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Determination of heavy metal concentrations in natural clay mineral samples from quarries in Turkey

Türkiye'deki ocaklardan alınan doğal kil mineral örneklerinde ağır metal konsantrasyonlarının belirlenmesi

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Determination of Heavy Metal Concentrations In Natural Clay Mineral Samples From Quarries In Turkey

Highlights

- *Environmental pollution of heavy metals is increasingly becoming a problem*
- *Turkey has the largest mineral resources in the world and is an important industrial mineral*
- *Sepiolite is widely used in industrial applications*
- *Analysis results revealed that the average concentration of as, Sr, Sn, and Cd in sepiolite samples was higher than the Earth's crust averages*
- *The values of cancer risk estimated to evaluate potentially health risks caused by PTEs in sepiolite.*

Graphical Abstract

In this study was analyzed the concentrations of PTEs (Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Rb, Sr, Zr, Cd, Sn, Ba and Pb) in sepiolite samples located in the Central Anatolian region of Turkey. A total of thirty sepiolite samples collected randomly from sepiolite open quarries (SQs) located in Polatlı-Ankara (SQ1), Beylikova-Eskişehir (SQ2), and Sivrihisar-Eskişehir (SQ3) in Central Anatolia of Turkey as shown in Figure.

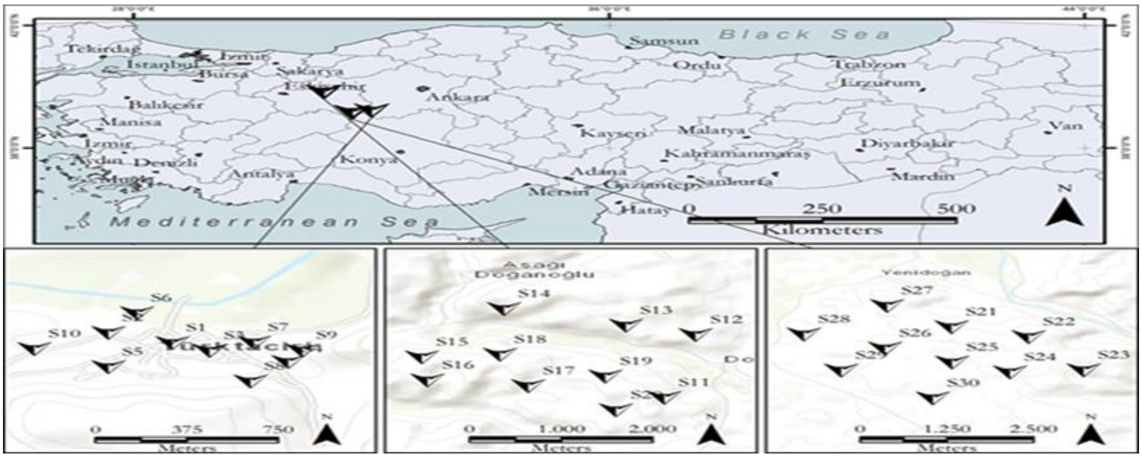

Figure. Locations of sampling points and sepiolite quarries

Aim

In this study of aim, the concentrations of some HMs in sepiolite samples collected from three quarries were examined. Located in the Central Anatolia Region of Turkey) were determined using energy-dispersive X-ray fluorescence spectroscopy and also the enrichment factor (EF) for HMs calculated.

Design & Methodology

This reseach particularly to aim the levels of 14 HMs in 30 sepiolite samples collected from 3 quarries located center area of Turkey by using (EDXRF) spectroscopy. The HM concentration distributions of sepiolite quarries and Earth's crust averages of HMs

Originality

In this study, for the first time,) the concentrations of PTEs in sepiolite samples from three selected commercial quarries located in the Central Anatolian region of Turkey were analyzed,

Findings

The contamination of sepiolite samples with PTEs was evaluated based on enrichment factors. However, large inconsistencies in the enrichment factor results associated with the selections of reference elements in the calculation of enrichment factors were observed

Sonuç (Conclusion)

In conclusion, this study highlighted the status of potentially toxic elements, enrichment factors, and risk characterization in sepiolite minerals. The data are information that can create awareness for both those who use sepiolite-added products and those who work in the quarries

