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Removal of Cd^{+2} and Pb^{+2} Ions from Aqueous Solutions Using Bentonite-Modified Magnetic Nanoparticles

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Abstract: The paper presents results of studies on the possibility of using bentonite modified by magnetic hematite nanoparticles to clean post-production water contaminated by Cd^{2+} and Pb^{2+} ions. The colloidal solutions of iron (III) hydroxide and iron (II) oxide were used to cover the surface of bentonite clay. The obtained products have tested for X-ray analysis which shows hematite nanoparticles of size 22.76 nm were covered the clay surface. The clay loaded with nanoparticles was used as active agent in the removal of Cd^{2+} and Pb^{2+} ions in their aqueous solutions. The efficiency of the removal process was studied using flame atomic absorption techniques. However, the removal efficiency towards Pb^{2+} ions was relatively higher than Cd^{2+} ions. This was related to the mode of interaction between the removed ions and surface of the prepared nanoparticles.

Keywords: hematite, nanoparticles, bentonite, Cd^{2+} and Pb^{2+} ions, removal efficiency

1 Introduction

Presence of heavy metals in the environment has been of great concern because of their growing discharge, toxicity and other adverse effects on receiving waters. Heavy metals contaminants in soils originate in the spreading of inorganic fertilizers, sewage sludge, and industrial wastes. Heavy metal ions like lead and cadmium, when present in the levels greater than the permissible limit become long-term hazardous contaminants because of their high toxicity causing severe damage to the kidney, nervous system, reproductive system, liver and brain[1,2]. Already the ground water systems are contaminated with lead and cadmium as inorganic Pb^{2+} and Cd^{+2} ions [3,4]. Pb^{2+} ions for example diffuse into water and the environment through effluents from lead smelters as well as from battery, paper, pulp and ammunition industries. In order to improve the quality of water, various desalination and purification methods are used, with particular emphasis on water intended for human consumption.

These methods include techniques like, adsorption, biodegradation, photodegradation, catalysis, photocatalysis, etc. Most of them are based on the use of advanced materials, such as: oxidants, microbiological substances, porous materials and polymer membranes. Bentonite is natural and cheap clay. It is a widespread material which has been used earlier as an alternative material for the removal of many wastes [5-10]. Bentonite exhibits strong adsorption capability due to its large surface area and surface energy. Many researchers modified bentonite by occupation of its exchange sites by organic cations. Previous studies showed that chitosan and organic modified bentonite have been widely used to adsorb heavy metals [11-13], dyes [14] and organic pollutants such as phenol [15]. Recently, there has been a growing interest in inexpensive high surface area materials, especially metal oxides, due to their unique applications, including adsorption and chemical catalysis [16,17]. Herrea et al. [18] have studied the effectiveness of hematite fine particles as adsorbent/ catalyst for the adsorption and catalytic combustion of azo-dye, Orange II, and obtained promising results. However, when these oxides were used in the form of fine powder or hydroxide flocculation, they retained their desirable high catalytic activity, high adsorptive capacity and rapid adsorptive rate, but the solid/liquid separation and the recovery of adsorbent were difficult to achieve. A technique for coating iron oxide onto a clay surface for the removal of metal ions and organic compounds has also been developed to overcome the separation and recovery difficulties [19-21].

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 their super adsorption capacities [22-24]. The combination between the properties of the natural clays and the unique properties of the nanoparticle can give rise to effective and economic

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adsorbent. Fe_3O_4 (hematite) nanoparticles, a fine brown powder, were used recently in several applications like magnetic storage media, solar energy transformation, electronics, ferrofluids and catalysis [25,26]. The aim of the present work is to investigate the capability of bentonite clay loaded with hematite nanoparticles for removal of Pb^{2+} and Cd^{2+} ions from their aqueous solutions compared to natural bentonite.

Table 1: Shows the sample notation used in this study.

