Extractive Treatment of Arsenic Contaminated Clay Soils (Vermiculite)

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Abstract
In this research, the capability of vermiculite in arsenic extraction, associated with characterizing its main properties was evaluated. To address this purpose, vermiculite was artificially contaminated with arsenic at 7 and 28-day intervals. Then, arsenic was extracted from contaminated soils by different extractants. Various physical and mechanical tests were performed to investigate the effect of arsenic as an anionic contaminant on the properties of the vermiculite, as well as to evaluate how the properties of the contaminated soil were altered by the extraction process. The carbonate bonding phase was probably mainly responsible for the adsorption and fixation of arsenic with more than 50% portion among measured fractions at different curing times. Based on the vermiculite condition, hydrochloric acid was the best extractant for removing arsenic in all studied samples (around 3 -18 % more than other extractants). The clay soil demonstrated few changes due to arsenic contamination and modification. In general, the most promising characteristics of vermiculite as clay liner are its stability after contamination due to high CEC and SSA; however, its workability and strength (UCS between 110 to 220 kPa at different soil conditions) is a challenge and must be improved by adding coarser fractions like silt particles. In general, the results of this study regarding the effects of arsenic contamination and extraction onto vermiculite's physical properties can provide appropriate information for researchers and geo-environmental engineers.

Keywords: Soil contamination, Soil properties, Extraction, Heavy metals, Vermiculite

INTRODUCTION

Arsenic is the 20th most abundant element in the earth's crust, a quasi-metallic element that belongs to the group of 15 periodic tables of elements and is in two oxidation states. (Abejón et al., 2015; Bagherifam et al., 2014). Contamination of water and soil with arsenic (As) is a global issue affecting human and living species health (Stachnik et al., 2020) and is a concerning issue in over 70 countries, including Vietnam, Mongolia, Greece, Hungary, the United States of America, Thailand, Ghana, Chile, Argentina, Mexico, etc. (Selim & Sparks, 2001). Over 140 million people worldwide are also affected by arsenic toxicity due to carcinogenic effects and keratosis associated with the consumption of As-contaminated food and water (Ravenscroft et al., 2011; UNICEF, 2018). However, arsenic contamination is mostly associated with India, Pakistan, Bangladesh, and Iran. Given that arsenic geology has been studied in different parts of the world; the reported contamination in Iran has mainly tectonic origin and is mostly related to adjacent areas of hot springs and young volcanic rocks (Ajili et al., 2016; National Research Council, 1999). Arsenic concentrations in topsoil are both geogenic and anthropogenic (Loukola-Ruskeeniemi et al., 2022). As the soil becomes contaminated, its geotechnical properties, including compressibility,

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subsidence, compressive strength, and so on, are affected. If this contamination occurs in the soil with different structures, it can cause irreversible effects, so it is necessary to clean the soils contaminated with heavy metals (Nazari, 2016). Soil leaching has several advantages, such as relatively low costs and far lower environmental impacts than drilling and landfilling methods (Lee et al., 2011). But it is also a complex method (Wei et al., 2016). Also, element extraction by soil leaching is an emerging method for clearing heavy metal-contaminated soils that need to be evaluated for its efficiency in simultaneous removal of different metals, soil quality after modification, and reusability of the recycled washing agents (Wang et al., 2016). In general, the leaching process consists of a set of physical and chemical techniques (Chen et al., 2016). Contaminants are mainly adsorbed in fine-grained soils and are cleaned by the addition of chemicals (Li & Li, 2000). A study on the extraction of heavy metals by Wang et al. (2013) investigated the effect of removal of lead from contaminated soil by leaching solution on soil engineering properties. Then various tests were carried out on the soils. The results showed that increasing EDTA (Ethylenediaminetetraacetic acid) concentration as an extractant decreased pH and, increasing the EDTA concentration from 0 to 15 mol/L increased the plastic limit from 21.8% to 23% and the liquid limit from 41.6% to 43.3% (Wang et al., 2013). Ouhadi et al. (2016) investigated the effect of lead removal on physical behavior from EDTA-extracted bentonite soil. A series of experiments including hydrometer test, Atterberg limits, and compaction on contaminated bentonite were performed before and after contamination. The results of this study demonstrated that soil mechanical behavior changes in the lead-contaminated bentonite after soil modification with EDTA. In this case, soil properties after the removal of pollutants are largely irreversible.

