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Removal of Mercury using Dibutyl-Disulfide Montmorillonite: Characterization of Adsorbent, Optimization, Isotherm, Kinetic and Real Samples Study

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Abstract

Dibutyl-Disulfide Montmorillonite (DD-MMT) was synthesized successfully and found to be an excellent adsorbent for Hg(II) removal. The fourier transform infrared spectroscopy (FT-IR), x-ray diffraction spectrum (XRD) and scanning electron microscopy (SEM) were used to characterize properties of the absorbent. The effects of several parameters such as solution pH, adsorbent dose, contact time and the initial concentration on the Hg(II) adsorption onto the composite were investigated. DD-MMT had a high capacity for Hg(II) removal that removed Hg(II) (10-100 mg/L) more than 95 % with 2 g/L of adsorbent in only 10 min. The adsorption equilibrium data fitted well to Langmuir isotherm. The maximum adsorption capacity of Hg(II) ions was 312.5 mg/g that was bigger than most of previous methods. Adsorption kinetics of Hg (II) on DD-MMT followed the pseudo-second-order kinetic model. In addition, the method has the advantages of environmental friendly, rapidity, simplicity, and low cost for Hg(II) removal.

Keywords: *Adsorption, Dibutyl-Disulfide, Mercury (II), Montmorillonite.*

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Introduction

In the recent decades, removal of toxic pollutants from environment is one of the major challenges for scientists. Without clean water, life is impossible. The most important sources of water pollution are untreated toxic industrial wastes. Mercury is known as a highly toxic heavy metal that is non-biodegradable. There are many way to enter Mercury into food chain. Industrial processes like chloralkali production, textile factories, oil refineries, burning of fossil fuels, paint, pulp, fertilizer, ores mining and smelting, etc. cause the release of mercury into the environment [1].Even in low concentration, the Hg(II) is toxic to the environment and human health. Mercury has harmful effects on human health and causes problems such as neurotoxicity, neurologic problems, risk of myocardial infarction, autism, alzheimer disease, and other related problems. The human central nervous system is damage permanent in contiguity with mercury even at very low concentration [2]. Accordingly, extensive studies have been done for removal of mercury from water samples and various techniques have been used such as reduction [3], coagulation [4], precipitation [5], ion exchange [6], membrane separation [7] and adsorption.

Probably the most attractive and efficient method for removing heavy metals is adsorption process. Several types of adsorbents for Mercury (II) removal have been considered in the literature such as WCNT-COOH [1], polydithiocarbamate [8], MCD-GO-R [9], Polyacrylonitrile fiber [10], CTS-g-P(AA-co-NANHT) [11], EDTA-m graphene oxide [12], conjugate nanomaterial [13], PPy/SBA- 15 [14], Si-APTMS-Py [15], thiol-incorporated AC [16], etc. Two factors are very important to select adsorbent: high surface area and suitable sites for adsorption. Therefore, in this study, Montmorillonite (MMT) was selected. Montmorillonite is nature nanoclay. The high specific surface area, environmental friendly, layered structure, high cation exchange capacity, etc., have made Montmorillonite very good adsorbent material [17-19]. Montmorillonite was modified by Dibutyl-Disulfide (DD) to produce suitable sites for Mercury (II) adsorption. The FT-IR spectroscopy, XRD and SEM techniques were applied to characterize modified Montmorillonite. Then, we used modified nanoclay to remove Hg(II) from aqueous sample.The effective variables in removal (i.e., solution pH, adsorbent dose, contact time, and agitation rate) were optimized. The Langmuir and Freundlich adsorption isotherms of Hg(II) on DD-MMT were also studied.

Experimental

Material

The chemical with analytical grade was used. A stock solution of 1000 mg/L of Hg (II) was prepared by dissolving 0.1713 g of Mercury(II) nitrate (monohydrate) (Merck-Germany) in water and diluting to 100 mL in a volumetric flask. The requested concentrations were prepared by successive dilutions. Montmorillonite (sodiumform) was supplied by F.C.C. (china). Dithizone was purchased from the Merck Company (Germany).

Apparatus

Absorption studies were carried out using Perkin-Elmer UV–vis spectrophotometer model Lambda35. A FT-IR Perkin-Elmer BX II was used for recording FT-IR spectra. Scanning electron microscope (SEM, Philips XL30) was used for the preparation of SEM images. The crystal structure of nanoclay and modified nanoclay were determined by an X-ray diffractometer (XRD) (XRD Seifert ID 3003, Germany) at ambient temperature.

