Journal of Hazardous Materials 184 (2010) 654–661

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Study of organically-modified montmorillonite clay for the removal of copper(II)

Khaled S. Abou-El-Sherbini [a], Mohamed M. Hassanien [b,*]

[a] Department of Inorganic Chemistry, National Research Centre, Dokki, Giza, Egypt
[b] Department of Chemistry, Industrial Education College, University of Beni-Suif, Beni-Suif, Egypt

ARTICLE INFO

Article history:
Received 6 May 2010
Received in revised form 19 July 2010
Accepted 23 August 2010
Available online 27 August 2010

Keywords:
Montmorillonite
2-Oxyhydrazino-*N*-(2-methylen-yl-hydroxyphenyl)pyridinium chloride
Intercalation
Removal
Copper(II)

ABSTRACT

2-Oxyhydrazino-*N*-(2-methylen-yl-hydroxyphenyl)pyridinium (OMHP) ion was immobilized onto Na-montmorillonite clay (MMT). The modified clay (OMHP-MMT) was used for the removal of Cu(II). Experiments were carried out as a function of solution pH, stirring time, effect of some common ions and eluent type, concentration and volume. MMT, OMHP-MMT, and OMHP-MMT-loaded Cu(II) were characterized by X-ray diffractometry, electronic and infrared spectra, and elemental and thermogravimetric analyses. OMHP is suggested to be intercalated into MMT parallel to the aluminosilicate layers, with a capacity of 56.4 mEq/100 g. OMHP-MMT shows good stability in 0.1–1 mol L^{-1} hydrochloric or nitric acids, ammonia hydroxide, concentrated Na^+, K^+, NH_4^+, Cl^- or SO_4^{2-}. It shows good removal efficiency and selectivity towards Cu(II) at pH 3.0–8.0 and stirring time 10 min with an removal capacity of 119 mEq/100 g. Most common ions do not interfere with the removal process except Fe^{3+}. Extracted Cu(II) could be quantitatively recovered by 10 mL 1% thiourea in 0.1 mol L^{-1} HCl with 100-fold preconcentration factor. OMHP-MMT was successfully applied to recover Cu(II) from different samples.

© 2010 Elsevier B.V. All rights reserved.

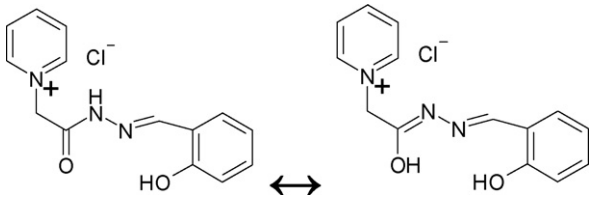
1. Introduction

More and more people are facing water scarcity that does not only mean its insufficiency but also its being contaminated by hazardous materials. Heavy metals such as lead, mercury, and copper are considered among the worst hazards as they cannot be decayed chemically [1]. Most of the traditional technologies developed for removing heavy metals from solutions such as ion exchange, adsorption [2], chemical precipitation [3], reverse osmosis, electrodialysis [4], and solvent extraction [5], whilst effective, are very often costly, time-consuming and/or themselves use hazardous materials. Solid phase extraction using functionalized materials, could avoid such drawbacks while maintaining selectivity and efficiency [6–10]. Natural, synthetic, and modified inorganic and organic solids have been successfully employed in this regard. Among this group, aluminosilicate minerals such as montmorillonite (MMT) act as potential ionic exchangers for heavy metals due to their low cost, high abundance, easy manipulation, and harmlessness to the environment [11–19]. MMT is a very soft phyllosilicate mineral of the smectite family, having two SiO_4-tetrahedral sheets sandwiching a central AlO_6-octahedral sheet (type 2:1). Chemically, it is hydrated sodium calcium aluminum magnesium silicate hydroxide $(Na, Ca)_x(Al)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$ [11–13]. It has a defective structure because of the isomorphic substitution of the Mg or Fe atoms for the Al atoms (octahedra) and the Al atoms for the Si atoms (tetrahedra) so that the negatively-charged aluminosilicate layers accommodate exchangeable cations such as Na^+, Ca^{2+} and/or Mg^{2+} in the interlayered-spacing for the sake of charge compensation [12]. These exchangeable cations are strongly hydrated in the presence of water, resulting in a hydrophilic environment at the clay surface [13].

MMT has recently attracted many separation applications with or without modification to enhance separation efficiency and selectivity. Despite its negative surface charge, MMT has little affinity for heavy metal ions such as Co^{2+}, Zn^{2+}, and Cu^{2+}, hence further functionalization is necessary [17]. Cu(II) ions were removed from an aqueous solution using heat-treated MMT and its poly(oxo zirconium) and tetrabutylammonium derivatives with extraction efficiencies 28.8, 7.1 and 27.3 mg/g despite their high cation exchange capacities (CEC) were 153.0, 73.2 and 47.6 mEq/100 g, respectively [14]. MMT was modified with hexadecyltrimethylammonium ions with a capacity of 96 mEq/100 g then the organo-clay was functionalized with 2-mercapto-5-amino-1,3,4-thiadiazole with a capacity of 23.5 mEq/100 g which is finally used to extract Hg(II) [15]. MMT modified with sodium dodecylsulfate could extract 0.032 and 0.083 mmol/g Zn^{2+} and Cu^{2+}, respectively at pH 3.3 [17]. Methylene blue was immobilized onto MMT-predominant bentonite with a capacity of 36 mEq/100 g and used to extract Hg^{2+} at pH 6.0 with a capacity of 37 mEq/100 g. [19]. However, the MMT is more favorable than bentonite as MMT has higher specific surface area and capacity whereas bentonite is a mixture of phases

* Corresponding author. Tel.: +2 0122219118.
E-mail addresses: kh_sherbini@yahoo.com (K.S. Abou-El-Sherbini), mmhassanien2002@yahoo.com (M.M. Hassanien).

0304-3894/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2010.08.088



Scheme 1. Resonance of 2-oxyhydrazino-*N*-(2-methylen-yl-hydroxyphenyl) pyridinium chloride.

[11,19]. Vermiculite, a 2:1 mineral clay, was applied as adsorbent for removal of Cd^{2+}, Mn^{2+}, Zn^{2+}, and Cr^{3+} from aqueous solutions with capacities of 0.50, 0.52, 0.60, and 0.48 mmol/g, respectively [20].