Declaration of Ethical Standards

The author(s) of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

Determination of Heavy Metal Concentrations In Natural Clay Mineral Samples From Quarries In Turkey

Araştırma Makalesi / Research Article

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ABSTRACT

Environmental pollution of heavy metals is increasingly becoming a problem and has become of great concern due to the adverse effects it is causing around the world. Today, various chemical, biological, and physical pollutants arising as a result of rapidpopulation growth, industrialization, and excessive mining activities have become a major problem that adversely affects people, animals, plants, organisms, and ecosystems all over the world. Sepiolite is a clay mineral containing hydrated magnesium silicate and widely used in construction, agriculture, food, fertilizer, pharmaceutical, detergent, cosmetics, paint, paper, etc. The average concentrations of Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Rb, Sr, Zr, Cd, Sn, Ba and Pb analyzed in sepiolite samples collected from three quarries (Polatlı, Beylikova, and Sivrihisar) located in the Central Anatolian Region of Turkey using EDXRF spectroscopy were found as 5456.5, 361.0, 42.0, 15.5, 65.2, 3831.5, 8.6, 23.7, 7.8, 11.8, 5.3, 13.7, 1183.2, 25.3, 3.7, 7.2, 131.9 and 5.3 mg/kg, respectively. The average enrichment factor values of V, Cr, Co, Ni, Cu, Zn, As, Sr, Cd, Sn, Ba, and Pb indicated minimal to extremely high enrichment in sepiolite. The values of non-carcinogenic risk index and cancer risk estimated to evaluate potentially health risks caused by PTEs in sepiolite samples were within the acceptable limit and the safe range except for the Beylikova quarry.

Keywords: Sepiolite, heavy metals, enrichment factor, EDXRF, Türkiye.

Türkiye'deki Ocaklardan Alınan Doğal Kil Mineral Örneklerinde Ağır Metal Konsantrasyonlarının Belirlenmesi

ÖZ

Ciddi çevre sorunları haline gelen ağır metaller (HM'ler), genellikle maden kaynaklarının geliştirilmesi de dahil olmak üzere insan faaliyetlerinden kaynaklanmaktadır. Sepiyolit, hidratlanmış magnezyum silikat içeren bir kil mineralidir ve inşaat, tarım, gıda, gübre, ilaç, deterjan, kozmetik, boya, kağıt vb. alanlarda yaygın olarak kullanılmaktadır. Bu çalışmada, üç ocaktan toplanan sepiolit numunelerindeki bazı HM'lerin konsantrasyonları incelenmiştir. Türkiye'nin İç Anadolu Bölgesi'nde bulunan (Polatlı, Beylikova ve Sivrihisar) enerji dağılımlı X-ışını floresans spektroskopisi kullanılarak belirlenmiş ve ayrıca HM'ler için zenginleştirme faktörü (EF) hesaplanmıştır. Sepiyolit numunelerinde analiz edilen Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Zr, Cd, Sn ve Pb ortalama konsantrasyonları 361, 42, 16, 65, 3832, 9, Sırasıyla 24, 8, 12, 5, 25, 4, 7 ve 5 mg/kg. V, Co, Ni, Pb, As, Cd ve Sn'nin ortalama EF değerleri, sepiolit numunelerinde önemli ila aşırı yüksek zenginleşmeyi göstermektedir.

Anahtar Kelimeler: Sepiyolit, ağır metaller, zenginleştirme faktörü, EDXRF, Türkiye

1. INTRODUCTION

Today, various chemical, biological, and physical pollutants arising excessive mining activities have become major problem that adversely affects people, animals, plants, organisms, and ecosystems all over the world [1-3].Contamination of agricultural soils, water resources, and food crops with heavy metals (HMs) or potentially toxic elements as chemical pollutants remains a major environmental issue the global in the environment [4-8]. The main sources of HMs are human activities such as chemical and metallurgical industries, mining, agriculture, combustion from vehicle emissions, power plants, coal burning, etc [9]. The availability of HM and its toxicity effects on human health and other organisms depend on its chemical properties Exposure to HMs can cause serious health diseases such as cardiovascular problems, insomnia, insanity, cancer, Alzheimer, anemia, abdominal discomfort, depression, headache, constipation, cramping in the abdomen, exhaustion, irritability, etc. [8,10-12].Mining activities containing exploration, construction, operation (grinding the rock and ores, etc.) maintenance, expansion, abandonment may have negative impacts on the environment such as erosion, deforestation, contamination, and alteration of soil profiles , and an

