Modification and Characterization of Nanoclay and Its Using for the Removal of Cr(VI): Optimization, Isotherm, Kinetic and Real Sample Studies

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Abstract

In this study, a simple and efficient method for removal of Cr (VI) from water samples was developed using modified nanoclay. A facile one-step method was employed to produce Dithizone-Montmorillonite (Dz-MMT) composite. The synthesized composite was characterized by scanning electron microscopy (SEM), X-ray powder diffraction (XRD), and Fourier transform infrared spectroscopy (FT-IR). The effectiveness of the composite in Cr (VI) removal from aqueous solutions at different adsorbent dose, solution pH, contact time, and agitation rate were examined. The composite had a high uptake capacity in room temperature and removed Cr (VI) (10 mg/L) of about 98% from aqueous solutions by 3 g/L of adsorbent in 90 min. The equilibrium adsorption isotherm data are tested by applying both Langmuir and Freundlich isotherm models. The composite effectively removed Cr (VI) from water, and the maximum adsorption capacity obtained from the Langmuir equation was 76.9 mg/g. Adsorption kinetics of Cr (VI) on the composite followed the pseudo-second-order kinetic model. The method was applied to the removal of Cr (VI) in tap water, river water, and industrial wastewater samples from different parts of Khouzestan, Iran.

Keywords: Hexavalent Chromium, Modified Montmorillonite, Removal.

1. Introduction

Hexavalent Chromium, Cr (VI), is one of the most toxic and harmful heavy metals, which is a serious wastewater pollutant causing environmental risk. The International Agency for Research on Cancer (IARC) has classified inhaled Cr (VI) as a human carcinogen [1]. The maximum concentration limit for Chromium (VI) for discharge into inland surface water is 0.1 mg/L and in potable water is 0.05 mg/L [2]. Chromium is extensively used in many modern industries. Effluents generated from different industries such as paint and pigment manufacturing, stainless steel production, leather, electroplating, wood preservation, fertilizer, textile, and aerospace industry, generally contain hexavalent Chromium. Therefore, the elimination of Chromium (VI) from wastewater is important to protect public health.

Adsorption is considered as a very effective and economical process for removal of metal ion from wastewaters [3]. Different adsorbents have been used for the removal of Chromium (VI) from water samples such as Ocimumamericanum L. seed pods [4],

Helianthus annuus (sunflower) stem waste [5], aniline formaldehyde condensate coated silica gel [6], Montmorillonite-supported magnetite nanoparticles [7], modified Ca-Montmorillonite with ionic liquids [8], green algae Ulvalactuca and its activated carbon [9], and UAE sand [10].

The adsorbents, which have high surface area and adequate sites for adsorption, are preferred in adsorption of heavy metals. Therefore, in this study, Montmorillonite (nanoclay) was selected. The high specific surface area, chemical and mechanical stability, layered structure, high cation exchange capacity, etc., have made the nanoclays excellent adsorbent materials [11]. Montmorillonite (MMT) was modified by Dithizone (Dz) to produce adequate sites for Chromium adsorption. Modified Montmorillonite was characterized by FT-IR spectroscopy, XRD and SEM techniques. Afterward, the synthesized composite was used for removal of Chromium (VI) from water samples. The effects of pH value of solution, adsorbent dose, adsorption time, and agitation rate on the adsorption of Chromium (VI) on Dz-MMT have been investigated. The Langmuir and Freundlich isotherms and adsorption kinetics of Chromium (VI) on Dz-MMT were also studied.

2. Experimental

2.1 Materials

All chemicals used were of analytical grade. Moreover, doubled distilled water was used throughout the study. Montmorillonite (sodium form) was supplied by F.C.C. (China). A stock solution of 1000 mg/L of Cr (VI) was prepared by dissolving 0.2828 g of potassium dichromate (Merck-Germany) in water and diluting to 100 mL in a volumetric flask. The desired concentrations were obtained by successive dilutions.

2.2. Apparatus

Absorption studies were carried out using Perkin-Elmer UV–vis spectrophotometer model Lambda35. A FT-IR Perkin-Elmer BXπ 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 Siefret ID 3003, Germany) at ambient temperature.

