

The use of natural and modified sepiolite for removal of arsenic in drinking water

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Abstract

The natural sepiolite clay mineral was obtained from General Directorate of Mineral Research and Exploration (MTA) of Turkey and modified with 2.5 M of NaOH. The natural and modified sepiolite samples were characterized by XRF, XRD, N₂ sorption, FTIR and SEM- EDS. The maximum As(III) and As(V) removal for natural sepiolite was achieved at an initial pH of 7 and 5.0, respectively; ca. 2.2 mg/g and 10.5 mg/g. The maximum As(III) and As(V) removal for modified sepiolite was achieved at an initial pH of 5.0; ca. 45.4 mg g⁻¹ and 38.4 mg g⁻¹, respectively. While the Langmuir isotherm fitted well with results obtained from the As(V) of SP and As(III) of Na-SP, the Freundlich isotherm model is more appropriate for the results obtained from As(V) of Na-SP.

Key words: Adsorption, arsenic, manganese, sepiolite,

1. Introduction

Sepiolite (Si₁₂)Mg₈O₃₀(OH)₆(OH₂)₄ · 8H₂O (magnesium hydrosilicate) is a natural clay mineral and has various industrial applications such as adsorptive, rheologic, and catalytic applications [1, 2]. Sepiolite has a large capacity for adsorbing heavy metals, organic molecules, dyes and pesticides from wastewater due to its channels running parallel to the fiber axis [3]. The abundance of sepiolite mineral reserves as a raw material source in Turkey and its relatively low cost attract attention for its utilization in water treatment [4].

Studies [5-13] showed that the sepiolite has high adsorption capacity for the removal of heavy metal ions such as Cu²⁺, Zn²⁺, Cd²⁺, Co²⁺, Pb²⁺, Sr²⁺, and Cr⁶⁺ from water. However, there are a few studies for the removal of arsenic and manganese from drinking water by natural sepiolite [10, 14, 15].

The problem of arsenic contamination in natural waters is a global interest concerning the different field researchers. Arsenic is found as form of As (V) and As (III) in groundwater in many regions around the world. Arsenic poisoning in Japan, China, Mexico, Argentina, India, and USA has been reported [16-18]. A maximum contaminant level for arsenic has been recommended to reduce in drinking water as 10 µg L⁻¹ by the World Health Organization (WHO). Therefore, research on improving the current methods or developing low-cost alternatives and new materials to remove arsenic from industrial effluents or drinking water is essential [19].

The aim of this study was to evaluate the capacity of natural and modified sepiolite to remove As(III) and As(V) from aqueous media via adsorption. The influence of the initial pH value, the initial metal concentration and the contact time were investigated. The chemical composition, morphology, phase composition, specific surface area and pore volume, and qualitative composition of the natural and modified sepiolite were determined.

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2. Materials and Method

2.1. Preparation of adsorbent

The natural sepiolite (SP) was obtained from General Directorate of Mineral Research and Exploration (MTA) of Turkey. The sepiolite was first ball milled to particle size in a range of 0.25–0.5 mm and dried in an oven at 120 °C overnight. The sepiolite was transformed to the Na-form by a treatment with a 2.5 M NaOH solution at 80 °C. After washing and drying, the sample was calcined at 500 °C for 2 h and denoted as Na- SP.

2.2. Characterization of samples

The chemical composition of the natural and modified sepiolites was analyzed using Energy – dispersive X- Ray spectroscopy (EDS) (OXFORD INSTRUMENTS INCA X-Act/51-ADD0013) on a scanning electron microscope (SEM) (JEOL/ JSM-6610). The morphology of the natural and modified sepiolites was examined by a Scanning Electron Microscope (SEM) (JEOL/ JSM-6610). X-ray powder diffraction (XRD) patterns of the sepiolites were recorded on a Rigaku SmartLab X-ray diffractometer using non-monochromotographic Cu K α 1-radiation (40 kV, 40 mA, $\lambda = 1.5$). Scanning was in the range 5–65 °C of 2 θ . The specific surface area and micropore volume of the samples were measured using N₂ adsorption–desorption (AUTOSORB 1C) at – 196 °C. The surface area, total pore volume and micropore volume were determined by multipoint BET, t-plot and DR (Dubinin–Radushkevich), respectively. Infrared absorption measurements of the natural and modified sepiolites were carried out using a Fourier Transform Infrared (FTIR) spectrophotometer (Bruker Optics- Alpha). The FTIR spectra were obtained in the wavenumber range 650–4000 cm⁻¹ using single bounce ATR with diamond crystal.

