



## Removal of lead from aqueous solutions with a treated spent bleaching earth

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### ABSTRACT

A spent bleaching earth from an edible oil refinery has been treated by impregnation with a normal sodium hydroxide solution followed by mild thermal treatment (100 °C). The obtained material (TSBE) was washed, dried and characterized by X-ray diffraction, FTIR, SEM, BET and thermal analysis. The clay structure was not apparently affected by the treatment and the impregnated organic matter was quantitatively removed. We have investigated the sorption of lead on this material, the spent bleaching earth (SBE) and the virgin bleaching earth (VBE). The kinetic results fit the pseudo second-order kinetic model and the Weber & Morris, intraparticle diffusion model. The pH had effect on the sorption efficiency. The sorption isotherms followed the Langmuir model for various sorbent concentrations with good values of determination coefficient. A comparison between the results obtained with this material and those of the literature highlighted a good removal capacity of the treated spent bleaching earth at low cost.

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### 1. Introduction

The increasingly various industrial activities produce liquid effluents containing toxic compounds for humans and the environment. Among these compounds, heavy metals are most dangerous due to their toxicity at very low concentration in water. Many works were devoted to their elimination, the objective being to develop an effective and economic process. Heavy metals removal methods cited in the literature generally involve adsorption processes on activated carbon [1,2], ions exchange mechanism [3,4] or complexation by natural and synthetic reagents [5–7]. The cost of these processes led to numerous studies on alternative removal methods by use of less expensive natural materials and waste by-products such as chitosan, zeolites, clays, peat moss, fly ash, rice husk and sawdust [8]. The waste by-product chosen in this work is a spent bleaching earth obtained from an edible oil refinery.

The refining process of crude edible oil includes four operations: degumming, neutralization, bleaching and deodorization. The bleaching step is performed by use of acid-activated clay, called bleaching earth. This bleaching operation produces great quantities of solid wastes which usually are disposed of in a landfill near the factory. In Algeria, edible oil refineries produce about 8000 tonnes of spent bleaching earth per year. This disposal poses an acute problem of management and storage.

The spent bleaching earth (SBE) contains about up to 30% (w/w) of residual oil that rapidly oxidizes to the spontaneous

auto-ignition point, and also produces unpleasant odors [9]. The constant changes in environmental legislation and the growing importance of safety in disposal techniques has led to many restrictions in solid waste management. In order to minimize the risk of pollution, many studies are devoted to the conversion and the reuse of these wastes in various applications [9–16]. Three methods were reported for the treatment of spent bleaching earth: (1) recovery of the entrapped oil by washing with non polar solvents followed by steam treatment or washing with a solution of anionic detergent and a solution of sodium triphenylphosphate, (2) regeneration by burning and (3) regeneration by solvent extraction [17].

Recently, the regeneration of spent bleaching earth was conducted by preliminary acid impregnation followed by thermal processing [9–11,13–16]. In a previous work we have studied the decolorizing properties of a spent bleaching earth regenerated by thermal treatment followed by acid leaching [14] and by impregnation with a sodium hydroxide solution followed by a mild thermal treatment [18]. The aim of this work is to apply our recently published spent bleaching earth regeneration method to heavy metals removal from aqueous solution. In our previous publication we have observed that the regenerated material removed only cationic dyes leading us to suppose that the process was an ion exchange one. The regeneration method reported was based on a saponification reaction of the edible oil, leading to the formation of fatty acids sodium salts which could be removed by washing with water and afforded the original bentonite with its well known cation exchange properties. The sorption properties of the treated material were studied for lead removal from aqueous solutions. Lead is one of the most toxic elements and is present in industrial wastewaters from

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**Table 1**  
Chemical analysis of VBE

Constituent	Chemical analysis (%)
SiO <sub>2</sub>	69.39
Al <sub>2</sub> O <sub>3</sub>	14.67
Fe <sub>2</sub> O <sub>3</sub>	1.16
MgO	1.07
CaO	0.30
Na <sub>2</sub> O	0.5
K <sub>2</sub> O	0.79
TiO <sub>2</sub>	0.16
SO <sub>3</sub>	0.91
Ignition loss	11

battery manufacturing, metallurgy, metal finishing, and chemical industry.

In this study, we have investigated the kinetics, sorption isotherms and pH effect of the lead sorption on the treated spent bleaching earth and we have compared the sorption capacities with those of the virgin and the untreated spent bleaching earth.

## 2. Experimental

### 2.1. Materials

The spent bleaching earth (SBE) was obtained from an edible oil-refining factory (ENCG at Oran, Algeria). The virgin bleaching earth (VBE) was provided by Bental company (Algeria). The chemical composition of the virgin bleaching earth is shown in Table 1. All chemicals used were of analytical grade.

