Preparation of Fe_3O_4 @ montmorillonite composite as an effective sorbent for the removal of lead and cadmium from wastewater samples

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Abstract: A magnetic Fe_3O_4 @ montmorillonite composite was prepared and used for the separation of lead and cadmium from aqueous solutions. For this purpose, magnetite (Fe_3O_4) was generated by co-precipitation of $FeSO_4$ and $FeCl_3$ onto montmorillonite. The effects of various experimental parameters such as pH of the solution, amount of sorbent, initial concentration of analytes, and contact time on the sorption efficiencies of lead and cadmium ions were investigated and optimized by applying a batch technique. The concentrations of analytes were determined by high resolution continuum source flame atomic absorption spectrometry. The maximum adsorption occurred at pH 2.0. The adsorption capacity of Fe_3O_4 @ montmorillonite composite was 5 mg g^{-1} Pb and 2 mg g^{-1} Cd. The quantitative retention in acidic medium was an advantage for the removal of metals from acidic water samples. Under optimized conditions, lead and cadmium were quantitatively removed from wastewater (between 95% and 98%) in a contact time of less than 5 min. The results showed that Fe_3O_4 @ montmorillonite can be efficiently used for the removal of lead and cadmium from aqueous solutions.

Key words: Removal, lead, cadmium, Fe_3O_4 @ montmorillonite, composite, atomic absorption spectrometry

1. Introduction

Lead is a nonessential, heavy metal element, assumed to be toxic and a potential danger to living beings and a pollution source.[1,2] Its most widespread toxic ions are within industrial wastewater, emissions from traffic, and pesticide residuals.[1,3] Cadmium is a toxic heavy metal of environmental concern as well and classified as a B1 carcinogen by the US Environmental Protection Agency.[4] Cadmium is widely used in various industries, which widely pollutes the environment. In order to remove hazardous pollutants from various environmental sources, e.g. aqueous media, many procedures such as co-precipitation, adsorption, ion-exchange, filtration, electrochemical techniques, and reverse osmosis were proposed. Because of their serious detrimental effects, it is important to determine trace levels of lead and cadmium in almost all matrices as well as to remove these pollutants effectively and cheaply.

Natural clays are often used for their metal adsorbent properties. The adsorption capacity of clays results from a relatively high surface area and a net negative charge in their structure, which attracts and holds cations such as heavy metals.[5] Montmorillonites have the smallest crystals with the largest surface area and highest cation exchange capacity.[6]

Recently, magnetic materials are being used because of their fast separation efficiency for investigating

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decomposition or deformation in chemical processes such as separation, purification etc. [7−9] Magnetic separation is a promising technique in water treatment because of the high separation rate using a simple magnetic process. [10]

In the present study, the preparation of a montmorillonite–Fe_3O_4 magnetic composite and its use as a sorbent for the separation of lead and cadmium from aqueous solutions was examined.

2. Results and discussion

2.1. Effect of sample pH on sorption

In order to investigate the optimum pH for quantitative retention of the analytes, the pH was changed in the range of 1–10 at room temperature. Cd^{2+} was quantitatively retained at pH range 2–7 while the best efficiency for Pb^{2+} was obtained at pH 2. In general, clays have negative surface charges in solution. In acidic samples, competitive reactions between H^+ and metal ions occur. [11] However, in this case, as shown in Figure 1, when the surface of the clay was modified with Fe_3O_4, optimum pH should be set to 2 for high retention fractions. It can be assumed that the magnetic attraction power of Fe_3O_4 contributes to the collection of analytes on the sorbent. The effect of pH on retention was examined several times and every time the analytes were insistently retained on the sorbent around 95% to 100% at pH 2.

2.2. Effect of contact time on sorption

The influence of shaking time on adsorption was also investigated over a time range of 1 to 30 min and no improvement with increasing time was found. It was observed even after 1 min that the adsorption reaches its maximum (nearly 100%) and remains constant at higher contact times. To be on the safe side, a 5-min shaking time was applied in all trials (Figure 2).
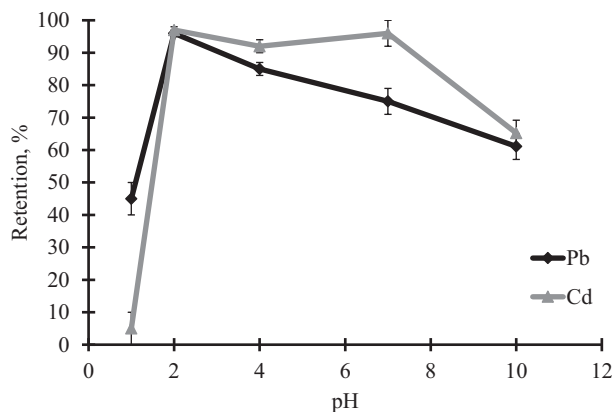

