



## Immobilization of methylene blue onto bentonite and its application in the extraction of mercury (II)

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### ABSTRACT

Methylene blue was immobilized onto bentonite (BNT). The modified clay (MB-BNT) was used to extract Hg<sup>2+</sup> at pH 6.0 yielding Hg-MB-BNT. BNT, MB-BNT and Hg-MB-BNT were characterized by X-ray diffractometry, infrared spectra, and elemental and thermogravimetric analyses. MB is suggested to be intercalated into the major phase of BNT; montmorillonite mineral (MMT), lying parallel to the aluminosilicate layers, with a capacity of 36 mequiv./100 g. MB-BNT shows good stability in 0.1–1 M hydrochloric or nitric acids, ammonium hydroxide, and concentrated Na<sup>+</sup>, K<sup>+</sup> or NH<sub>4</sub><sup>+</sup> chlorides or iodides. It shows good selectivity towards Hg<sup>2+</sup> with an extraction capacity of 37 mequiv./100 g in the presence of I<sup>-</sup> giving rise to a ratio of MB/Hg<sup>2+</sup>/I<sup>-</sup> 1:1:3 in the clay phase. Extracted Hg<sup>2+</sup> could be quantitatively recovered by ammonia buffer at pH 8.5. MB-BNT was successfully applied to recover Hg<sup>2+</sup> from spiked natural water and cinnabar mineral samples using the optimum conditions; pH 6.0, time of stirring 10 min and 10 mL of 0.05 M NH<sub>4</sub>Cl/NH<sub>4</sub>OH at pH 8.5 as eluent.

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### 1. Introduction

The presence of heavy metals in environment is a potential problem to water and soil quality due to their high toxicity to plant, animal, and human life. Moreover, heavy metals cannot be decayed chemically as organic pollutants can. Therefore, several treatment technologies have been developed for eliminating heavy metal from solution such as chemical precipitation [1], adsorption, and solid phase extraction (SPE) [2,3]. Among these techniques, SPE has been preferably applied using natural, synthetic, and modified inorganic, organic supports. In this group, aluminosilicate minerals act as potential ionic exchangers for heavy metals due to their low cost, high abundance, easy manipulation, and harmlessness to the environment [4–10]. They form different varieties of natural minerals having definite chemical structures. Among them, the most important are layered clays such as montmorillonite (MMT); a member of the smectite family, having two SiO<sub>4</sub>-tetrahedral sheets sandwiching a central AlO<sub>6</sub>-octahedral sheet (type 2:1) [4]. Due

to the isomorphous substitution of the Mg and Al atoms for the Al and Si atoms, respectively, the aluminosilicate layers are negatively charged hence they accommodate exchangeable cations such as Na<sup>+</sup>, Ca<sup>2+</sup> and/or Mg<sup>2+</sup> in the interlayered-spacing for the sake of charge compensation [5]. So MMT has recently been employed in many separation applications with or without modification. Cu (II) ions were removed from an aqueous solution using MMT and its poly(oxo zirconium) and tetrabutylammonium derivatives with extraction efficiencies 153.0, 73.2 and 47.6 mequiv./100 g, respectively [7]. MMT modified with di-p-anisyltelluritrichloride, bi-phenyltelluride, octadecyltrimethylammonium, tetrabutylammonium and cetylpyridium cations was used to extract the contaminants chlorinated phenols from aqueous solutions [8]. MMT-predominant clay was used for the adsorption of methylene blue (MB) with a capacity up to 58.3 mg/g (i.e. 20.5 mequiv./100 g) at pH 5.65. The capacity was observed to increase as the initial concentration increases due to agglomeration [9].

The volcanic ash weathering product; bentonite (BNT), includes MMT as the main active constituent in variable compositions depending upon its origin [10,11]. Hence, BNT with various guest ions was used as adsorbents for quinalizarin from cotton-dyeing waste [12]. Furthermore, BNT was intercalated with nonyl- and dodecylammonium cations [13]. Maximum adsorption of malachite green dye; >90%, was achieved in aqueous solutions at pH 9 using BNT with cation exchange capacity, CEC, 95 mequiv./100 g [14]. The clay was also used to adsorb MB<sup>+</sup> with a capacity

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150 mg/g (i.e. 52.7 mequiv./100 g) [15]. A 93% extraction of Cr (III) was achieved from tannery wastewater onto BNT at pH 2.4–2.5 and a 99% recovery was achieved with 3 M sulfuric acid solutions [16]. The treatment of BNT with inorganic or organic reagents increases the sorption capacity and selectivity. For example, hexadecyltrimethylammonium–BNT was efficiently used to adsorb textile dyes in contrary to pristine BNT [17].

On the other hand, many new ion collectors were developed for mercury removal due to its high toxicity [18–22]. Hg (II) could be extracted with crystal violet loaded on polyurethane foams with breakthrough and critical capacities of 10.8 and 8.1 mg/g (i.e. 5.4 and 4.0 mequiv./100 g), respectively [18]. Silica gel modified with 2-mercaptobenzimidazole was used in removing Hg(II) from aqueous media [19]. Although, these sorbents are selective but the synthesis processes are tedious, expensive, time-consuming and/or the sorbents themselves are irrecoverable. Recent experimental data revealed that MB<sup>+</sup> combines to mercuric halides or nitrate to form a variety of salt or complex compounds depending on the counter ion [23]. The present work aims to immobilize MB<sup>+</sup> onto BNT for the removal of Hg (II) from aqueous environments.