### 2.2. SBE treatment

The spent bleaching earth sample was impregnated with 1N NaOH solution (solid/solution ratio: 1/5, w/w) and heated at 100 °C overnight. The obtained solid was washed with distilled water, dried at 80 °C during 24 h, crushed and 0.250 mm sieved. This treated spent bleaching earth is noted TSBE.

### 2.3. Characterization of the materials

X-ray powder diffraction data of the virgin bleaching earth, the spent bleaching earth and the treated spent bleaching earth were collected with monochromatic Cu K $\alpha$  radiation using a Phillips X'Pert MPD diffractometer. Thermal analysis curves of the same materials were recorded with a NETZSCH STA 409 PC/PG simultaneous thermal analyser. BET analysis was performed on a micromeritics ASAP 2010 apparatus. The IR spectra of the samples in the 4000–400 cm<sup>-1</sup> were obtained with a Nicolet Avatar 330 FTIR spectrophotometer. SEM observation of the three materials (VBE, SBE and TSBE) with the same magnification factor was carried out with a scanning electron microscope Jeol 1200 EX.

Iodine number and the zero point of charge (pHzpc) of VBE, SBE, and TSBE were determined according to a procedure reported in the literature [19,20]. These results and the BET surface area are reported in Table 2.

**Table 2**  
Characteristic data of VBE, SBE and TSBE samples

Sample	BET surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> )	Iodine number (mg/g)	pHzpc
VBE	147.45	0.21	19.04	3.65
SBE	–	–	38.07	4.52
TSBE	47.45	0.093	24.11	4.53

Samples pretreated under vacuum at 200 °C, for the BET measurements.

### 2.4. Kinetic study

The kinetic study was carried out in batch mode on 50 mg suspensions of SBE, VBE and TSBE in 100 mL of lead aqueous solutions at Pb(II) concentration values of 100 mg/L for SBE and VBE and 150 mg/L for TSBE.

The suspensions were stirred during different time intervals (10–240 min) then centrifuged. The pH was fixed at 4.5 with HNO<sub>3</sub>. The lead concentration in the supernatants was measured by flame atomic absorption spectroscopy (AAS) using a PYE UNICAM SP9 at 383.6 nm.

### 2.5. Sorption isotherms

The sorption isotherms were established using VBE, SBE and TSBE suspensions in solutions (solid–solution ratio = 0.5 g/L) with lead concentration values from 25 to 200 mg/L. The pH of each suspension was adjusted to 4, stirred for 90 min and centrifuged. The equilibrium lead concentrations in the supernatants were determined by atomic absorption spectroscopy at 383.6 nm. The removal capacities of the materials were calculated from the difference between the lead initial and final concentrations.

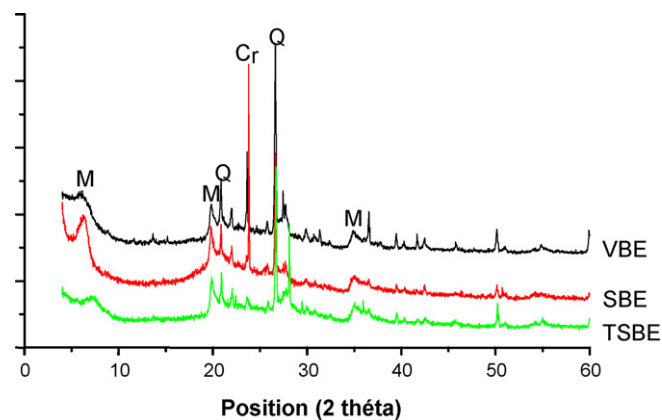
### 2.6. pH effect on lead removal

Experiments were conducted on suspensions of 50 mg of TSBE in 100 mL of lead solutions with initial concentrations from 25 to 200 mg/L. The pH of each suspension was adjusted in the range 3–6 with of 1N NaOH and 1N HCl solutions, then stirred during 90 min. The solid phase was separated by centrifugation and the supernatants were analyzed.

## 3. Results and discussion

### 3.1. Characterization of materials

The X-ray powder diffraction patterns (Fig. 1) of VBE, SBE and TSBE show the same diffraction peaks of the montmorillonite (M) and the presence of quartz impurities in the samples (at  $2\theta = 20.89^\circ$  and  $26.65^\circ$ ). From this observation, we deduce that the edible oil bleaching process and the treatment of the SBE with NaOH did not affect the main structure of the used bentonite. Fig. 1 also shows that the (001) reflection of SBE and TSBE did not correspond to any organic intercalation product after the bleaching process and the NaOH treatment. The reported intercalation of long chain organic molecules in the interlayer space of a bentonite led to an increase of the  $d_{001}$  value from 12–14 Å to near by 18 Å [21].