2.3. Adsorption experiments

Batch adsorption experiments were carried out in glass flasks (0.1 L) using a magnetic shaker at 25 °C at a constant agitation of 200 rpm. In the kinetic studies, suspensions containing a range of 25–100 mg·L⁻¹ arsenic were stirred for different periods of time at initial pH of 5. After the reaction, suspensions were centrifuged at 5000 rpm for 5 min in order to separate the solution and the solids. The initial and non-adsorbed concentrations of arsenic in supernatants were determined by Atomic Absorption Spectroscopy (AAS) (GBC A4382). All results were expressed as averaged values of duplicate tests.

The adsorption capacity (q_e , mg·g⁻¹) and removal percentage (%) of arsenic were determined using Eq.2.1 and 2.2.

$$q_e = \frac{(C_o - C_e)V}{m} \quad (1)$$

$$\text{Removal efficiency (R, \%)} = \frac{(C_o - C_e)}{C_o} \times 100 \quad (2)$$

where C_0 and C_e are the initial and final concentrations of arsenic (mg L^{-1}), V is the volume of solution (L) and m is the amount of adsorbent (g). Equilibrium data for natural and modified sepiolites were fitted to the Langmuir and Freundlich models as reported in reference [20].

3. Results and Discussion

3.1. Chemical composition of sepiolites

SEM-EDS analysis in Table 1 indicate that sepiolite is the major components along with traces of Al, K and Fe oxides. The treatment of the SP with NaOH leads to insignificant change of almost all cations except dealumination and desilication in SP. The removal of Mg^{2+} and formation of hydroxysodalite are significant.

Table 1. The composition of natural and modified sepiolites.

Sample	Mg	Al	Si	K	Na	Ca	Ti	Fe	Cl
SP	20.08	9.45	66.97	0.46	-	0.97	0.20	1.68	0.05
Na-SP	14.76	4.24	27.12	0.55	46.86	1.84	-	4.42	-

3.2. XRD results of samples

A comparison of XRD patterns of SP and Na-SP are shown in Fig. 1. The presence of peaks distinctive for sepiolite is obvious. After the treatment with NaOH, peaks at $21, 35^\circ$ of 2θ appeared because of the formation of hydroxysodalite as reported by Kang et al. [21]. Additionally, peaks at $7, 19$ and 23° of 2θ disappeared because of significant dealumination and desilication of the SP.

3.3. Surface area and pore size distribution of samples

The nitrogen adsorption and desorption isotherms of natural and modified sepiolites are shown in Fig. 3, and the surface characteristics calculated from isotherms are listed in Table 2. The shape of SP is consistent with Type I according to the I.U.P.A.C [25], which is characteristic of microporous materials with a plateau at high relative pressures. The BET surface areas of the SP and Na-SP samples demonstrated that treatment with NaOH caused the formation of mesopores in the solid particles, resulting in a lower surface area, revealing $187.8 \text{ m}^2 \text{ g}^{-1}$ for SP and $7.09 \text{ m}^2 \text{ g}^{-1}$ for Na-SP. The pore diameters change in the same direction, varying from 194 \AA to 264 \AA through significant desilication and dealumination.