2.3. Preparation of adsorbent

The Montmorillonite (5 g) was suspended in 500 mL distilled water and stirred magnetically for about 24 h at room temperature. Then, the pH of the solution was adjusted to 2.5 using nitric acid and 1.0g Dithizone (that it has been solved in acetone) was added. The suspension was stirred for 3 h at room temperature. The green precipitation was filtered and washed several times with double distilled water. In the end, the precipitation was dried in an oven at 60 °C for 24 h.

2.4. General method

All the experiments were carried out in batch mode. Batch mode was selected because of its relative simplicity. The experiments were run in Erlenmeyer flasks (100 mL) using shaker. Prior to each experiment, predetermined amount of adsorbent was added to each flask with 50 mL of aqueous Chromium (VI) solution. The desired pH was maintained using dilute NaOH or HCl solutions. All the adsorption experiments were carried out at room temperature (25 ±2 °C) and a pH of 2, unless stated otherwise. The shaking was kept constant for each run throughout the experiment ensuring equal mixing. Samples of 10 mL were taken, centrifuged and analyzed for Chromium (VI) concentration measurements. The concentration of Chromium (VI) ions was determined spectrophotometrically by developing a purple-violet color with 1, 5-diphenyl carbazide in acidic solution as a complexing agent. The absorbance of the purple-violet colored solution is read at 542 nm.

The percentages of Chromium (VI) removal are calculated based on the following equation:

$$\text{Re}\,moval(\%) = (\frac{C_{0-}C_e}{C_0}) \times 100 \qquad (1)$$

In this equation, C_0 is the initial Chromium (VI) concentration (before being mixed with the adsorbent), and C_e is the equilibrium concentration (after being mixed with the adsorbent). The equilibrium

concentration was obtained through a calibration curve for the Chromium.

3. Results and Discussion

3.1 Adsorbent characterization

3.1.1. FT-IR Spectroscopic Studyalysts

The FT-IR spectra of MMT and Dz-MMT were studied (Fig. 1). The FT-IR spectrum of Dz-MMT indicated the presence of new bands at about 1498, 1458, 1438 and 1316 cm^{-1} corresponding to the N-H (bending), aromatic compound, N-N, C-N (stretching) absorption bands, respectively[12].These results confirmed that MMT was modified by Dithizone because Dithizone has the bands (N-H, N-N and C-N) but Montmorillonite doesn't have them.
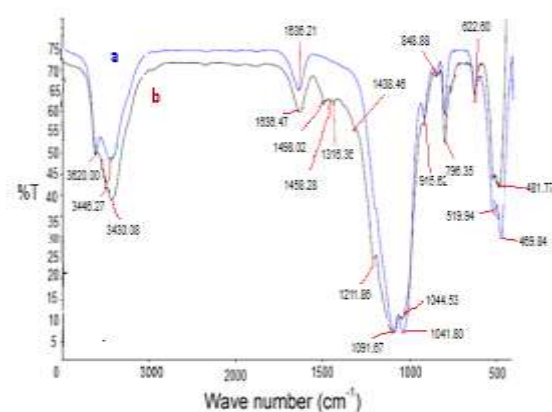

Fig. 1. FT-IR spectra of (a) MMT (b) MMT-DZ

3.1.2. X-ray diffraction Study

To investigate the modification, the diffraction spectrum of x-ray was taken between 2 theta of 5° to 15° from pure Montmorillonite and also for modified Montmorillonite (Figure 2). The shift of the XRD peak from 7.24 to 6.12 can be attributed to re-orientation of the organic compound between MMT layers [13, 14]. The modification process occurred in such a way that the Dithizone ions were adsorbed in the interlamellar space of the clays. The adsorption was through an exchange reaction between the inorganic cations on the clay and the Dithizone ions in the solution [15].

