Removal of cadmium from drilling fluid using nano-adsorbent

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HIGHLIGHTS

• The use of magnetic nanoparticles for Cd removal from drilling fluid was investigated.
• The method is feasible, environmental-friendly and economically attractive.
• The removal efficiency was highly pH-dependent.
• The adsorption equilibrium was described well by the Freundlich isotherm model.

ABSTRACT

Magnetic nanoparticles are exceptional adsorbent materials due to their unique magnetic properties and good adsorption capacity. In this study, a new method combining nanoparticle adsorption and magnetic separation was investigated for the removal of cadmium ions from the drilling fluid and its efficiency was studied. Magnetic iron oxide nanoparticles were successfully synthesized, characterized and evaluated by X-Ray Diffraction (XRD), Transmission Electron Microscopy (TEM) and Infrared spectroscopy (IR). The effects of various factors, e.g. pH, shaking rate, retention time and magnetic adsorbent doses on the adsorption process were also studied. The concentrations of cadmium ions were measured with both Atomic Absorption Spectroscopy (AAS) and Electrochemical Method. Adsorption reached equilibrium within 10 min. The maximum adsorption occurred at pH of 6 and shaking rate of 50 rad/s (480 RPM) with 3.2 mg of adsorbent for an initial Cd concentration of 5 mg/L. The adsorption data were analyzed and fitted well by Freundlich isotherm.

1. Introduction

Materials in the nanosized range are considered the best candidates in the removal of organic and inorganic pollutants from the environment because of their unique physicochemical properties and the availability of different forms of nanomaterials [1–4]. Compared to the most commonly used traditional techniques suggested for the treatment of industrial effluents in terms of heavy metals (i.e. precipitation, adsorption, ion exchange, reverse osmosis, and ion flotation), they not only possess quite good performance owing to high efficient specific surface area and the absence of internal diffusion resistance, especially in low concentrations of metal ions where traditional methods are inefficient, but also can be recovered simply and rapidly by an external magnetic field [5]. In addition, loaded metal ions could be simply stripped off by acid washing and it is possible for regeneration or activation of the adsorbent to reuse. This desorption process was discussed in many studies and it was shown that magnetic nano-adsorbents could be used several times effectively [6–9].

With the rise of the environmental protection movement, the petroleum industry has placed greater emphasis on minimizing the environmental impact of its operations [10]. One of the environmental concerns in drilling industry is drilling fluid wastes. Some researchers have been done on the effects of drilling activities using NAF (non-aqueous fluid) on the metal contents of the marine sediments [11,12]. Also a recent study in Iran has shown that drilling fluid discharged in mud pit has considerable amounts of heavy metals that are not naturally found. These heavy metals are toxic and have the potential to spread all over the land, surface and ground water [13].

Several studies have shown the efficiency of nanoparticles in the removal of cadmium ions from aqueous solutions [3,14–20]. They investigated the efficiencies of different nanoparticles in cadmium removal from water samples and the study on the drilling mud was first studied in this research.

In the present study, a method combining nanoparticle adsorption and magnetic separation was investigated for the removal of
cadmium ions from drilling fluid waste and its efficiency was studied. Magnetic iron oxide nanoparticles were successfully synthesized, characterized and evaluated by X-Ray Diffraction (XRD), Transmission Electron Microscopy (TEM) and Infrared spectroscopy (IR). The effects of various factors, e.g., pH, shaking rate, retention time and magnetic adsorbents doses were also studied.

2. Materials and methods

2.1. Materials

Polyacrylic acid, carbodiimide, ferric chloride hexahydrate, Ferrrous chloride tetrahydrate, ammonium hydroxide, diethylenetriamine (DETA), hydrogen tetrachloroaurate (III) trihydrate, were the guaranteed or analytic grade reagents and used without further purification. The water used throughout this work was distilled water.

