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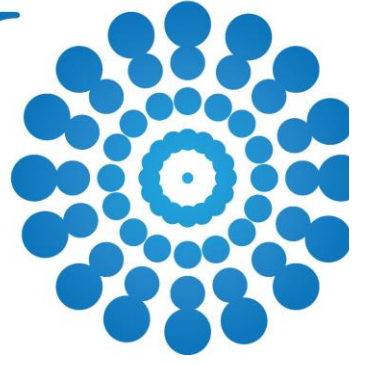
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Grinding of Calcite to Nano-Size: Effect of Mill Capacity and Grinding Media Shape

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The fabrication of nano-sized materials with conventional ball mill is a very difficult process. But it is not impossible. When the capacity of the mill is reduced, the nano-sized product can be reached. In this study, nano-sized calcite was produced by conventional ball mill. Firstly, the mill capacity (feed amount) was reduced, then, the effect of the grinding media type was investigated. Spherical ball and cylindrical shaped “Cylpebs” are used as grinding media. Comparative tests have been performed using Cylpebs and spherical balls in a 20 tph capacity industrial ball mill under the same conditions. The results showed that Cylpebs was more efficient than conventional spherical balls. In addition, the capacity of the conventional ball mill for the fabrication of nano-sized products should be significantly reduced. When the mill capacity is reduced by 75% (5 tph) and grinded with Cylpebs, the fineness (d_{90}) of the product reaches 1300 nanometers.

Key words: Ball Mill, Ball, Calcite, Cylpebs, Nano Grinding

1. Introduction

In many different industries today, such as, plastics, ceramics, cement, metallurgy, paint, food, cosmetics and energy, there is a growing need for materials identified as nano-sized. Nanomaterials fabrication methods can be classified according to whether their assembly followed either the so called “*bottom-up*” approach or the “*top-down*” approach. The bottom-up approach is one where smaller components of atomic or molecular dimensions self-assemble together, according to a natural physical principle or an externally applied driving force, to give rise to larger and more organized systems. The top-down approach is where a process starts from a large piece and subsequently uses finer and finer tools for creating correspondingly smaller structures [1]. Namely, nano-sized grains are produced by physical processes such as grinding. In the top-down approach there are two options such as wet and dry grinding. In this study, dry grinding was preferred to eliminate the cost of drying. The general flow diagram of the nano-calcite fabrication using an industrial scale ball mill is given in Figure 1.

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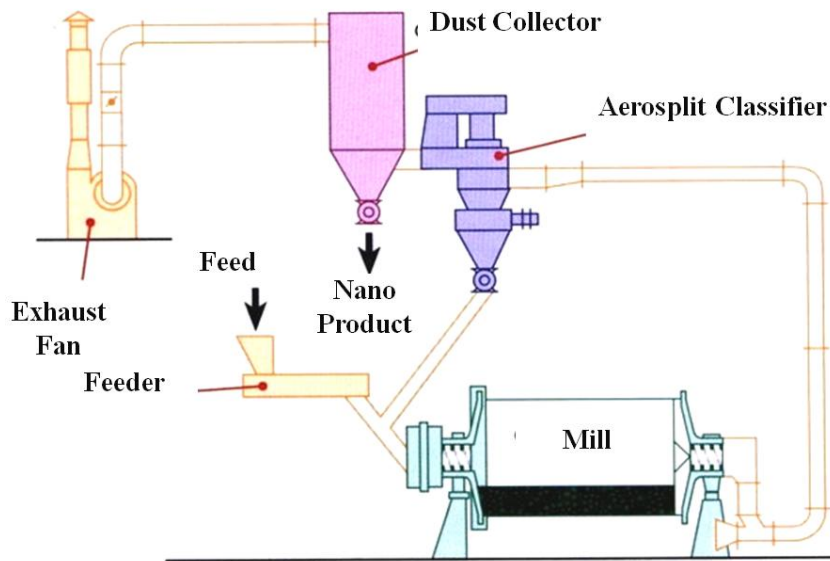


Figure 1. Nano calcite fabrication flow diagram [“top-down” approach]

The primary function of grinding media is to crush and grind ore particles inside rotating mills, such as ball, rod, and semi-autogenous mills, and sometimes in stirred mills such as Vertimill, SVM mills, Sala Agitated Mill, HIGMill, Tower Mill, and ISAMill [2]. In recent years, grinding charges with unconventional shapes have appeared on the market. One example is the cylindrically shaped media called Cylpebs. Cylpebs have greater surface area and higher bulk density than balls of similar mass and size, due to their shape. Cylpebs of the same diameter and length have 50% greater surface area, and 45% greater weight, than balls of the same material. In addition, they have 9% higher bulk density than steel balls, and 12% higher than cast balls. The objective of this paper is to compare Cylpebs and ball grinding media in terms of grinding efficiency for fabrication of nano sized calcite [3-4]. Calcite (CaCO_3) was chosen as test material for this study. It is a salt, widely used in the ground nano-form, in paints, food or pharmaceuticals industries and as filler in the paper making process (Garsia et al., 2002).

