montmorillonite (MMT) is a natural clay with chemical and mechanical stability, layered structures and large surface area for adsorption of guest species.  

In this research, sodium montmorillonite nanoclay particles were modified using physical vapor deposition method with 3-aminopropyltrimetoxysilane (APMS) and applied for simultaneous removal of Cd, Zn, Pb and Ni heavy metals from wastewater samples. Both batch and column studies were carried out for studying adsorption process and all affecting parameters on adsorption were studied and optimized.
**Experimental**

**Reagents and materials**

Stock standard solution of Cd, Zn, Pb and Ni heavy metals \((1000 \text{ mg.L}^{-1})\) was purchased from Merck KGaA (Darmstadt, Germany). Sodium montmorillonite nanoclay particles were purchased from Sigma-Aldrich Co. (MO, USA). All chemicals were of analytical grade and used without further purification. 3-aminopropyltrimethoxysilane (APMS) compound, supplied by Merck was utilized to surface-modification of MMT. Working standard solutions of analytes were prepared daily with dilution of stock standard solution.

**Apparatus**

A graphite furnace atomic absorption spectrometer (GFAAS, model GFA 7000, Shimadzu, Kyoto, Japan) was used for the determination of heavy metals. With a model 630 Metrohm (Switzerland) pH meter, pHs were determined. Scanning electron microscopy (SEM) observations were performed on a 20 kV MIRA 3-TESCAN (Czech Republic) scanning electron microscope after using a gold coating. A Fourier transform infrared (FTIR) spectrometer PerkinElmer (Bucks, UK) was applied employed for qualitative spectra interpretations as well as for structure elucidation. The powder X-ray diffraction (XRD) investigations were performed on a Bruker instrument (model D8 advance, Germany).

**Removal procedure**

In order to study the efficiency of simultaneous removal of heavy metals by sand, two techniques of batch and column adsorption techniques were used for their adsorption; and for both, parameters affecting adsorption were optimized. An aqueous standard solution
containing 10 μg.L\(^{-1}\) of a mixture of heavy metals was used for this purpose. For studying the effect of interfering ions, different amounts of several salts including sodium nitrate, potassium nitrate, calcium nitrate, sodium chloride and sodium sulfate were added to the mixed solution individually.

For batch removal studies of HMs, 10.0 mL of standard solution was added to a test tube containing 10 mg of sorbent and mixture was vortex stirred for 30 min at room temperature. To investigate the adsorption isotherm, a suspension of 5 mg of adsorbent in each single metal ion solution (5–50 mg.L\(^{-1}\)) was prepared and stirred for 45 min. The solid adsorbent was then separated by centrifugation at 3500 rpm for 5 min. All experiments were repeated at least three times.

For column removal, a 10 mL polyethylene column was packed with appropriate amount of nanoclay and 20 mL of pH adjusted solution of mixture of HMs was passed through it. Flow rate of solution passage was adjusted by means of a valve at the bottom of the column using a vacuum manifold (Supelco, USA). Fresh nanoclay powder was used for each experiment. Again, each experiment was performed at least in triplicates. For finding the extraction efficiency, residual HMs concentrations in the solutions after removal were determined by GFAAS and removal efficiency of HMs was calculated using eq. 1:

\[
\text{Removal efficiency (\%)}: \left( \frac{C_0 - C_f}{C_0} \right) \times 100 \quad (\text{eq. 1})
\]

Where \(C_0\) and \(C_f\) are initial and equilibrium concentration of HMs (mg.L\(^{-1}\)), respectively.

To obtain the best performance of the adsorption process for simultaneous removal of four target HMs and achieving satisfactory efficiency in the shortest possible time, several parameters influencing adsorption were studied and optimized while all target compounds were exist in the solution. Parameters studied were the amount of sorbent, pH of sample
solution, effect of contact time, ionic strength of the sample solution, and initial concentration of each analyte. Each experiment was run in triplicates.