Preparation of adsorbent

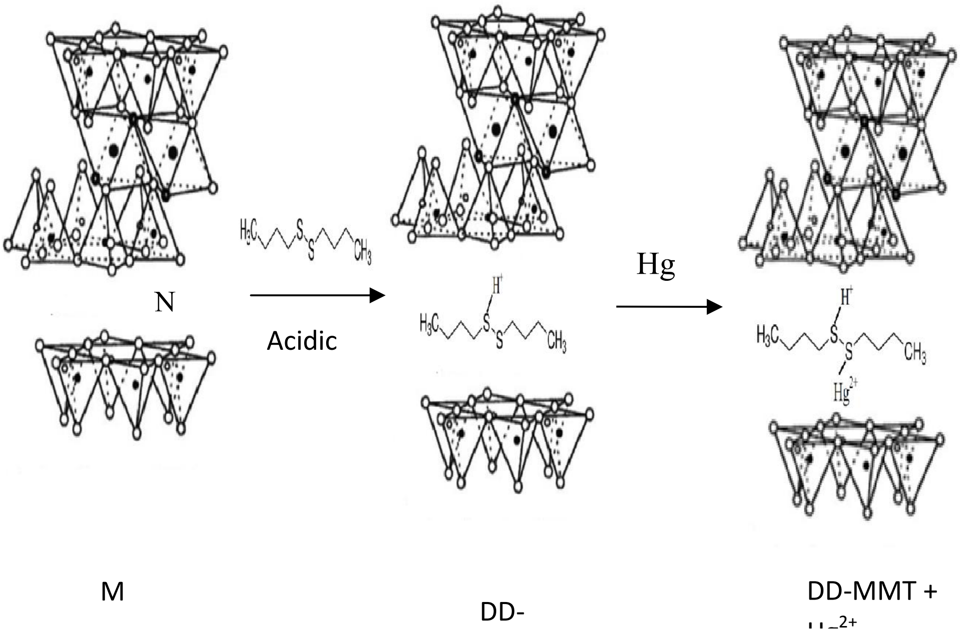
The Montmorillonite (5 g) was stirred magnetically in 500 mL distilled water for about 24 h at room temperature. Then, the pH of the solution was adjusted to 2.5 using nitric acid and 1.0g Dibutyl-Disulfide (that it has been solved in acetone) was added. The suspension was stirred for 3 h at room temperature. The precipitation was dried in an oven at 40 °C for 24 h, after filtration and washing with distilled water.

General method

Batch mode was selected for all the experiments. The diluted NaOH or HCl solutions were used to adjust the desired pH.To remove of Hg(II) from aqueous solutions, 50 ml of Hg(II) solution (certain pH and concentration) was added to Erlenmeyer flasks (100 mL) that contained a certain amount of adsorbent. The Erlenmeyer flasks were placed on the shaker. All the adsorption experiments were performed at room temperature (25 ±2 °C). After determined time, samples of 10 mL were taken, centrifuged and analyzed for Mercury (II) concentration measurements. The concentration of Mercury (II) ions was determined spectrophotometrically with dithizone solution as a complex agent. The absorbance of the solution is read at 480 nm.

Results and discussion

As mentioned before, Monmorillonite has layered structure and high cation exchange capacity. On the other hand, Dibutyl-Disulfide can accept a proton in acidic medium and then exchange with cation in Monmorillonite layers. The presence of S donor atoms of Dibutyl-Disulfide made suitable sites for adsorption of Hg(II). The probable mechanism is shown in Scheme1**.** The preliminary experimental observations showed that DD-MMT had a high capacity to remove Hg(II) in comparison with MMT so that DD-MMT removed Hg(II) more than 90 % but MMT removed Hg(II) less than 60 % in same conditions.



Scheme 1*. Schematic illustration for adsorption of Hg on modified Montmorillonite.*

Adsorbent characterization

The FT-IR spectrum of Dibuthyl-Disulfide has a band at about 2900 cm $^{-1}$. The FT-IR spectrum of Montmorillonite does not have any band at about 2900 cm^{-1}. The presence of a sharp band was observed at about 2900 cm^{-1} for the FT-IR spectrum of DD-MMT. The results revealed that MMT was modified by Dibuthyl-Disulfide.