## 2. Experimental

### 2.1. Materials

All chemicals were of analytical reagent grade otherwise stated. Double distilled water (DDW) was used throughout. BNT was purchased from ACMA Company, Egypt. Hg (II) stock standard solution (1000 mg L<sup>-1</sup>) from Merck was used for the preparation of intermediate standard solutions by an appropriate dilution with 0.1 M hydrochloric acid (HCl). MB chloride trihydrate was purchased from Riedel-de Haën Co. (Germany). Its formula is C<sub>16</sub>H<sub>18</sub>N<sub>3</sub>SCl·3H<sub>2</sub>O. A stock solution (1 × 10<sup>-3</sup> M) was prepared by dissolving MB in DDW. Due to the acid–base character of the MB dye, all solutions were buffered with 5 × 10<sup>-3</sup> M acetate buffer (CH<sub>3</sub>COOH/NH<sub>4</sub>OH) at pH 6. Acetate buffer was chosen as it is a weak ligand and can buffer a wide range of pH. Sulphide ores of mercury; cinnabar, were kindly obtained from Prof. I.M. Kenawy, Mansoura University, Egypt. They (50–80 mg) were dissolved by boiling under reflux in aqua regia and hydrofluoric acids for 15 min, then filtered off using a G4 glass frit and completed to a volume of 1 L with DDW.

### 2.2. Apparatus

A Perkin Elmer 2380 atomic absorption spectrometer equipped with a hydride generation kit was used for direct measurement of Hg (II) by the cold vapor technique (CV-AAS). 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 Kα1 radiation source operated at a generator voltage, 45 kV and current, 40 μA. The instrument was run at step scan mode within 2θ angle 4–40°. The collected data was refined using Profit software. For reliability of data, each sample was scanned several times. X-ray fluorescence (XRF) analysis for BNT was carried out for powder (<74 μm) samples using X-ray fluorescence equipment PW 2404 with six analysis crystals. Crystals (LIF-200), (LIF-220) were used for estimating Ca, Fe, K, Ti, Mn and other trace elements from nickel to uranium while crystal (TIAP) was used for determining Si and Al and PXI for determining sodium and magnesium. 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%. BET surface area of the clay was investigated

by Sorpty – 1750 (Carlo Erba Instrumentation). The estimation of the major and trace elements were done as powder pellets (Pellets method) which were prepared by pressing the powder of the sample in Aluminum Cup using Herzog presser and 10 ton pressure. The IR absorption spectra were recorded in KBr tablets on a Mattson 5000 FTIR spectrometer. Electronic spectra were recorded on a Unicam UV/Vis UV2. Thermogravimetric analysis (TGA) of the modified clays was carried out using a Shimadzu thermobalance at a rate of heating 10 °C min<sup>-1</sup> in a purified N<sub>2</sub> atmosphere. The pH was adjusted within the range 3–9 using a Hanna 8519 digital pH meter using 0.5 M of NH<sub>4</sub>OH and 0.2 M of CH<sub>3</sub>COOH.

### 2.3. Batch-mode SPE of Hg (II) onto MB–BNT

#### 2.3.1. Optimization of separation conditions

A total of 20 mg of MB–BNT was suspended with constant stirring for different time intervals in 25 mL of 100 μg L<sup>-1</sup> of Hg (II) as mercuric chloride plus 82.8–331.2 μg L<sup>-1</sup> of KI (equivalent to Hg<sup>2+</sup>/I<sup>-</sup> 1:1–1:4) at different pH values. The concentrations of the investigated ions in the filtrates were determined by CV-AAS. The distribution coefficient (*K<sub>d</sub>*) was determined using Eq. (1), where *C<sub>clay</sub>* is the metal concentration in the clay (solid phase) and *C<sub>sol</sub>* is the metal ion concentration in the solution phase

$$K_d = \frac{C_{\text{clay}} (\mu\text{g/g})}{C_{\text{sol}} (\mu\text{g/mL})} \text{mL g}^{-1} \quad (1)$$

#### 2.3.2. Optimization of recovery conditions

The effect of the volume and the pH of the eluent (0.1 M NH<sub>4</sub>Cl/NH<sub>4</sub>OH) on the recovery of 100 μg of Hg<sup>2+</sup> from 1 L of DDW, collected from two-times batch-mode separation processes onto 2 × 75 mg MB–BNT, was studied using the optimum conditions of separation; pH 6.0, stirring time of 10 min and Hg<sup>2+</sup>/I<sup>-</sup> ratio 1:3.

The effect of interfering ions on the recovery of 100 μg of Hg<sup>2+</sup> extracted onto 75 mg MB–BNT from 1 L of solution using the optimum conditions. The batch-mode SPE was repeated on the filtrate using another fresh 75 mg of MB–BNT using the same conditions then both residues were gathered and the collected Hg<sup>2+</sup> was eluted with 10 mL of 0.1 M NH<sub>4</sub>Cl/NH<sub>4</sub>OH at pH 8.5.

### 2.4. Synthesis of methylene blue loaded BNT (MB–BNT) and mercury (II) loaded MB–BNT (Hg–MB–BNT)

BNT was further homogenized by milling in a ball-mill for 2 h to a particle size <90 μm then 100 g was activated by stirring in 500 mL of 1 M HCl for 2 h, washed with DDW, filtered and dried at 80 °C for 24 h to yield 98.1 g of the activated clay coded BNT<sub>A</sub>.

For the synthesis of MB–BNT, 1.0 g of BNT<sub>A</sub> was suspended in 1 × 10<sup>-3</sup> M MB (500 mL) and shaken for 3 h on a mechanical shaker. The resulting blue suspension was then centrifuged. The supernatant solution was discarded, and the residual MB was estimated by UV spectrometry at 620.3 nm (isobestic point) by using calibration curve of MB solution. Isobestic point was chosen for measurement to avoid fluctuations due to different MB species which is known to form aggregates depending upon concentration and ionic strength [9,24,25]. About 500 mL DDW was then added to the clay slurry and shaken overnight. The resulting suspension was centrifuged and the supernatant solution was discarded. This was repeated three times. No MB was detected in the supernatant washing solutions. Finally, MB–BNT was dried at 60 °C for 48 h and the yield (1.12 g) was stored in a desiccator.