The paper aims at functionalizing Na-montmorillonite clay with 2-oxyhydrazino-*N*-(2-methylen-yl-hydroxyphenyl)pyridinium (OMHP) chloride as a chelating hydrazone derivative to extract Cu(II) ions from water samples.

2. Experimental

2.1. Materials

All chemicals were of analytical reagent grade otherwise stated. Double distilled water (DDW) was used throughout. MMT (sodium montmorillonite) was provided by Southern clay products, Inc. A Cu(II), as chloride, stock standard solution, (1000 mg L^{-1}) from Merck was used for the preparation of intermediate standard solutions by an appropriate dilution with DDW. Salicylaldehyde and Girard P (2-oxyhydrazinopyridinium chloride) were purchased from Aldrich. OMHP chloride was synthesized according to literature [21,22]. Ethanol and Toluene was supplied by EDWIC, Egypt. Granite samples were kindly supplied from Prof. Dr. IM.M. Kenawy, Mansoura University, Egypt.

2.2. Synthesis of OMHP-loaded MMT (OMHP-MMT)), and Cu(II)-loaded OMHP-MMT (Cu-OMHP-MMT)

OMHP (Scheme 1) was synthesized according to literature [21,22]. 5 g of Girard-P were refluxed with 4 mL salicylaldehyde in 50 mL of absolute ethanol over water bath for 4 h. The reaction mixture was left to cool till white crystals were separated out. These were filtered off, recrystalized from ethanol and finally dried in vacuum desiccators over anhydrous calcium chloride. Yield: 6.5 g (74%) of (OMHP). Found: C, 57.93; H, 4.78; N, 14.25; Cl, 11.75. Calc. for $C_{14}H_{14}N_3O_2Cl$ (291.71): C, 57.64; H, 4.84; N, 14.41; Cl, 12.15%.

MMT (100 g) was activated by stirring in 500 ml of 0.1 mol L^{-1} HCl for 2 h, washed with DDW, filtered and dried at 80 °C for 24 h to yield 99.4 g of the activated clay coded MMT_A. Then 10 g of MMT_A were added to 200 ml ethanolic solution (95%) containing 2 g of OMHP and refluxed with vigorous stirring for 24 h. The yellowish yield was centrifuged, the supernatant solution was discarded, and the yield washed and centrifuged three times with ethanol followed by water. OMHP-MMT was dried in vacuum oven at 80 °C for 6 h and the yield was 10.95 g.

To synthesize Cu-OMHP-MMT, 1 g of OMHP-MMT was suspended in 100 mL of 10 mg L^{-1} of the metal ions at pH 5.5. The mixture was stirred for 1 h at a constant rate. The resulting greenish suspension was centrifuged, the supernatant solution was discarded and the procedure was repeated with increasing the initial metal ion concentrations (100 mL of 0.1, 0.5 and 1 g L^{-1} of the metal ions) at pH 6.0. This graduation in concentration of metal ions is to reach the "saturation" till the plateau values (adsorption capacity values) were obtained. The clay suspension was centrifuged, washed three times with 5 mL DDW then Cu-OMHP-MMT was dried in vacuum oven at 80 °C for 6 h and the yield (1.15 g) was stored in a desiccator.

The cation exchange capacity (CEC) of MMT was determined according to the literature [23] by back-titrating excess 1 mol L^{-1} ammonium acetate. Analysis of ammonia was performed in a well-ventilated room, where no ammoniacal solutions were stored, using the Koroleff method [24]. For the determination of Cl^- in OMHP or OMHP-MMT, 0.5 g was enrolled in a piece of sodium and heated gently for 10 min then heated vigorously for another 10 min and dropped in 25 mL DDW. Cl^- was determined by gravimetric determination as silver chloride. Cu(II) in 0.5 g Cu-OMHP-MMT was determined by flame atomic absorption spectrometer (FAAS) after elution with 10 mL of thiourea in 0.1 mol L^{-1} HCl.

2.3. Apparatus

A Perkin Elmer 2380 atomic absorption spectrometer was used for direct measurement of Cu(II) at wavelength 324.8 nm. An automatic VARIO EL ELEMENTAR instrument was used to determine the percentage of C, H, N and S. X-ray diffraction (XRD) characterization was carried out using a powder diffractometer Philips 'X-pert Pro' attached with secondary monochromator, automatic divergence slit, nickel filter and a $Cu_{k\alpha 1}$ radiation source operated at a generator voltage, 45 kV and current, 40 μA. The instrument was run at step scan mode within 2θ angle 4–70°. For reliability of data, each sample was scanned several times. X-ray florescence (XRF) analysis for MMT was carried out for powder (<74 μm) samples using X-ray fluorescence equipment PW 2404 with six crystals. Crystals (LIF-200), (LIF-220) were used for estimating Ca, Fe, K, Ti, Mn and other trace elements from nickel to uranium while the crystal (TIAP) was used for determining Si and Al and PXI for determining Na and Mg. The concentration of analyzed elements is determined by using software Super Q and Semi Q programs with accuracy of 99.99% and confidence limit 96.7%. For the analysis, the clay was formed as powder pellets (Pellets method) which were prepared by pressing the powder of the sample in aluminum cup using Herzog presser and 10 t pressure. BET surface area of the clay was investigated by Sorpty-1750 (Carlo Erba Instrumentation). The IR absorption spectra were recorded in KBr tablets on a Mattson 5000 FTIR spectrometer. Electronic spectra were recorded for the sample in Nujol, on a Unicam UV/Vis UV2. Thermogravimetric analysis (TGA) was carried out using a Shimadzu thermobalance at a rate of heating 10 °C min^{-1} in a purified N_2 atmosphere. The pH was adjusted within the range 2–10 using a Hanna 8519 digital pH meter using 0.5 mol L^{-1} of NH_4OH and 0.2 mol L^{-1} of CH_3COOH.