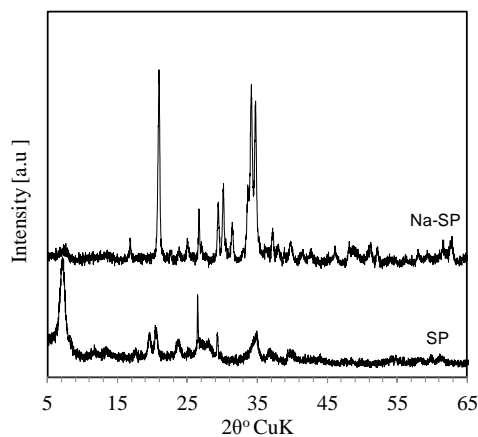


Figure 1. XRD patterns of natural and modified sepiolites

3.4. SEM images of samples

SEM images of SP and Na-SP are shown in Fig. 2. After the NaOH treatment, the particles seemed to be melted and became very irregular, indicated that the severe desilication and dealumination may destroy the structure to some extent as seen in the XRD pattern [22]. NaOH treatment led to not only a decrease in particle size but also crystal deagglomeration as reported in references [23, 24].

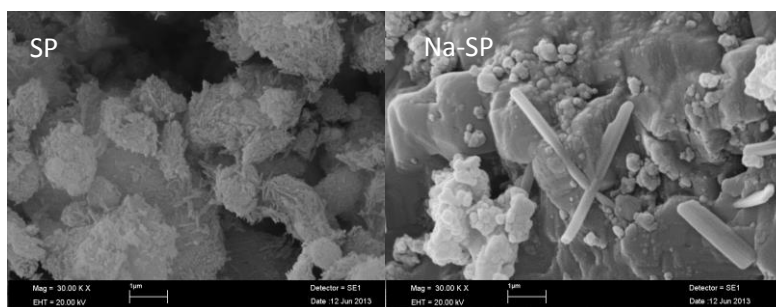


Figure 2. SEM images of natural and modified sepiolites.

Table 2. Surface area and pore characteristics of natural and modified sepiolites

Sample	SA (m ² g ⁻¹) ^a	V _T (cm ³ g ⁻¹) ^b	V _{MP} (cm ³ g ⁻¹) ^c	d (Å) ^d
SP	187.8	0.91	5.66x10 ⁻²	194
Na-NSP	7.09	0.04	5.4x10 ⁻⁴	268

^a Multipoint BET method ; ^b Volume adsorbed at $p/p_0 = 0.99$.; ^c Micropore volume calculated by DR method ; ^d Average pore diameter