Since soil elemental contamination is measured not only by their total concentration but also by considering their availability and mobility, arsenic extraction, leaching test and speciation analysis were must be evaluated (Migoni et al., 2021). Types of methods used to determine the contents of heavy metals in soil include column leaching, single-stage extraction, sequential extraction method, soil content determination method, complete sample analysis method (Emami Heidari & Adinehvand, 2016). But the use of sequential extraction, as the most efficient method in estimating the mobility of elements in soil and sediment, has become very common in the last two decades. This method provides information on the distribution of elements across different phases of the soil and allows the researcher to predict the severity of the impact of metal pollution on the soil (Moore et al., 2014). Zhao et al. (2022) by studying the geochemical fractions of arsenic in soils with varying particle sized showed the geochemical fractions of As was mainly residual, accounting for 50% in the ≤ 0.05 mm.

As mentioned, arsenic is an important anionic contaminant in soil and water that can have an anthropogenic and geogenic origin. As a result of anthropogenic activities, arsenic has been found in terrestrial environments globally. Heavy metal contaminated soil entails a high cost for remediation procedures. To improve risk assessments and inform remediation efforts, a clear understanding of the factors controlling levels of risk is required. The bioavailability and toxicological properties of soil-borne contaminants are generally influenced by the age of metalloids (Abbasi et al., 2021). It is a noteworthy fact that despite Arsenic's importance as a terrestrial contaminant, relatively little research has been conducted on the effects Arsenic aging has had on phytotoxicity and ecotoxicology as a whole. The vermiculite clay soil, a natural clay mineral with proper potentialities for cost-effective treatments of metal contamination, can extract heavy elements and adsorb various contaminants as a liner. Therefore, due to the importance of arsenic toxicity, the efficiency of the fractional extraction method in assessing the severity of soil contamination, and the importance of its analysis in the contamination of subsurface layers and, above all, the choice of a method to extract with the least effect on the important physical properties of the soil, this study was conducted with the following objectives:

-Analysis of arsenic extraction and evaluation of the effect of extractant type on important

physical and mechanical properties of vermiculite clay soil

   - Analysis of clay vermiculite application as clay liner in landfills containing arsenic leachate

MATERIALS AND METHODS

In this study, Vermiculite clay soil passing the mesh # 10 sampled from Jiroft (Kerman province-Iran) was used; because vermiculite can be used for the preparation of engineering materials, extraction of heavy metals from wastewater, and adsorption of various contaminants in this field (Rashad, 2016).

To identify the clay properties and impact of the extraction, experiments such as particle size distribution, Atterberg limits, specific gravity, modified soil compaction, unconfined compressive strength, falling head permeability coefficient were performed by ASTM standard. Also, standard methods were used for the determination of CCE and gypsum (Nelson & Sommers, 1983), pH (0.01 M $CaCl_2$ suspension), cation exchange capacity (CEC) (Chapman, 1965) of vermiculite clay soil. The water-vapor-based SSA (Specific Surface Area) for vermiculite clay soil was obtained by the Brunauer-Emmett-Teller (BET) approach (Brunauer et al., 1938).

Scanning electron microscopy (SEM) analysis equipped with EDX analyzer TESCAN model MIRA III was used to evaluate the dimensions and morphology of the clays as adsorbents. X-ray diffraction (XRD) was used to study the mineral composition of the samples, micrographs were prepared by X-ray diffraction (Philips XRD-D6792, glass Cu Anode tube with a maximum power of 3 kW). Elemental analysis of clay soil used in this study was performed by X-ray fluorescence (XRF) spectroscopy PHILIPS Model PW1410.