2.4. Batch mode removal of Cu(II) onto OMHP-MMT

A total of 20 mg of OMHP-MMT was suspended with constant stirring for different time intervals in 25 mL of 20 mg L^{-1} of Cu(II), as chloride, at different pH values. The concentrations of the investigated ions in the filtrates were determined by FAAS. The removal efficiency (E, %) was determined using Eq. (1), where C_i and C_f are the initial and final metal concentration in the solution phase, respectively.

$$E = \frac{C_i - C_f\,(\mathrm{mg/L})}{C_i\,(\mathrm{mg/L})} \times 100\% \quad (1)$$

The effect of the volume of the eluent (1% thiourea in 0.1 mol L^{-1} HCl) on the recovery of 50 μg of Cu(II) from 1 L of DDW, collected from one batch-mode separation processes onto 100 mg OMHP-MMT, was studied using the optimum conditions; pH 6.0, and stirring time = 10 min.

The effect of interfering ions on the recovery of 50 μg of Cu(II), extracted onto 100 mg OMHP-MMT from 1 L of solution, was studied using the optimum conditions. The residue was filtered and the

Table 1
XRF analysis of MMT clay.

Metal	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2
%	61.32	21.54	3.82	2.45	0.23	2.63	0.15	0.1

LOI at 105 °C is (6.42%), LOI at 1000 °C is (13.52%).

collected metal ions were eluted with 1% thiourea in 0.1 mol L^{-1} HCl.

2.5. Application of removal process of Cu(II) onto OMHP-MMT

Pool water from Sakaka and well water from Tabarjel, Saudi Arabia were filtered using a sintered glass G4. One liter of DDW or the water samples was spiked with 10 and 50 μg of Cu(II), and 100 mg of OMHP-MMT was dispersed in each. The mixture was buffered to pH 6.0 with acetate buffer (CH_3COOH/NH_4OH), stirred for 10 min, and filtered. Another fresh 75 mg of OMHP-MMT was added to the filtrate, adjusted again to pH 6.0, stirred for another 10 min, and filtered. The residues were, gathered, washed with DDW buffered to pH 6.0 then the separated Cu(II) was eluted with 10 mL of 1% thiourea in 0.1 mol L^{-1} HCl and determined with FAAS. In each case, the samples were analyzed in triplicate otherwise stated.

The suggested separation method was also applied to the referenced granite samples [25,26]. 0.5 g of the sample was dissolved in boiling HF and HNO_3 acids till near dryness, diluted, filtered and completed to 1 L. Then the removal process follows as illustrated for the pool water sample.

3. Results and discussion

3.1. Characterization of MMT clay and its modifications

MMT has a reasonable BET surface area (S_{BET} = 86 m^2 g^{-1}) compared with the literature 19.8, 235, and 128 m^2 g^{-1} [7, 15, 27, respectively]. It has a density of 2.7 g cm^{-3}. The total CEC of the clay is found to be 83.2 mmol/100 g indicating that it is moderately charged clay as expected in similar clays; 153, 34.4, and 90 mmol/100 g [7, 9, 16, respectively]. XRF analysis of MMT is shown in Table 1. It shows that it is composed of typical constituents of MMT [11–13].

The powder XRD patterns of MMT, OMHP-MMT and Cu-OMHP-MMT are shown in Fig. 1. MMT shows the presence of a single phase of MMT, PDF 13-259. The high background of the diffraction pattern and the broad peaks indicate that MMT is poor crystalline which is common for such clays [13]. The basal interlayered-spacing of MMT is found to be 13.55 Å as concluded from the 0 0 1 diffraction line observed at 2θ 6.523°. This indicates the presence of a single water layer in the van der Waals gab of MMT [13]. The basal interlayered-spacing of OMHP-MMT was found to increase to 13.9 Å as concluded from the 001 diffraction line observed at 2θ 6.357°. This negligible enlargement suggests that OMHP is intercalated into the interlayered-spacing of MMT, lying parallel to the aluminosilicate layers and replacing the interlayered cations and water molecules. This agrees with the literature as in the slightly charged clays such as montmorillonite and hectorite, the organic cations are oriented lying flat between the aluminosilicate sheets [28]. Upon intercalation of Cu(II) into OMHP-MMT, the basal interlayered-spacing almost did not change. Its value was observed to be 13.42 Å (2θ 6.44°). This indicates that Cu(II) is inserted in the interlayered-spacing.

The results of FTIR spectra of MMT, OMHP-MMT and Cu-OMHP-MMT are tabulated in Table 2. Multiple broad bands were detected for MMT in the range 3700–3000 cm^{-1} that are attributed to the OH stretching frequencies. This indicates the presence of at least three types of OH groups that are suggested to be isolated OH groups, indicated from the band at 3630 cm^{-1} [29], and those involved in hydrogen bonding. The band of the OH bending vibration is observed at 1637 cm^{-1} whereas the Al–Al–OH bending frequency was observed at 916 cm^{-1}. This may be considered characteristic of a di-octahedral smectite-type 2:1 layer [30,31]. A strong band was observed at 1044 cm^{-1} characteristic of the Si–O stretching frequency. The tetrahedral bending modes for Al–O–Al, Si–O–Al, Si–O–Mg, and Si–O–Si were observed at 621, 524, 468, and 432 cm^{-1}, respectively [32]. IR absorption spectra of OMHP-MMT showed the development of additional small bands at 1709, 1633, 1624, 1565, 1491, and 1278 cm^{-1}. They are assignable to νC=O, C=C/C=N, Secondary amine δNH, N–C–O, δC=C of aromatic ring, and C–O, respectively [33]. This confirms the intercalation of OMHP onto MMT. IR absorption spectra of Cu-OMHP-MMT showed the disappearance of the bands due to C=O, and δNH observed in the pattern of OMHP-MMT. Also, the bands at 1561 (N–C–O), and

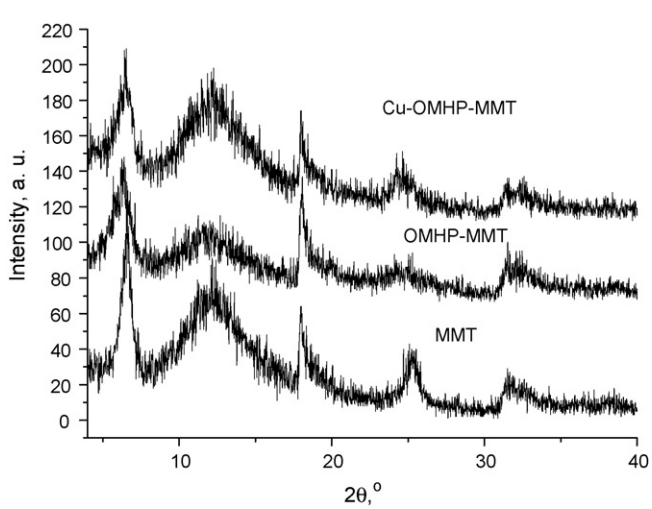


Fig. 1. XRD patterns of MMT (1), OMHP-MMT (2) and Cu-OMHP-MMT. $Cu_{k\alpha 1}$ radiation source.