Sample name	Description
B	Natural Bentonite
B/H	Bentonite loaded with hematite nano particles
B/H-Pb-1	Bentonite loaded with hematite nano particles and soaked in Pb solution(1000 mg/l) for 72 hrs
B/H-Pb-2	Bentonite loaded with hematite nano particles and soaked in Pb solution (3000 mg/l) for 72 hrs
B/H-Cd-1	Bentonite loaded with hematite nano particles and soaked in Cd solution for 72 hrs(1000 mg/l)
B/H-Cd-2	Bentonite loaded with hematite nano particles and soaked in Cd solution for 72 hrs(3000 mg/l)

2 Experimental

2.1 Materials

The materials used in this study were natural occurring bentonite clay. The bentonite samples were washed by distillated water and dried in oven at 100ºC for 24 hrs. $Cd(NO_3)_2$ and $Pb(NO_3)_2$ (BDH) were used as source for Cd^{2+} and Pb^{2+} ions respectively. Other agents used were all analytical grade and all solutions were prepared with distilled water.

2.2 Preparation of hematite suspension

Hematite suspension was obtained according to the following equations:

$$FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 + 3HCl$$

$$Fe(OH)_3 + HCl \rightarrow FeOCl + 2H_2O$$

$$nFe(OH)_3 + mFeO^+ + mCl^- \rightarrow nFe(OH)_3 \cdot mFeO^+ + mCl^-$$

In order to obtain magnetic nanoparticles comprising iron oxide (II, III), the following synthesis was performed:

$$FeCl_2 + 2\ FeCl_3 + 8\ NH_3 + 4\ H_2O \rightarrow Fe_3O_4 + 8\ NH_4Cl$$

A solution containing iron (II) chloride (0.02 molar) and iron (III) chloride (0.04 molar) was prepared at room temperature. The suspension was slowly acidified with 1 M HCl until the pH = 4-5. 60 ml of 0.35M $Fe(NO_3)_3$ was added and the solution boiled for one hour. 20 g of bentonite clay was introduced to the resulted suspension and the suspension was left to settle down then filtrated. The solid obtained washed with distilled water several times and dried in an oven at 60ºC for 24 hrs.

The structure properties of natural bentonite (B) and bentonite loaded with hematite nanomaterial (B/H) were identified using X-ray diffraction (XRD). For X-ray examination, a stabilized X-ray generator was used fitted using copper target and nickel filter under working conditions of 40 kV and 25 mA.

2.3 Removal Experiments

Table 2: Operational conditions for AAS measurements.

Conditions	**Cd**	**Pb**
Wavelength, nm	228.8	283.3
Lamp current, mA	7.5	10
Slit width	1.3	1.3
Heating program		
Drying temp., C°	80-120	80-120
Time/sec	30	30
Ashing temp., C°	300	400
Time/sec	30	30
Atomization temp., C°	1700	2100
Time/sec	7	7
Cleaning temp., C°	2600	3000
Time/sec	30	30

The removal efficiency of both natural bentonite and bentonite coated with nano hematite particles towards Pb^{2+} and Cd^{2+} cations was examined. This was done by agitated 50 ml of each metal ions solution (3000 mg/l) to 0.5 g of both bentonite(B sample) and bentonite loaded with hematite nano particles (B/H sample) for 2, 4, 6, 12, 24 and 72 hrs at 25ºC. At each time interval, filtration was carried out and the concentrations remained of each heavy metal were determined using atomic absorption spectrometer (AAS). The AAS measurements were carried out with AA spectrometer; model Z-8100 polarized Zeeman, manufactured by Hitachi, Ltd., from Japan Hitachi single – element hollow cathode lamps were used with air-acetylene flow rate ranging from 0.5 to 4.0 l/min with an auxiliary oxidant gas pressure ranging from 140 to 120 kpa. The instrument is provided with temperature regulation device and automated sampling by a built in auto sampler, type SSC -200. Selection of wavelength ranged from 190 to 900 nm. AAS measurements were carried out under a constant air flow rate or (15.0 l/min), according to the following operational condition for each element as in Table (2).