Vermiculite clay soil is a natural hydrated silicate mineral with a majority of magnesium, iron, calcium, and aluminum elements (Table 1). Also, impurities of clay soil were gypsum and lime as 25% and 5%, respectively. Vermiculite clay soil has a very high cation exchange capacity and a very high specific surface area of about 58 meq/100 g and 118.1 m^2/g, respectively.

Two combinations of sodium meta-arsenite As(III) and sodium hydrogen arsenate heptahydrate (As(V)) were used to prepare arsenic-contaminated clay soils (Georgiadis et al., 2006). To contaminate the soil, arsenic at a concentration of 1000 ppm was added to the soil clay with optimum moisture content (ω_{opt}) and was treated with three replications at 7 and 28 curing days. The sample with 28 days of treatment was used to extract arsenic due to the effect of time on the distribution of different forms of arsenic.

To investigate the total extraction of arsenic from soil medium, six chemical materials including 10% hydrochloric acid, 10% sulfuric acid, 10% nitric acid, 10% acetic acid (Alam & Tokunaga, 2006), 1 mM potassium phosphate (Georgiadis et al., 2006), and 1 mM potassium dichromate were used. Then, to determine the chemical with the highest amount of pollutant removal from the clay soil, the arsenic content was measured using an atomic absorption spectroscopy (AAS) (Perkin Elmer-800 graphite furnace).

Fractional extraction was performed on one gram of contaminated soil sample and the contribution of arsenic in four phases including soluble and exchangeable phases, carbonate bonding, iron, and manganese bonding, organic matter bonding was determined (Table 2). By sequential addition of acids or chemical solvents at different phases, initially, the more unstable

Table 1. Chemical analysis of vermiculite clay according to X-ray fluorescence

Chemical Compounds	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	MgO	K_2O	TiO_2	MnO	LOI
%	49.0	3.50	5.78	4.76	0.82	28.1	0.21	0.03	0.13	7.3

Table 2. Laboratory conditions and required reactant for sequential extraction of arsenic per gram of clay soil sample (Tessier et al., 1979)

Fraction	Experimental condition	Reactant
Exchangeable and water soluble	1 h at 25˚C	8 ml $CaCl_2$ (1 M – pH=7)
Bond to carbonates	5 h at 25˚C	8 ml CH_3COONa (1 M – pH=5)
Bond to Fe/Mn Oxides	6 h at 96˚C	20 ml $H_3NO.HCl$ (0.04 M) in 25% CH_3COOH (1 M – pH=2)
Bond to Organic Matter (OM)	2 h at 85˚C	3 ml HNO_3+5ml H_2O_2 (30%)

Table 3. Extracted arsenic concentration (mg/kg) by the selective method of arsenic-contaminated soil sample with different time treatments

Treatment	Exchangeable fraction	Organic Fraction	Fe/Mn oxide Fraction	Carbonate Fraction
		mg/Kg		
V_1	21.3	ND	27.6	70.5
V_2	ND	ND	34.3	35.2

V_1: contaminated vermiculite soil-treatment 7 days incubation, V_2: contaminated vermiculite soil-treatment 28 days incubation, ND: not detected

phases reacted with weak bonds such as soluble and exchangeable components and at last organic components (Tessier et al., 1979). Finally, the arsenic content of each component was determined by AAS.