Table 2
Infrared spectra of MMT, OMHP-MMT and Cu-OMHP-MMT.

MMT	OMHP-MMT	Cu-OMHP-MMT
3630	3626	3625
3443 (broad)	3428 (broad)	3426 (broad)
	3091	3091
	1709	
	1633	1633
1637	1624	
	1565	1561
	1491	1490
		1447
		1362
	1278	1277
1044	1047	1047
916	916	917
799	792	797
	763	753
	727	
	676	677
621	624	623
524	522	523
467	464	464

Table 3
Elemental analysis of OMHP-MMT, Cu-OMHP-MMT and their corresponding capacities.

Clay	C (%)	N (%)	H (%)	Cl^- (%)	Cu(II) (%)	Capacity (mEq/100 g)
OMHP-MMT	9.51 ± 0.09	2.36 ± 0.03	1.49 ± 0.05	–	–	56.4 ± 0.6 OMHP/OMHP-MMT
Cu-OMHP-MMT	8.56 ± 0.05	2.10 ± 0.03	1.61 ± 0.06	3.82 ± 0.05	6.73 ± 0.15	119 ± 3 Cu(II)/OMHP-MMT

Values are given in mean values ($\bar{x}$) ± its standard deviation (σ) for three measurements.

1490 cm^{-1} (δC=C) were red shifted and new bands were developed at 1447 and 1362 cm^{-1}. These mean that Cu(II) is bonded to OMHP in the enol form via O and N atoms.

The elemental analysis data of OMHP-MMT and Cu- OMHP-MMT are shown in Table 3. The percentage of C and N (C% and N%) and was used to calculate the functionalization capacity of OMHP (C_{OMHP}) according to Eq. (2):

$$C_{OMHP} = 500 \times \left(\frac{C\%}{(\text{Mol. wt. of OMHP} \times \text{mole fraction of C in OMHP}} + \frac{N\%}{\text{Mol. wt. of OMHP} \times \text{mole fraction of N in OMHP}} \right) \times \text{mEq}/100\,\text{g} \quad (2)$$

The organic capacity of OMHP-MMT derived from the elemental analysis was found to be 56.4 mEq/100 g, which is comparable to those obtained for reported organically-modified layered clays [14,15,18]. No chloride was found in OMHP-MMT. XRF analysis of OMHP-MMT for CaO and Na_2O indicates the decrease of their concentration to 0.14% and 0.23%, respectively. This indicates that they may be replaced by OMHP in the interlayered-spacing of MMT. The elemental analysis of Cu-OMHP-MMT indicated the uptake of 119 mEq Cu(II)/100 g of OMHP-MMT. This indicates that OMHP-MMT has high removal capacity towards Cu(II) compared to modified MMT [14,17]. The ratio of Cu(II):OMHP in Cu-OMHP-MMT is 2:1 whereas, chloride was detected in 1:1 ratio in respect to Cu(II).

TGA curves of MMT, OMHP-MMT and Cu-OMHP-MMT are shown in Fig. 2. MMT shows the presence of three major thermal decomposition stages. The 1st stage (6.01%) occurs at 65 °C and is attributed to the adsorbed and interlayered water [19,32,34]. The 2nd stage (1.43%) occurs at 482 °C and may be attributed to the gradual loss of structural water suggested to represent the adjacent OH groups. The 3rd stage (2.97%) occurs at 667 °C and may be attributed to the loss of structural water, initially present as isolated OH groups. Similar thermal decomposition stages were previously observed and described for Ca-rich MMT [32]. They also agree with the IR findings of the presence of multiple types of OH. OMHP-MMT shows a sharp decrease in the amount of adsorbed and interlayered waters (1.66%) which may be due to the exchange of the van der Waals cations with the large hydrophobic OMHP molecules. Also, a new weight loss stages (12.03%) developed within the range

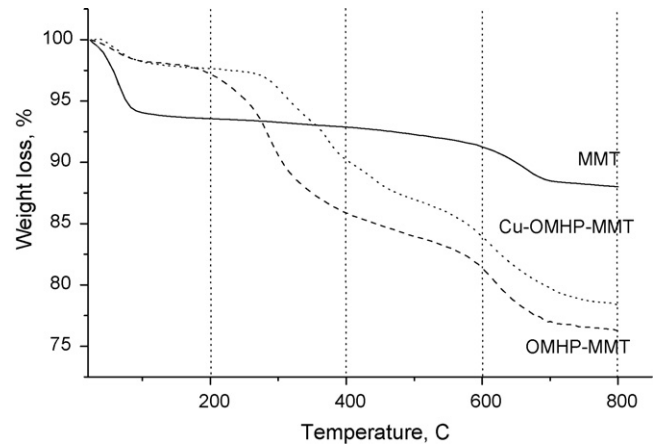


Fig. 2. Thermogravimetric analysis of MMT (solid line), OMHP-MMT (dashed-line) and Cu-OMHP-MMT (dotted-line). Rate of heating 10 °C min^{-1} in a purified N_2 atmosphere.