**Fig. 1.** X-ray powder diffraction patterns of virgin bleaching earth (VBE), spent bleaching earth (SBE) and treated spent bleaching earth (TSBE). Montmorillonite (M), quartz (Q), cristobalite (C).

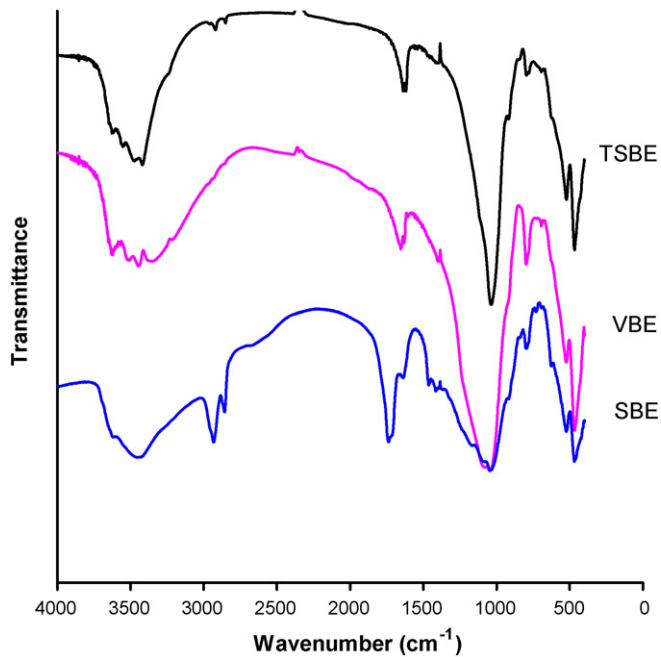


Fig. 2. FTIR spectra of VBE, SBE and TSBE.

The infrared spectrum of VBE (Fig. 2) shows the characteristic absorption bands of a montmorillonite, particularly the bands near  $3460\text{ cm}^{-1}$  with a shoulder at  $3446\text{ cm}^{-1}$  attributable, respectively, to the absorption by the interlayer water and the stretching vibrations of structural hydroxyls. It also shows the absorption bands at  $1654\text{ cm}^{-1}$  (interlayer water hydroxyl bending vibration),  $1048\text{ cm}^{-1}$  (Si–O stretching),  $794\text{ cm}^{-1}$  (Si–O vibrations of quartz impurities),  $516$  and  $462\text{ cm}^{-1}$  (Si–O–Al bending). These results are in agreement with the literature [22]. The VBE, TSBE and SBE spectra are similar but the latter exhibits the edible oil characteristic bands. These bands, observable in Fig. 2, are those corresponding to C–H stretching at  $2925$  and  $2854\text{ cm}^{-1}$  and the ester carbonyl vibration at  $1736\text{ cm}^{-1}$ . This carbonyl band disappears after the treatment of SBE with NaOH leading to sodium salt of fatty acids totally removed after washing operation. The spectrum of TSBE is similar to that of VBE, but near  $2800\text{ cm}^{-1}$  there is the existence of two bands, indicating the presence of some organic matter (probably glycerol formed during the saponification reaction and this will be also detected by thermal analysis).

The thermal properties of the three materials can be summarized as follows: TGA and DSC plots of VBE (Fig. 3a) show an initial endothermic weight loss starting at  $40^\circ\text{C}$  and ending at  $160^\circ\text{C}$ . This first weight loss was due to removal of adsorbed water. A second weak endothermic weight loss at the temperature around  $500^\circ\text{C}$  was due to the OH group release from different position of the montmorillonite structure.

The TGA and DSC plots of SBE (Fig. 3b) did not show the first endothermic weight loss around  $100^\circ\text{C}$  corresponding to adsorbed water removal. This is due to the edible oil bleaching process conditions which produce the spent bleaching earth in anhydrous medium, low pressure and a temperature of  $80^\circ\text{C}$ . Fig. 3b presents an important exothermic weight loss starting at  $160^\circ\text{C}$  and ending at  $450^\circ\text{C}$  due to decomposition and burning of the organic content of the SBE. We show also the DSC weak endothermic peak around  $500^\circ\text{C}$  corresponding to the loss of structural hydroxyl groups.

The TGA and DSC plots of TSBE (Fig. 3c) present the same two endothermic peaks that of VBE with an additional exothermic peak at  $316^\circ\text{C}$  corresponding probably to the loss of residual glycerol (dec.  $290^\circ\text{C}$ ) formed during the treatment.