RESULTS AND DISCUSSION

The distribution of elements in the four fractions of the selective extraction technique has been shown in Table 3. The abundance order of arsenic chemical forms in soil V_1 can be expressed as carbonate bonding phase > iron phase and manganese phase > exchangeable phase > organic phase and in V_2 soil as carbonate bonding phase > iron phase and manganese phase > exchangeable phase = organic phase. The most important controlling factor for arsenic fixation in soil with 7-day and 28-day pollution treatment is the carbonate bonding phase. This may be due to the presence of lime in vermiculite clay soil. The carbonate component of V_2 is higher than V_1 because when organic matter and iron and manganese oxides are less abundant in the system, carbonates can be an important adsorbent for a large number of elements. The reason for the low exchangeable phase is the weak electrostatic bonding. The exchange form contains elements that are weakly adsorbed on the solid surfaces by weak electrostatic bonding and can be released by ion exchange processes. This form comprises a portion of the low elements that can be released in the soil more than the others and usually comprises a small fraction of the total amount of the element in the soil (Azari, 2015). As can be seen, the exchangeable phase of V_2 is less than the exchange phase of V_1, due to the passage of time. The passage of time causes the ions to enter the non-exchangeable phases from the exchange phase that, in this study, arsenic has entered the iron and manganese bonding phase over time. Also, due to the absence of organic matter in the clay, the soil organic matter bonding component is zero. As a result, the majority of Arsenic in silt and clay fractions was associated with amorphous and well-crystalline Fe and Al oxides, whereas the highest portion of As in bulk soil and clay fractions were tightly bound to residual phases, showing that sediment and clay fractions were more vulnerable to As pollution than

sand fractions (Gerdelidani et al., 2021). Migoni et al. (2021) assessed the sequential extraction of arsenic in an agricultural soil, the speciation chemical analysis showed that As(V) was by far the most abundant species, whereas As(III), which represents the most soluble and available species, was only a very small fraction. No arsenic organic species were detected in the soil samples. The As sequential extraction protocol showed that the most abundant As amount was contained in the final residue of the sequential extraction procedure. Therefore, less soluble and available species of As in studied soils shown that As(V) was more than As(III).

Figures 1 and 2 show that the hydrochloric acid extractant had the highest removal efficiency for all soils. Hydrochloric acid has a removal efficiency of 27.3% and 36.4% of arsenic from soil samples V_1 and V_2, respectively. Therefore, the results showed that the V_2 soil sample had the lowest arsenic adsorption. The cause can be stated based on the vermiculite clay structure that the vermiculite clay is a 2: 1 silicate sheet. The structure of this mineral consists of an octahedral sheet (alumina octahedral), which is located between two tetrahedral sheets (silica tetrahedral) (Hundakova et al., 2013). Vermiculite clay soil can adsorb heavy metals through two different mechanisms (Malandrino et al., 2006):
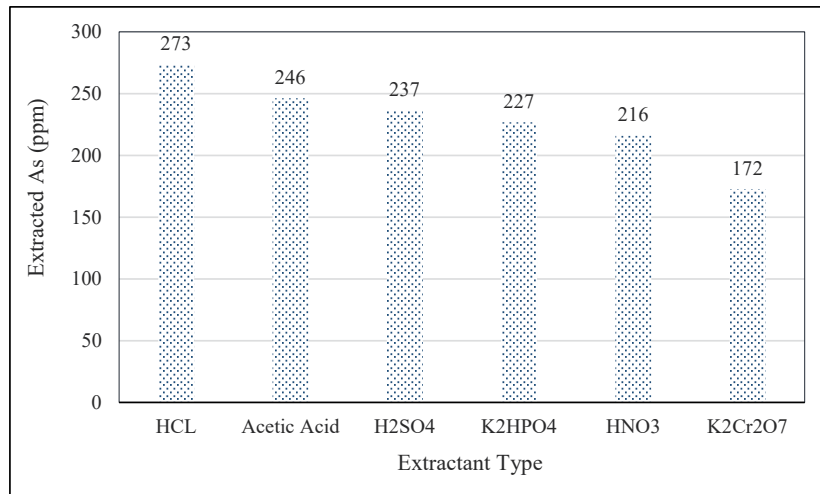