2.2. Synthesis and characterization of magnetic adsorbent

The novel magnetic nano-adsorbent required for the adsorption experiments, prepared in Shahid Chamran University, was synthesized by the procedure presented by Chen et al. This magnetic nano-adsorbent has been developed using Fe₃O₄ nanoparticles as cores and polyacrylic acid (PAA) as ionic exchange groups. The Fe₃O₄ magnetic nanoparticles were prepared by co-precipitating Fe²⁺ and Fe³⁺ ions in an ammonia solution and treating under hydrothermal conditions and then developed by the covalent binding of polyacrylic acid (PAA) on the surface of Fe₃O₄ nanoparticles and the followed amino-functionalization using diethylenetriamine (DETA) via carbodiimide activation [1,14]. The particle size and morphology of aminated magnetic nanoparticles were determined using a LEO transmission electron microscope (TEM) model 902E. In order to determine the crystal structure of the products, they were analyzed using an X-ray diffractometer (XRD) model PW1840. All samples were also characterized using a Perkin Elmer Fourier transformation infrared (FT-IR) spectroscopy model LX185256.

2.3. Synthesis of drilling fluid and measuring its properties

Drilling fluid used in these sets of experiments was a simple water-based mud consists of water and bentonite that was prepared as follows:

First, a specific volume of distilled water was taken in a graduated cylinder and moved into a clean plastic vessel mixed by a mixer with the rotational speed of 1257 rad/s (12,000 RPM). Definite amount of bentonite, required for the desired rheological properties of the mud sample, was weighted carefully and added to water gradually. Then they were mixed well for about 20 min. After preparation, its rheological properties were measured.

2.4. Adsorption studies

To study the capability of amino-functionalized magnetic nanoparticles in Cd removal from the drilling fluid and obtain optimum conditions of the adsorption process, several sets of experiments were done in different conditions of pH, shaking rate and retention time with different amounts of magnetic nanoparticles used. All these experiments were done in laboratory temperature of 25 °C. To obtain the desired concentration of Cd in solution media, specific amount of Cadmium Nitrate (Cd(NO₃)₂·4H₂O) (MERK) was added to mud samples. Drilling mud pH was adjusted by 0.1 M HCl (MERK) and 0.1 M NaOH (MERK) and measured by an electronic pH Meter Kent model EIL 7045/46.

At first, several experiments were done in different values of pH and constant conditions of temperature, shaking rate and retention time. Then at optimum pH, different shaking rates and retention times along with several adsorbent doses were tested to obtain optimum conditions.

The equilibrium adsorption capacity of adsorbent was calculated by the following equation:

\[ Qe = \frac{(C_0 - C_e)V}{W} \]  

where \( Qe \) is the equilibrium adsorption capacity of adsorbent in mg metal/g adsorbent, \( C_0 \) is the initial concentration of the metal ions in mg/L, \( C_e \) is the equilibrium concentration of metal ions in mg/L, \( V \) is the volume of metal ions solution in L, and \( W \) is the weight of the adsorbent in g.

2.5. Adsorption isotherm

Analysis of the equilibrium data is important to develop an equation, which accurately represents the results and can be used for the design purposes. Several isotherm equations have been used for the equilibrium modeling of adsorption systems. The equilibrium data for metal ions over the concentration range from 5 to 200 mg/L at 25 °C were correlated with Freundlich isotherm. The Freundlich sorption isotherm, one of the most widely used mathematical descriptions, usually fits the experimental data over a wide range of concentrations. This isotherm gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies [19].

\[ \ln q_e = \ln K_f + \frac{1}{n} \ln C_e \]  

where \( q_e \) is the amount of metal ions adsorbed at equilibrium per gram of adsorbent (mg/g), \( C_e \) is the equilibrium concentration of metal ion in the solution (mg/L), \( K_f \) and \( n \) are the Freundlich model constants.