2. Materials and Methods

Experimental studies were carried out in an industrial-scale ball mill shown in Figure 2. The diameter of the mill is 3 m in length and 7 m in length. The total internal volume of the mill is 49 m^3 . The mill capacity for the production of $d_{90} \sim 60\text{-}100$ microns calcite is 20 tph. The Cylpebs and spherical balls shown in Figure 3 were separately charged and their grinding performances tested. The charging rates of Cylpebs and spherical balls are given in Table 1. The material (calcite) which is grinded to the nano size is taken with the Alpine type air separator. The calcite mineral was broken to -8 mm by impact crusher before feeding to the mill. The grain size (d_{90}) of the calcite feed to the mill is ~ 4 mm.



Figure 2. Image of calcite grinding mill (Classic ball mill)

Cylpebs
(cylindrical media)



Conventional Balls
(spherical media)



Figure 3. Image of different types of grinding media

Table 1. Grinding media features and charging rates

Grinding Media Types	Sizes and Weights of Grinding Media				Total Media Weight	Media Charge Rate
	15-20mm	20-30mm	30-40mm	40-55mm		
Conventional Balls	14520 kg	14700 kg	14700 kg	14700 kg	70630	37%
Cylpebs	14x17x16mm 28000 kg	21x25x26mm 2100 kg	29x35x34mm 2100 kg	-	7000	31%

3. Results and Discussions

Table 2 shows the d_{90} dimensions of the products obtained depending on the capacity of the mills. Accordingly, when the capacity of the mill was reduced from 20 tph to 5 tph, the fineness of the product was reduced from 60 microns to 3.9 microns (Figure 4). Reducing the capacity means increasing the contact time of the material (calcite) with the grinding media. The same applies if Cylpebs are used. When the capacity was reduced from 20 tph to 5 tph, the fineness of the product obtained decreased from 30 microns to 1.3 microns. Cylpebs grinder media has more efficient grinding than conventional balls. For example, if the mill is operated with a capacity of 10 tons per hour, the products obtained are 10 microns with cylpebs balls and 20 microns with conventional balls.

Table 2. d_{90} sizes vs mill capacity of products using with Balls and Cylpebs

Conventional Spherical Balls		Cylpebs	
Mill Capacity	d_{90} sizes of product	Mill Capacity	d_{90} sizes of product
20 tph	60 μm	20 tph	30 μm
10 tph	20 μm	10 tph	10 μm
5 tph	3.8 μm	5 tph	1.3 μm

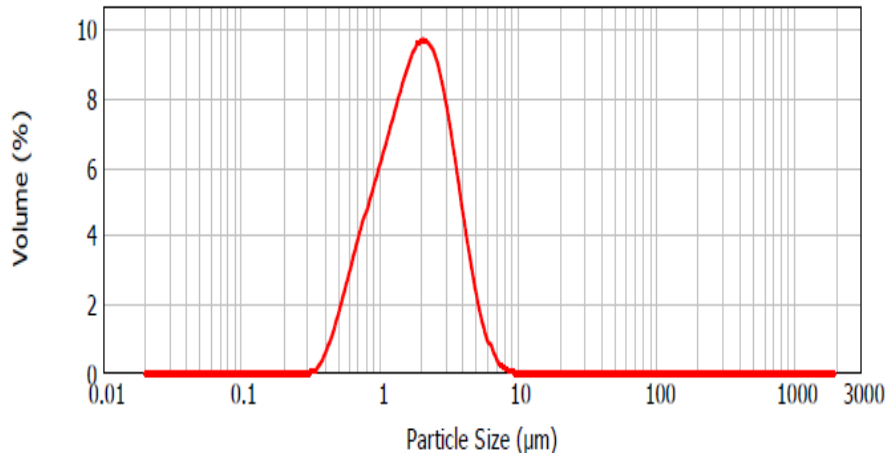


Figure 4. Particle size distribution in grinding with Spherical Balls (5 tph capacity)