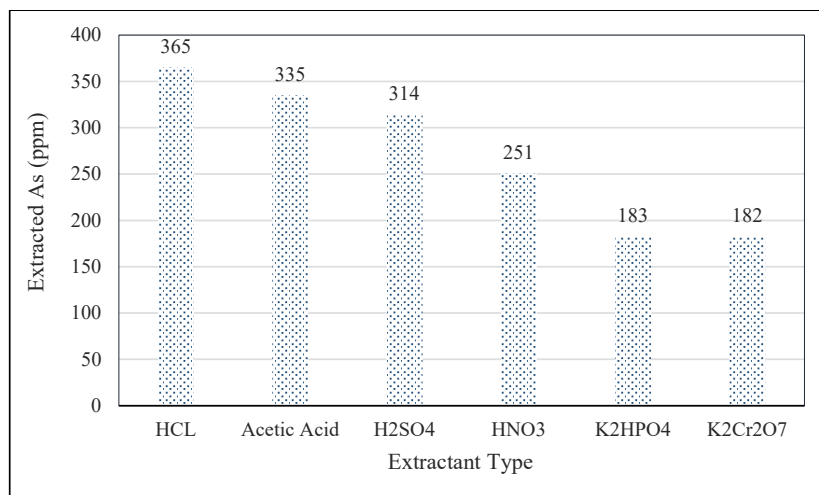**Figure 1.** Effect of extractant type on the extraction of total arsenic from the soil by a 7-day treatment

Figure 2. Effect of extractant type on the extraction of total arsenic from vermiculite clay soil by a 28-day treatment

Table 4. Vermiculite clay soil properties in different contamination and extraction treatments

Soil sample	Gs	pH	PI	Clay	Silt	Sand	Soil classification		γ_{dmax} (KN/m³)	ω_{opt} (%)	K (cm/s)	UCS (KPa)
							USCS	AASHTO				
V_0	2.48	8.53	12.3	4	82	14	ML	A-7-5	16.7	18.8	$5.6*10^{-8}$	110
V_1	2.58	6.90	12.1	4	84	12	MH	A-7-5	15.9	19.4	$3.1*10^{-6}$	220
V_2	2.24	6.28	10.7	3	84	13	MH	A-7-5	16.1	17.6	$2.7*10^{-7}$	140
EV_2	2.26	4.14	4.7	12	65	23	MH	A-5	15.8	18.5	$9.1*10^{-7}$	120

V_0: vermiculite soil, V_1: contaminated vermiculite soil-treatment 7 days incubation, V_2: contaminated vermiculite soil-treatment 28 days incubation, EV_2: As extracted vermiculite soil

1- At planar sites, cation exchange occurs as a result of metal ions interacting with permanent negative charges (outer domain complexes).

2- Formation of inner-sphere complexes through silanol and aluminol groups at the edges of clay particles.

On the other hand, because of the anion nature of arsenic, the latter mechanism could be more dominant in the long-term absorption and exchange of arsenic anion. Initially due to the high concentration of arsenic, its ability to exit OH⁻ from the silanol and aluminol groups has been high. But over time due to the alkalinity of the soil, OH⁻ overcomes arsenic at the sites of silanol and aluminol. Therefore, the arsenic content in the soil solution is increased and extraction is easier. Dos Anjos et al. (2014) extracted adsorbed elements such as (As, Ba, Cd, Cu, Cr, Co, Mn, Ni, Pb, Sr, V, and Zn) using vermiculite and montmorillonite clays by acids. The results showed that the extraction of most elements adsorbed to vermiculite and montmorillonite by hydrochloric acid and nitric acid was satisfactory. It is notable, however, that an inorganic acid such as HCl can effectively remove heavy metals from contaminated soils, but usually require a certain concentration to achieve greater removal efficiency. However, soil acidity destroys the physical, chemical, and biological structures of the soil and results in the loss of large amounts of soil elements for agriculture (Yang et al., 2009). Tokunaga and Hakuta (2002) investigated capability of different extractants to leach arsenic from artificially contaminated Kuroboku soil. Results showed phosphoric acid (9.4% concentration) in 6 h can extract 99.9% of arsenic. This efficiency of phosphoric acid is probably due to ligand exchange between phosphate ions and arsenic. In another study, three extractants (1 M HCl, 0.5 M H_3PO_4, and 2% Na dithionite in 0.01 M HCl) were compared for As extraction. As extraction efficiency for 0.5 M H_3PO_4 was the greatest. After that 2% Na dithionite in 0.01 M HCl and 1 M HCl (Im et al., 2015).

