

EFFECTIVENESS OF MODIFIED BENTONITE ON CD AND PB IMMOBILIZATION IN ARTIFICIALLY CONTAMINATED SOILS

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The goal of this study was to know how the modified bentonite mineral can immobilize cadmium and lead in soils. Cadmium and lead chloride solutions were used to contaminate soils. Total levels of Cd were 31.12 and 39.80 mg kg⁻¹ corresponding to 63.83 and 146.87 mg kg⁻¹ of total Pb in experimentally contaminated clay and sandy loam soils. Clay soil had the highest total metal contents because of its highest adsorption capacity. Raw bentonite (RB), thermal activated bentonite (TB), acid activated bentonite (AB), and combination of acid thermal activated bentonite (ATB) were added to soils at rates of 0.5 and 1.0% (w/w) and incubated for 2, 14, 30, and 60 days at 25°C. The results indicate that, the extracted DTPA-Cd and Pb decreased with increasing incubation time, accompanied by decreases in EC due to the ATB-treatment. As the rate of the modified bentonite increased, the effectiveness of these treatments to immobilize Cd and Pb improved, and they can be organized in the following order: ATB > AB > TB > RB. ATB-treatment was the most efficient in decreasing DTPA-Cd and Pb with maximal immobilization efficiencies (E %) 91.42 and 90.99% for Cd and 98.46 and 97.85% for Pb in the clay and the sandy loam soils, respectively. RB-treatment exhibited the least ability among other treatments to immobilize these metals, reducing contents of DTPA-Cd and Pb by 79.25 and 90.61%, respectively. According to the statistical analysis utilizing the LSD test and in terms of practicality and cost, 1% ATB was the most effective treatment for immobilizing Cd and Pb in contaminated soils.

Keywords: artificially contaminated soils, heavy metals, immobilization efficiency and modified bentonite

INTRODUCTION

Heavy metal contamination of soil is becoming a worldwide concern due to the threat it poses to the environment, including soil, water, plants, animals, and human life. Cadmium (Cd) and lead (Pb) are heavy metals that

are non-biodegradable in the soil. Cd and Pb have long-term resistance in the environment and become toxic to human, plants and animals (Bolan et al., 2014 and Lu et al., 2017). These metals have the ability to move in a soil solution or along the surface water and leach into the underground water because of their dissolution from soil minerals by acidic water or through industrial discharge, mining waste and landfill (Hussain et al., 2017). Therefore, to reduce their mobility and bioavailability sorbent materials and precipitating agents are usually applied to achieve these goals (Bolan et al., 2014 and Hussain et al., 2017). The immobilization technique is well-known for the in-situ treatment of heavy metal-contaminated soils. Immobilization is the process of making heavy metals less mobile or hazardous by reducing their solubility through chemical reactions (ion-exchange, adsorption, precipitation, and complexation processes) (Wang et al., 2009 and Hashimoto et al., 2009). Natural sources, industrial wastes, agricultural wastes, and food waste have all been used as adsorbent materials (Wang et al., 2019 and Meng et al., 2020). A variety of adsorbents have been developed to provide high adsorption capacity at a low cost. Clay materials, zeolites, cement, phosphates, and organic composts are among the most commonly used adsorbents (Fin̄zgar et al., 2006). Clays are low cost-effective adsorbents (Selim et al., 2014), because they have high cation exchange capacity, readily available and low-cost adsorbents which can be recycled and utilized for subsequent cycles. Clay minerals in the soil operate as natural scavengers, eliminating and collecting pollutants in water passing through the soil by exchange and adsorption. Clays have great adsorbent capacity due to their large specific surface area and ability to store water in interlayer sites, which may be augmented by acid activation and/or thermal treatment (Toor, 2010).

Bentonite is an aluminum phyllosilicate mineral. It is basically composed of montmorillonite (smectite) with other clays and inorganic minerals. Types of bentonite depend on their dominant cations (K, Na, Ca and Al). Clays have exceptional adsorption capacity which would be increased by acid activation and/or thermal treatment (Ehssan, 2013). Thermal treatment is a physical behavior which requires calcination of clays at high temperatures. Thermal treatment significantly alters the surface properties of bentonite; it improves porosity by increasing mesopore volume, increases the number of surface adsorption sites, while reducing the number of hydroxyl groups (Gupta et al., 2015 and Nones et al., 2015). One of the most successful methods for producing active materials for adsorption and catalysis proposals is acid activation of clays (Boroomand et al., 2017). Clay minerals are generally acid activated by treating them with HCl or H₂SO₄, and the cost of manufacturing these clays is minimal. It enhances the porosity of the surface as well as the number of adsorption sites in the clay, both of which are critical for pollutant adsorption (Komadel, 2016). In addition to these structural changes, acid-activated bentonite is ideal for the removal or elimination of contaminants. The surface area of clays grows dramatically when acid

activation is followed by thermal treatment. As previously stated, acid and heat treatments, for example, can improve heavy metal adsorption performance. Several researches have been conducted using bentonite clay as a heavy metal adsorbent. Clay activated with 2 mol L⁻¹ acid had the maximum removal efficiency of Ca, Pb, Zn, and Ba, according to Oduola and Okwonna (2016), with removal efficiencies of 99.6, 98.6, 100, and 90%, respectively. Acid activated clays improve their specific surface area 22 times and their adsorption capacity 6 times, according to Afolabi et al. (2016). Lead and zinc removal efficiency were 99.67 and 99%, respectively, when modified bentonite was activated with a combination of acid and heat. Cu²⁺ and Cd²⁺ removal efficiency onto natural bentonite were 84.49 and 87.02%, respectively, according to Karapinar and Bonatb (2009). Inglezakisa et al. (2007) reported that the removal efficiency of Pb²⁺ reached 100%.