3.1.3. SEM photographs study

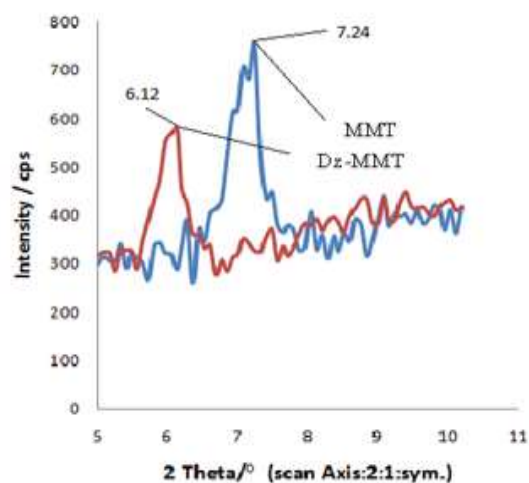The surface morphologies of the MMT, Dz-MMT and Dz-MMT after adsorption of metal ion were studied

Fig. 2. XRD spectra of MMT and MMT-DZ

using scanning electron microscopy. Micrographs of the surface of each material are shown in Fig. 3(a)–(c) at 5000 times magnifications. They are typical of the overall surface of each sample. Fig. 3(a) corresponds to the raw MMT which shows that MMT consists of small particles and has a nonporous surface; however, it was not compact. After the fabrication of the Dz-MMT composite, as it is presented in Fig 3(b), the sharp sheets were observed due to the coating of Dz onto the surfaces of MMT. As shown in Fig. 3(c), metal ions are trapped on the sharp sheets such as snow on earth.
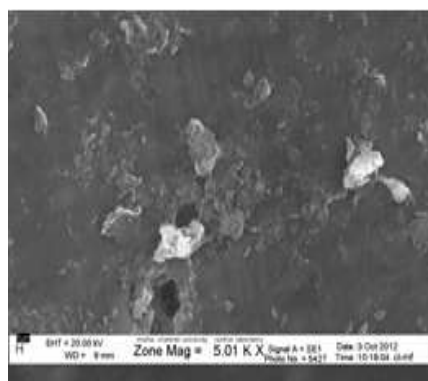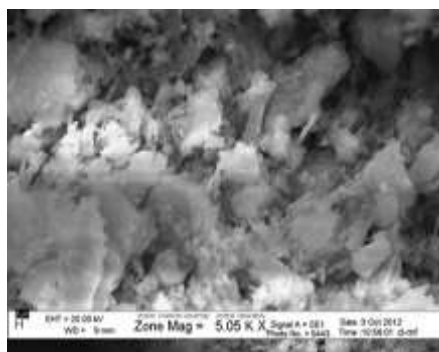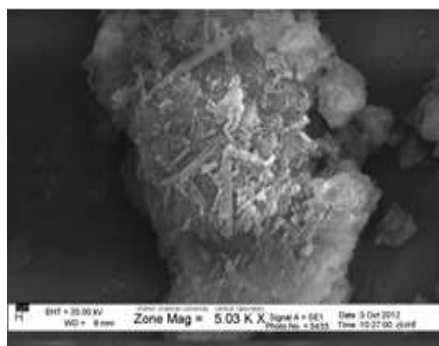

Fig. 3. Small angle X-ray diffraction pattern of (a) Vanadyl Schiff base complex@Mont and (b) Na-montmorillonite

Fig. 3. SEM images of (a) MMT (b)MMT-DZ (c) MMT-DZ-Cr(VI) at 5000 times magnification