To synthesize Hg–MB–BNT, 1 g of MB–BNT was suspended in 100 mL of 10 mg L<sup>-1</sup> of Hg (II) + 33 mg L<sup>-1</sup> of I<sup>-</sup> as KI at pH 6.0. The mixture was stirred for 1 h with a constant rate. The resulting suspension was centrifuged, the supernatant solution was discarded and the procedure was repeated with increasing the initial metal

**Table 1**  
XRF analysis of BNT clay.

Metal	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	Cl <sup>-</sup>	SO <sub>3</sub>
%	51.47	1.35	17.84	8.88	0.05	1.64	1.54	2.7	0.82	0.1	2.91	1.50

LOI at 105 °C is (8.42%), LOI at 1000 °C is (17.43%).

ion concentrations (100 mL of 0.1, 0.5 and 1 g L<sup>-1</sup> of Hg (II) + 0.33, 1.65 and 3.3 g L<sup>-1</sup> of I<sup>-</sup> as KI, respectively, at pH 6.0). This graduation in concentration of Hg<sup>2+</sup> 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 Hg-MB-BNT was dried at 60 °C for 48 h and the yield (1.2 g) stored in a desiccators.

The cation exchange capacity (CEC) of BNT was determined according to the literature [26] by back-titrating excess 1 M ammonium acetate. Analysis of ammonia was performed in a well-ventilated room, where no ammoniacal solutions were stored, using the Koroleff method [27]. For the determination of Cl<sup>-</sup> and I<sup>-</sup> in MB-BNT and Hg-MB-BNT, respectively, 0.5 g of the clay 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<sup>-</sup> and I<sup>-</sup> were determined by gravimetric determination as silver chloride and iodide, respectively. Hg<sup>2+</sup> in 0.5 g Hg-MB-BNT was determined by CV-AAS after elution with 10 mL of 0.05 M ammonia buffer (NH<sub>4</sub>OH/NH<sub>4</sub>Cl) pH 10.

### 2.5. Application of SPE of Hg (II) onto MB-BNT

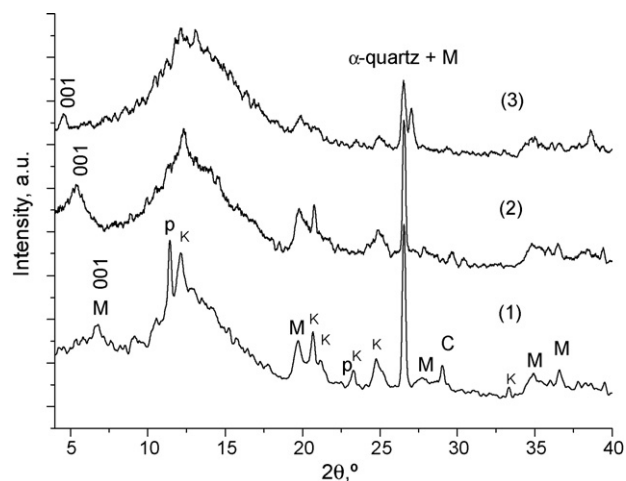
Sewage water from Lake Domat Al Gandel, well water from Tabarjel, Alquryyat, and Sakaka cities—Saudi Arabia were filtered using a sintered glass G4. One liter of DDW or each sample was spiked with 1 and 5 μg of Hg<sup>2+</sup> plus 2.5 and 12.5 μg of KI, respectively, and 75 mg of MB-BNT was dispersed in each. The mixture was buffered to pH 6.0 with acetate buffer (CH<sub>3</sub>COOH/NH<sub>4</sub>OH), stirred for 10 min, and filtered. Another fresh 75 mg of MB-BNT 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 Hg<sup>2+</sup> was eluted with 10 mL of 0.05 M NH<sub>4</sub>Cl/NH<sub>4</sub>OH at pH 8.5 and determined with CV-AAS. In every case, all samples were analyzed in triplicate otherwise stated.

In case of cinnabar samples, 10 mL of their solutions was diluted to 1 L with DDW, then treated similar to water samples.

## 3. Results and discussion

### 3.1. Characterization of BNT and its modifications

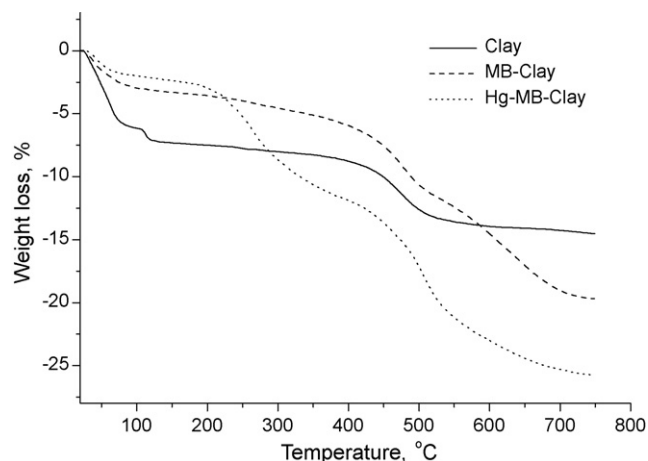
XRF analysis of the used clay is shown in Table 1. It shows that the BNT is composed of typical constituents of other bentonites [28]. BNT has BET surface area ( $S_{BET}$ ) of 35 m<sup>2</sup> g<sup>-1</sup> and pore radius ( $r$ ) of 69.3 nm. BET surface area of this clay was low compared with other BNT clays [4–6]. It has a density of 2.6 g cm<sup>-3</sup> and a particle size <100 μm. The powder XRD pattern of the activated bentonite (Fig. 1) shows the presence of the clay minerals; MMT, powder diffraction file (PDF) 13-259, as a major phase and kaolinite A1, PDF 83-971, as a minor phase. Other minor non-clay mineral phases are α-quartz, PDF 85-1054, pyroaurite, 86-181 and calcite, PDF 88-1812. The basal interlayered-spacing of MMT phase is found to be 13.04 Å as concluded from the 001 diffraction line observed at 2θ 6.774°. This indicates the presence of a single water layer in the Van der Waal's gap of MMT [6]. The total CEC of BNT is found to be 65 mequiv./100 g that is slightly charged clay as expected in BNT clays [13]. Consequently, XRF, XRD, surface area, and CEC analyses indicate that BNT is a mixture of clay and