200–400 °C that may be attributed to the pyrolysis of the intercalated OMHP. The suggested OMHP capacity from TGA loss is 46.8 mEq/100 g which is less than that estimated from elemental analysis due to the inaccuracy of separation of the overlapped TGA stages. The appearance of the weight loss stage of the sandwiched organic constituent into a Na-MMT was observed previously in the same range [35]. The gradual loss of structural water, attributed to vicinal OH groups, remained almost unchanged (1.16%) while that attributed to isolated OH groups doubled (5.67%). This increase may be due to the overlapping of the organic pyrolysis with the water loss stages, or could be related to a change of the geometry of the octahedral sheet into a transvacant configuration produced by the mechanical deformation of a starting *cis*-vacant montmorillonite happening during the intercalation process [32]. Cu-OMHP-MMT shows the same major stages observed for OMHP-MMT but with lower total weight loss at 800 °C which is due to the presence of Cu with the modified clay. The stages attributed to the pyrolysis of organic constituent are ca. 70 °C-shifted to higher temperature which indicates the stabilization of OMHP upon bonding to Cu(II). However, the decomposition stage of adsorbed and intercalated water, was almost the same as that of OMHP-MMT whereas the stage of structural water increased to 8.81% upon Cu(II) intercalation compared with OMHP-MMT. This increase may be due to the

Table 4
TGA results of MMT, OMHP-MMT and Cu-OMHP-MMT.

Weight loss stages	MMT		OMHP-MMT		Cu-OMHP-MMT	
	T_{DTG} (°C)	Weight loss (%)	T_{DTG} (°C)	Weight loss (%)	T_{DTG} (°C)	Weight loss (%)
Adsorbed and intercalated water	65	6.01	59	1.66	55	2.00
Organic constituent			226	4.11	224	0.17
			284	4.52	307	2.80
			343	3.4	374	3.94
Structural water						
Adjacent OH	482	1.43	487	1.16	439	2.54
Isolated OH	667	2.97	619	5.67	555	2.26
					616	3.68
					702	2.87
Total weight loss at 800 °C	–	11.99	–	23.77	–	21.54

Table 5
Characteristic values of the removal of metal ions on clay materials.

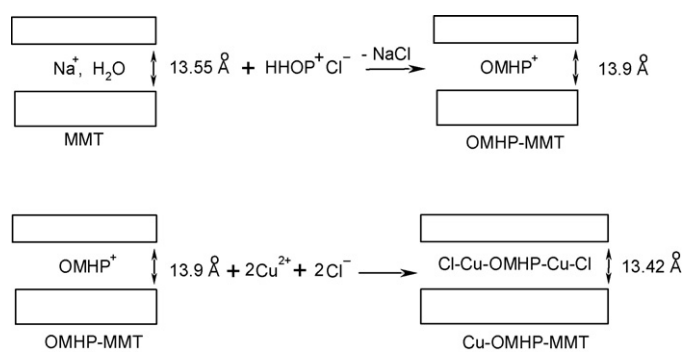
Material	CEC (mEq/100 g)	Removed metal ion	Capacity (mmol/100 g)	pH	Reference
Heat-treated MMT	153.0	Cu(II)	45.3	6	[14]
Heat-treated MMT modified with poly(oxo zirconium)	73.2	Cu(II)	11	6	[14]
Heat-treated MMT modified with tetrabutylammonium	47.6	Cu(II)	43	6	[14]
Kaolinite	11.3	Cu(II)	6.9	6	[14]
Kaolinite modified with poly(oxo zirconium)	10.2	Cu(II)	4.7	6	[14]
Kaolinite modified with tetrabutylammonium	3.9	Cu(II)	5	6	[14]
MMT-modified with hexadecyltrimethylammonium ions/2-mercapto-5-amino-1,3,4-thiadiazole	95.5	Hg(II)	52	1-8	[15]
		Cd(II)	≈30	7–8	
		Pb(II)	≈22	7–7.5	
		Cu(II)	≈15	7–7.5	
		Zn(II)	≈12	7.5–8	
		Ni(II)	≈8	8	
MMT modified with sodium dodecylsulfate	37.2	Zn(II)	3.2	3.3	[17]
		Cu(II)	8.3		
MMT-predominant bentonite modified with methylene blue	65	Hg(II)	37	6.0	[19]
Vermiculite	135	Cd(II)	50	9.0	[20]
		Mn(II)	52		
		Zn(II)	60		
		Cr(III)	48		
Bentonite Volclay	81.9	Cu(II) complex with triethylenetetramine	84.5	7	[37]
Bentonite SAz-1	120		122	7	
Illite Massif Central	19		20	7	
OMHP-MMT	83.2	Cu(II)	119	3–8	Present work

incorporation of water in bonding with Cu(II). Also, it may be partially due to the overlapping of the stages of organic constituent pyrolysis with the structural water loss as well as the change of the geometry of the octahedral sheet. The total weight loss in the range of heating 25–800 °C increases in the order MMT < Cu-OMHP-MMT < OMHP-MMT which confirms the intercalation of Cu(II), and OMHP in MMT. The details of TGA results are given in Table 4.

The electronic spectral band of Cu-OMHP-MMT, in Nujol, appeared broad at 595 nm due to the d–d transition which is an evidence for the existence of Cu(II) in a tetrahedral geometry [36].

The resistance of the OMHP-MMT against OMHP loss was investigated in concentrated solutions of Na^+, K^+ or NH_4^+ as chlorides or iodides; 0.1–2 mol L^{-1} of HCl, HNO_3, NaOH or NH_4OH. For this aim, 0.1 g OMHP-MMT was shaken for 2 h with 25 mL of each solution, described above, in a batch mode state. OMHP-MMT was then washed, centrifuged, dried and the elemental analysis for C and N was repeated. No loss >2% could be observed. Surprisingly an increase was observed in case of NaOH and to lower extent for NH_4OH down to pH 9. This was attributed to the dissolution of the clay network leaving the organic constituent. Hence, for any application in aqueous media, the pH should be kept below 9. Only DMF and DMSO can strip OMHP from OMHP-MMT by reflux.

According to these results, it can be concluded that OMHP is intercalated into the interlayered-spacing of MMT and this modified clay can extract Cu(II) via bonding to the intercalated OMHP in the enol form, via O and N atoms of OMHP, according to Scheme 2.



Scheme 2. Scheme of synthesis of Cu-OMHP-MMT from MMT.