The X-ray diffraction (XRD) spectrum of Montmorillonite and modified Montmorillonite were studied in the range from 5^{o} to 15^{o} of the 2θ angle. The XRD peak was shifted from 7.24 to 6.10 implying the reorientation of the organic compound between MMT layers. The modification process occurred in such a way that the Dibutyl-Disulfide ions were adsorbed in the interlayer space of the clays therefore there was exchange between the inorganic cations on the clay and the Dibutyl-Disulfide ions in the solution.

The scanning electron microscopy was used to study the surface morphologies of the MMT and DD-MMT. Micrographs of the surface at 8000 times magnifications are shown in Fig 1a b. The raw MMT (Fig 1a) has surface with low compression. The DD-MMT composite (Fig 1b) has surface with high compression that it is compact. The high compression was observed due to the adsorption of DD onto MMT.

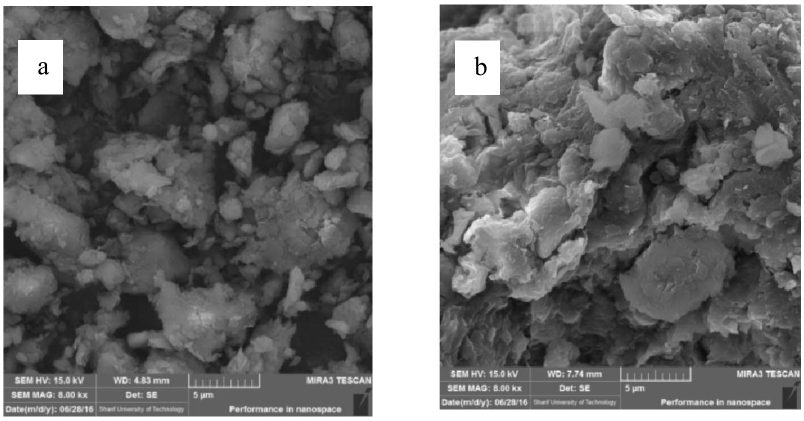


Figure 1. SEM images of (a) MMT (b) DD-MMT at 8000 times magnification.

Effect of Variables

The pH of the Hg(II) solution was found to be the most important factor influencing on the adsorption process. The solution pH was studied as a variable of removal at the initial Hg(II) concentration of 20 mg/L (Figure 2). The removal of Hg(II) was maximum at pH of 4.0.

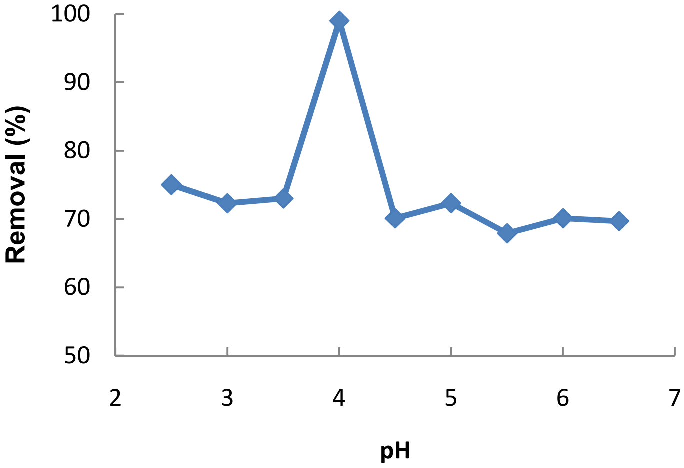


Figure 2. Effect of pH on Hg(II) removal (initial Hg(II) concentration 20 mg/L, adsorbent dose=3 g/L, contact time=60 min, agitation rate= 100 rpm).

Another important parameter that was analyzed is the dose of adsorbent (Fig 3). An increase in effectiveness of Hg(II) removal with increasing dose of adsorbent was observed. The adsorbent dose increase means functional groups increase which arrive to an increase in the removal of Hg(II). It was confirmed that adsorbent dose of 2 g/L and 60 min time is enough to remove about 100 % Hg(II).