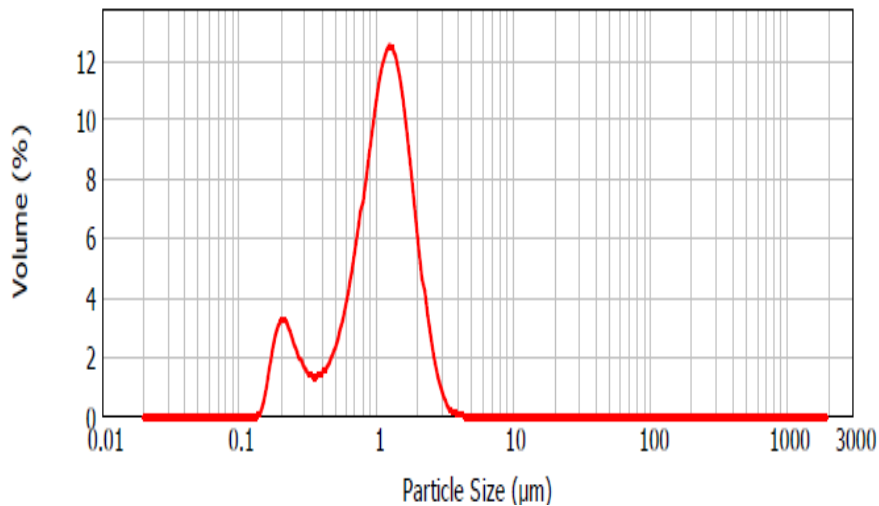


Figure 5. Particle size distribution in grinding with Cylpebs (5 tph capacity)

4. Conclusions

In this study, industrial scale grinding tests were carried out for the fabrication of nano calcite. The normal capacity of the mill used in the tests is 20 tph. However, it was not possible to produce nano-sized calcite with this capacity. Therefore, the capacity of the mill has been reduced. In other words, the amount of calcite feed is reduced. This increases the contact time between the calcite and the balls. When the residence time of Calcite in the mill was increased by 4 times, the fineness (d_{90}) of the products obtained fell below 4 microns. When the mill capacity was 20, 10 and 5 tph, respectively, the fineness of the products were 60, 20, and 3.8 microns, respectively. These results

were obtained in case of grinding with conventional balls. In case of using Cylpebs instead of conventional balls, the product fineness was 30, 10 and 1.3 microns, respectively. According to these results; the fineness of the products is inversely proportional to the mill capacity. As the mill capacity is reduced, finer products are obtained. This is due to increased grinding time and material-to-ball contact.

As a result, mill capacity is an important operating parameter in the fabrication of nano-sized calcite. It is not possible to fabricate nano-sized material with a conventional ball mill operated with normal capacity (20 tph). If the capacity is reduced by 75%, it is possible to produce nano-sized material. Furthermore, cylpebs should be used instead of conventional balls in this grinding process. Cylpebs gives finer products than conventional spherical balls.

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Determination of Some Biological Activities and Elemental Content of Methanol Extracts of *Psylliostachys spicata* (Willd.) Nevskis' Specimens Collected from Two Different Locations

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Abstract - *Psylliostachys spicata* is a species of Plumbaginaceae family which are used for medical aromatic purposes. In this study, *Psylliostachys spicata* that collected from Üzümlük and Gölgekonak (Siirt, Turkey) salts areas were evaluated with regard to element content, total phenolic content (Folin-Ciocalteu) and antioxidant activity (1,1-diphenyl-2-picrylhydrazine-DPPH). While for both regions some heavy metal contents (Pb, Zn, Fe) were below the allowed by the World Health Organization, toxic metals such as Cd and As were not detected. As a result of the analysis of the extracts obtained with methanol, it was determined that the total amount of soluble phenolics and antioxidant activity were among the acceptable values for both localities. According to the results, it is thought that *P. spicata* is a potential source of antioxidant which is not a concern in terms of toxic metal content.