**Fig. 1.** XRD patterns of BNT (1), MB-BNT (2) and Hg-MB-BNT. Cu Kα1 radiation source. 'M'=montmorillonite, PDF 13-259, 'K'=kaolinite A1, PDF 83 971, 'P'=pyroaurite, PDF 86-181 and (C)= calcite, PDF 88-1812.

non-clay minerals which are responsible for the low CEC and BET values.

The FTIR spectra of BNT showed multiple broad bands in the range 3650–3400 cm<sup>-1</sup> that are attributed to the OH stretching frequencies of adsorbed water. This indicates the presence of at least two types of OH groups that are suggested to be isolated OH groups and those involved in hydrogen bonding. The band of the OH bending vibration is observed at 1640 cm<sup>-1</sup> whereas the Al–Al–OH bending frequency was observed at 915 cm<sup>-1</sup>. This may be considered characteristic of a di-octahedral montmorillonite 2:1 layer [29,30]. An intense broad band was observed at 1100–1020 cm<sup>-1</sup> characteristic of the Si–O stretching frequency. The tetrahedral bending modes for Si–O–Al, Si–O–Mg, and Si–O–Si were observed at 524, 456, and 429 cm<sup>-1</sup>, respectively. TGA curve of BNT (Fig. 2) shows the presence of four thermal decomposition stages. The 1st stage (6.12%) occurs at 64 °C and is attributed to the adsorbed water. The 2nd stage (1.37%) occurs at 112 °C and is attributed to the



**Fig. 2.** Thermogravimetric analysis of BNT (solid line), MB-BNT (dashed-line) and Hg-MB-BNT (dotted-line). Rate of heating 10 °C min<sup>-1</sup> in a purified N<sub>2</sub> atmosphere.

**Table 2**

TGA results of BNT, MB–BNT and Hg–MB–BNT.

Clay	BNT			BNT–MB			Hg–BNT–MB		
	%	$T_{DTG}$ (°C)	Range (°C)	%	$T_{DTG}$ (°C)	Range (°C)	%	$T_{DTG}$ (°C)	Range (°C)
1st stage	6.12	64	25–74	3.40	39	25–97	2.16	44	25–84
2nd stage	1.37	112	109–117	0.24	213	205–218	3.30	228	192–255
3rd stage	0.33	252	245–255	6.22	477	425–502	6.10	264	255–395
4th stage	5.86	472	426–517	7.54	637	537–694	4.00	456	395–488
5th stage	–	–	–	–	–	–	5.12	504	488–542
6th stage	–	–	–	–	–	–	4.21	635	542–670
Total loss, %	13.77	–	–	17.54	–	–	24.89	–	–

interlayered-water. The 3rd and 4th stages (0.33 and 5.86%) occur at 252 and 472 °C, respectively, and are attributed to the structural water. These results agree with the IR findings of the presence of multiple types of OH. The details of TGA results are given in Table 2. These results are in agreement with those reported for Indian BNT clay [31].

The basal interlayered-spacing of MMT phase was found to increase to 16.29 Å in MB–BNT as concluded from the 001 diffraction line observed at  $2\theta$  5.421° (Fig. 1). This enlargement suggests that MB is intercalated into the interlayered-spacing of MMT, lying parallel to the aluminosilicate layers. In relatively slightly charged clays such as montmorillonite and hectorite, the organic cations are oriented lying flat between the aluminosilicate sheets [13]. Compared with the IR absorption spectra of BNT, MB–BNT showed the development of additional small bands at 2934, 2862, 2817, 2712, 1607, 1491, 1449 and 1339  $\text{cm}^{-1}$ . The bands at 2934, 2862, 2817 and 2712 are assignable to asymmetric and symmetric stretching vibrations of methyl and methylene groups whereas 1607 and 1339  $\text{cm}^{-1}$  are characteristic of stretching vibrations of C=C in aromatic rings, and C–N stretching of tertiary amines of MB, respectively [32]. This confirms the intercalation of MB onto the MMT component of BNT.

The elemental analysis data of MB–BNT are shown in Table 3. The percentage of C (C%) was used to calculate the functionalization capacity of MB ( $C_{MB}$ ) according to Eq. (2):

$$C_{MB} = \frac{C\%}{M. \text{ wt. of MB} \times \text{mole fraction of C in MB}} \times 10 \text{ mmol g}^{-1} \quad (2)$$

The organic capacity of MB–BNT derived from the elemental analysis was found to be 36 mequiv./100g, which is comparable to those obtained for reported MB-immobilized layered clays;  $40 \pm 2$  mg/g (equal to 14.1 mequiv./100g) of clay mixture of palygorskite (86%) and sepiotite (14%) [33], 60 mg/g (equal to 21.1 mequiv./100g) of clay mixture of montmorillonite and nontronite [9] and 150 mg/g (equal to 52.7 mequiv./100g) of BNT [34].  $\text{Cl}^-/\text{MB}^+$  mole ratio in MB–BNT was found to be 1:2 which indicates that MB–BNT capacity is ca. one quarter of the CEC capacity of the clay. This may be attributed to the large size of the MB molecules which may even exist as a dimer or as aggregates at the surface, as well as a single protonated form depending on the concentration and the surface properties [24,25,33].