The present work aims at strengthening immobilization performance of natural bentonite through improving its characteristics by thermal and acid activation and to evaluate the efficiency of modified bentonite to stabilize/immobilize Cd and Pb in two different artificially contaminated soils.

MATERIALS AND METHODS

1. Materials

The natural Egyptian bentonite (bent.) was obtained from Egypt Company for Mining and Drilling Chemicals under the brand name (MB1100). It is composed primarily of sodium montmorillonite. It was used in the current research without further purification. Its cation exchange capacity (CEC) is 85.2 cmol_c kg⁻¹ by using ammonium acetate (pH 7) (Rhoades, 1982). Salts of Cd and Pb chlorides were used as sources of heavy metal ions. Hydrochloric acid and ammonium hydroxide were used for pH adjustment.

2. Preparation of Modified Bentonite

2.1. Thermal activation of bentonite

The preparation of thermal activated bentonite (TB) was carried out by heating of raw bentonite in Muffle Furnace at 200°C for a period of 90 min. When the heating was obtained the sample was taken out of Muffle and cooled in a desiccator for 2 h.

2.2. Acid activation of bentonite

Raw bentonite was treated with 2N hydrochloric acid (HCl) (37% purity, Merck) at 30°C. The clay to acid ratio is 1:10 for 3 h with agitation shaker. At the end of treatment, the bentonite was washed several times with distilled water and dried over night at 105°C (Eloussaief and Benzina, 2010).

2.3. Combined acid and thermal activation of bentonite

A portion of 100 g weight of the obtained acid activated bentonite (AB) was placed in a Muffle Furnace at a temperature of 200°C for 90 min then placed in a desiccator for 2 h to cool.

3. Clay Characterization Techniques

More than one method was utilized to conceive a better assessment of characterization. X-ray diffraction (XRD) was performed on dried powdered samples. The XRD patterns of natural and modified bentonite were recorded using Cu-radiation. The diffractogram was scanned from (2θ) 5 to 50 at scan rate of $0.5^\circ \text{ min}^{-1}$. The analysis of the infrared absorption of the clay samples was carried out in Nicolet isso thermo scientific FTIR=ATR spectrometer from wave number of 400 to 4000 cm^{-1} . The morphology of the samples and its homogeneity was investigated by field emission scanning electron microscopy (SEM FET Quantum FEG250). The cation exchange capacity (CEC) was determined by ammonium acetate (pH 7) (Rhoades, 1982).

4. Batch Immobilization Experiment

Two soil samples with different textures were chosen in Abo Zabil district. The physical and chemical properties were determined according to the standard methods outlined by Sparks (1996), and the findings are presented in Table (1).

Table (1). Some indigenous physical and chemical properties of the investigated soil samples.

Soil texture	Particle size distribution %			pH	EC (dSm^{-1})	OM (%)	CaCO ₃ (%)	CEC (cmol.kg^{-1})
	Sand	Silt	Clay					
Clay	36.02	9.82	54.16	7.28	0.762	1.64	4.27	21.86
Sandy loam	67.75	21.86	11.39	7.52	0.951	0.25	10.58	4.14

	Soluble cations (mmol.L^{-1})				Soluble anions (mmol.L^{-1})				Cd (mg.kg^{-1})		Pb (mg.kg^{-1})	
	Ca ⁺²	Mg ⁺²	Na ⁺	K ⁺	CO ₃ ⁻²	HCO ₃ ⁻	Cl ⁻	SO ₄ ⁻²	Total	DTPA	Total	DTPA
Clay	1.38	1.05	4.83	0.36	-	1.29	4.62	1.73	3.05	0.047	17.52	1.11
Sandy loam	3.15	1.69	4.23	0.39	1.08	2.25	4.68	2.35	1.03	0.060	8.31	0.52

DTPA means DTPA extractable

Solutions of different concentrations of Cd and Pb were prepared using metal chlorides, were prepared then sprayed onto the soil samples with continuous mixing to homogenize the applied heavy metals distribution. The spiked soils were air-dried after each portion of sprayed metals solution. The total amounts of the studied metals were applied to exceed their maximum concentrations in soils as reported by EPA (2001). After spiking, the soils were supersaturated with de-ionized water and then mixed periodically for two weeks. The procedure of wetting and air drying cycle was repeated five times to allow sufficient mixing of the applied metals and soil to imitate field

conditions (Lin et al., 1998). The total metal contents of soils were extracted with a ternary acids mixture of HNO₃, H₂SO₄ and HClO₄ as described by Hesse (1972). The available metal contents of soils were extracted with DTPA - ammonium bicarbonate according to Lindsay and Norwell (1978). An atomic absorption spectrometer (AAS) was used to determine the total and DTPA-extractable metal contents. The variance and LSD analyses were used to compare treatment means. All the statistical analyses were carried out by using costat software (2010). The chemical and physical properties of the artificially contaminated soils and treatments are presented in Table (2).