3.2. Removal of Cu(II) using OMHP-MMT

Fig. 3 shows the effect of pH on the removal efficiency of Cu(II) on OMHP-MMT in a batch-mode removal process after stirring for 30 min. The modified clay shows excellent removal efficiency towards Cu(II) >98.0% within a wide pH range 3.0–8.0. The applicability of the removal procedure to such wide pH range is quite important for on-field treatment of contaminated water of different criteria and pH values [1–4]. At higher pH the removal

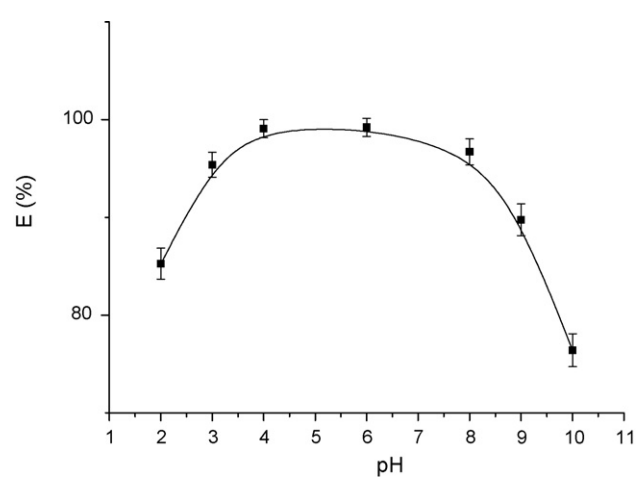


Fig. 3. Effect of pH on the removal efficiency (*E*, %) of Cu(II) using OMHP-MMT. Weight of OMHP-MMT = 20 mg. Volume = 25 mL. Time of stirring = 30 min. Concentration of Cu(II) = 20 μg mL^{-1}.

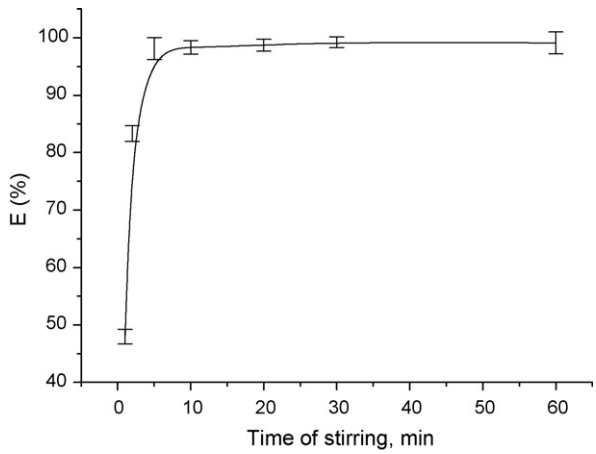


Fig. 4. Effect of time of stirring on the removal efficiency of Cu(II) using OMHP-MMT.

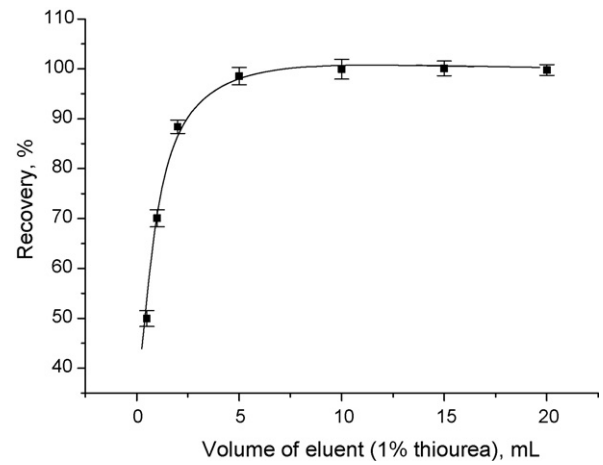


Fig. 5. Effect of volume of the eluent (1% thiourea in 0.1 mol L^{-1} HCl) on the recovery of 50 μg of Cu(II) from 1 L of DDW.

efficiency decreases likely due to the hydrolysis of the clay in alkaline solutions [11,12]. Maximum removal efficiency (99.2 ± 0.9%) was obtained at pH 6.0. On the other side, the introduction of Cu(II) as sulphate or nitrate instead of chloride had no influence on the removal process which means that the major role owing to OMHP.

Comparing the parameters of Cu(II) removal using OMHP-MMT with the those obtained for some alike clays (Table 5), the following advantages could be concluded: (1) OMHP-MMT has the highest capacity for free Cu(II). (2) It has also a wide applicable pH range suitable for most natural waters.

The effect of time of stirring on the removal efficiency of Cu(II) using OMHP-MMT at pH 6.0, is shown in Fig. 4. The time of stirring needed for sorption of 50% of the metal ions ($t_{1/2}$) was found to be 1.3 min which indicates the rapid kinetics of diffusion and that the sandwiched OMHP ions are easily accessible for bonding to Cu(II) ions without steric hindrance. Hence, 5 min of stirring was enough to reach maximum value of separation. This is attributed to the large and open 2D structure of OMHP-MMT. Therefore, it is suitable for the Cu(II) removal in flow systems at trace level of concentration. Although 5 min was enough to reach maximum value of separation, 10 min was recommended to assure complete separation.

Consequently, optimum conditions of the removal of Cu(II) using OMHP-MMT are pH 6.0, and stirring time = 10 min.

A series of selected eluents such as dithizone, thiourea, sodium citrate, sodium oxalate, sodium thiocyanate, different acids and bases were used in order to find the best eluent for desorbing Cu(II) ion from OMHP-MMT. Dithizone in chloroform and thiourea in 0.1 mol L^{-1} HCl can release Cu(II) from OMHP-MMT as they forms stable complexes with Cu(II). 0.1% thiourea in 0.1 mol L^{-1} HCl was preferably chosen as eluent to avoid the toxicity of chloroform. The effect of the volume of the eluent on the recovery of Cu(II) collected twice from batch-mode separation using 2 × 75 mg OMHP-MMT was studied using the optimum conditions of separation (Fig. 5). The use of 5 mL of 1% thiourea in 0.1 mol L^{-1} HCl completely releases Cu(II) ions but 10 mL was recommended for guaranteeing complete scavenging of the metal ions which gives 100-fold concentration. $CuSO_4$ could be obtained from the eluate by adding concentrated H_2SO_4, then boiling to decompose thiourea. The mixture was filtered to remove precipitated sulfur, dried and heated to 300 °C in open air.

An average loss of 0.45% of OMHP-MMT capacity was noticed upon each cycle of removal and recovery which may be due to the hydrolysis of the clay support [11,12]. The sorbent reserved 89.3% of its initial Cu(II) capacity when used for 25 cycles of elution. Hence, the used eluent was considered optimal for quantitative recovery of Cu(II) and preserving OMHP-MMT capacity.