TGA curve of MB–BNT (Fig. 2) shows a sharp decrease in the amount of adsorbed and intercalated-waters which may be due to the displacement of the Van der Waals cations with the large hydrophobic MB molecules. In contrary, the structural water

amount almost did not change. Also, a new weight loss stage (7.54%) developed at 637 °C that may be attributed to the pyrolysis of the intercalated MB. The suggested MB capacity from TGA loss is 27 mequiv./100g which is less than that estimated from elemental analysis due to the inaccuracy of separation of the overlapped TGA stages.

XRF analysis of MB–BNT for CaO and Na<sub>2</sub>O indicates the decrease of their concentration to 0.14 and 0.23%, respectively. This indicates that they may be replaced by MB in the interlayered-spacing of MMT in addition to the decomposition of calcite as confirmed from the disappearance of its reflection in the diffraction pattern (Fig. 1).

The resistance of the MB–BNT against MB loss was investigated in concentrated solutions of Na<sup>+</sup>, K<sup>+</sup> or NH<sub>4</sub><sup>+</sup> as chlorides or iodides; 0.1–2 mol L<sup>-1</sup> of HCl, HNO<sub>3</sub>, NaOH or NH<sub>4</sub>OH. For this aim, 0.1 g MB–BNT was shaken for 2 h with 25 mL of each solution, described above, in a batch-mode state. The clear liquor was collected and stripped MB if present was determined by spectrophotometric method. The results indicated that the MB–BNT was unaffected by water, 0.1–1 M hydrochloric or nitric acids, ammonium hydroxide, concentrated Na<sup>+</sup>, K<sup>+</sup> or NH<sub>4</sub><sup>+</sup> chlorides or iodides. This chemical stability in aqueous media enables the application of MB–BNT in different aqueous media. Methanol, ethanol, isopropyl alcohol, n-butanol, carbon tetrachloride, acetone, chloroform, benzene, DMF and DMSO easily strip MB from MB–BNT so organic media are inappropriate for application.

It is noteworthy to mention that the suspension of either BNT or MB–BNT in water is very stable that can be separated only by centrifugation. This may be explained that the main component of BNT; MMT is composed of the negatively charged aluminosilicate layers which are stable in water. In wet conditions, they can host up to three layers of water in addition to the compensated cations such as Na<sup>+</sup>, Ca<sup>2+</sup> or (2MB)<sup>+</sup> in case of MB–BNT in the interlayered-spacing [6]. Upon the addition of Hg<sup>2+</sup> to MB–BNT suspension in order to synthesize Hg–MB–BNT, a quick coagulation of the precipitate occurs and the separation process could be easily achieved by filtration.

The basal interlayered-spacing of MMT phase increased again to 19.25 Å in Hg–MB–BNT as concluded from the 001 diffraction line observed at  $2\theta$  4.586° (Fig. 1). This enlargement in the basal spacing is attributed to the intercalation of Hg<sup>2+</sup> in the interlayered-spacing upon reaction with the sandwiched MB<sup>+</sup>. IR absorption spectra of Hg–MB–BNT showed the same pattern of MB–BNT. Elemental analysis of Hg–MB–BNT (Table 3) indicated the uptake of 37 mequiv. Hg<sup>2+</sup>/100g of MB–BNT. The ratio of Hg<sup>2+</sup>:MB:I<sup>-</sup> in Hg–MB–BNT

**Table 3**

Elemental analysis of MB–BNT and Hg–MB–BNT and their corresponding capacities.

Clay	C (%)	N (%)	H (%)	S (%)	Cl <sup>-</sup> (%)	Hg <sup>2+</sup> (%)	I <sup>-</sup> (%)	Capacity (mequiv./100g)
MB–BNT	6.90 ± 0.11	1.48 ± 0.02	1.02 ± 0.06	1.15 ± 0.03	0.64 ± 0.03	–	–	36 ± 1 MB/MB–BNT
Hg–MB–BNT	5.72 ± 0.05	1.25 ± 0.02	1.15 ± 0.04	0.97 ± 0.02	–	6.19 ± 0.14	11.52 ± 0.12	37 ± 1 Hg <sup>2+</sup> /MB–BNT

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



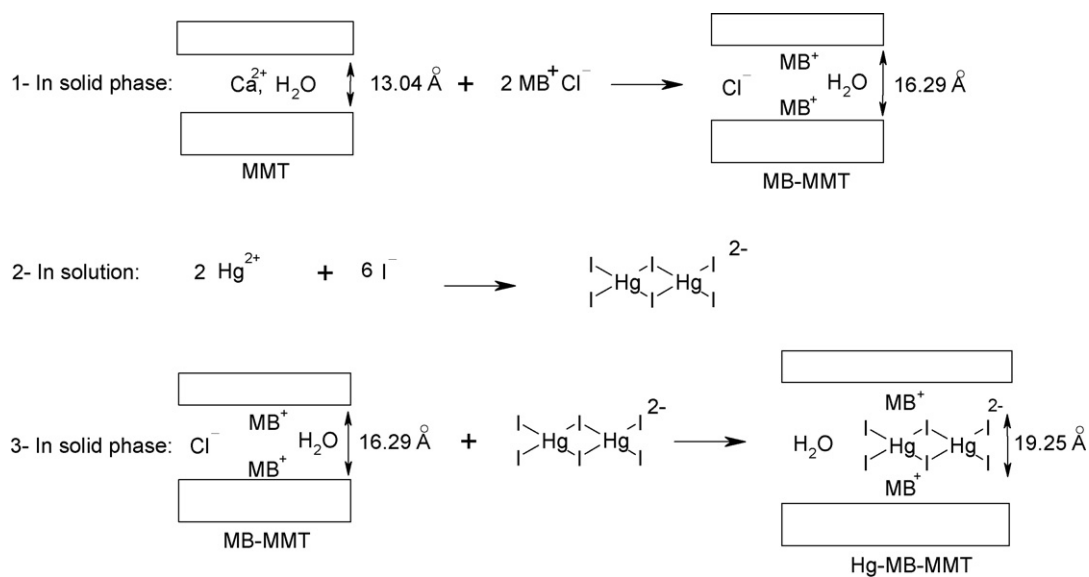


Fig. 3. Scheme of synthesis of Hg-MB-BNT from BNT.

is 1:1:3 which may suggest the formation of an ion pair of the type  $2\text{MB}^+ \text{Hg}_2\text{I}_6^{2-}$  [23]. The capacity of MB-BNT towards  $\text{Hg}^{2+}$  is an important factor because it determines how much MB-BNT is required to quantitatively remove a specific amount of  $\text{Hg}^{2+}$  from solutions.