Table (2). Chemical properties of the artificially contaminated soil samples and the applied incubation treatments.

		pH	EC	Cd		Pb	
			(dSm ⁻¹)	(mg kg ⁻¹)		(mg kg ⁻¹)	
		1: 2.5 extract		Total	DTPA	Total	DTPA
Spiked soils	Clay	7.44	0.978	39.80	4.39	146.87	15.89
	Sandy loam	7.74	1.149	31.12	5.43	63.83	4.33
Treatments	RB	10.52	1.322	0.001	ND*	0.015	ND
	TB	10.54	0.126	ND	ND	ND	ND
	AB	2.87	0.058	ND	ND	ND	ND
	ATB	2.90	0.048	ND	ND	ND	ND

Raw bentonite (RB), thermal activated bentonite (TB), acid activated bentonite (AB) and acid thermal activated bentonite (ATB). ND*= Not detected

Four treatments were carried out, i.e., raw bentonite (RB), thermal activated bentonite (TB), acid activated bentonite (AB) and combined acid thermal activated bentonite (ATB). Portions of 100 g from the artificially contaminated soils were mixed with 0.5 g and 1.0 g of each treatment. Each treatment was carried out in triplicates. Replications of the homogeneous soil mixtures were watered to saturation level and placed in sealed small polyethylene pots in order to maintain the moisture level. The sealed soil mixture pots were incubated for 2, 14, 30 and 60 days at 25±2°C. The soil pots were thoroughly mixed during the incubation process. At each period, a replicate from each treatment was removed from the incubator and the DTPA extractable fractions of the studied metals in soils were determined after incubation. The difference in initial concentration and final concentration, knowing dry mass of soil, allowed for the calculation of the exact amount of heavy metals immobilized per gram of soil. The efficiency (E %) of different applied treatments for immobilization of the heavy metals can be evaluated using the expression:

$$E (\%) = [(C_o - C_e)/C_o] \times 100$$

Where E represents immobilization efficiency in percent; C_e represents the equilibrium extractable concentration (mg kg^{-1}) and C_0 represents the initial extractable concentration (mg kg^{-1}) at zero time.

RESULTS AND DISCUSSION

1. The XRD Study

Fig. (1) shows that the XRD pattern of raw and modified bentonite clay approved montmorillonite as the dominant clay mineral and presence of quartz as the main impurity mineral with traces of kaolinite. The result of the XRD analysis for basal d-spacing in RB showed that characteristic peaks (d_{001}) at $2\theta = 6.30$ was 14.05 \AA , which is a characteristic of divalent cations located in the interlayer space and solvated by water molecules (Novakovića et al., 2008). The decrease in the basal d-spacing to 13.5 \AA of thermal activated bentonite (TB) indicates alterations in the interlayer of the clay layers after heat treatment at 200°C (Cótica et al., 2011). This decrease was caused by the removal of interlayer water and the migration of exchangeable cation. Moreover, the peak (d_{001}) expanded to 15.04 \AA and 15.14 \AA in AB and ATB clays, respectively after the samples were treated with acid, indicating that the expandable layers of smectite type. Similar results were reported by Tomić et al. (2011). X-ray diffraction results showed the presence of other peaks in the ranges: 7.12 \AA (corresponding to kaolinite) and 4.45 \AA (corresponding to the smectite clay mineral) and the additional peaks of quartz prevailing at 3.5 \AA , 2.54 \AA . and 1.81 \AA .

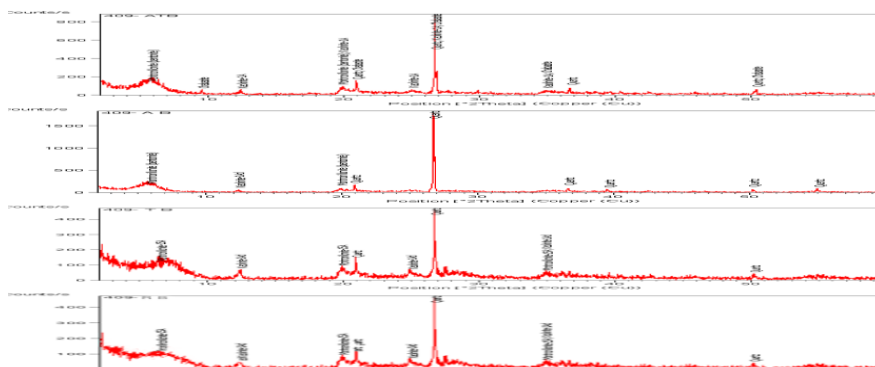


Fig. (1). XRD patterns for natural and modified bentonite.