3.2 Effect of pH

The adsorption of Chromium (VI) onto the composite as a function of pH was investigated at the initial Chromium concentration of 10 mg/L and the contact time of 60 min (Figure 4). The removal of Chromium was maximum at pH of 2.0. Dithizon have N,S-coordination sites that formed complex with Chromium at acidic media (pH=2) [16].
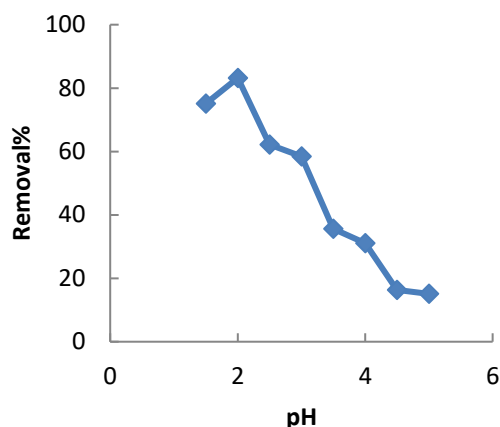
Fig. 4. Effect of pH on Cr(VI) removal (initial Cr(VI) concentration 10 mg/L, adsorbent dosage=2 g/L, contact time=60 min, agitation rate= 100 rpm).
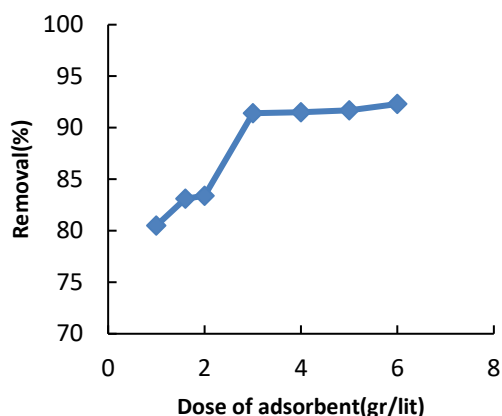
3.3. Effect of adsorbent dose

The influence of adsorbent dose on Chromium removal was studied by varying the adsorbent dose from 1.0 to 6.0 g/L at an initial Chromium concentration of 10 mg/L in 50 mL solutions. Increased adsorbent dosage implied a greater surface area and a greater number of binding sites available for the constant amount of Chromium (VI). An adsorbent dose of 3 g/L was chosen as an optimum value. The results showed (Figure 5) that 1 g/L of Dz-MMT is required for the 80.5% removal of Chromium (VI) from initial concentrations of 10 mg/L. However, for a removal of about 92%, 3 g/L of Dz-MMT was needed. The results are better than some of the previously reported methods [4-6].
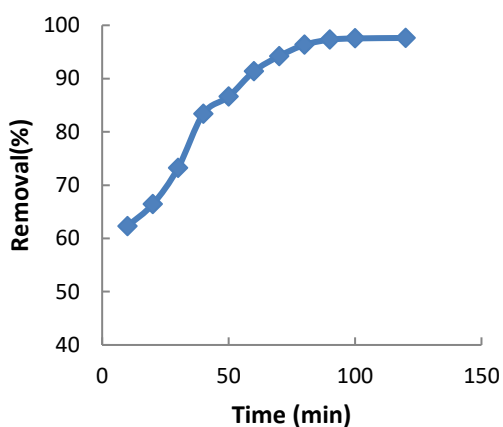
3.4. Effect of contact time and Agitation Rate

The adsorption of Chromium onto composite adsorbent has been investigated as a function of time in the range of 10-120 min (Fig. 6). It was found that about 62 % removal of Chromium occurs within 10 min. However, for a removal of more than 97%, a time interval of 90 minutes was needed. The method is rapid compared to similar methods [1,6,8].

The agitation speed ranging between 80 and 120 rpm was maintained (Figure not shown). In the all speed, the removal was not varied significantly. An agitation speed of 100 rpm was chosen as an optimum value.

Fig. 5. Effect of adsorbent dose on adsorption of Cr(VI) (initial Cr(VI) concentration 10 mg/L, pH=2.0, contact time=60 min, agitation rate= 100 rpm)

Fig. 6: Effect of contact time on adsorption of Cr (VI) (initial Cr(VI) concentration 10 mg/L, adsorbent dosage=2 g/L, pH=2.0, agitation rate= 100 rpm)

3.5. Isotherms of Adsorption

In this study, Langmuir and Freundlich isotherms were employed for the study of the adsorption of Cr (VI) onto modified Montmorillonite. Such isotherms were achieved for an initial concentration of 5-30 mg/L in the previous optimization condition, contact time of 120 min and temperature of $25 \pm 2 \ ^0C$.