The results of the main properties of vermiculite clay under different treatments of contamination and extraction with hydrochloric acid have been presented in Table 4. As a fact, the pH results indicate that the soil has become more acidic due to contamination and extraction treatments. It can be stated that when hydrochloric acid is added to heavy metal contaminated soil, it caused the H⁺ ion concentration in the soil to increase and the pH to decrease. After extraction of arsenic from the soil, the fine fraction decreased and coarse fraction increased rather than the arsenic contamination with 28-day treatment sample, which increased soil permeability coefficient. But after the extraction of arsenic from contaminated vermiculite clay, the plastic index (PI) decreased. The specific gravity of soil and optimum moisture content did not change significantly after extraction of contaminants. In general, characteristics of the extracted clay soil were more similar to non-contaminated clay soils than those contaminated with arsenic anion.

The X-ray diffraction graph of samples V_2, EV_2, V_0 has been shown in Figure 3. The contamination increased the main clay peak at an angle of about 5.8 and the height of the

structural unit, which could be due to the increased gap between layers. On the other hand, increasing the thickness of the double layer has played a major role in increasing the XRD peak. But the intensity of this peak decreased as a result of the extraction. The reason can be stated that the hydrochloric acid caused irregularity in the vermiculite sheet structure and the gap between the layers. The inclusion of cationic contaminants (lead and cadmium) in the vermiculite sheet structure causes irregularity in the vermiculite layers (Rabiei, 2019).

According to SEM studies, vermiculite clay platelet is seen in Figure 4a; but after the contamination (Figure 4b), it caused the decreased platelets' size and increased diffusion while extracting the arsenic with hydrochloric acid (Figure 4c), the acid partly dissolves the compounds in the soil, making clay uniform and separating the platelets from each other. Also, the results of SEM-EDX images showed the presence of oxygen, silicon, and aluminum as clay vermiculite constituents and, the high levels of arsenic in EDX in Figure 4b indicate that arsenic-contaminated the soil and, the decrease in arsenic peak in EDX in Figure 4c shows the extraction of contamination by acid.

Since clays have high hydraulic properties, they are frequently used to contain wastes in landfills (Oluwapelumi, 2015). These materials are typically used to line the sides, base, and capping of landfills. Natural or artificial materials or a combination of them can be used for linings and capping. (Guney et al., 2008). Until about 1982, the predominant liner material used in landfills was clay. A typical liner material needs to be hydraulically permeable (permeability less than or equal to 1×10^{-7} cm/s) and strong enough to withstand 200 kN/m² of pressure (Guney et al., 2014). Vermiculite soils have a coefficient of permeability that is less than 1×10^{-7} cm/s, which is recommended as the requirement for proper hydraulic conductivity for clays used as landfill liners. Vermiculite soils have a UCS that is below 200 kN/m², which means that a layer of lining used with this clay cannot withstand the loads imposed by wastes disposed of in landfills. However, V_1 soils have the higher UCS and Ks; it means at the short time, the cloding helped workability with higher UCS and higher permeability. It was recommended by
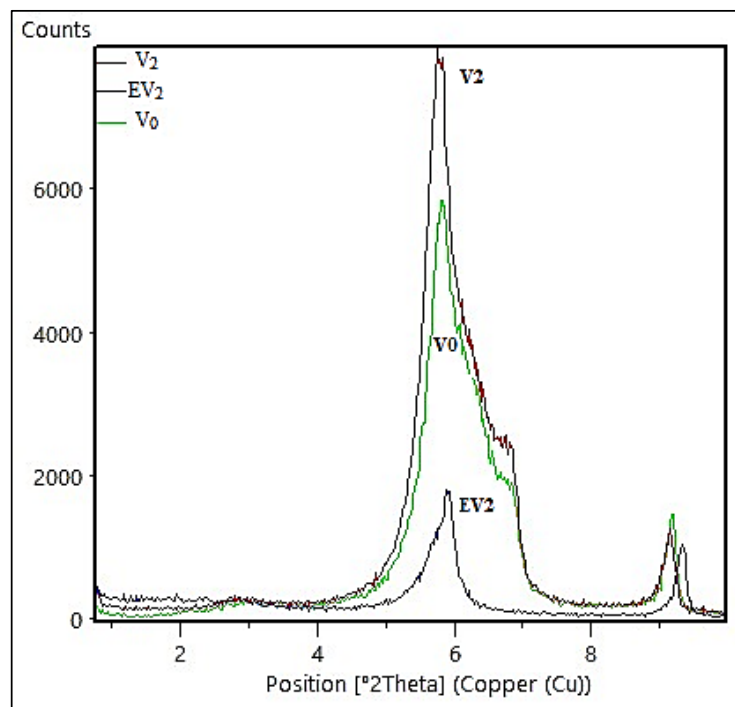