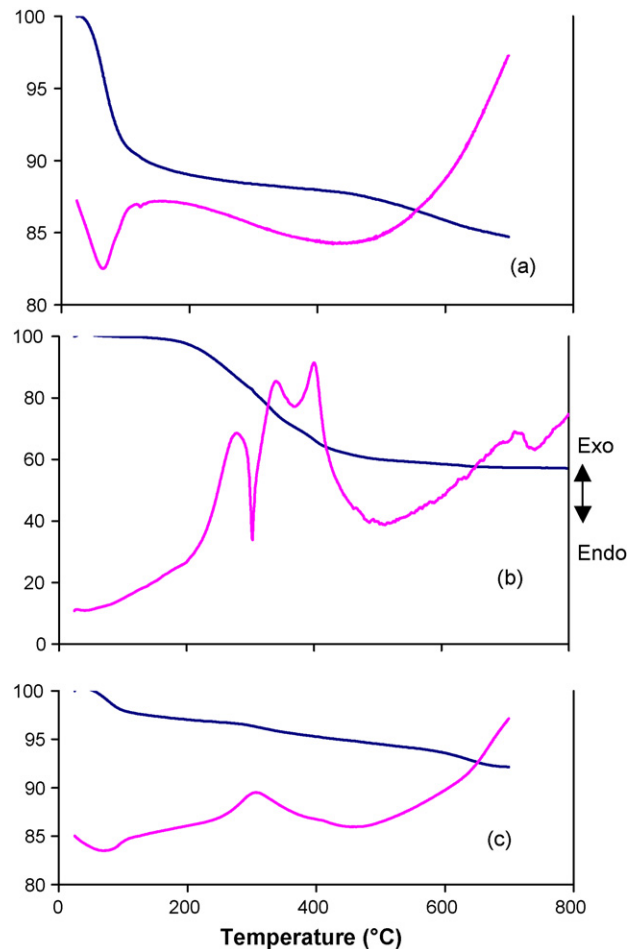


Fig. 3. Thermogravimetric and DSC plots of (a) VBE, (b) SBE and (c) TSBE.

The SEM micrographs of VBE and SBE (Fig. 4a and b) show a similar morphology while that of TSBE (Fig. 4c) show flattened and vermicular texture resulting from the basic and heat treatment.

### 3.2. Contact time effect on lead sorption

Fig. 5 shows the sorption capacities for lead of VBE, SBE and TSBE versus contact time. The lead removal with TSBE is faster than with VBE and SBE at the same concentration. Thus, the sorption equilibrium reached after 60 min for the first and second material. The different initial concentration of lead ions solution affected the sorption kinetics for the third material for which the equilibrium reached after 90 min at the highest initial lead concentration ( $C_0 = 200\text{ mg/L}$ ).

From these preliminary results and for the following sorption isotherm study, we have chosen a contact time of 90 min to ensure sorption equilibrium.

### 3.3. Kinetic modeling

The sorption kinetics is an important aspect of the pollutants removal process control. The Lagergren's first-order kinetic model, the Ho's pseudo second-order model and the Weber & Morris intraparticle diffusion model are the most frequently used in the literature to predict the mechanism involved in the sorption process [23,24].