Keywords: Total phenolic content; element analysis; *Psylliostachys spicata*; Siirt

Psylliostachys spicata (Willd.) Nevski'nin İki Farklı Lokasyondan Toplanan Örneklerinin Metanol Ekstraktlarının Bazı Biyolojik Aktiviteleri ve Element İçeriğinin Belirlenmesi

Öz - *Psylliostachys spicata*, bir çok üyesi tıbbi aromatik amaçla kullanılan Plumbaginaceae familyasından bir türdür. Bu çalışmada Üzümlük ve Gölgekonak (Siirt, Türkiye) tuzlası çevresinden toplanan *Psylliostachys spicata* bitkisi, element içerik, toplam fenolik madde miktarı (Folin-Ciocalteu) ve antioksidan aktivite (1,1-difenil-2-pikrilhidrazin-DPPH) açısından değerlendirilmiştir. Element miktarları ICP-OES (İndüktif Eşleşmiş Plazma-Optik Emisyon Spektrometresi) cihazıyla ppm düzeyinde belirlenmiş olup her iki bölge için bazı ağır metal içerikler, (Pb, Zn, Fe) Dünya Sağlık Örgütü'nün izin verdiği max. değer in altında çıkarken; Cd ve As gibi toksik metaller ise tespit edilememiştir. Metanol ile elde edilen ekstraktların analizi sonucunda, toplam çözünebilir fenolik madde miktarı ve antioksidan aktivitesinin kullanım açısından her iki lokalite için kabul edilebilir değerler arasında olduğu belirlenmiştir. Elde edilen sonuçlara göre *P.spicata*'nın toksik metal içerik bakımından endişe vermediği potansiyel bir antioksidan kaynağı olduğu düşünülmektedir.

Anahtar kelimeler: Toplam fenolik içerik; element analizi; *Psylliostachys spicata*; Siirt

1. Giriş

Plumbaginaceae familyası üyeleri özellikle İran-Turan ve Akdeniz Bölgeleri başta olmak üzere dünyanın hemen hemen her yerinde yayılış göstermektedir. Familyanın bir çok üyesi ekstrem (uç) ortamlarda yaşayan (halofit, soğuğa uyumlu, kumlu topraklarda büyüyen) türlerdir.

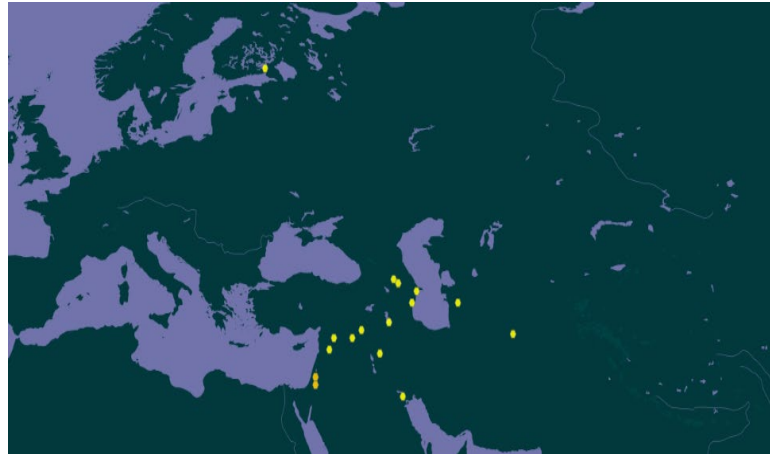
Plumbaginaceae, 28 cins ve yaklaşık 650 türü temsil etmekle beraber [1-3] Türkiye'de 84 taksonu vardır [4].

Psylliostachys spicata, bir çok üyesi tıbbi aromatik amaçla kullanılan Plumbaginaceae familyasından bir türdür. Türkiye'de *Psylliostachys* cinsi ilk kez Siirt ili Akdoğan köyü tuzcul alanından tanımlanmıştır [5].

Bitkisel ilaçlar yüksek oranda biyolojik aktif molekül, mineral ve eser element içermekle beraber birçok hastalığın tedavisinde yaygın olarak kullanılmaktadır [6]. Bitkisel ilaçlar geleneksel tıp sistemlerinin önemli bir basamağını oluşturmakla beraber son yıllarda hem gelişmiş hem de gelişmekte olan ülkelerde birinci basamak sağlık hizmeti olarak kullanımı giderek artmaktadır. Dünya Sağlık Örgütü, dünya nüfusunun yaklaşık %65-80' inin öncelikli olarak alternatif tıbbi tercih ettiğini (çoğunlukla tıbbi bitkilerden elde edilen ilaçlar) rapor etmiştir [7,8].

Bitkisel ürünlerin terapötik yararlarına artan ilgiye paralel olarak doğal bitki ve piyasada mevcut olan formülasyonlarının toksisitesi ve güvenliği ile ilgili endişeler giderek artmaktadır. Doğal bitkilerin tabiatı gereği her zaman güvenli olduğuna dair yaygın bir yanlış kanı olsa da tıbbi bitki ve onların formülasyonlarının yan etkiler ve toksisite vakaları üzerine birçok rapor bulunmaktadır [9].