Figure 3. Clay X-ray diffraction graph in different treatments

the National Rivers Authority (NRA) that soil to be used as a clay liner have liquid limits and plasticity indices below 90% and 65%, respectively, and have clay content above 10% (National Rivers Authority, 1995). A soil plasticity index (PI) of greater than 10 percent is generally recommended. On the other hand, soils with extremely high PI levels (more than 30%) tend to be cohesive and sticky, which makes them difficult to work with. The problem with high PI soils is that they tend to form hard clumps (clods) during placement, so they are difficult to compact. The creation of preferred flow paths around clods allows leachate to migrate as quickly as possible (EPA, 1993).
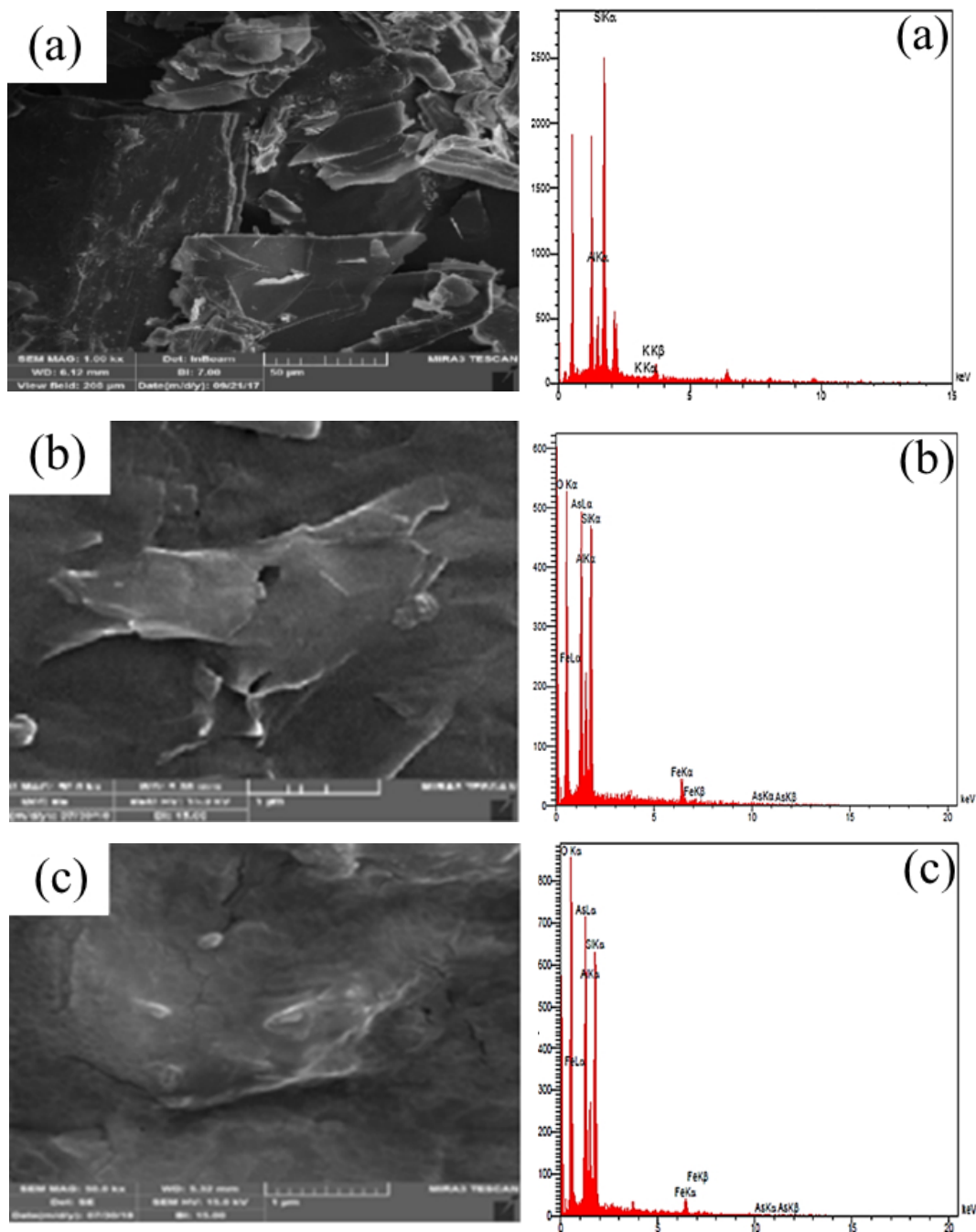