**Modification of MMT**

The modification trend of MMT particles was as follows: 3 g as-received MMT and 3 mL APMS were dispersed in a solution having 5 mL water and 95 mL ethanol using a probe ultrasonic. The resultant suspension was refluxed at 80°C for 7 h. The modified MMT was then separated by centrifugation and washed using ethanol for removing the extra APMS on the surface of MMT. Finally, the powders were dried at 80°C for 12 h.

**RESULTS AND DISCUSSION**

**Morphology and characterization of adsorbent**

As can be seen in scanning electron microscope (SEM) image of APMS-MMT (Fig. 1), it has an irregular surface structure. The average size of adsorbent particles was 250 µm which was determined using ImageJ® software. Irregular surface structure, porosity and fractured structure of the adsorbent is obvious as well. Fig. 2 shows the FTIR spectra of as-received and modified MMT. The specimen was scanned by FT-IR at wavelength range of 400-4000 cm⁻¹ with a resolution of 4 cm⁻¹. The main peak at 3444 cm⁻¹ is assigned to the stretching vibration of hydroxyl (-OH) groups and the peak at 1643 cm⁻¹ represents the H-O-H bending vibration.¹³ Besides, the peak observed at around 3636 cm⁻¹ is attributed to the stretching vibration of the OH groups bonded to the Al atoms. The absorption band observed at 1058 cm⁻¹ corresponds to the stretching vibration of the Si-O-Si and Si-O and a broad peak observed at 802 cm⁻¹ is attributed to the symmetric stretching of the Si-O-Si.¹⁴ The FTIR spectrum of modified MMT, however, shows additional peaks at 2925 cm⁻¹ and 2859 cm⁻¹ (CH₃ asymmetric stretching and CH₂
stretching), and 1506 cm\(^{-1}\) (bending vibration of \(–\text{NH}_2\) group)\(^{15}\) which confirms the successful grafting of silane agent onto the MMT.

Fig. 3 shows XRD patterns of as-received and modified MMT. The diffraction peak angle for as-received MMT is observable at 2\(\theta\)=6.14°, which corresponds to the interlayer d-spacing (\(d_{001}\)) of 14.4 Å. On the contrary, for the modified MMT, the diffraction peak angle is 4.95° (i.e. \(d_{001}=17.9\) Å). This means that silane-modification enhances the interlayer d-spacing of MMT by 24%.

**Effect of contact time on removal efficiency of heavy metals by APMS-MMT**

Removal of HMs by APMS-MMT was carried out after 5, 10, 30, 50, 70, 90 and 120 min of starting the adsorption process. Results are shown in Fig. 4. As can be seen, for all HMs, when contact time increases, removal percent goes up and finally reaches to a constant level which deals with reaching equilibrium after 30 min.

**Effect of pH on removal efficiency of heavy metals by APMS-MMT**

The effect of pH on removal efficiency of HMs on APMS modified MMT is depicted in Fig. 5 which shows a maximum sorption capacity at pHs 4.0-6.0. At the beginning, when pH of the solution increases, the adsorption efficiency of all heavy metals increases. That’s because hydrogen ions which are in competition with metal ions for the binding sites, reduce. At pHs around 5.0, functional groups such as carboxyl on the sorbent are dissociated to carboxylate ions and cations can rapidly adsorbed and adsorption efficiency was increased. This phenomenon also indicates that the adsorption mechanism of heavy metals on Na-Mt nano clay obeys a complexation with ion exchange. At pHs greater than 6.0, HMs are converted to their hydroxide and because there is no charge on them, they may precipitate or have low tendency to adsorb on the clay surface.
Adsorption isotherm of heavy metals on APMS-MMT

The adsorption isotherm was investigated with two models Langmuir (eq. 2) and Freundlich (eq. 3).

\[
\frac{C_{eq}}{q_{eq}} = \frac{1}{Q^0K} + \frac{C_{eq}}{Q^0} \\
\log(q_{eq}) = \log(K_f) + \frac{1}{n} \log(C_{eq})
\]

where \(C_{eq}\) is the concentration of cations at equilibrium (mg.L\(^{-1}\)), \(q_{eq}\) is amount of metal ions per gram of sorbent at any time, \(K\) is the Langmuir constant (mg.L\(^{-1}\)) related to the affinity of the binding sites, \(Q_0\) is the maximum adsorption of metal ions adsorbed per gram of sorbent (mg.g\(^{-1}\)) and \(K_f\) and \(n\) are Freundlich constants indicating capacity and intensity of adsorption, respectively. The Langmuir model illustrates that the maximum adsorption of heavy metals corresponds to the saturated monolayer of adsorbed analytes on the surface of sorbent\(^{16}\).