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increase in dust and emissions [13]. Turkey has the largest mineral resources in the world and is an important industrial mineral (boron, sepiolite, feldspar, barite, marble, pumice, bentonite, gypsum, etc.) [14]. The proven sepiolite reserves of the world are approximately million tons [15].

Sepiolite ($Mg_8Si_{12}O_{30}(OH)_4(OH_2)_4{\cdot}8H_2O$) [16]. Sepiolite is widely used in industrial applications such as agricultural carries, adhesives, industrial floor absorbents, drilling fluids, animal feed bonds, paint and coatings, paper, pharmaceuticals, polishes, suspension fertilizers, and raw materials in the ceramics [17]. Thus, there is a need for a study containing data on the determination of the concentration levels of HMs in sepiolite. However, many previous studies have investigated the mineralogical and radiometric characterization of sepiolite minerals and the removal of radioactive elements or HMs from various environmental samples using sepiolites. [18-28]. This reseach particularly to aim the levels of 14 HMs in 30 sepiolite samples collected from 3 quarries located center area of Turkey by using (EDXRF) spectroscopy.

2. MATERIAL AND METHOD

2.1. Sample Gathering

A total of thirty sepiolite samples collected randomly from sepiolite open quarries (SQs) located in Polatlı-Ankara (SQ1), Beylikova-Eskişehir (SQ2), and Sivrihisar-Eskişehir (SQ3) in Central Anatolia of Turkey as shown in Figure- 1 [2,24-32]. Detailed information analysis given by [29,32].

2.2. Enrichment factor(EF)

EF is the HM pollution level estimating the difference concentrations by given ***[29-30,33].***

$$EF = \frac{(C_{HM})_{sample} / (C_R)_{sample}}{(C_{HM})_{crust} / (C_R)_{crust}}$$