2. Fourier Transforms Infrared Spectroscopy (FTIR)

Fig. (2a) represents the raw bentonite clay FTIR spectrum. The first zone (3693.81 to 3619.8 cm^{-1}) is the characteristic region of the O–H bonding stretch that lies between the tetrahedral and octahedral bentonite sheets

(Bhattacharyya et al., 2014). The 3693.81 cm^{-1} signal belongs to the stretching of the structural O–H bond in the kaolinite network, confirming the presence of this mineral as an impurity (Torres et al., 2013). The stretches vibrations of Al–OH and deformation of the water H–O–H occurring at 910 and 1663 cm^{-1} . Stretching in the 992 cm^{-1} band is associated with Si–O–Si vibrations, the presence of octahedral layers in the range of 992 and 789.46 cm^{-1} , finally a peak in the 445 to 414.95 cm^{-1} band indicates the presence groups Al–O–Si. Fig. (2b) shows that the FTIR spectrum of thermal activated bentonite reveals that on heating Na- montmorillonite up to 200°C , the peaks at 3619.89 cm^{-1} disappeared. The beak of Si-O-Si at 992 cm^{-1} remained unchanged. The increased peak strength at 796.12 cm^{-1} indicates the alteration of tetrahedral sheet. The intensity of peak at 688 cm^{-1} (Al-OH-Si bending) increased with increase in temperature to 200°C . FTIR spectrum of acid activated bentonite in Fig. (2c) reveals that during acid activation of bentonite, the protons penetrate into clay layers attacking the OH groups causing variation in adsorbent peaks attributed to the OH vibrations and octahedral cations. The strength of stretching bands noticed at 3619.89 cm^{-1} (Al-OH-Al). The attack of acid resulted in a decrease of bands associated with the adsorbed water at 3605 cm^{-1} (H-O-H stretching) and 1636 cm^{-1} (H-O-H bending). The peak of Si-O-Si at 988 cm^{-1} has been remained unchanged. The FTIR spectrum of ATB shown in Fig. (2d) reveals that deeper penetration of protons into the activated clay layers occurred reflecting a structural change because of the acid attack. These results suggest a significant decrease of cations that are part of the clay octahedral layer, which causes the loss of water and hydroxyl groups (3693.81 to 2356.61 cm^{-1}).

3. Scanning Electron Micrograph (SEM)

The morphologic analysis of four types of clay particles by scanning electron microscopy is shown in Fig. (3). The distinctive morphology characters of raw montmorillonite are thin and short leaves, onion-shape, honeycombed, lath-shape and distributed thin flake. Small pore establishment occurred due to impurities removal and water in thermal activated bentonite (TB). These keep the pores open up and the surface appears as more porous and homogenous. The leaching of cations on acid activation due to replacement of exchangeable cations by H^+ ions making the clay surface more porous at low acid concentration, the surface is getting highly porous with even distributing pores. This means that acid activation increases porosity. Acid activation followed by thermal activation provides more porous clay than that of acid activated only due to absence of any water which is presented in clay and was adsorbed during washing. This finding agrees with that of Yeon and Bai (2015), who stated that clay minerals are heated after using acid to remove any impurities or moisture attached to clay particles.

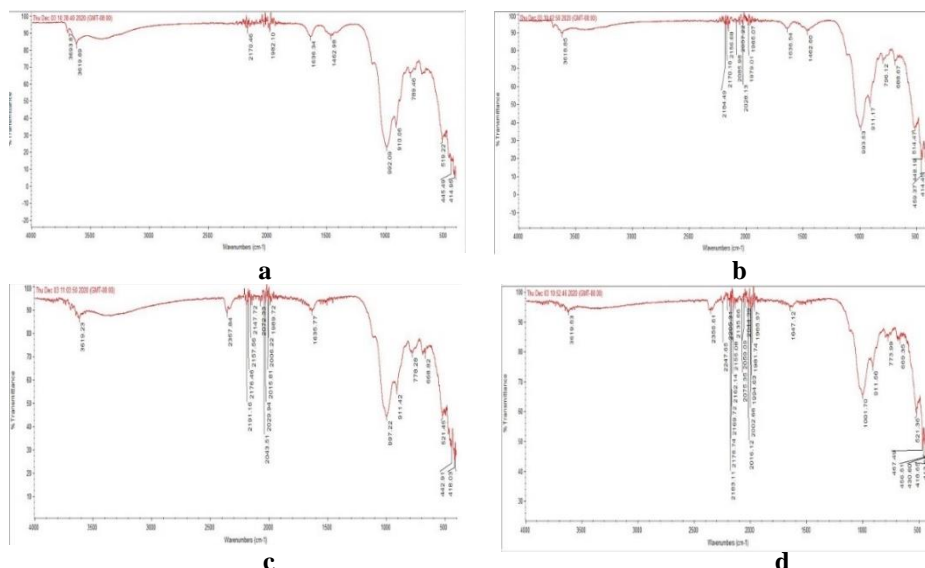


Fig. (2). FTIR spectra for (a) Raw bentonite (RB), (b) Thermal activated bentonite (TB), (c) Acid activated bentonite (AB) and (d) combined acid thermal activated bentonite (ATB).