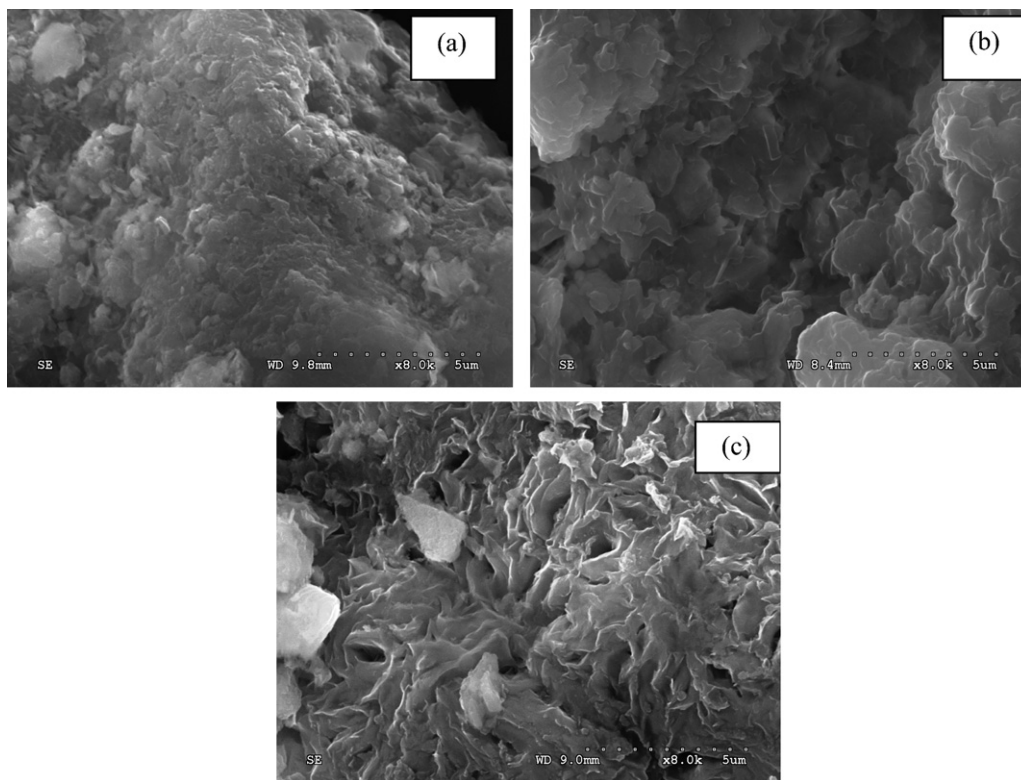


Fig. 4. SEM photographs of (a) VBE, (b) SBE and (c) TSBE.

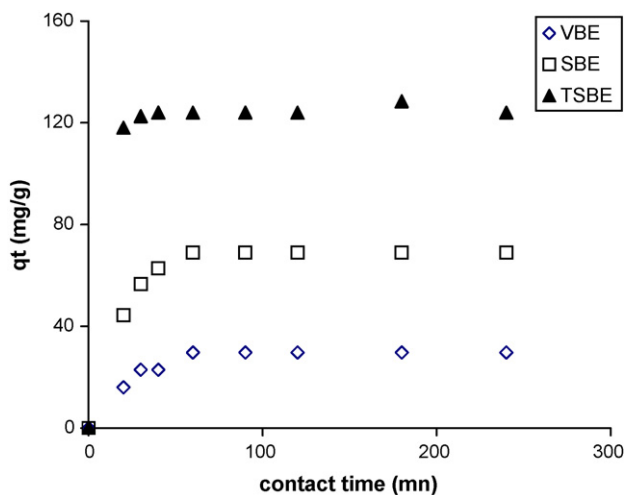


Fig. 5. Effect of contact time on lead sorption capacities of VBE (■), SBE (◆) and TSBE (▲).

The Lagergren’s first-order model is expressed by the equation [23]:

$$\frac{dq}{dt} = k_1(q_e - q_t) \tag{1}$$

where  $q_t$  and  $q_e$  ( $\text{mg g}^{-1}$ ) are, respectively, the amounts of sorbed lead at time  $t$  and at equilibrium and  $k_1$  ( $\text{min}^{-1}$ ) is the first-order rate constant. Integration of Eq. (1) gives the expression:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} \times t \tag{2}$$

Eq. (2) shows a linear relationship between  $\log(q_e - q_t)$  and  $t$ . Linear regression calculations allow the determination of the rate con-

stant  $k_1$  and the equilibrium removal capacity  $q_e$ . These parameters were calculated for the sorption of lead. The results are reported in Table 3.

The calculated values from the first-order kinetic model show that the experimental results did not fit this model. The determination coefficient is very low for the three materials. Moreover large differences between experimental and calculated values of the equilibrium sorption capacities are observed (Table 3).

The more recent pseudo second-order model has been extensively used by several researchers in the same field due to its very good correlation with experimental results. This model is expressed by Eq. (3) [23]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{3}$$

where  $k_2$  is the pseudo second-order rate constant ( $\text{g mg}^{-1} \text{min}^{-1}$ ).

The integration of Eq. (3) and its linearization gives the expression:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \times t \tag{4}$$

The plots of  $t/q_t$  versus  $t$  (Fig. 6) are straight lines of which slope and intercept values are, respectively,  $1/(k_2 q_e^2)$  and  $1/q_e$ . The values of the rate constant  $k_2$  and of the equilibrium sorption capacity  $q_e$  are calculated from these parameters. The calculated  $k_2$  and  $q_e$  values and the corresponding linear regression determination coefficient  $R^2$  values for VBE, SBE and TSBE are reported in Table 3. A very good correlation was observed between experimental data and the pseudo second-order kinetic model with determination coefficient values higher than 0.99. The values of the rate constant  $k_2$  are of the same order of magnitude as those observed in the literature [25].