where CHM and CR are sepiloit and in Earts of the concentration

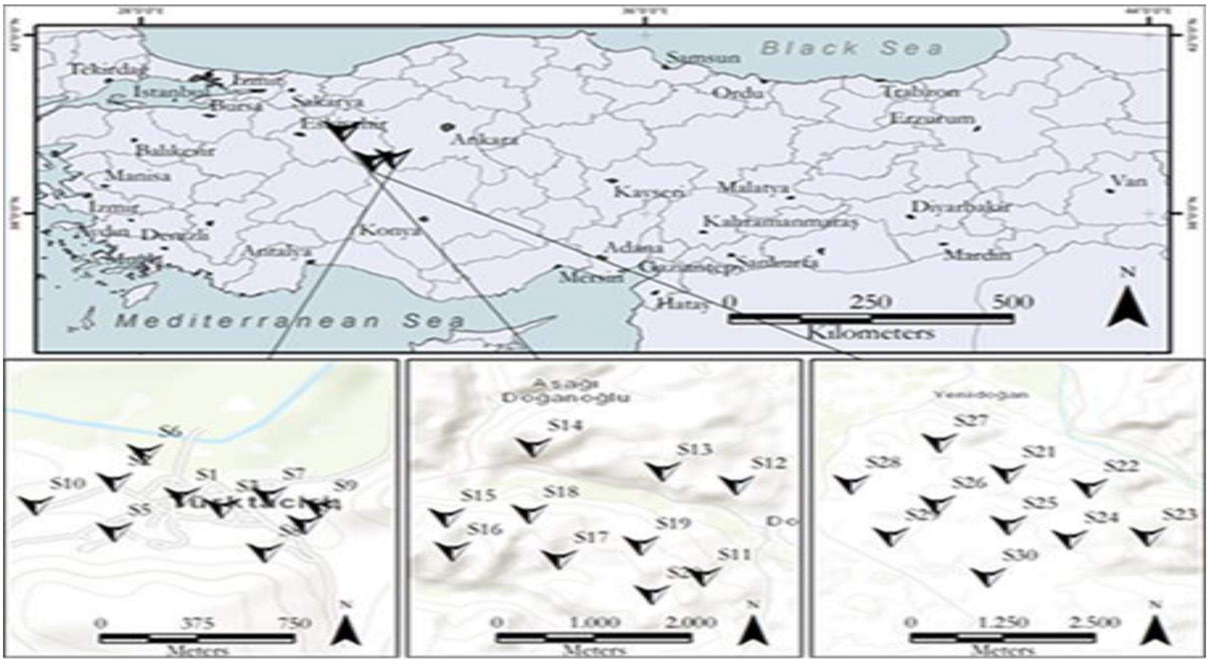

Figure 1. Locations of samling points and sepiolite quarries

Table 1. Some descriptive statistical data on theconcentration of HMs in sepiolite samples

Heavy metal	Concentration (mg/kg)								N
	Average	Median	SD	SE	Kurtosis	Skewness	Min	Max	
Ti	361.0	161.2	315.3	57.6	-1.0	0.9	109.6	942.7	30
V	42.0	21.6	31.2	5.7	-1.4	0.4	3.5	104.4	30
Cr	15.5	5.3	16.6	3.0	-0.2	1.1	1.8	54.8	30
Mn	65.2	43.7	40.4	7.4	-0.6	1.0	19.6	158.2	30
Fe	3831.5	1655.5	3451.8	630.2	-1.1	0.9	942.7	9853.0	30
Co	8.6	6.2	6.9	1.3	-1.0	0.7	2.1	22.6	30
Ni	23.7	10.5	21.0	3.8	-1.1	0.9	7.4	61.0	30
Cu	7.8	4.9	5.5	1.0	-1.0	0.8	2.6	18.2	30
Zn	11.8	7.8	6.7	1.2	-1.3	0.7	5.2	24.9	30
As	5.3	4.0	4.4	0.8	-1.0	0.7	0.8	13.4	30
Zr	25.3	26.9	3.0	1.0	-1.7	-0.4	21.3	29.2	10
Cd	3.7	3.4	1.0	0.3	-0.7	0.3	2.1	5.4	10
Sn	7.2	7.6	2.2	0.6	0.8	0.0	3.4	11.7	13
Pb	5.3	5.5	1.4	0.3	1.9	-1.3	1.4	7.2	26

Table 2. The average and range of concentrations of HMs in sepiolite quarries

Heavy metal	Concentration (mg/kg)						Earth's crust
	SQ1		SQ2		SQ3		
	Average	Range	Average	Range	Average	Range	
Ti	136.5	109.6-153.3	786.2	524.2-942.7	160.2	124-226.8	4500
V	26.6	3.5-75.9	68.1	47.5-85.4	31.2	11.5-104.4	90
Cr	4.4	2.6-6.1	37.2	25.3-54.8	4.9	1.8-10.5	83
Mn	37.7	19.6-45.7	117.6	70.2-158.2	40.2	26.2-47.0	1000
Fe	1432.9	942.7-1962.0	8457.5	4824-9853	1604.2	1245-2305	46500
Co	4.0	2.1-10.0	17.2	11.1-22.6	4.5	2.4-10.8	18
Ni	9.0	7.4-10.9	52.0	34.8-61.0	10.1	8.4-12.6	58
Cu	4.2	2.6-6.2	15.2	10.9-18.2	4.1	2.7-5.9	47
Zn	8.0	5.2-21.5	18.9	12.7-24.9	8.4	6.1-21.8	83
As	2.6	1.4-4.7	11.1	7.8-13.4	2.4	0.8-5.3	1.7
Zr	< 1.0		25.3	21.3-29.2	< 1.0		170
Cd	< 2.0		3.7	2.1-5.4	< 2.0		0.13
Sn	< 3.0		7.2	3.4-11.7	7.3	5.6-9.1	2.5
Pb	4.6	1.9-6.1	6.1	5.1-7.2	5.1	1.4-7.1	16