In order to evaluate the suitability of OMHP-MMT for the removal of Cu(II) from environmental samples, the effect of some common ions, was studied by adding different amounts of diverse ions to 1 L of 100 μg L^{-1} of Cu(II) solution, and the optimum condition for batch-mode removal was applied. Errors are considered tolerable up to ±2%. No interference from macroamounts (up to 10,000 times the concentration of Cu(II)) of many foreign ions was detected in the given conditions as shown in Table 6. However, a strong competition for Cu(II) removal on OMHP-MMT was observed from Cr(III), Al(III) and Fe(III) and (II). A 1% thiocyanate solution could mask all competing ions except for Fe(III). These ions are practically much tracer in water samples than Cu(II) at the applied pH [1,3,4]. However for on field application, its presence should be taken into consideration.

3.3. Application of OMHP-MMT for the removal of Cu(II) from natural samples

The removal method was applied for the removal of Cu(II) ions from water samples. Table 7 shows the results of the application process. The spiked amounts of Cu(II) were quantitatively recovered from the DDW sample whereas additional amounts were identified in the pool and well water samples which are due to background originally present (2.35 and 33.7 ng mL^{-1}, respectively). It

Table 6
Effect of interfering ions on the removal of Cu(II) [50 μg L^{-1}] using 2 × 75 mg OMHP-MMT at pH 6.0.

Interfering ion	Tolerance limit
Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, In^{3+}, NH_4^+, Mo^{6+} (as MoO_4^{2-}), Cl^-, ClO_3^-, BrO_3^-, F^-, Br^-, NO_3^-	10,000-fold
S^{2-}, SCN^-, Pb^{2+}, Tl^+, oxalate	1000
SO_3^{2-}, I^-, tartarate	500
Cd^{2+}, $S_2O_3^{2-}$, citrate,	100
Fe^{2+}, Al^{3+}, Cr^{3+}	10
Fe^{3+}	1

Table 7
Removal of Cu(II) and Fe(III) from 1 L of spiked natural water samples using 2 × 75 μg of OMHP-MMT at pH 6.0 after a time of stirring of 10 min.

Sample	Cu(II) added (μg)	Expected [Cu(II)] in 10 mL of extract (μg mL^{-1})	Found (ng mL^{-1})	RSD (%)	$\|t\|_1$
DDW	10	1	0.99 ± 0.01	1.42	1.59
	50	5	5.03 ± 0.06	1.14	1.17
Swimming pool	10	1	4.41 ± 0.04	1.02	–
	50	5	8.33 ± 0.15	1.79	–
Well water from Tabarjel	10	1	1.23 ± 0.02	1.49	–
	50	5	5.24 ± 0.09	1.74	–
Granite (1)*	–	0.634 ± 0.021^{R}	0.64 ± 0.011	1.72	0.44
Granite (2)*	–	0.095 ± 0.004^{R}	0.091 ± 0.002	1.87	1.59

The data are given as $\bar{X} \pm \sigma$ where $\bar{x}$ is the mean value, σ is the standard deviation $n = 5$. In case of water samples $|t|_1$ was applied whereas in case of granite samples $|t|_2$ was applied. * marks values given in μg g^{-1} and R refers to the reported values in references [25,26].

is noteworthy to mention that direct applying of the original pH of the pool and well water samples (7.1 and 7.7, respectively) brings the same removal results which indicates the possibility of direct application of the method for treatment of Cu-polluted water.

A comparison between the experimental means for the recovered Cu(II) amounts from DDW and the granite samples with the spiked or reported values, respectively, was carried out using the null hypothesis of $|t|$ for $P = 0.05$ and $n = 5$ in the case of spiked DDW sample and $n = 10$ in the case of granite samples. It was found out that $|t|_1$ and $|t|_2$ for the investigated metal ion are less than the tabulated values ($|t|_1 = 2.78$ and $|t|_2 = 2.31$) [38]. Consequently, no significant difference was found between the values obtained by the present method and the real or the reported values. This indicates that the proposed method is accurate and efficient for the removal of Cu(II) from polluted waters.

4. Conclusion

OMHP could be successfully intercalated into MMT with a capacity of 56.4 mEq/100 g. The grafted clay OMHP-MMT showed an removal efficiency for Cu(II) of 119 mEq/100 g at pH 6 which can be easily eluted by 1% thiourea in 0.1 mol L^{-1} HCl. OMHP-MMT well tolerates most common ions. OMHP-MMT was applied for the removal of Cu(II) from spiked natural water and granite samples and the method was found accurate. Consequently, OMHP-MMT can be applied for the removal of Cu(II) from contaminated environs.

Acknowledgement

The authors wish to express their thanks for Mr. Dame Bassel, English lecturer, Faculty of Science and Arts of Sharurah, Najran University, Saudi Arabia.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2010.08.088.