The TSBE plots of Fig. 5 show three steps suggesting an intraparticle diffusion kinetic control. In the fast first step (from 0

**Table 3**  
Kinetic parameters of lead removal by VBE, SBE and TSBE

	C <sub>0</sub> (mg L <sup>-1</sup> )	q <sub>e</sub> exp. (mg g <sup>-1</sup> )	First-order kinetics			Pseudo second-order kinetics			
			q <sub>e</sub> (mg g <sup>-1</sup> )	K <sub>1</sub> × 10 <sup>+2</sup> (min <sup>-1</sup> )	R <sup>2</sup>	q <sub>e</sub> (mg g <sup>-1</sup> )	K <sub>2</sub> × 10 <sup>+3</sup> (g mg <sup>-1</sup> min <sup>-1</sup> )	R <sup>2</sup>	k <sub>D</sub>
VBE	100	29.71	28.73	3.96	0.941	31.65	2.77	0.995	3.82
SBE	100	68.93	73.30	6.01	0.993	71.43	2.19	0.998	10.06
TSBE	150	136.37	123.19	7.02	0.983	138.89	2.96	0.999	7.39

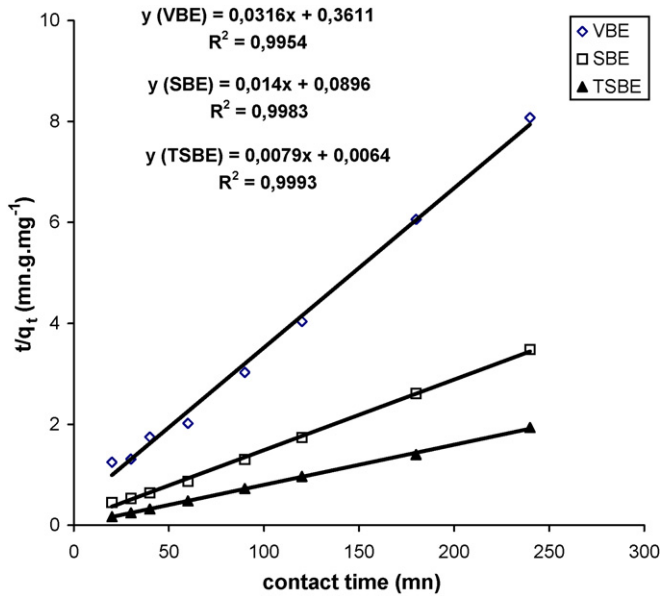


Fig. 6. Pseudo second-order plot lead removal from aqueous solution.

to 40 min) the lead cations are exchanged with external sodium cations. The more slower second step corresponds to the ion exchange with the interlayer sodium cations until equilibrium. This second step is probably intraparticle diffusion controlled.

The Weber & Morris intraparticle diffusion model is expressed by the equation:

$$q_t = k_D \times t^{0.5} \tag{5}$$

where k<sub>D</sub> is the intraparticle diffusion rate constant.

According to this model, the plots of q<sub>t</sub> versus t<sup>0.5</sup> (Fig. 7) show that the VBE and SBE lines pass through the origin, then, the lead sorption on these materials is intraparticle diffusion controlled rate.

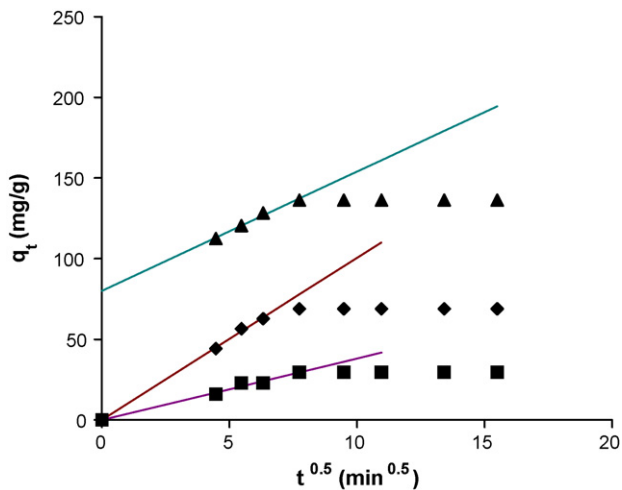


Fig. 7. Weber & Morris plots of lead sorption on VBE (■), SBE (◆) and TSBE (▲).

For TSBE, the plot did not pass through the origin, this is indicative of some degree of boundary layer control and then, the intraparticle diffusion is not the only rate-limiting step [26].

The mechanism of lead sorption on the three materials is an ion exchange process with the interlayer compensating ions of montmorillonite, which is the main component of the bentonite.

### 3.4. Sorption isotherms

The equilibrium sorption experimental data obtained in this study were analyzed using the commonly used Freundlich and Langmuir isotherm models.

The empirical Freundlich model which is known to be satisfactory for low concentrations is expressed by the equation:

$$q_e = K_F \times C_e^{1/n} \tag{6}$$

where q<sub>e</sub> is the equilibrium sorption concentration of solute per gram of adsorbent (mg/g), C<sub>e</sub> is the equilibrium aqueous concentration of the solute (mg/L); K<sub>F</sub> and n are Freundlich constants which are related to adsorption capacity and intensity of adsorption.