The Freundlich model represented a multilayer adsorption of heavy metals on the sorbent. Results are shown in Table 1. Calculated data derived from maximum adsorption capacity (\(Q_0\)), \(K\) and \(R^2\) parameters, indicate that the adsorption of all heavy metals on nanoclay obey Langmuir isotherm model. Values of \(K\) illustrate that cadmium has strongest binding affinity among metal ions studied. As an example, adsorption isotherm of Pb on sorbent is shown in Fig. 6.

Effect of sample-loading flow rate on the removal efficiency of heavy metals by APMS-MMT
In removal of the analyte in column adsorption, loading flow rate of sample solution is a key factor in the extraction processing that affects extraction time and quantitative retention of adsorbed metals. For this purpose, six flow rates, i.e. 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 mL.min\(^{-1}\) were studied and results are shown in Fig. 7. As can be seen, the flow rate did not affect removal efficiency significantly; however, the removal efficiencies for Zn and Ni at 3 mL min\(^{-1}\) were higher than those at 0.5 mL min\(^{-1}\). This is may be because at lower flow rates, sample cannot properly spread on the entire sorbent, which is packed, very compact in the column with fine particles. When higher vacuum applies, probably molecules of sample can better penetrate in the fine structure of the sorbent. Effect of flow rate depends on both initial concentration of metal ions and amount of adsorbent. Finally, flow rate of 3.0 mL.min\(^{-1}\) was selected as optimum loading flow rate for all of the analytes.

*Effect of amount of adsorbent on removal efficiency of heavy metals by APMS-MMT*

What is illustrated in Fig. 8 is the effect of amount of adsorbent packed in column on percent of simultaneous removal of Cd, Zn, Pb and Ni heavy metals. As can be seen, due to the increment of the available sorption sites, percent of dye removing increases with increasing of adsorbent dosage and at 0.5 g of sorbent, removal percentage of all heavy metals is higher than 99%. Also, Pb and Zn adsorb better than Cd and Ni. These results are in agreement with maximum adsorption capacity mentioned earlier.

*Elution study of adsorbed heavy metals from APMS-MMT*

The elution of adsorbed metal ions from column was studied at flow rates of 0.5 to 5 mL.min\(^{-1}\) using 10% (V/V) HNO\(_3\) as eluent. The results showed that the flow rate of eluent did not affect the removal efficiency of metal ions and removal percentage of heavy
metals was ≥94% at all flow rates studied. For prevention of dissociation of sorbent in strong acidic medium, fresh nanoclay was used in the each adsorption processes.

Effect of co-existing ions on removal efficiency of heavy metals by APMS-MMT

Adsorption process can be affected strongly by interfering ions exist in real samples. In order to study this parameter, cations and anions were chosen according to their major abundance in wastewater samples; such as K⁺, Na⁺, Ca²⁺, Mg²⁺, Cl⁻, NO₃⁻ and SO₄²⁻ at three concentration levels of 10, 100 and 1000 mg.L⁻¹. The results showed that the interfering ions did not influence the removal efficiency of target metal ions. That’s because complexation of functional group of sorbent with studied heavy metals is better than with alkali or alkali-earth metals.

Application of proposed method for removal of heavy metals from real samples

A real wastewater sample was collected from urban wastewater of Zabol city in east of Iran. The sample was filtered and pH was adjusted to 5.0. The filtered wastewater was analyzed by GFAAS and no traces of the target analytes were observed. An aliquot (50 mL) of the sample was spiked with 10 mg.L⁻¹ of each heavy metal and treated with modified nanoclay by both batch and column removal methods. The removal efficiency of all metal ions from wastewater was quantitative and close to 100%. Moreover, the elution efficiency of all adsorbed heavy metals from wastewater sample was found to be over 94%. These results indicate the great potential of APMS-modified nanoclay for adsorption of heavy metals from samples with complicated matrices.