TGA curve of Hg-MB-BNT (Fig. 2) shows more decrease in the amount of adsorbed water whereas the intercalated-water increased to 3.3% upon  $\text{Hg}^{2+}$  intercalation compared with MB-BNT. Moreover, new stages (6.1, 5.12 and 4.21%) appeared in Hg-MB-BNT at 264, 504 and 635 °C, respectively, which may be due to the intercalated  $2\text{MB}^+ \text{Hg}_2\text{I}_6^{2-}$ . The total weight loss in the range of heating 25–750 °C increases in the order BNT < MB-BNT < Hg-MB-BNT which confirms the intercalation of MB and  $\text{Hg}_2\text{I}_6^{2-}$  in the MMT phase.

According to these results, it may be concluded that MB is intercalated into the interlayered-spacing of MMT component of BNT and this modified clay can extract  $\text{Hg}^{2+}$  as  $\text{Hg}_2\text{I}_6^{2-}$  with MB/Hg ratio 1:1 according to Fig. 3. The bonding between  $\text{MB}^+$  and  $\text{Hg}_2\text{I}_6^{2-}$  is suggested to be ionic as previously reported [23]. It is noteworthy to mention that the attempt to use other halo- or nitrate-forms of mercury was unsuccessful.

### 3.2. SPE of Hg (II) using MB-BNT

Fig. 4 shows the effect of pH on  $\log K_d$  of the batch-mode SPE of  $100 \mu\text{g L}^{-1}$  Hg (II) using MB-BNT in the presence of  $331.2 \mu\text{g L}^{-1}$  of KI (equivalent to  $\text{Hg}^{2+}/\text{I}^-$  1:4). MB-BNT shows good extraction efficiency towards Hg (II) and the maximum  $\log K_d$  values is 4.65 corresponding to a metal extraction efficiency of  $97.28 \pm 1.87\%$  at pH 6.0.

The effect of  $\text{Hg}^{2+}/\text{I}^-$  ratio on the separation efficiency of  $\text{Hg}^{2+}$  using 20 mg of MB-BNT was studied with a time of stirring 30 min at the optimum pH 6.0. The separation efficiency ( $E\%$ ) was determined by using formulae (3):

$$E (\%) = \left( \frac{C_0 - C_e}{C_0} \right) \times 100 \quad (3)$$

where  $C_0$  and  $C_e$  are the initial and remaining concentrations ( $\mu\text{g L}^{-1}$ ) of the metal ion, respectively. Fig. 5 shows that maximum separation efficiency could be obtained from ratio of 1:3 up to 1:4. This may confirm the intercalation of Hg (II) in the form  $\text{Hg}_2\text{I}_6^{2-}$  according to Fig. 3 which is in accordance with the literature [23].

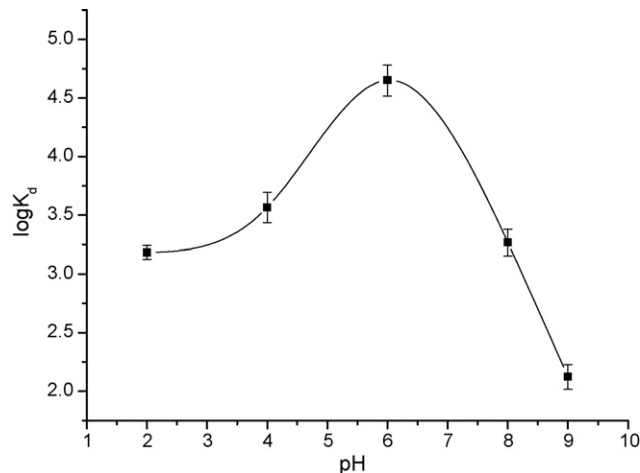


Fig. 4. Effect of pH on the distribution coefficient of Hg (II) using MB-BNT. Weight of MB-BNT = 20 mg. Volume = 25 mL. Time of stirring = 30 min. Concentration of Hg (II) =  $100 \mu\text{g L}^{-1}$  as mercuric chloride plus  $331.2 \mu\text{g L}^{-1}$  of KI.

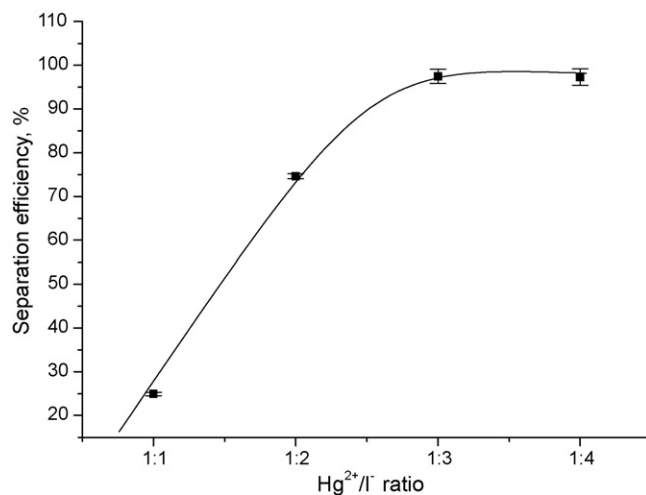
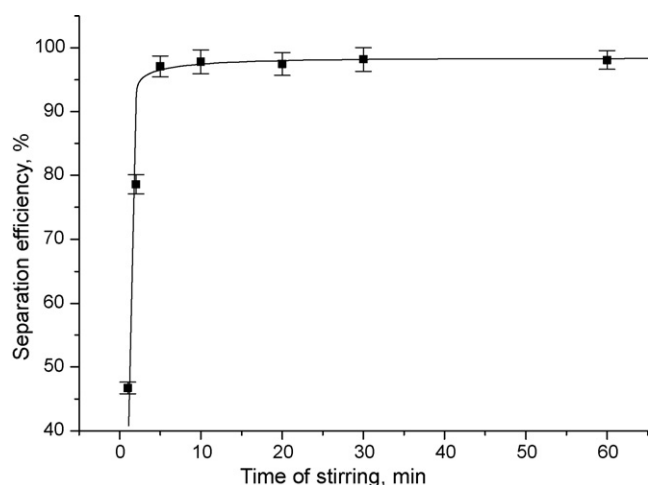