Eq. (6) can be linearized in its logarithmic form which enables the determination of Freundlich constants as below:

$$\log q_e = \frac{1}{n} \times \log C_e + \log K_F \tag{7}$$

The calculated values of Freundlich constants are reported in Table 4, the determination coefficient values for the three materials are lower than 0.94 and led us to conclude that our results did not fit the Freundlich sorption model.

The Langmuir isotherms model is described by the following equation:

$$q_e = \frac{Q_{max} K_L C_e}{1 + K_L C_e} \tag{8}$$

where q<sub>e</sub> (mg/g) is the amount of lead removed per gram of sorbent, Q<sub>max</sub> (mg/g) is the maximum sorption capacity, C<sub>e</sub> (mg/L) is the lead concentration in the equilibrium solution, and K<sub>L</sub> (L/g) is the Langmuir constant related to the adsorption energy.

The Langmuir equation can be rearranged to linear form for the convenience of plotting and determining the Langmuir constants as below:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_{max}} + \frac{1}{Q_{max} K_L} \tag{9}$$

**Table 4**

Constant values of Langmuir and Freundlich isotherms for lead sorption by VBE, SBE and TSBE at solid solution ratio R = 0.25 g/L

Material	pH	Langmuir model			Freundlich model			
		Q <sub>max</sub> (mg g <sup>-1</sup> )	K <sub>L</sub> (L.mg <sup>-1</sup> )	R <sup>2</sup>	R <sub>L</sub>	K <sub>F</sub> (L.mg <sup>-1</sup> )	n	R <sup>2</sup>
VBE	4	48.54	0.099	0.992	0.08	8.36	2.57	0.902
SBE	4	62.5	0.162	0.997	0.05	14.53	2.89	0.858
TSBE	3	47.17	0.20	0.995	0.05	12.35	2.98	0.791
	4	104.17	0.24	0.995	0.02	45.67	5.84	0.803
	5	156.25	0.29	0.996	0.02	55.94	4.28	0.860
	6	322.58	0.13	0.996	0.03	108.72	4.55	0.940

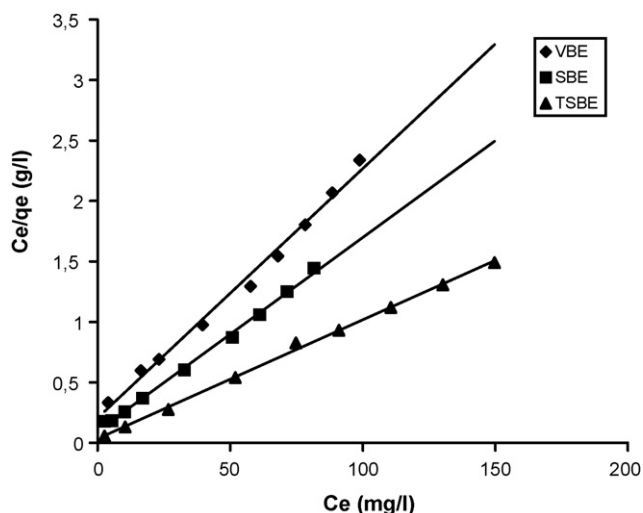


Fig. 8. Langmuir sorption isotherms of lead on VBE (■), SBE (◆) and TSBE (▲) at pH 4.

The essential characteristic of Langmuir can be expressed in terms of dimensionless separation factor  $R_L$  which is defined by:

$$R_L = \frac{1}{1 + K_L C_0} \quad (10)$$

where  $C_0$  is the initial metal concentration (mg/L) and  $K_L$  is the langmuir constant. The  $R_L$  value between zero and one indicate favourable adsorption. Our results reported in Table 4 were found to be values between zero and one for all materials.

Fig. 8 shows Langmuir sorption isotherms for lead (solid/solution ratio = 0.50 g/L) on VBE, SBE and TSBE. The slopes which are representative of the maximum sorption capacity are practically of similar values except for TSBE. This indicates that the maximal sorption capacity of TSBE toward lead is the highest value of these series. The calculated Freundlich and Langmuir parameters are reported in Table 4. The best fits were observed with the Langmuir model. The determination coefficient values for this model were higher than 0.992, while those of Freundlich model were lower.

Table 5 shows the sorption capacity values of various sorbents toward lead. It can be seen that our result (156.25 mg of lead/g of TSBE at pH 5) is better than most of results shown in the references cited on Table 5 [27–34].