Comparison of proposed APMS-MMT adsorbent with existing methods

A comparison of proposed technique with other reported methods for removal of heavy metals by various sorbents are shown in Table 2. As can be seen, APMS-modified
nanoclay has a higher adsorption capacity rather than all adsorbent depicted in the table. Also, this method has additional advantages such as shorter contact time, easy to operate and better selectivity than the other adsorbents reported.

CONCLUSION
In this research, a natural with 3-aminopropyltrimetoxysilane (APMS) and applied for simultaneous removal of Cd, Zn, Pb and Ni heavy metals from wastewater samples. Affecting parameters on removal efficiency in both batch and column technique were studied and optimized. At the optimal condition adsorption capacity of Cd, Zn, Pb and Ni were 143.3221, 142.9865, 144.1294 and 140.3581 mg.g$^{-1}$, respectively. Removal efficiency of all heavy metals was quantitative and elution efficiency was over 94%. Also, interfering ions such as sodium, potassium, magnesium, chloride, nitrate and sulfate did not affect the removal efficiency of analytes. This technique successfully applied for removal of heavy metals from real waste water samples.

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Conflict of interest
The authors have declared no conflict of interest.
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Table 1. Obtained fitted parameters of Langmuir isotherm for adsorption of HMs on APMS-MMT

| Metal ion | $Q_0$ (mg.L$^{-1}$) | $R^2$ |
|-----------|---------------------|-------|
| Cd        | 143.3221            | 98.57 |
| Zn        | 142.9865            | 98.20 |
| Pb        | 144.1294            | 99.27 |
| Ni        | 140.3581            | 98.11 |
Table 2. Comparison of proposed sorbent with other reported adsorbent for removal of heavy metals

| Sorbent                          | Metal ion(s)     | Adsorption capacity (mg.g\(^{-1}\)) | Ref |
|----------------------------------|------------------|-------------------------------------|-----|
| Activated alumina powder         | Cr, Ni, Cu       | 0.31, 0.15, 0.125                   | [17]|
| Hickory wood                     | Pb, Cu, Cd       | 153.1, 34, 28                       | [18]|
| Camel bones magnetic             |                 |                                     |     |
| Nanocomposite                    | Pb, Cd, Co       | 344.8, 322.6, 294.1                 | [19]|
| Sugarcane leaf modified with     |                 |                                     |     |
| Nanosized MgO                    | As, Pb           | 157, 103                            | [20]|
| Zero valent iron                 | Co               | 134                                 | [21]|
| graphene composites              |                 |                                     |     |
| Dithiocarbamate CNTs             | Cd, Zn, Cu       | 235, 202.4, 101.2                   | [22]|
| Montmorillonite/Humic Acid       | Cu, Cd, Cr       | 15.6, 15.25, 14.14                  | [23]|
| APMS-MMT nanoclay                | Cd, Pb, Zn, Ni   | 143.32, 142.98, 144.12, 140.35      | This work |
|                                  |                  |                                     |     |
Figures' captions

Fig. 1. SEM image of Na-Mt nanoclay

Fig. 2. FTIR spectra of a) as-received MMT, and b) modified MMT

Fig. 3. XRD patterns of as-received and modified MMT

Fig. 4. Effect of contact time on removal efficiency of heavy metals

Fig. 5. Effect of pH on removal efficiency of heavy metals

Fig. 6. Langmuir and Freundlich plots of Pb adsorbed on APMS-MMT

Fig. 7. Effect of flow rate on removal efficiency of heavy metals.

Fig. 8. Effect of amount of adsorbent on removal efficiency of heavy metals
Fig. 1.
Fig. 2.
Fig. 3.
Fig. 4.
Fig. 5.
Fig. 6.
Fig. 7.
Fig. 8.
Graphical Abstract