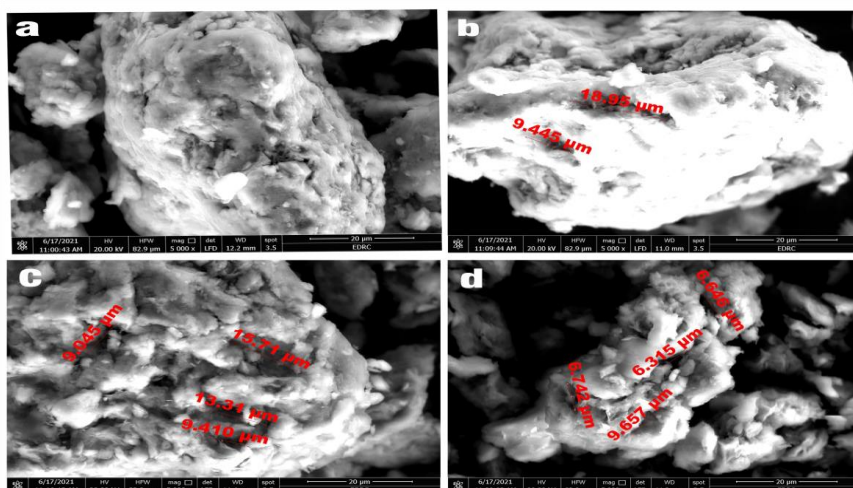


Fig. (3). SEM images for (a) Raw bentonite (RB), (b) Thermal activated bentonite (TB), (c) Acid activated bentonite (AB) and (d) combined acid thermal activated bentonite (ATB).

4. Estimation of Cation Exchange Capacity (CEC)

The cation exchange capacity values were 85.21, 72.26, 59.26 and 59.08 cmol.kg^{-1} for RB, TB, AB and ATB, respectively. The results showed that heat and acid treatments significantly reduced the cation exchange

capacity, which was consistent with previous research (Didi et al., 2009 and Vieira et al., 2009). These results did not prevent cadmium and lead adsorption onto bentonite because ion exchange is not the only mechanism involved here. The decrease in CEC value caused by acid treatment is due to cationic leaching, whereas low CEC values caused by heat treatment can be explained by a charge reduction caused by the migration of small radii cations into unoccupied octahedral sites and the establishment of covalent bonds. Another argument is that when the cation is heated, it becomes more tightly bonded to the surface, making NH_4^+ exchange more difficult. The amount of charge reduction, however, is determined by the heating temperature and the cation's type.

5. Immobilization of Cadmium and Lead

The total levels of Cd and Pb in the two spiked soil samples rose rapidly in direct proportion to the doses given. Total concentration of Cd was 31.12 and 39.80 mg kg^{-1} and of Pb was 63.83 and 146.87 mg kg^{-1} in intentionally contaminated sandy loam and clay textured soil samples, respectively. Because of great adsorption ability of the clay soil, it had the highest total level of Cd and Pb, while sandy loam soil had the lowest total content. In both two soils, Pb had the highest concentration while Cd had the lowest. Pb has a higher geochemical affinity for reacting with soil elements to build inner-sphere complexes and even precipitate in various ways. In contrast to Pb, Cd tends to be less and weakly adsorbed by the two soils, which facilitate its leaching (Irhaa et al., 2009). Table (2) indicates also that the concentration of DTPA-Cd was higher in the spiked sandy loam soil compared to the clay one due to the lack of adsorbing/active surfaces in the sandy loam soil. This finding agrees with that of Selim (2012), who concluded that the free heavy metal ion concentrations in clay soils were lower than in the sandy one receiving the same pollutants.

The initial fixed Cd and Pb concentrations in the intentionally polluted soils are shown in Fig. (4). These values were calculated by subtracting the DTPA-Cd and Pb concentrations from the total metal content. The clay soil originally absorbed the highest quantities of Cd and Pb, whereas the sandy loam soil initially adsorbed the lowest levels. Because of its strong adsorption affinity and the creation of inner-sphere complexes with the active surfaces of soil elements, Pb showed the largest amounts initially adsorbed in the two examined soils. This is in agreement with the results of Gomes et al. (2001), who found that Cr and Pb were the heavy-metal cations most strongly absorbed by seven Brazilian soils in competitive situations, whereas Cd, Ni, and Zn were the least adsorbed elements. The results revealed that the different treatments had no influence on the pH value of all the investigated soils. While EC reduced dramatically within 2 days of incubation in all treatments, with the smallest decrement between 30 and 60 days. As the rate

of amendment application increased, the soil EC value declined. EC values fell in the sequence ATB> AB > TB> RB when the same treatment rates were used.

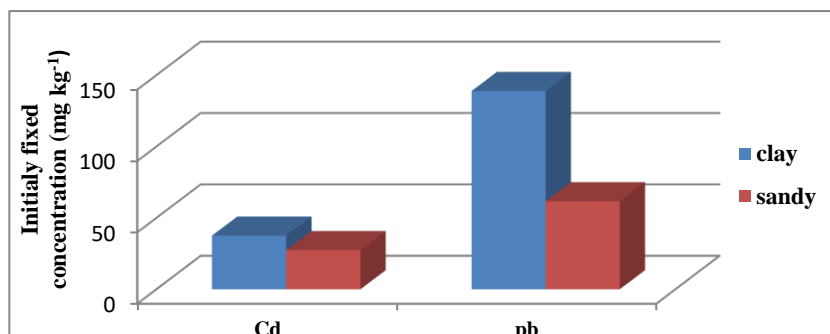


Fig. (4). Initially fixed Cd and Pb concentrations in the artificially contaminated soils.