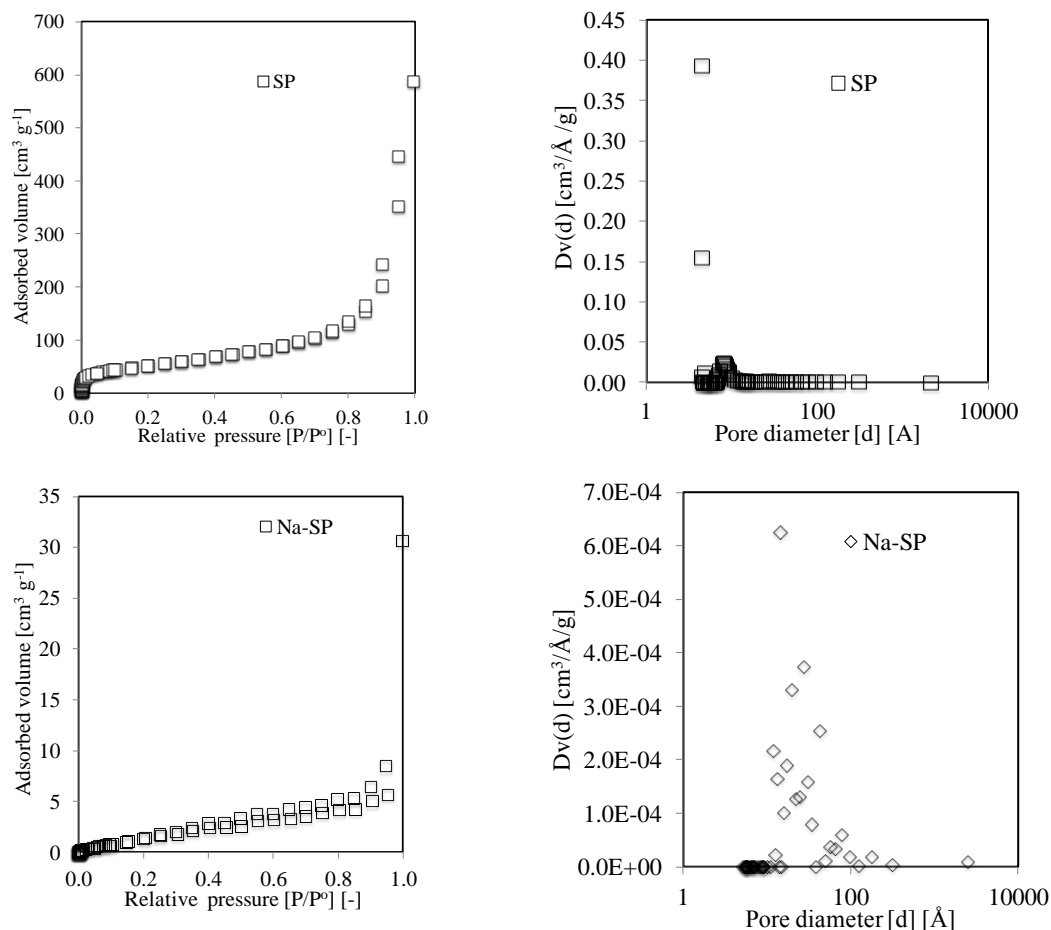


Figure 3. N_2 adsorption–desorption isotherm and differential pore size distribution of natural and modified sepiolites

3.5. FTIR of the samples

The FTIR spectra of the SP and Na-SP samples are shown in Fig. 4. FTIR bands of the SP and Na-SP samples can be observed in three regions [26, 27].

Bands in the $4000\text{--}3000\text{ cm}^{-1}$ range correspond to the vibrations of the Mg–OH group (3690 cm^{-1}), coordinated water (3568 cm^{-1}) and zeolitic water (at 3422 cm^{-1}); the intensity of these bands disappeared after the alkali treatment due to dealumination and removal of Mg cation based on EDS results.

The band at 1671 cm^{-1} is due to the vibration of zeolitic water, disappeared after the NaOH treatment.

Bands in the $1200\text{--}400\text{ cm}^{-1}$ are related with silicate. The band centered at 1016 and 460 cm^{-1} corresponds to Si–O–Si vibration that NaOH treatment not only shifts, which it lower

wavenumbers from 1016 cm^{-1} to 876 cm^{-1} , but also decreases its intensity. Bands at 1215 , and 980 cm^{-1} correspond to Si–O bonds that they disappeared after NaOH treatment. Bands at 690 and 637 cm^{-1} correspond to Mg–OH bond vibrations. After alkali treatment, the band intensity at 637 cm^{-1} decreased and the band 690 cm^{-1} disappeared because of removal of manganese as seen in EDS results.

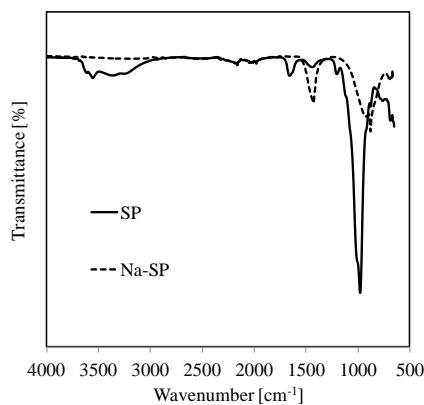


Figure 4. FTIR spectra of the natural and modified sepiolites

3.6. Adsorption of arsenic by natural and modified sepiolites

3.6.1. Effect of initial pH

The initial pH value of the solution is an important controlling parameter in the arsenic adsorption process because it affects the chemistry of arsenic [30, 31] and surface properties of the adsorbent.

The dependence of the sorption capacity on the pH value is shown in Table 3. In the case of As (III) and As (V), maximal adsorption capacity of the SP is obtained at 1.5 of pH. With increasing initial pH value, the adsorption capacity of SP decreased because of an increase in negative charge of the adsorbent surface. On the other hand, maximal adsorption capacity of the SP for As (III) and As (V) were obtained at 5 of pH. This difference can be explained by the changed surface charge of natural sepiolite by NaOH treatment.