2.4 Removal efficiency

The removal efficiency was calculated by using equation (1):

$$\text{Removal efficiency \%} = [(C0 - Ct) / C0] \times 100 \qquad (1)$$

Where C0 is the initial concentration of the heavy metal introduced in the solution (3000 mg/l) and Ct is the concentration of the each heavy metal in the filtrate (mg/l).

3 Results and Discussion

3.1 Structure and composition of the prepared materials

Fig. 1 shows a schematic model of bentonite clay which loaded in its surface with hematite nanoparticles. It shows how the magnetic hematite nanoparticles covered the surface of the bentonite clays. These nanoparticles increase the roughness and surface defects. As a consequence the surface area and the adsorption properties of the bentonite clay will be increased notably.

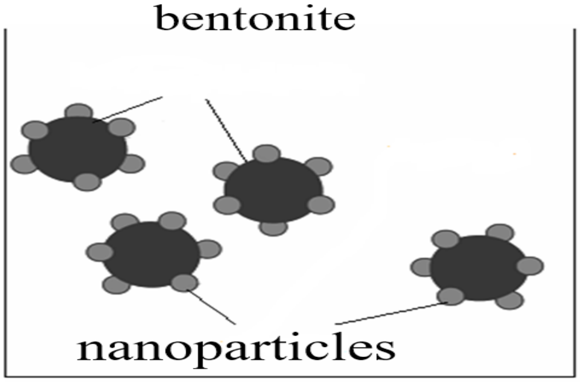

Fig. 1. Schematic model of the prepared solid.

Generally, XRD can be used to characterize the phase composition of the used clay and the crystallinity of the prepared nano-particles. Fig. 2 shows the XRD patterns of natural bentonite and bentonite loaded with hematite nanoparticles.

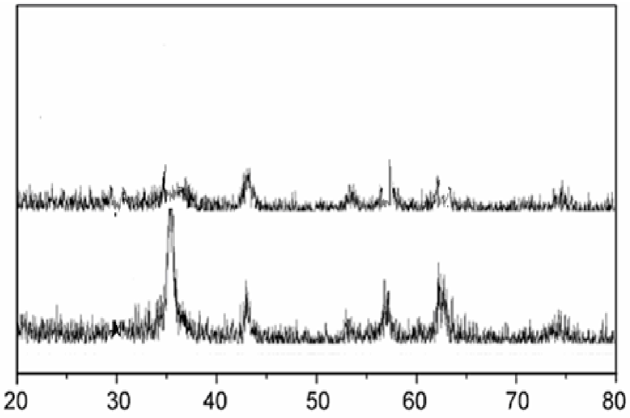

Fig. 2. XRD of bentonite and hematite/bentonite nanopaticles.

The XRD pattern of natural bentonite (B sample) shows small peaks of ill-crystalline silicon dioxide (SiO_2) which indicates it is the major constituent of used bentonite. This low in the crystallinity of SiO_2 besides its high surface area explain the high absorption properties of the used bentonite. The patter of bentonite sample loaded with hematite (B/H sample) shows peaks at 2θ = 36º , 43.7º and 63º in addition to the peaks of SiO_2 which are just the evidence of the existence of the Fe_3O_4 nano particles loaded on the surface of bentonite. Calculating the grain size according to Debye-Scherrer formula, we obtained 22.76 nm for the Fe_3O_4 particles indicting they are in the nano scale.

3.2 XRD of (B/H-Pb) and (B/H-Cd) samples

XRD patterns of the bentonite samples loaded with hematite nanoparticles and in soaked in Pb (B/H-Pb) and Cd ions (B/H-Cd) for 72 hrs are shown in Fig. 3.