Fig. (5) show the highest reductions of the combined ATB treatment in the two investigated soils. Where the ATB treatment reduced the DTPA-Cd from approximately 4.391 to 0.465 mg kg⁻¹ (78.84% decrease) in the clay soil and 2.713 to 0.199 mg kg⁻¹ in the sandy loam soils (71.99% decrease) in the first 2 days while it gradually decreased from 0.465 to 0.188 mg kg⁻¹ (12.58% decrease) and 0.199 to 0.07 mg kg⁻¹ (14.3% decrease) in the next 58 days in the clay and the sandy loam soils, respectively. Data show also that combined ATB treatment was the most effective one in reducing DTPA-Pb by 98.46 and 97.85% as compared to the un-amended soils after 60 days of incubation in the clay and the sandy loam soils, respectively, The data show that DTPA-Cd decreased by 79.25 and 81.45% in the clay and sandy loam soils, respectively, while DTPA-Pb decreased by 70.31 and 88.6% in the clay and the sandy loam soils, respectively. Extractable DTPA-Cd and Pb in Fig. (5) showed consistent decreases with time down to nearly 86 & 89% and 91.29 & 93.77% of un-amended soils due to the effect of the added TB and AB after 60 days of incubation, respectively.

The combined acid thermal activated bentonite (ATB) was substantially more successful in lowering the DTPA extracted Cd and Pb, as revealed by the LSD test, in the two examined metals and treatments, according to the statistical analysis (Table 3). It was found that only 1% ATB was sufficient to fix up to 91.42 and 98.46% of the applied Cd and Pb, respectively. Also increasing the applied ATB rate from 0.5 to 1.0% showed significant differences, indicating that 1% ATB was sufficient to get the lowest DTPA extracted metals in the two investigated soils.

Table (4) shows the immobilized Cd and Pb concentrations as a result of the applied treatments. They were calculated by subtracting the concentration at the end of the incubation experiment, i.e., 60 days (C₆₀) from

the relevant concentration in the contaminated soil at zero time (C_0). The results in Table (4) reveal that the immobilized concentrations by the various treatments may be in the following order: $Pb > Cd$ in all of the investigated treatments. Also, combined ATB was found to be the most effective immobilizer of Cd and Pb in polluted soils. Cadmium (Cd) had a lower response to the treatments because its immobilized concentration ranged from 1.887 to 2.450 $mg\ kg^{-1}$, compared to 4.238 $mg\ kg^{-1}$ for immobilized Pb.

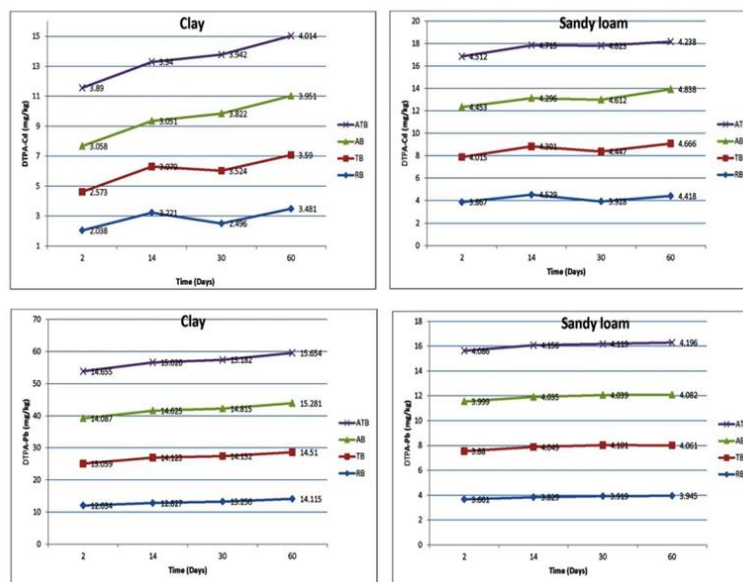


Fig. (5). DTPA-Cd and Pb extractable from contaminated soils during the incubation period as a function of the different treatment rate.

Fig. (6) shows that the maximum immobilization efficiencies were for ATB-treatment, whose immobilization efficiency ($E\%$) values were 91.42 and 98.46% for Cd and Pb in the clay soil while 90.99 and 97.85% for Cd and Pb in the sandy loam soil whereas for AB-treatment immobilization efficiencies were 89.45 and 88.62% for Cd and 94.56 and 93.25% for Pb in the clay and the sandy loam soil samples, respectively. Data also showed that the immobilization efficiencies of TB-treatment were 81.32 and 86.95% for Cd and 90.25 and 92.85% for Pb in the clay and sandy loam soil samples, respectively. While the RB showed the lowest ability among these treatments to immobilize Cd and Pb in soils, as $E\%$ for Cd and Pb were 79.25 and 90.61% in the clay soil, while were 81.45 and 88.79% in the sandy loam soil. However, the present study showed that from the practical and economic points of view, 1% ATB was the best treatment to immobilize Pb and Cd from two artificially contaminated soils. These results are in agreement with those of Luz et al.