Table 3. The values of EF calculated for HMs in sepiolite samples

Heavy metal	The value of the enrichment factor			Enrichment level
	Average	Min	Max	
Ti	1.3	0.9	1.7	Deficiency to minimal
V	10.5	2.6	55.3	Moderate to extremely high enrichment
Cr	2.6	0.7	4.5	Minimal to moderate enrichment
Mn	1.3	0.5	2.4	Deficiency to moderate enrichment
Fe	1.3	0.7	1.9	Deficiency to minimal
Co	8.9	4.2	28.6	Moderate to very high enrichment
Ni	6.6	4.2	10.1	Minimal to significant enrichment
Cu	3.2	1.3	7.1	Minimal to significant enrichment
Zn	3.2	1.0	12.6	Minimal to significant enrichment
As	56.8	16.3	144.2	Significant to extreme enrichment
Zr	1.0	0.7	1.4	Deficiency to minimal
Cd	187.3	112.7	265.6	Extreme enrichment
Sn	40.4	10.1	137.2	Significant to extreme enrichment
Pb	8.4	1.7	18.4	Minimal to significant enrichment

3. RESULTS AND DISCUSSION

HMs analyzed in all sepiolite samples is given in Table 1. The HM concentration distributions of sepiolite quarries and Earth's crust averages of HMs are presented in Table 2. The levels of HMs in all sepiolite samples can be ranked as follow: Fe > Ti > Mn > V > Zr > Ni > Cr > Zn > Co > Cu > Sn > As > Pb > Cd. The concentration of Hg, which is a very toxic element, was found below the detection limit of 1.0 mg/kg.

According to the average values of HMs, except for As and Cu, the sepiolite quarries are ranked in descending order as follows: SQ2 > SQ3 > SQ1.HM enrichment of sepiolites evaluated based on EFs. For the calculation of EFs of HMs, Al was taken as a reference element, and background values of HMs given by Yaroshevsky [35] were considered as the Earth's crust average [33,34]. All sepiolite samples and enrichment levels of HMs are given in Table 3. The average Co concentration is lower than the earth's crust average of 18 mg/kg [35].

4. CONCLUSION

In this study, for the first time, (1) the concentrations of PTEs (Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Rb, Sr, Zr, Cd, Sn, Ba and Pb) in sepiolite samples from three selected commercial quarries located in the Central Anatolian region of Turkey were analyzed, (2) potential non-carcinogenic and carcinogenic health risk caused by PTEs contained in the investigated sepiolite samples was evaluated and (3) enrichment factor was calculated for the enrichment status of PTEs in sepiolite samples by using six different reference elements. Analysis results revealed that the average concentration of As, Sr, Sn, and Cd in sepiolite samples was higher than the Earth's crust averages. The contamination of sepiolite samples with PTEs was evaluated based on enrichment factors. However, large inconsistencies in the enrichment factor results associated with the selections of reference elements in the calculation of enrichment factors were observed. In this study, it was shown that the choice of six commonly-used reference elements (Al, Mn, Fe, Ca, Sr, and Ti) used in the calculation of the enrichment factor can lead to large differences between the enrichment factor values of the element of interest, although the results were assumed to be similar regardless of which reference elements being used. This situation may lead to serious misinterpretation of the result of evaluating the sepiolite quality in terms of PTEs. Potential health risk evaluation results indicated that some PTEs in sepiolite samples from the SQ2 quarry may pose carcinogenic and non-carcinogenic risks to adults and quarry workers. Therefore, at least, it should be necessary to take necessary precautions such as not breathing dust to eliminate situations that may threaten the health of the quarry workers. In conclusion, this study highlighted the status of potentially toxic elements, enrichment factors, and risk characterization in sepiolite minerals. The data are information that can create awareness for both those who use sepiolite-added products and those who work in the quarries.

ACKNOWLEDGMENTS

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DECLARATION OF ETHICAL STANDARDS

The author(s) of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

AUTHORS'CONTRIBUTIONS

Aybaba HANÇERLIOĞULLARI:Performed the experiments and wrote the manuscript.

Şeref TURHAN: Performed the experiments and wrote the manuscript.

Arif BAŞTUĞ: Analysed the results and calculated.

Yosef G.A MADEE:Collected of all sample and mesurement in laboratory

CONFLICT OF INTEREST

There is no conflict of interest in this study

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