In order to study the adsorption of Chromium according to Langmuir Isotherm [17] a plot of $1/q_e$ versus $1/Ce$ was drawn. Langmuir constants are shown in Table 1.

The Freundlich model assumes a heterogeneous adsorption surface with sites that have different adsorption energies which are not equally available

[18]. For this isotherm, log qe was plotted versus log Ce. The results were presented in Table 1.

Table 1: Langmuir and Freundlich isotherm parameters for the adsorption of Cr(VI) on MMT-DZ

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
76.92	0.05	0.4	3.54	1.61

Both of the isotherms are well adapted with the adsorption of Chromium (VI) on Dz-MMT (Table 1). The coefficients of correlation were high (R^2 =0.991 for Langmuir isotherm and R^2=0.847 for Freundlich isotherm) showing a good linearity. The adsorption isotherms fit both Langmuir and Freundlich isotherms but Langmuir isotherm is found to be more favorable than Freundlich isotherm. The maximum adsorption capacity is bigger than most reported methods (Table 2).

3.6. Adsorption kinetic studies

The adsorption was considered as the pseudo-first order and pseudo-second-order kinetic models. Parameters for pseudo-first and pseudo-second order models from linear regression for concentrations of 10 and 20 (mg/L) of Chromium (VI) are summarized in Table 3. According to Table 2, the adsorption kinetics well fitted using a pseudo second-order kinetic model.

3.7. Real Samples Study

The researchers studied Chromium (VI) removal from real samples of the waters from Ahvaz city water, Persian Gulf water and the industrial wastewaters. To do this, 25 mL of each real sample was examined, different amounts of Chromium (VI) were added to

Table 2. Comparison of the maximum adsorption capacity of Cr (VI) on various adsorbents.

Adsorbent	Maximum capacity	Reference
Kaolinite	11.6	1
Acid-Activated Kaolinite	13.9	1
ZrO-Kaolinite	10.9	1
TBA-Kaolinite	10.6	1
seed pods	83.3	4
Montmorillonite-supported magnetite nanoparticles	15.3	7
green alga	10.6	9
green alga's activated carbon	112.3	9
White sand	62.5	10
Yellow sand	9.8	10
Red sand	2.38	10
Fe_3O_4 nanoparticle	34.87	19
Carbon bead-supported Hollow carbon nanofiber	51	20
Dz-MMT	76.9	Present study

Table 3. Kinetic parameters for the adsorption of Cr(VI) on MMT-DZ

Pseudo- First -order equation				
Concentration (mg/L)	$q_{e, exp}$ (mg/g)	K_1 (min^{-1})	q_e (mg/g)	R^2
10	4.879	0.0552	5.754	0.907
20	5.623	0.0161	7.473	0.847

Pseudo-second-order equation				
Concentration (mg/L)	q_e, exp (mg/g)	K_1 (min^{-1})	q_e (mg/g)	R^2
10	4.879	0.033	4.945	0.993
20	5.623	0.0145	7.518	0.998

them and the removal process was studied on them. Chromium (VI) removal, in all the samples, was more than 90%, which reveals the effectiveness of this method for all samples.

4. Conclusion

The results show that the chemically modified Montmorillonite with Dithizone can be used as an effective adsorbent for the removal of Chromium (VI) from different water samples. The SEM images clearly showed that after modified, a lot of pores were produced and the FT-IR spectra showed that modification was successfully occurred. The high efficiency of adsorbent may be due to the high specific surface area of Montmorilonite and the presence of S and N donor atoms of Dithizone, which play a key role in binding with Cr (VI). Thus, the adsorbent is very effective for the removal and separation of Chromium (VI). The proposed method has several advantages.

1. The adsorbent is easily obtained. A facile one-step method was employed to produce Dithizone-Montmorillonite (Dz-MMT) composite.

2. The removal method is effective, simple, rapid and low cost.

3. The adsorption equilibrium data obeyed the Langmuir isotherm. The maximum adsorption capacity is bigger than those of the most widely adsorption method for the removal of Cr (VI) (Table 2).

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