(2013), who found that the maximum removal efficiencies were 97.62 and 91.08% for Cd (II) and lead (II), respectively using chemically and thermally modified bentonite.

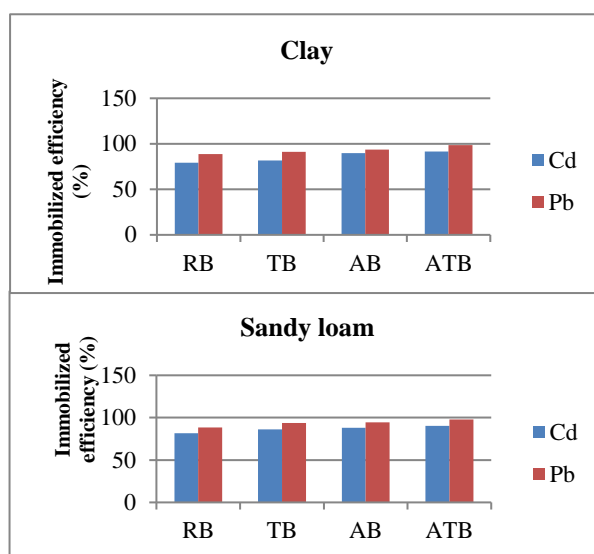
Table (3). LSD analyses of the mean concentrations of Cd and Pb in the two artificially contaminated soils as a result of the applied treatments at the end of the incubation period.

Soil Samples	Treatments	Concentration (mg/kg soil)			
		Cd		Pb	
Clay	Control	4.391	a	15.899	a
	RB 0.5%	1.365	b	2.225	b
	RB 1%	0.911	c	1.663	c
	TB 0.5%	1.194	b	1.671	c
	TB 1%	0.799	d	1.364	d
	AB 0.5%	0.637	d	0.976	e
	AB 1%	0.441	e	0.701	f
	ATB 0.5%	0.408	e	0.618	f
	ATB1%	0.376	f	0.444	g
LSD 0.05		41.43		97.56	
Sandy loam	Control	5.426	a	4.332	a
	RB 0.5%	0.366	b	0.606	b
	RB 1%	0.264	c	0.407	c
	TB 0.5%	0.241	c	0.386	c
	TB 1%	0.199	d	0.269	d
	AB 0.5%	0.195	d	0.257	d
	AB 1%	0.154	e	0.244	d
	ATB 0.5%	0.141	f	0.135	e
	ATB 1%	0.138	f	0.093	f
LSD 0.05		89.06		99.35	

*According to Fisher's Protected LSD test at p 0.05, means within a column followed by the same letter are not statistically different.

Table (4). Immobilized concentrations of Cd and Pb in the two artificially contaminated soils amended with applied treatments (C₀ - C₆₀) mg kg⁻¹.

Soil sample	Incub. time (days)	Immobilized concentration (mg kg ⁻¹)							
		RB		TB		AB		ATB	
		0.5%	1%	0.5%	1%	0.5%	1%	0.5%	1%
Clay		DTPA- extra. Cd (mg kg⁻¹)							
	2	1.887	2.038	2.362	2.771	2.383	3.058	3.463	3.891
	14	2.054	3.201	2.472	3.079	2.969	3.051	3.711	3.940
	30	2.496	2.891	2.798	3.524	3.754	3.822	3.844	3.941
	60	3.024	3.483	3.196	3.594	3.752	3.953	3.983	4.014
Sandy loam	2	1.615	1.944	1.615	2.013	1.785	2.233	1.952	2.421
	14	1.683	2.263	2.022	2.155	1.994	2.154	2.132	2.191
	30	1.836	1.962	2.173	2.223	2.285	2.396	2.253	2.412
	60	2.002	2.211	2.255	2.331	2.347	2.436	2.316	2.453
	Clay		DTPA- extra. Pb (mg kg⁻¹)						
2		11.178	12.034	11.951	13.059	13.42	13.89	14.087	14.655
14		12.205	12.828	13.353	14.000	13.999	14.649	14.625	15.026
30		13.255	13.60	13.698	14.152	14.504	15.048	14.815	15.182
60		13.674	14.116	14.228	14.510	14.922	14.879	15.281	15.654
Sandy loam	2	2.745	3.000	3.661	3.880	3.894	3.999	4.086	4.168
	14	3.343	3.665	3.829	4.049	4.030	4.035	4.156	4.205
	30	3.353	3.792	3.919	4.101	4.032	4.039	4.119	4.181
	60	3.724	3.837	3.945	4.061	4.074	4.082	4.196	4.238