2.6. Digestion of mud samples

To measure remaining metal concentration in the mud samples by AAS, transparent solutions should be prepared from dry mud powder. A standard method called alkaline fusion was used for this purpose. The concentration of remaining Cd was determined by two methods, i.e., Atomic Absorption Spectroscopy (by AAS – TG Instruments) and Electrochemical Method (Steroglass ION 3 Potentiometric Stripping Analyzer).

To reduce the effects of materials used for the preparation of the samples and minimize the error, a blank sample was also prepared and its Cd concentration was measured. It was prepared by the procedure mentioned earlier, but without the mud sample.

3. Results and discussion

3.1. Characterization of amino-functionalized magnetic nano-adsorbents

Transmission electron microscopy images as shown in Fig. 1 revealed that the amino-functionalized Fe₃O₄ nanoparticles were multidispersed and quite fine with a mean diameter of around 16 nm. The electron diffraction pattern indicated that the magnetic nanoparticles were highly crystalline. X-ray diffraction pattern is shown in Fig. 2. It is known that magnetic particles of less than 30 nm will exhibit paramagnetism [20]. The binding of DETA on the PAA-coated Fe₃O₄ nanoparticles was demonstrated by the analyses of Infrared (IR) spectroscopy. Fig. 3 shows the IR spectra of PAA-coated and amino-functionalized magnetic nanoparticles.
It was observed, after amino-functionalization, that the characteristic peaks of PAA at 1710 cm\(^{-1}\) (C=O stretch), 1450 and 1410 cm\(^{-1}\) (C–O stretch) disappeared and new peaks appeared at 1331 cm\(^{-1}\) (N–H bend) and 1044 cm\(^{-1}\) (C–N stretch). This revealed that the carboxylic acid groups of PAA have been amino-functionalized successfully by reacting with the amino groups of diethylenetriamine [21].

3.2. Drilling mud properties

Measured properties of the synthetic drilling mud are given in Table 1.

3.3. Effects of variable parameters on the adsorption of metal ions

3.3.1. Effect of solution pH

Knowledge of the optimum pH is very important since pH not only affects the surface charge of adsorption, but also the degree of ionization and speciation of adsorbent during reaction. To establish the effect of pH on the adsorption efficiency of Cd\(^{2+}\) ions onto the nanoparticles, batch equilibrium experiments were repeated at different pH values in the range of 4.5–10. Fig. 4 illustrates the effect of solution pH on the adsorption of Cd\(^{2+}\) ions by the magnetic nanoparticles at an initial Cd\(^{2+}\) ion concentration of 5 mg/L. It showed that acidic media improves the adsorption process and the amount of adsorbed Cd\(^{2+}\) on the surface of the adsorbent increases in lower pH. And the optimum pH for this purpose was 6.

3.3.2. Effect of adsorbent dose

As it is shown in Fig. 5, cadmium uptake per gram of adsorbent was drawn versus amount of adsorbent while keeping other parameters constant. From this figure it can be observed that for such cadmium concentration, removal efficiency per gram of the adsorbent generally improved with decreasing adsorbent dose. This shows that 3.2 mg adsorbent has enough exchangeable sites to remove the ions, so that RE% of the ions was not changed after 3.2 mg of adsorbent was applied. This suggests that after a certain dose of adsorbent, the maximum adsorption sets in and hence the amount of ion bound to the adsorbent and the amount of free ions remain constant even with further addition of the dose of adsorbent.
3.3.3. Effect of shaking rate

Since an optimum shaking rate is essentially required to maximize the interactions between metal ions and adsorption sites of the adsorbent in the solution, the effect of shaking rate on Cd\textsuperscript{2+} adsorption was investigated in optimum conditions of pH and obtained adsorbent amount (pH = 6 and 3.2 mg adsorbent) and the results are shown in Fig. 6. It was found that Cd\textsuperscript{2+} removal efficiency gradually increased with an increase in shaking rates from 25 to 50 rad/s (240–480 RPM) and then remained almost constant after that. This phenomenon can be explained by the fact that, for a relatively lower shaking rate, the system is incompletely mixed; hence, the poor dispersion of nanoparticles in the solution resulted in only a small portion of surface area of adsorbent being exposed and reacted with the Cd\textsuperscript{2+} ions. The optimum shaking rate, according to this graph, was 50 rad/s (480 RPM).