Fig. 5. Effect of  $\text{Hg}^{2+}/\text{I}^-$  ratio on the separation efficiency Hg (II) using MB-BNT. Weight of MB-BNT = 20 mg. Time of stirring = 30 min. Volume = 25 mL. pH = 6.0. Concentration of Hg (II) =  $100 \mu\text{g L}^{-1}$  as mercuric chloride plus  $82.8$ – $331.2 \mu\text{g L}^{-1}$  of KI.



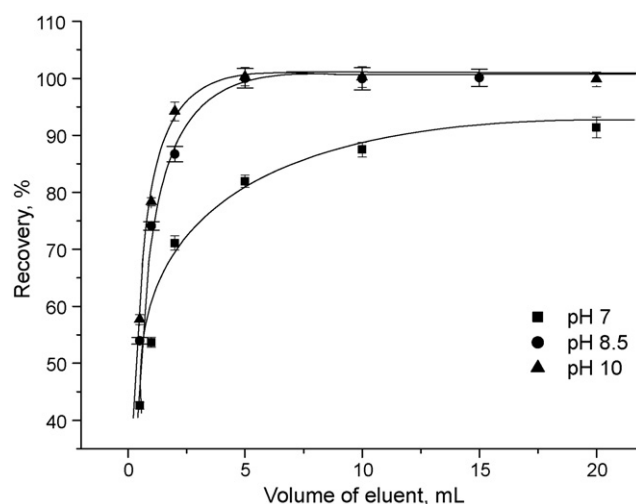
**Fig. 6.** Effect of time of stirring on the separation efficiency Hg (II) using MB-BNT. Weight of MB-BNT = 20 mg. Volume = 25 mL. pH = 6.0. Concentration of Hg (II) = 100  $\mu\text{g L}^{-1}$  as mercuric chloride plus 248.4  $\mu\text{g L}^{-1}$  of KI ( $\text{Hg}^{2+}/\text{I}^-$  ratio 1:3).

Furthermore, it is noteworthy to mention that no separation of  $\text{Hg}^{2+}$  was obtained by replacing  $\text{F}^-$ ,  $\text{Cl}^-$  or  $\text{Br}^-$  for  $\text{I}^-$  at any ratio.

The effect of time of stirring on the separation efficiency of  $\text{Hg}^{2+}$  using 20 mg of MB-BNT at pH 6.0 using  $\text{Hg}^{2+}/\text{I}^-$  ratio of 1:3, is shown in Fig. 6. The time of stirring needed for sorption of 50% of the metal ions ( $t_{1/2}$ ) was found to be 1.2 min which indicates the rapid kinetics of diffusion and that the sandwiched  $\text{MB}^+$  ions are easily accessible for bonding to the metal ions without steric hindrance. Hence, 5 min of stirring was enough to reach maximum value of separation. This is attributed to the open 2D structure of MB-BNT. Therefore, it is suitable for the  $\text{Hg}^{2+}$  extraction 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 SPE of  $\text{Hg}^{2+}$  using MB-BNT are found to be pH 6.0, stirring time of 10 min and  $\text{Hg}^{2+}/\text{I}^-$  ratio 1:3.

A series of selected eluents such as sodium thiosulfate, sodium citrate, sodium oxalate, different acids and bases were used in order to find the best eluent for desorbing mercury ion from the sorbent surface. Ammonia buffer was chosen to release  $\text{Hg}^{2+}$  from



**Fig. 7.** Effect of volume and the pH of the eluent (0.1 M  $\text{NH}_4\text{Cl}/\text{NH}_4\text{OH}$ ) on the recovery of 100  $\mu\text{g}$  of  $\text{Hg}^{2+}$  from 1 L of DDW, collected from two-times batch-mode separation processes using  $2 \times 75$  mg MB-BNT. pH of extraction process = 6.0, stirring time = 10 min and  $\text{Hg}^{2+}/\text{I}^-$  ratio 1:3.

**Table 4**

Effect of interfering ions on the SPE of Hg (II) [100  $\mu\text{g L}^{-1}$ ] using  $2 \times 75$  mg MB-BNT at pH 6.0 (acetate buffer,  $\text{CH}_3\text{COOH}/\text{NH}_4\text{OH}$ ).