**Fig. (6).** The immobilization efficiency (E%) of Cd and Pb for different applied treatments at rate 1%.

CONCLUSIONS

Bentonite has high adsorbent capacity, which can be improved through acid activation and/or thermal treatment. The dominant minerals in raw bentonite were montmorillonite and quartz, with traces of kaolinite. According to the XRD patterns, the basal spacing characteristic peaks (d001) had structural changes as a result of heat and acid treatments. Acid treatment followed by thermal activation at 200°C resulted in deeper protons penetration into activated clay layers, according to FTIR. SEM scans revealed that acid treatment followed by heat treatment produces more porous clay than acid or thermal treatment alone because any impurities or moisture connected to clay particles are removed. The amount of Cd and Pb immobilized by activated bentonites was higher than the corresponding ones immobilized by the raw bentonite, according to obtained results. These treatments' ability to immobilize Cd and Pb improved as the rate of application and incubation period increased, and they could be grouped in a descending order as follows: ATB > AB > TB > RB. After 60 days of soil incubation, the ATB-treatment was the most effective in lowering DTPA-Cd and Pb as compared to the other treatments, with maximum immobilization efficiencies of 91.42 and 90.99% for Cd and 98.46 and 97.85% for Pb in the clay and the sandy loam soil samples, respectively. The LSD test revealed that the ATB treatment had the greatest effect on decreasing the DTPA extracted Cd and Pb. Only 1% ATB was found to repair up to 91.42 and 98.46% of the applied Cd and Pb, respectively. However, the present investigation found that the 1% ATB-treatment was the optimal treatment for immobilizing Cd and Pb in the two artificially contaminated soils from practical and economic standpoint.

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فاعلية البنتونيت المعدل على تثبيت الكاديوم والرصاص في الأراضي الملوثة صناعياً

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أجريت هذه الدراسة لتقييم قدرة معدن البنتونيت المصري المعدل حرارياً وحامضياً على تثبيت أيونات الكاديوم (Cd^{2+}) والرصاص (Pb^{2+}) في التربة الملوثة. اختبرت عينتين تربة ذات قوام مختلف وتم تلويثهما صناعياً بمحلول كلوريد الكاديوم والرصاص. تراحت تركيزات المحتوى الكلي للكاديوم من 31.12 إلى 39.8 ملجم/كجم وللرصاص من 63.83 إلى 146.87 ملجم/كجم في عينات التربة الرملية اللومية والطينية، على التوالي. أظهرت النتائج أن المحتوى الكلي للكاديوم والرصاص كان الأعلى في التربة الطينية بسبب قدرتها العالية على الامتصاص. استخدمت تقنيات حيود الأشعة السينية (XRD) والتحليل الطيفي للأشعة تحت الحمراء المحولة (FTIR) والسعة التبادلية الكاتيونية (CEC) وصور الميكروسكوب الإلكتروني (SEM) لدراسة الصفات المورفولوجية والكيميائية لمعدن البنتونيت المعدل. تم خلط البنتونايت الخام (RB) والبنتونيت المعدل حرارياً (TB) والبنتونيت المعدل حامضياً (AB) والبنتونايت المعدل حامضياً وحرارياً معاً (ATB) بمعدلي 1 و 0.5% (وزن/وزن) مع التربة الملوثة وحضنت في درجة حرارة 25 درجة مئوية لمدة 2 و 14 و 30 و 60 يوماً. في هذا الصدد، أظهرت النتائج أن المستخلص الكيميائي من كل DTPA-Pb و DTPA-Cd انخفض بشكل معنوي بمقادير مختلفة مع زيادة فترة التحضين مصحوباً بانخفاض في EC بسبب تأثير المعالجات المضافة محققاً أعلى انخفاضاً لمعاملة ATB في كلاً من نوعي التربة التي تم فحصها. زادت قدرة هذه المعاملات في تثبيت الكاديوم والرصاص مع زيادة معدل الأضافة إلى 1% ويمكن ترتيبها بترتيب تنازلي حسب قدرتها التثبيتية لعناصر الدراسة على النحو التالي $ATB > AB > TB > RB$ وأظهرت الدراسة أيضاً أن البنتونيت المعدل حامضياً وحرارياً كان الأكثر فاعلية في خفض تركيزات DTPA-Pb و DTPA-Cd مقارنةً بالمعاملات الأخرى في نهاية فترة التحضين (بعد 60 يوماً) حيث كانت أقصى كفاءة للتثبيت (E%) 91.42 و 90.99% للكاديوم و 98.46 و 97.85% للرصاص في عينات التربة الطينية والرملية، على التوالي. بينما أظهر البنتونيت الخام (RB) أقل قدرة على تثبيت هذه المعادن في التربة مقارنةً بالمعاملات الأخرى، حيث انخفض DTPA-Pb و DTPA-Cd بنسبة 79.25 و 90.61% في عينات التربة الطينية و 81.45 و 88.79% في عينات التربة الرملية. أشار التحليل الإحصائي باستخدام اختبار LSD إلى أن معاملة ATB كانت أكثر كفاءة معنوية في خفض Pb و Cd المستخلصة كيميائياً بمحلول DTPA. وجد أن ما يقرب من 91.42 و 98.46% من الكاديوم والرصاص، على التوالي تم تثبيتهما بنسبة 1% من ATB. ومن وجهة النظر العملية والاقتصادية البنتونيت المعدل حامضياً وحرارياً (ATB) بنسبة 1% كان أفضل معاملة لتثبيت الرصاص والكاديوم في الأراضي الملوثة صناعياً.