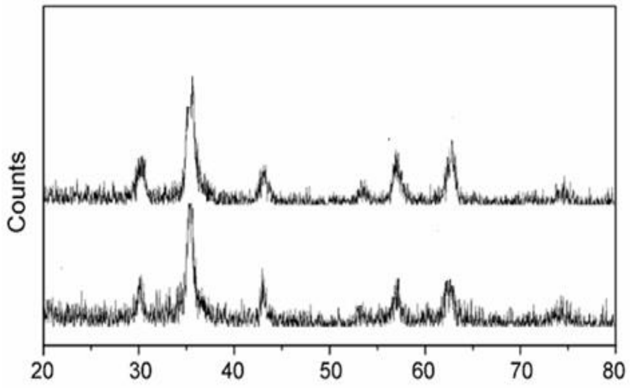

Fig. 3. XRD of bentonite and hematite/bentonite nanoparticles.

Besides the peaks characterized to Fe_3O_4 particles, a new peak appeared in the XRD patterns at 30.9º. That peak is slightly broader in B/H-Pb sample than in B/H-Cd sample which is related to $PbFe_2O_4$ and $CdFe_2O_4$ respectively. The appearance of such peaks is an evidence of the ability of the prepared bentonite loaded with nanoparticles for the removal of Pb^{+2} and Cd^{+2} ions from their aqueous solutions

3.3 Removal efficiency

3.3.1 For Pb^{+2} ions

The absorption isotherm of B and B/H samples toward lead ions from its aqueous solution is represented in Fig. 4 as a function of soaking time.

The natural bentonite (B) is showed a potential removal for Pb^{+2} ions which increased by increasing the soaking time. This efficiency of removal is more notable on the first 2 hrs of soaking and reached its highest value (66.7%) after 24 hrs of soaking. The bentonite loaded with hematite nano materials, B/H sample, showed a similar trend of the variation of removal efficiency with the soaking time as in B sample but with relatively higher values. There is an increase in the efficiency of removal by about 50 %

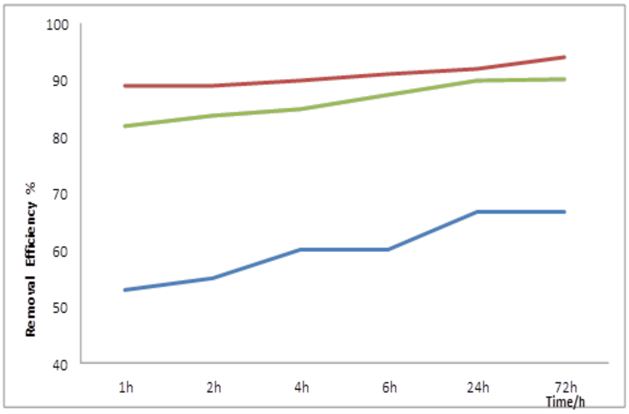

Fig. 4. Percentage of Removal efficiency of lead ions.

compared to natural bentonite from the first hour of the soaking experiment. After 72 hrs of soaking about 90 % of Pb^{+2} ions are removed from its aqueous solution by B/H sample. This increase in the removal efficiency of B/H sample compared to B sample is related to various modes of interaction between Pb^{+2} ions and B/H sample. Presence of hematite nano materials can act as super absorbent to Pb^{+2} ions. Besides, Pb^{+2} ions can react with hematite particle to form double oxide $PbFe_2O_4$ as indicted from X-ray results.

Decreasing the initial concentration of Pb^{+2} ions in the soaking solution from (3000 mg/l) to (1000 mg/l) was resulted in slight increase in the removal efficiency as noticed from Fig. 4. The recorded removal efficiency for solution with initial concentration of Pb^{+2} ions (1000 mg/l) was 94% while as for solution with initial concentration (3000 mg/l) is 90.1 % after 72 hrs of soaking. Such finding can be related to the mode by which Pb^{+2} ions interact with B/H surface and by which they removed from the pollutant solutions. Many authors studied the removal of lead ions by many effective binders and they showed that the removal process was controlled by the adsorption phenomena. At the adsorbed-adsorbent interface, increasing the adsorbent amount leads to overcrowding of the adsorbent particles. This will lead to reduce their diffusion velocities in the boundary layer and in consequence reduces the overall removal efficiency [27]. Also, increasing the adsorbed amounts reduces the ratio between the numbers of active sites on the adsorbent surface to the numbers of the adsorbed molecules which results to comparatively lower adsorption.