Interfering ion	Tolerance limit
$\text{Na}^+$ , $\text{K}^+$ , $\text{Mg}^{2+}$ , $\text{Ca}^{2+}$ , $\text{Sr}^{2+}$ , $\text{Ba}^{2+}$ , $\text{Al}^{3+}$ , $\text{Cr}^{3+}$ , $\text{Mn}^{2+}$ , $\text{Fe}^{3+}$ , $\text{Ni}^{2+}$ , $\text{Co}^{2+}$ , $\text{Cu}^{2+}$ , $\text{Zn}^{2+}$ , $\text{In}^{3+}$ , $\text{NH}_4^+$ , $\text{Mo}^{6+}$ (as $\text{MoO}_4^{2-}$ ), $\text{Cl}^-$ , and $\text{ClO}_3^-$ , $\text{BrO}_3^-$ , $\text{F}^-$ , $\text{Br}^-$ , and $\text{NO}_3^-$	10,000-fold
$\text{Pb}^{2+}$ , $\text{Ti}^+$ , and oxalate	1000
$\text{SO}_3^{2-}$ , $\text{I}^-$ , and tartarate	500
$\text{S}^-$ , $\text{S}_2\text{O}_3^{2-}$ , and citrate	100
$\text{Cd}^{2+}$	50

MB-BNT as it forms a stable diamine complex with it. The effect of the volume and the pH of the eluent (0.1 M  $\text{NH}_4\text{Cl}/\text{NH}_4\text{OH}$ ) on the recovery of  $\text{Hg}^{2+}$  collected from twice batch-mode separation using  $2 \times 75$  mg MB-BNT was studied using the optimum conditions of separation (Fig. 7). The use of 5 mL of pH buffer 8.5 or 10 completely releases  $\text{Hg}^{2+}$  ions. However, an average loss of 1.15% of MB-BNT capacity was noticed upon each cycle of separation and recovery using 10 mL of pH buffer 10 which may be due to the hydrolysis of

**Table 5**

Extraction of Hg (II) from 1 L of spiked natural water samples and cinnabar minerals using  $2 \times 75$   $\mu\text{g}$  of MB-BNT at pH 6.0 after a time of stirring of 10 min.

Sample	Hg (II) added ( $\mu\text{g}$ )	Expected [ $\text{Hg}^{2+}$ ] in 10 mL of extract ( $\text{ng mL}^{-1}$ )	Found ( $\text{ng mL}^{-1}$ )	RSD (%)	$ t_1 $
DDW	1	100	99.9	1.73	0.13
	5	500	500.5	1.31	0.17
Lake Domat Al Gandel	1	100	101.0	1.22	1.81
	5	500	501.4	1.30	0.48
Well water from Tabarjel	1	100	100.9	1.24	1.61
	5	500	498.8	1.43	0.38
Well water from Alquryya	1	100	100.5	1.44	0.77
	5	500	501.0	0.92	0.49
Well water from Sakaka	1	100	101.1	1.12	2.17
	5	500	502.8	1.10	1.13
Cinnabar mineral (crimson red), Marsa-Alam, Central Eastern Desert, Egypt <sup>a</sup>	–	$15.1 \pm 0.3^{\text{R}}$	$14.8 \pm 0.3^{\text{R}}$	1.79	1.3
Cinnabar mineral (red), El-Quseir, Central Eastern Desert, Egypt <sup>a</sup>	–	$12.5 \pm 0.5^{\text{R}}$	$12.6 \pm 0.2^{\text{R}}$	1.32	0.33
Cinnabar mineral (gray), El-Quseir, Om Khog, Central Eastern Desert, Egypt <sup>a</sup>	–	$6.5 \pm 0.4^{\text{R}}$	$6.4 \pm 0.1^{\text{R}}$	1.36	0.42

The data are given as  $\bar{X} \pm \sigma$  where  $\bar{X}$  is the mean value,  $\sigma$  is the standard deviation for  $n = 5$ . In case of water samples  $|t_1|$  was applied whereas in case of cinnabar samples  $|t_2|$  was applied.

R refers to the reported values in Ref. [35].

<sup>a</sup> Values given in % (wt/wt).

the clay support [4,5]. The sorbent reserved 96.1% and 94.9% of its initial MB and Hg<sup>2+</sup> capacities, respectively, when pH buffer 8.5 was used for 25 cycles of elution. Hence, 10 mL of pH buffer 8.5 is considered optimal for quantitative recovery of Hg<sup>2+</sup> and preserving MB–BNT capacity.

In order to evaluate the suitability of MB–BNT for the extraction of Hg<sup>2+</sup> 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<sup>-1</sup> of Hg<sup>2+</sup> solution, and the optimum condition for batch-mode extraction was applied. An error higher than ±2% was considered to be tolerable. No interference from macroamounts (up to 10,000 times the concentration of Hg<sup>2+</sup>) of many foreign ions was detected as shown in Table 4.

### 3.3. Application of MB–BNT for the SPE of Hg (II) from natural samples

The SPE method was applied for the removal of Hg (II) ions in water samples. Table 5 shows the results of the application process. The spiked amounts of Hg (II) were quantitatively recovered from the different water samples. No background could be identified.

A comparison between the experimental means for the recovered Hg (II) amounts with the real and reported values was carried out using the null hypothesis of  $|t|$  for  $P$  0.05 and  $n$  5 in the case of spiked natural water samples and  $n$  10 in the case of cinnabar samples. The  $|t|_1$  and  $|t|_2$  were found to be 0.13–2.17 and 0.42–1.3, respectively, for the investigated metal ions, which are less than the tabulated values ( $|t|_1$  2.78 and  $|t|_2$  2.31) [36]. 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 removal of mercury (II) from polluted waters.

## 4. Conclusion

Methylene blue could be successfully intercalated into montmorillonite phase present in the Egyptian bentonite with a capacity of 36 mequiv./100 g. The grafted BNT; MB–BNT showed an extraction efficiency for Hg (II), as Hg<sub>2</sub>I<sub>6</sub><sup>2-</sup>, of 37 mequiv./100 g at pH 6 which can be easily eluted by ammonia buffer at pH 8.5. MB–BNT showed also good tolerance against most common ions. MB–BNT was applied for the extraction of Hg (II) from spiked natural water and cinnabar samples and the method was found accurate. Consequently, MB–BNT can be applied for the removal of Hg<sup>2+</sup> from contaminated environs.

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