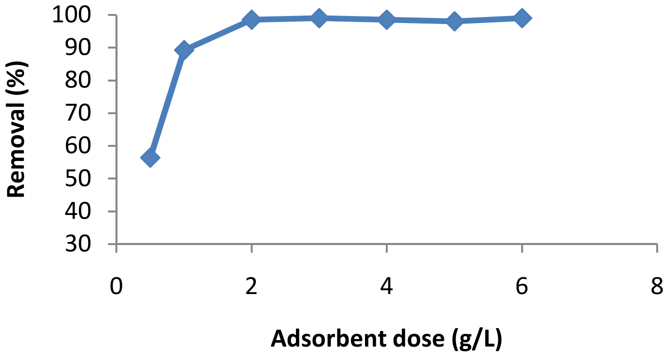


Figure 3. Effect of adsorbent dose on adsorption of Hg(II) (initial Hg(II) concentration 20 mg/L, pH=4.0, contact time=60 min, agitation rate= 100 rpm).

The adsorption of mercury onto composite adsorbent has been investigated as a function of time in the range of 5-120 min (Figure 4). It was found that more than 90 % removal of mercury occurs within 5 min. Time of 60 min is enough to remove about 100 % Hg(II). This method is very fast and it's one of advantages of the method.

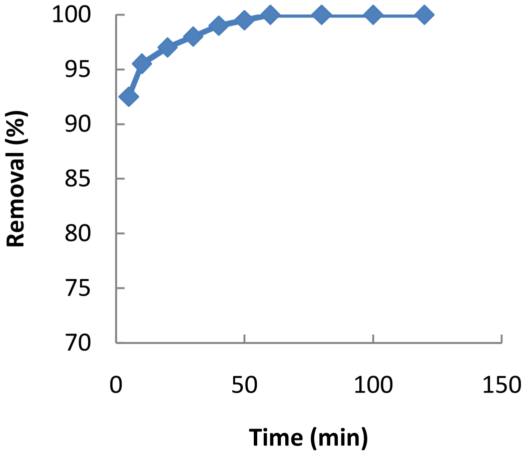


Figure 4. Effect of contact time on adsorption of Hg(II) (initial Hg(II) concentration 20 mg/L, adsorbent dose=2 g/L, pH=4.0, agitation rate= 100 rpm).

The agitation speed was sustained ranging between 60 and 140 rpm (Figure not shown). In the all speed, the removal was approximately the same. Therefore, an agitation speed of 100 rpm was exerted for further study. In order to study effect of mercury initial concentration, the solutions that have different concentrations were prepared and at the optimization condition were studied. The results showed that Hg(II) removal will be 100-95% (Table 1) for concentrations 10-100 mg L^{-1} at the optimization condition(pH=4.0, Adsorbent dose=2 g/L, Contact time=10 min, agitation speed=100 rpm). As can be seen from the table, the results are comparable to the previously reported method [20]; dithizone-montmorillonite removed Hg(II) (98-90%)only for concentrations 10-50 mg L^{-1} at the long time=90 min[20].The results confirmed that DD-MMT has extraordinary capacity on mercury(II) removal.

Table1. Effect of the initial concentration of Hg(II).

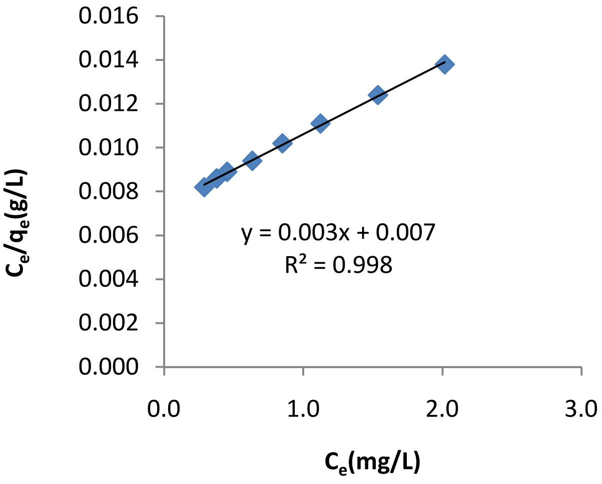
Initial Concentration of Hg(II) (mg/L)	Removal (%)
10	~100.0
20	~100.0
30	~100.0
40	99.5
50	99.0
60	99.0
80	98.1
90	96.3
100	95.2

Adsorption equilibrium isotherms

The researchers, two most popular models of isotherms, Langmuir and Freundlich, were used to evaluate adsorption isotherms. Mercury according to Langmuir Isotherm a plot of C_e/q_e versus C_e was drawn (Figure 5). Langmuir constants are presented in Table 2.

In order to study Freundlich isotherm, log q was plotted versus log C_e and then data were presented in Table 2.