Figure 1. Effects of pH on the retention of lead and cadmium (volume of sample solution: 10 mL, amount of sorbent: 0.1 g, initial concentrations of lead and cadmium: 1 mg L^{-1}, N: 3).
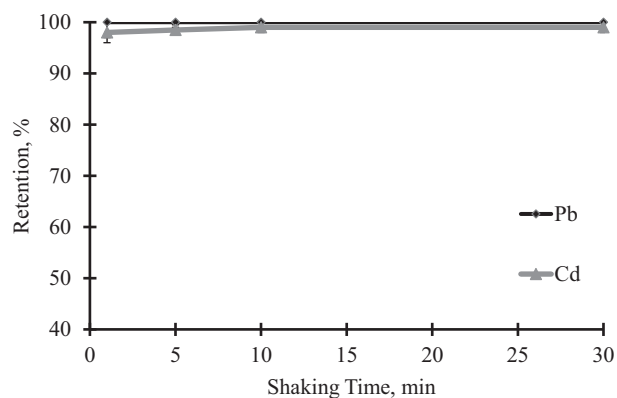
Figure 2. Effects of shaking time on retention of lead and cadmium (pH: 2, volume of sample solution: 10 mL, amount of sorbent: 0.1 g, initial concentrations of lead and cadmium: 1 mg L^{-1}, N: 3).

2.3. Effect of sorbent amount on sorption

Amount of adsorbent is an important parameter for determining the capacity of an adsorbent. Different amounts of sorbent within the range of 0.01 to 0.5 g were shaken with 1 mg L^{-1} of analytes at pH 2 for 5 min. Quantitative

retentions were obtained when 0.1 g of sorbent was used. Although maximum retention was achieved for lower sorbent amounts, since the mixture of the two analytes was treated at the same time, 0.1 g of sorbent was used in all experiments (Figure 3).

2.4. Effect of initial metal concentration on sorption

The adsorption capacity is the highest metal quantity taken up by the sorbent.[12] In order to find out the adsorption capacity of the Fe_3O_4 @ montmorillonite, 0.1 g of sorbent was shaken with increasing concentrations of 10 mL of metal solutions at pH 2. As can be seen from Figure 4, after 20 mg L^{-1} of cadmium and 50 mg L^{-1} of lead, quantitative retention efficiencies began to decrease.
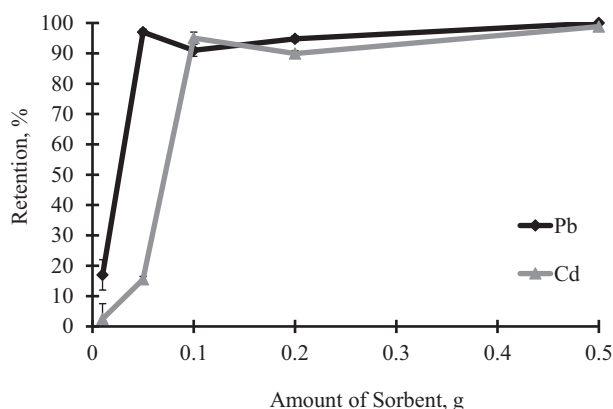

Figure 3. Effects of sorbent amount on the retention of lead and cadmium (pH: 2, volume of sample solution: 10 mL, amount of sorbent: 0.1 g, initial concentrations of lead and cadmium: 1 mg L^{-1}, N: 3).
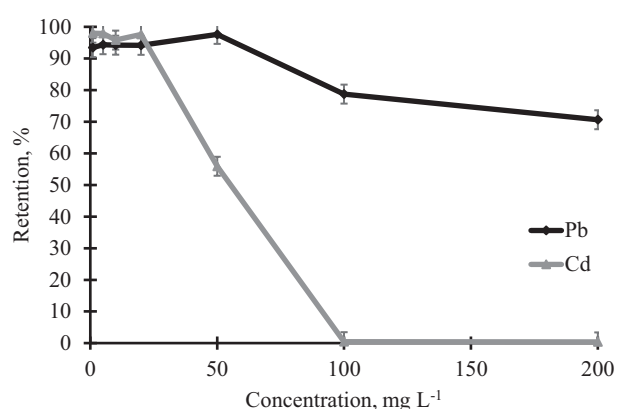
Figure 4. Effects of initial concentrations of lead and cadmium on retention (pH: 2, volume of sample solution: 10 mL, amount of sorbent: 0.1 g, N: 3).

2.5. Effect of interfering ions

The effects of various foreign ions on the sorption of the analyte were also investigated. For this purpose, 1 mg L^{-1} Pb and Cd were mixed with different chemical species in different concentrations prepared and shaken for 10 min. Then the concentrations of Pb and Cd in the eluent were investigated. Tolerance limits of foreign ions described as the retention of Pb and Cd are depicted in Table 1. The tolerance limit was taken as the maximum concentration of the foreign substances that caused less than 5% error. Obviously, lead and cadmium could be removed from water samples containing high concentrations of cations and anions.

2.6. Validation of method

In order to validate the method, the sorbent was tried in different wastewaters. The concentrations of the analytes were determined before and after being treated with the sorbent and the removal efficiency was calculated. As can be seen from Table 2, after shaking 0.1 g of sorbent with different wastewater matrices, Pb and Cd can be quantitatively removed from samples.