The percent of adsorbed Cd ions by the adsorbents was calculated by the following equation:

\[
R = \frac{C_0 - C_t}{C_0} \times 100
\]  

where \( R \) is the removal efficiency of the metal ions, \( C_0 \) is the initial concentration of the metal ions in mg/L, and \( C_t \) is the final concentration of the metal ions at any step in mg/L.

3.3.4. Effect of contact time

The analysis of batch adsorption of metal ions was carried out in different time steps and the results were recorded and the time profile of Cd ions adsorption was plotted. As it is shown in Fig. 7, the rate of Cd\textsuperscript{2+} uptake was initially quite high, followed by a much slower subsequent removal rate leading gradually to an equilibrium condition. About 90% of the Cd\textsuperscript{2+} was removed during the second minutes of the reaction, while only a very small part of the additional removal occurred during the following 10 min of contact. The rapid adsorption of Cd\textsuperscript{2+} by magnetic nanoparticles is a main advantage of this method; especially in industrial applications that the applied method should be time effective.

3.4. Freundlich adsorption isotherm

Freundlich parameters, \( K_f \) and \( n \), were determined by plotting \( \ln q_e \) versus \( \ln C_e \). As it is shown in Fig. 8, the adsorption data were fitted well with Freundlich model \( (R^2 = 0.997) \). According to this graph, Freundlich adsorption isotherm constants, \( K_f \) and \( n \), were found to be 2.683 mg/g and 1.1136, respectively. The value of 1/\( n \) less than one is indicative of chemisorption and indicates the favorability of cadmium sorption onto the magnetic nanoparticles under the studied condition. Comparison of this isotherm constants for different sorbents reported in the literature is given in Table 2 [16–18,22–26]. Differences between the constants obtained in this study and of other sorbents, could be due to the com-

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Table 1
Synthetic mud properties.

<table>
<thead>
<tr>
<th>Mud property, unit</th>
<th>Measured value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mud system WBM*</td>
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</tr>
<tr>
<td>Mud weight, pcf</td>
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</tr>
<tr>
<td>pH</td>
<td>9.8</td>
</tr>
<tr>
<td>YPa, lbs/100 sqft</td>
<td>18</td>
</tr>
<tr>
<td>PVc, cp</td>
<td>6</td>
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<tr>
<td>Apparent viscosity</td>
<td>15</td>
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<tr>
<td>Initial gel, lbs/100 sqft</td>
<td>14</td>
</tr>
<tr>
<td>10 Min gel, lbs/100 sqft</td>
<td>15</td>
</tr>
<tr>
<td>Water loss, ml/30 min</td>
<td>15</td>
</tr>
</tbody>
</table>

* WBM: water base mud, YP: yield point, and PV: plastic viscosity.
plexity and completely different nature of the drilling fluid compared to water as used in previous works.

4. Conclusions
It is conclusively evident from batch adsorption studies that the use of magnetic nanoparticles for the Cd removal from drilling mud is technically feasible, environmentally-friendly, and economically attractive. Other advantages of this method compared to conventional methods, are its relatively high efficiency at low concentrations, rapidness, space-saving, and simplicity. The removal efficiency was highly pH-dependent and the optimal adsorption occurred at pH 6. Adsorption efficiency increased with the shaking rates from 25 to 50 rad/s (240–480 RPM) but remained almost constant thereafter. The adsorption equilibrium was described well by the Freundlich isotherm model with its constants, \( K_f \) and \( n \), equal to 2.683 mg/g and 1.1136, respectively.

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References