The coefficients of correlation were high (R^2 =0.998 for Langmuir isotherm and R^2=0.987 for Freundlich isotherm) showing good linearity. The adsorption isotherms were fitted both Langmuir and Freundlich isotherms but Langmuir isotherm was found to be more favorable than Freundlich isotherm. The comparison of maximum adsorption capacity of Mercury (II) onto different synthetic adsorbents is presented in Table 3. DD-MMT demonstrates a significant adsorption capacity, which means that it may be successfully used as an effective adsorbent of Mercury (II).



Adsorbent	q_m (mg/g)	Reference

Figure5. The plot of Hg(II) adsorption on Langmuir isotherm model.

Table 2. Langmuir and Freundlich isotherm parameters for the adsorption of Hg(II) on DD-MMT.

Langmuir isotherm parameters			Freundlich isotherm parameters	
q_m (mg/g)	k_l (L/mg)	R_L	K_f ($mg^{1-n} L^n$ /g)	n
312.5	0.432	0.0076	89.97	1.37

Table 3. Comparison ofthe maximum adsorption capacity of Hg (II) on various adsorbents.

poly(vinylalcohol)/poly(vinylimidazole)	118.3	[7]
WCNT-COOH	200	[1]
conjugate nanomaterial	164.22	[13]
Si-APTMS-Py	174.3	[15]
polydithiocarbamate	22.03	[8]
thiol-incorporated AC	129	[16]
MCD-GO-R	63.25	[9]
Polyacrylonitrile fiber	275.76	[10]
EDTA-m graphene oxide	203.1	[12]
Silica-based	355.9	[23]
CTS-g-P(AA-co-NANHT)	1145.5	[11]
PPy/SBA- 15	200	[14]
DD-MMT	312.5	Present study

Adsorption kinetic

The equations of the pseudo-first order [21] and pseudo-second order [22] models were used to study adsorption kinetic and to determine the rate constants of adsorption.The rate constants and correlation coefficients for both models are shown in Table 4. Studying of kinetic parameters confirmed that the experimental data obey pseudo-second-order kinetic model.

Table 4. Kinetic parameters for the adsorption of Hg(II) on DD-MMT.

Pseudo- First -order equation				
Concentration (mg/L)	$q_{e,\ exp}$ (mg/g)	K_1 (min^{-1})	q_e (mg/g)	R^2
20	10.00	0.0014	10.71	0.9362
Pseudo-second-order equation				
Concentration (mg/L)	q_e, exp (mg/g)	K_2 (min^{-1})	q_e (mg/g)	R^2
20	10.00	0.163	10.05	0.9999

Treatment of real sample

In order to investigate practical application of the proposed method, real samples have been treated with DD-MMT at optimum experimental condition. The samples have been selected from Khouzestan in Iran. The initial concentration of mercury(II) ions in the water samples which has been determined by spectrophotometric method were less than detection limit. The result (Table 5) approved that DD- MMT has a substantial ability for mercury(II) removal from water solutions.

Table 5. Removal of Hg(II) in spiked water samples.

Sample	Added Hg(II) (mg/L)	Removal (%)
	20	90.6
Tap water	50	91.3
	100	95.3
	20	91.9
River water	50	91.4
	100	95.3
	20	89.5
Persian Gulf water	50	98.3
	100	96.4
	20	90.5
Industrial wastewater	50	93.6
	100	96.5

Conclusion

A facile synthesis method for DD-MMT was proposed in the present work. The Hg(II) ion adsorption investigations demonstrated that an efficient adsorbent was successfully created by this method. High efficiency of the adsorbent may owe to the high specific surface area of Montmorilonite and also the presence of S donor atoms of Dibutyl-Disulfide, which play a key role in binding with Hg (II). Thus, the adsorbent is very effective for the removal and separation of Hg (II). The proposed method has several advantages:

- Montmorillonite is natural nanoclay so the adsorbent is environmental friendly.
- The adsorbent is easily obtained. Dibutyl-Disulfide -Montmorillonite (DD-MMT) composite was prepared by a facile one-step method.
- The removal method is very effective, simple, rapid and low cost.
- The adsorption equilibrium data complied with the Langmuir isotherm. The DD-MMT composite had high capacity to remove Hg (II) to compare with other methods (Table 3).
- The different water samples were used as real sample that in all cases, removal was more than 90 percent.

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