3.6.2. Sorption isotherms studies and modeling

Adsorption capacity of SP and Na-SP with adsorption time is shown in Fig. 6. The equilibrium time of As(V) on SP and Na-SP were determined as 100 min and 300 min respectively and the equilibrium time of As(III) on Na-SP was determined as 300 min. Slow adsorption rate of arsenic on Na-SP can be modification of the structure and surface with NaOH treatment.

The isotherm constants calculated from experimental data in Fig. 6 are shown in Table 3. For adsorption of As (V) on SP and As(III) on the Na-SP the correlation coefficients (R^2) obtained from the Langmuir isotherm model were higher than those obtained from the Freundlich model and therefore, the Langmuir equation represents the adsorption processes better. Adsorption of As (V) on Na-SP showed opposite behavior. The maximum adsorption capacity of As(V) on the SP and Na- SP is 10.52 and 38.46, respectively that treatment of SP with NaOH increased almost four times its adsorption capacity for As(V). Because As(III) adsorption capacity of SP is low, the equilibrium time investigation for As(III) on SP was not studied. In contrast to SP, maximum adsorption capacity of Na-SP for As (III) is found as 45.4 mg g⁻¹.

Table 3. The influence of pH on the adsorption capacity (mg g⁻¹) of natural and modified sepiolites for As(III) and As(V).

Sample	SP		Na-SP	
	As(III)	As(V)	As(III)	As(V)
pH				
1.5	8.92	26.84	5.68	5.07
3	n.d	1.77	2.99	0.78
5	n.d	13.48	46.70	35.96
7	2.15	2.62	n.d	0.11
9	2.05	1.45	-	-

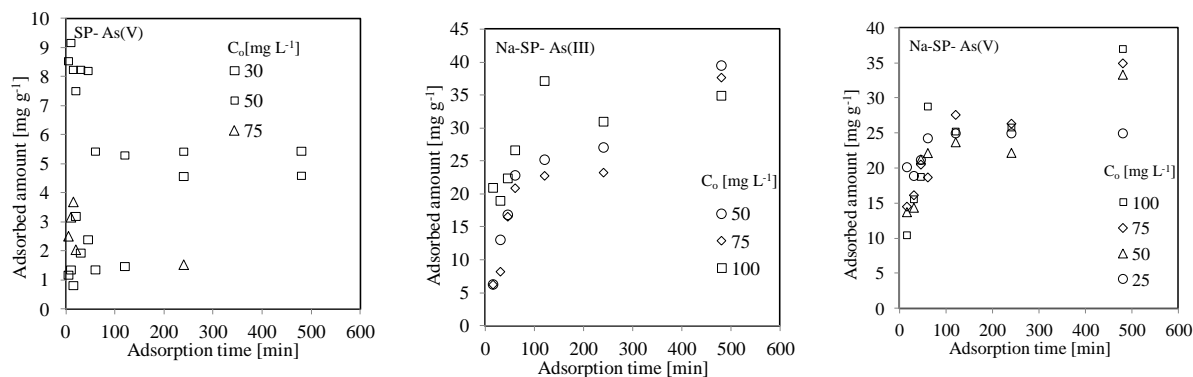


Figure 6. The plot of arsenic ions removal rates against adsorption time (200 rpm, 0.02 g, 25 °C).

Table 4. Adsorption isotherm constants of As (III) and As (V).

Sample	Langmuir isotherm			Freundlich isotherm		
	$Q_{\max}(\text{mg g}^{-1})$	$B (\text{L mg}^{-1})$	R^2	$k_F (\text{L g}^{-1})$	$1/n$	R^2
	As(V)					
SP	10.52	0.0034	0.95	0.036	1.06	0.93
Na-SP	38.46	0.44	0.87	26.84	0.07	0.94
	As(III)					
Na-SP	45.4	0.13	0.89	18.17	0.18	0.63

Conclusions

NaOH treatment increases arsenic adsorption capacity for both arsenic species (III and V). While the Langmuir isotherm fitted well with results obtained from the As(V) of SP and As(III) of Na-SP, the Freundlich isotherm model is more appropriate for the results obtained from As(V) of Na-SP.

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