References

[1] M.M. Benjamin, Water Chemistry, McGraw-Hill, Singapore, 2002.
[2] D. Clifford, Ion Exchange and Inorganic Adsorption. Water Supply and Treatment, 5th ed., McGraw-Hill, New York, NY, 1999.
[3] L.W. Canter, R.C. Knox, Ground Water Pollution Control, Lewis Publishers, Inc., Chelsea, MI, 1985, pp. 110.
[4] R. Swarup, S.N. Mishra, V.P. Jauhari, Environmental Water Pollution and Its Control, 1st ed., K.M. Rai Mittal for Mittal Publications, New Delhi, 1992, pp. 140–142.
[5] M. Cerna, Use of solvent extraction for the removal of heavy metals from liquid wastes, Environ. Monit. Assess. 34 (2) (1995) 151–162.
[6] N.J.K. Simpson, Solid Phase Extraction, Principles, Techniques and Applications, Marcel Decker, New York, 2000.
[7] V. Camel, Solid phase extraction of trace elements, Spectrochim. Acta Part B 58 (2003) 1177–1233.
[8] Kh.S. Abou-El-Sherbini, M.M. Hassanien, I.M.M. Kenawy, Selective separation and preconcentration of total tin using quercetin as chelating agent, Sep. Sci. Technol. 42 (2007) 3447–3463.
[9] M.M. Hassanien, Kh.S. Abou-El-Sherbini, Synthesis and characterisation of morin-functionalised silica gel for the enrichment of some precious metal ions, Talanta 68 (5) (2006) 1550–1559.
[10] G.A.E. Mostafa, M.M. Hassanien, Kh.S. Abou-El-Sherbini, V. Görlitz, Controlled-pore silica glass modified with N-propylsalicylaldimine for separation and preconcentration of trace Al(III), Ag(I) and Hg(II) in water samples, Anal. Sci. 19 (8) (2003) 1151.
[11] M. Kuzvart, Bentonite and montmorillonite clay, in: Industrial Minerals and Rocks, Elsevier, Amsterdam, 1984, pp. 280–287.
[12] Composition and mineralogy of clay minerals, in: B. Velde (Ed.), Origin and Mineralogy of Clays, Springer-Verlag, Berlin, 1995, pp. 27–33.
[13] M.M. Duane, C.R. Robert, X-Ray Diffraction and the Identification and Analysis of Clay Minerals, Oxford University Press, Oxford, 1989.
[14] K.G. Bhattacharyya, S. Sen Gupta, Kaolinite, montmorillonite, and their modified derivatives as adsorbents for removal of Cu(II) from aqueous solution, Sep. Purif. Technol. 50 (2006) 388–397.
[15] N.L. Dias Filho, D.R. do Carmo, Selective sorption of mercury(II) from aqueous solution with an organically modified clay and its electroanalytical application, Sep. Sci. Technol. 41 (2006) 733–746.
[16] M. Boufatit, H. Ait-Amar, W.R. Mc Whinnie, Development of an algerian material montmorillonite clay-Intercalation with selective long chain alkylammonium cations (octadecytrimethylammonium, cetylpyridium and tetrabutylammonium) and with tellerium complexes, Desalination 223 (2008) 366–374.
[17] S.-H. Lin, R.-S. Juang, Heavy metal removal from water by sorption using surfactant-modified montmorillonite, J. Hazard. Mater. B92 (2002) 315–326.
[18] A. Güses, Ç. Doğar, M. Yalçın, M. Açıkyıldız, R. Bayrak, S. Karaca, The adsorption kinetics of the cationic dye, methylene blue, onto clay, J. Hazard. Mater. B131 (2006) 217–228.
[19] M.M. Hassanien, Kh.S. Abou-El-Sherbini, N.S. Al-Muaikel, Immobilization of methylene blue onto bentonite and its application in the extraction of mercury (II), J. Hazard. Mater. 178 (2010) 94–100.
[20] M.G. da Fonseca, M.M. de Oliveira, L.N.H. Arakaki, Removal of cadmium, zinc, manganese and chromium cations from aqueous solution by a clay mineral, J. Hazard. Mater. B137 (2006) 288–292.
[21] F. Taha, M. Moussa, A. Shallaby, M. Hafez, Egypt. J. Chem. 19 (3) (1976) 527.
[22] F. Taha, M. Moussa, A. Shallaby, M. Hafez, Egypt. J. Chem. 19 (1) (1976) 17.
[23] R.C. Mackenzie, A micromethod for determination of cation-exchange capacity of clay, J. Coll. Sci. 6 (1951) 219–222.
[24] F. Koroleff, in: K. Grasshoff (Ed.), Methods of Seawater Analysis, Verlag Chemie, N.Y., 1976, p. 721.
[25] I. Kenawy, M. Hafez, M. Akl, R. Lashein, Determination by AAS of some trace heavy metal ions in some natural ad biological samples after their preconcentration using newly chemically modified chloromethylated polystyrene-PAN ion-exchanger, Anal. Sci. 16 (2000) 493–500.
[26] Kh.S. Abou-El-Sherbini, M.M. Hassanien, Synthesis of controlled-pore silica glass functionalised with quercetin and its application for the separation and preconcentration of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II), Sep. Sci. Technol. 39 (5) (2004) 1177–1201.
[27] F. Camposa, L. de la Torrea, M. Romána, A. Garcíab, A.A. Elguézabal, Montmorillonite clay intercalated with nanoparticles for hydrogen storage, J. Cer. Proc. Res. 9 (5) (2008) 482–485.
[28] G. Akcay, M. Yurdakoc, Nonyl-and dodecylamines intercalated bentonite and illite from Turkey, Turk. J. Chem. 23 (1999) 105–113.
[29] P.K. Jal, S. Patel, B.K. Mishra, Chemical modification of silica surface by immobilization of functional groups for extractive concentration of metal ions, Talanta 62 (2004) 1005.
[30] J.R. Ferraro, The Sadtler Infrared Spectra Handbook of Minerals and Clays, Sadtler Research Laboratories, Philadelphia, Pennsylvania, 1982, pp. 354–356.
[31] J.E. Mark, Ceramic-reinforced polymers and polymer-modified ceramics, Polym. Eng. Sci. 36 (1996) 2905–2920.
[32] F. Dellisanti, V. Minguzzi, G. Valdrè, Thermal and structural properties of Ca-rich Montmorillonite mechanically deformed by compaction and shear, Appl. Clay Sci. 31 (2006) 282–289.

[33] V.M. Parikah, Absorption Spectroscopy of Organic Molecules, Assison-Wesley Publishing Company, London, 1974.
[34] R.A. Rowland, Differential thermal analysis of clays and carbonates, Clays Clay Technol. 1 (1952) 151.
[35] Z. Gao, W. Xie, J.M. Hwu, L. Wells, W.-P. Pan, The characterization of organic modified montmorillonite and ITS filled PMMA nanocomposite, J. Therm. Anal. Calor. 64 (2001), pp. 475–467.
[36] A.B.P. Lever, Inorganic Electronic Spectroscopy, Elsevier, Amsterdam, 1968.
[37] L.P. Meier, G. Kahr, Determinatiom of the cation exchange capacity (CEC) of clay minerals using the complexes of copper(II) ion with triethyleneteramine and tetraethylenepentamine, Clays Clay Miner. 47 (3) (1999) 386.
[38] J.C. Miller, J.N. Miller, Statistics for Analytical Chemistry, 1st ed., Ellis Horwood Limited, England, 1986, pp. 43, 53, 59, 189, 192.