Figure 4. SEM-EDX images of various study clay soil samples: (a): V_0, (b): V_2, (c): EV_2

CONCLUSION

1. The selective extraction results showed that in the short and long term, the most important controlling factor is the stabilization of arsenic carbonate bonding phase and then the iron and manganese hydroxide phase and the passage of time cause the element to enter the non-exchangeable phases.

2. It was concluded that the passage of time on the geotechnical properties of anion-contaminated soils is an important and influential factor regarding changes in As fractions amount, UCS, K, particle size, and pH values which are substantial characteristics for soil application.

3. The contamination affected the geotechnical properties of vermiculite. To improve the geotechnical properties of this contaminated soil, vermiculite was extracted with hydrochloric acid and initial soil mechanics experiments were performed on the composites. In these experiments, after the extraction, a decrease of Atterberg limits, a decrease in pH, an increase in sand percentage and a decrease in fine percentage and no specific gravity change were observed. In other words, arsenic extraction improved some of the geotechnical properties.

4. The extent of adsorption appeared to have varied with the variation of time in the soils. For example, exchangeable portion was not detectable at 28-day soil treatment, while the amount of As in 7-day soil treatment was measured 21.3 mg/kg. Therefore, the arsenic content in the soil solution has decreased. Therefore, vermiculite clay with better absorption of arsenic has better performance as clay adsorbent in the short term.

5. Although the evaluation of arsenic adsorption capacity of vermiculite soils accompanied with the modification of soil properties by various extractants at different concentrations of contamination are valuable characteristics for soil contamination studies, soils workability and strength are challenges which must be improved by adding coarser fractions. However, this change should be to the extent that the minimum values of Atterberg limits meet the standard thresholds based on the properties of landfill liner design or other uses.

6. As a suggestion for future studies, in order to examine the influence of anions on clay soils, more anions (two or more) need to be assessed with different clay soil types. Furthermore, the addition concentrations chosen in this study are high. To evaluate how much stabilization disturbance occurs at different limits, the same anions need to be investigated at different concentrations similar to the natural soil concentrations.

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CONFLICT OF INTEREST

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

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