### 3.5. pH effect on lead removal

The pH value of the solution is an important controlling parameter in the adsorption process. Fig. 9 shows the Langmuir sorption

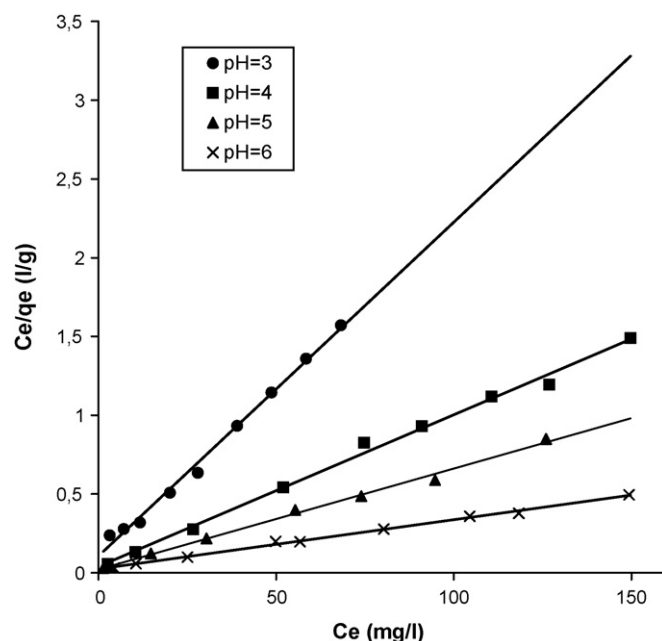


Fig. 9. Langmuir sorption isotherms of lead on TSBE at different pH values.

isotherms of lead on TSBE for pH values ranging from 3 to 6. From this figure, it was clearly observed that the maximum sorption capacity  $Q_{max}$  of TSBE sample increase with increased pH (a lower value of the slope corresponding to a higher value of  $Q_{max}$ ). An exponential relationship was found between  $Q_{max}$  and the pH with a good determination coefficient value (Fig. 10). In general, heavy metal adsorption is small at low pH value because of the  $H_3O^+$  ions competition. Similar observation was made in the literature with other sorbents [27,31,32]. Conclusion

The treatment of a spent bleaching earth by impregnation with a sodium hydroxide solution followed by a mild heat treatment led to an efficient sorbent for removal of lead from aqueous solutions. X-ray diffraction analysis has shown that the clay structure was not apparently affected by the treatment.

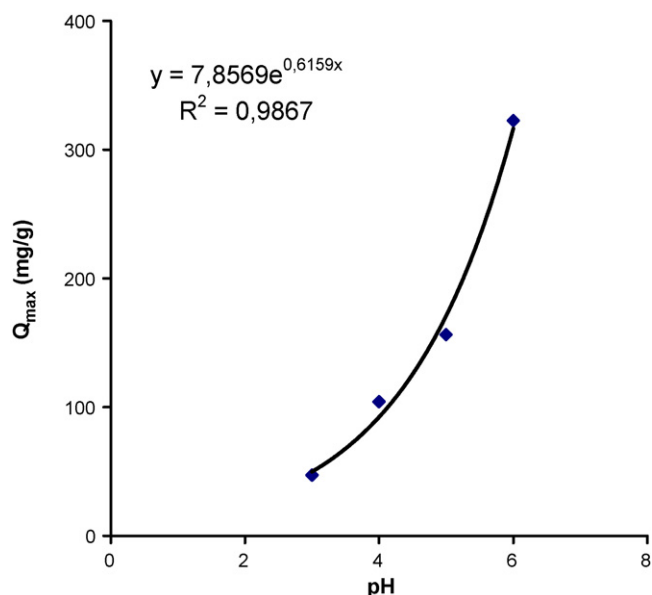


Fig. 10. Plot of calculated maximal sorption capacity ( $Q_{max}$ ) of TSBE vs. pH.

Table 5  
Lead removal capacities of different sorbents

Sorbent	$Q_{max}$ (mg g <sup>-1</sup> )	References
Composite (charcoal + kieselerde)	114.94	[27]
Chitosan	99.3	[28]
Palm kernel fibre	40.2	[29]
Tree tern	40.0	[30]
Chitosan	398	[31]
Na-montmorillonite	9.58	[32]
Sawdust	21.05	[33]
Modified peanut husk	29.14	[33]
Fly ash	17.2	[34]
Treated spent bleaching earth (pH 6)	322.3	This work
Treated spent bleaching earth (pH 5)	156.2	This work
Virgin bleaching earth	48.5	This work
Spent bleaching earth	62.5	This work

The kinetic results fit the pseudo second-order model with determination coefficient values higher than 0.99. The intraparticle diffusion is the rate-limiting step of the sorption process.

The lead sorption isotherms fit the Langmuir model for virgin bleaching earth, spent bleaching earth and TSBE.

The maximum sorption capacity for the materials VBE, SBE and TSBE increased with increasing pH.

The comparison between our results and those of the literature shows that the spent bleaching earth and the treated spent bleaching earth are among the cheaper materials and present very good lead sorption efficiency.

Work is in progress in order to explore other applications for this material and other cheap treatments of the spent bleaching earth to minimize solid wastes.

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