3.3.2 For Cd^{+2} ions

The removal efficiency of natural bentonite (B sample) and bentonite loaded with hematite nanoparticles are illustrated as a function of soaking time in Fig. 5. Here also there is a great tendency of the used bentonite to removal the Cd^{+2} from its aqueous solution. This tendency is notable from the first 2 hrs of soaking. After 24 hrs about 46.7 % of Cd^{+2} ions were removed from the solution by using natural bentonite.

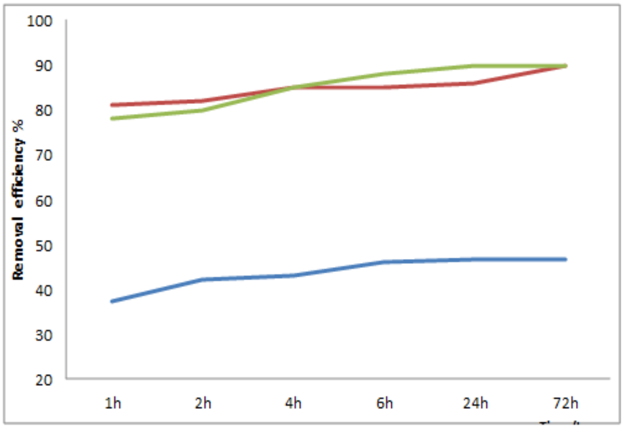

Fig. 5. Percentage of Removal efficiency of cadmium ions.

Using bentonite loaded with hematite nonmaterials results in a notable increase in the removal efficiency towards Cd^{+2} ions from aqueous solution. About 81% of Cd^{+2} ions were removed from solution in the first 1 hrs of soaking and 90% of these ions were removed after 72 hrs of soaking. Here and in contrast to that observed in case of Pb^{+2} ions, decreasing the initial concentration of Cd^{+2} in the soaking solution not greatly affects the percentage of the removal efficiency. 90% of removal efficiency is recorded for initial concentration 1000 and 3000 mg/l. Such finding gives rise to the mode of interaction between Cd^{+2} ions and B/H sample, Cd^{+2} ions can replace could replace exchangeable ions in B/H sample like Ca^{+2} and Fe^{+3}. These exchangeable reactions could be expressed as follows:

$$Cd^{+2} + Ca^{+2}\text{- B/H} \rightarrow Ca^{+2} + Cd^{+2}\text{- B/H}$$

$$Cd^{+2} + Fe^{+3}\text{- B/H} \rightarrow Fe^{+3} + Cd^{+2}\text{- B/H}$$

After a certain dose of Cd^{+2} ions, the exchangeable site become saturated and hence ratio between the amount of ions bounded to the adsorbent and the amount of the free ions remain constant even with further increase in the dose of Cd^{2+} ions [22]. This explains why decreasing the initial concentration of Cd^{2+} in the soaking solution not greatly affects the percentage of the removal efficiency.

4 Conclusion

It is conclusively evident from the above results that the use of bentonite clay loaded with magnetic nanopaticles for removal of Pb^{+2} and Cd^{+2} ions from their aqueous solutions is technically feasible and economically attractive. Also, it has a high efficiency at both low and high concentrations. Pb^{+2} ions are preferably adsorbed by the modified clay and the removal efficiency depends on the initial concentration of adsorbed ions in the soaking solution. However, Cd^{+2} ions can replace the exchangeable ions in the modified clay like Ca^{+2} and Fe^{+3} ions and the removal efficiency not greatly changed by the initial concentration of the adsorbed ions.

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