All those experimental results proved that montmorillonite modified with magnetic Fe_3O_4 was an effective sorbent for the removal of lead and cadmium from aqueous solutions. The magnetic properties of the composite provided rapid and effective separation of the sorbent from the sample medium using an external

magnetic field. Quantitative retention of analytes even at low pH values (pH > 2) is another advantage. The other advantages of the method are that montmorillonite is a cheap material and abundantly found in nature and the synthesis of Fe_3O_4 is an easy procedure and well defined in the literature.

Table 1. Effect of interfering ions on sorption (N: 3).

Species	Added as	Concentration of the diverse ion, mg L^{-1}	Retention of Pb, %	Retention of Cd, %
Na$^+$	NaCl	3800	96.7	97.3
Mg^{2+}	Mg(NO$_3$)$_2$.6H$_2$O	800	98.8	95.0
K$^+$	KCl	800	95.3	95.0
Ca^{+2}	CaCl$_2$	160	97.1	94.5
Cu^{+2}	CuSO$_4$.5H$_2$O	35	95.6	99.1
Cl$^-$	NaCl	5800	96.7	97.3
	KCl	720	95.3	95.3
	CaCl$_2$	280	97.1	94.2
NO$_3^-$	Mg(NO$_3$)$_2$.6H$_2$O	4000	98.8	95.0
SO$_4^{2-}$	CuSO$_4$.5H$_2$O	55	95.6	99.1

Table 2. Applications on wastewater samples.

	Pb		Cd	
	Concentration, mg L^{-1}	Removal, %	Concentration, mg L^{-1}	Removal, %
Wastewater-1	12.0	95.2	15.0	98.2
Wastewater-2	20.0	99.4	24.0	97.4
Wastewater-3	25.0	98.5	32.0	94.3
Wastewater-4	40.0	94.6	42.0	93.5
Wastewater-5	25.0	92.3	23.0	97.2

3. Experimental

3.1. Instruments

An Analytik Jena ContrAA 700 High Resolution Continuum Source Atomic Absorption Spectrophotometer (Analytik Jena, Jena, Germany) equipped with a 300 W xenon short-arc lamp as a continuum radiation source was used throughout the work. Pb (217.005 nm) and Cd (228.801 nm) were used with 3 pixels (central pixel $\pm$ 1). All measurements were carried out in triplicate. In order to shake samples, a VWR Minishaker was used.

3.2. Chemicals

High-purity water was obtained from a TKA reverse osmosis system connected to a deionizer (TKA Wasser-aufbereitungsysteme GmbH, Niederelbert Germany). All chemicals were from Merck (Darmstadt, Germany). The standard solution of each metal ion was prepared by diluting stock solution of 1000 mg L^{-1}. In order to adjust the pH of the solution 0.1 M NaOH and 0.1 M HNO$_3$ were used.

The Montmorillonite K10 (CAS 1318-93-0) with 250 m^2 g^{-1} surface area and pH 3–4 was obtained from Sigma-Aldrich (Taufkirchen Germany). For Fe_3O_4 modification, FeCl$_3$, FeSO$_4$, and NaOH (Merck, Darmstadt, Germany) were used.

3.3. Preparation of montmorillonite @ Fe_3O_4 magnetic composite

The magnetic composite was prepared very simply and quickly using inexpensive chemicals. The montmorillonite (3.3 g) was suspended in a 400-mL solution of $FeCl_3.6H_2O$ (7.8 g, 28 mmol) and $FeSO_4$ (3.9 g, 14 mmol) at 70 °C. To this solution was added 100 mL of 5 mol L^{-1} NaOH dropwise to precipitate the iron oxide. The composite was washed and then dried in a furnace at 100 °C for 2 h. To verify the magnetism, a basic test can be applied to composites with a simple magnet. The composite was collected by magnet, which showed that the material was magnetic.[13]

3.4. Elemental sorption by the sorbent

The adsorption experiments were carried out in 50-mL centrifuge tube by mixing 0.1 g of Fe_3O_4 @ montmorillonite and 10 mL of aqueous solution containing Pb^{+2} and Cd^{+2} at pH 2. After 5 min of mixing at 500 rpm in a shaker, the sorbent was separated effectively with the aid of a magnet. All the sorbent was collected at the bottom of the tube in less than 10 s (Figure 5).
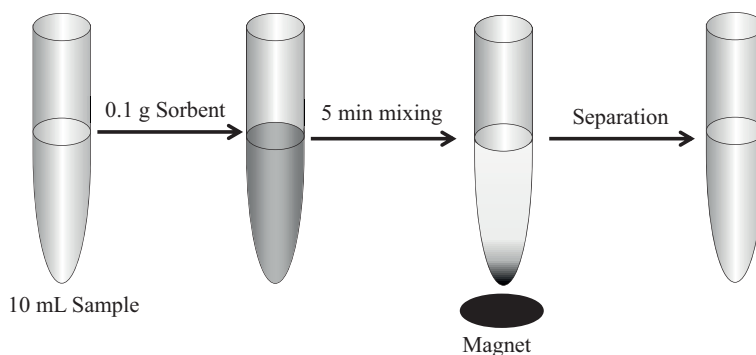

Figure 5. Experimental scheme.

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