Bu çalışmada, Siirt ilinin farklı iki bölgesinde toplanan *P. spicata*'nın iki farklı lokaliteden toplanan örneklerinin bazı biyolojik aktiviteleri yanında element içerikleri de araştırılmıştır.



Şekil 1. *P. Spicata* bitkisinin yayılış haritası [10].

2. Malzeme ve Yöntem

Çalışmanın materyalini oluşturan *P.spicata* bitkisi (Şekil 2), Siirt ilinin Üzümlük (37°, 46'69, 90"K, 42°, 5'44, 3"D, yükseklik 730m) ve Gölgekonak (37°, 46'21, 46"K, 42°, 6'53, 96"D, yükseklik 768m) tuzlu alanlarından 2013 yılında toplanmıştır. Toplanan bitki örneklerin sistematik analizi yapıldıktan sonra bir örneği Siirt Üniversitesi Herbaryumunda muhafaza edilmiştir. Bitkilerin kalan diğer kısmı, laboratuvar ortamında hava akımının olduğu gölgelik bir alanda kurutulup, toprak üstü kısımları öğütüldükten sonra cam kavanozlarda çalışmalarda kullanılmak üzere oda sıcaklığında muhafaza edilmiştir.

2.1. Bitki Ekstraktlarının Hazırlanması

Toplam fenolik madde miktarı ve antioksidan aktivite çalışmaları için 4 gr toz haline getirilmiş bitki örneği 40 mL metanol (%80) içerisinde çalkalayıcıda oda sıcaklığında 24 saat süreyle ekstrakte edilmiştir. Süzgeç kâğıdında süzülen ekstraktlar daha sonra vakum altında evapore edilip yoğunlaştırılmıştır. Son konsantrasyon 20 mg mL⁻¹ olacak şekilde stok çözeltiler hazırlanarak analize kadar +4 °C'de saklanmıştır. Tüm analizler 1 mg mL⁻¹ konsantrasyon üzerinden hesaplanmıştır.

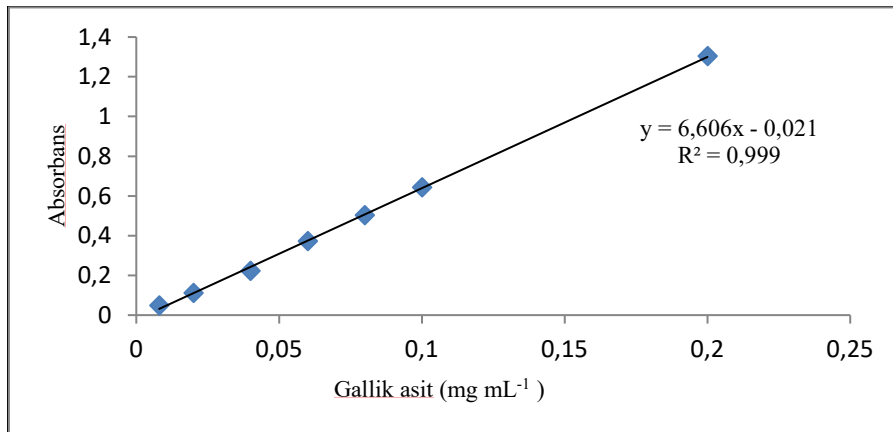


Şekil 2. *P. spicata* bitkisinin doğal alandaki görüntüsü

2.2. Toplam Fenolik Madde İçeriği

Bitki metanol ekstraktlarının toplam fenolik bileşik içeriği, gallik asit eşdeğeri olarak Folin-Ciocalteu yöntemi kullanılarak belirlenmiştir [11]. Bunun için 1 mL ekstrakt üzerine 1 mL FCR reaktifi ilave edilip 3 dk oda sıcaklığında inkübasyona bırakılmıştır. Bu çözeltiye, daha sonra doymuş Na_2CO_3 (%7, 1 mL) eklenerek, karışım oda sıcaklığında karanlıkta 90 dk süreyle çalkalanıp 760 nm de absorpsiyon ölçülmüştür. Aynı işlemler kontrol numunelere ve gallik asit standart ($0.05\text{-}1\text{ mg mL}^{-1}$) çözeltilerine de uygulanıp kalibrasyon eğrisi çizilmiştir (Şekil 3). Elde edilen kalibrasyon denkleminde, bitki ekstraktlarının toplam fenolik madde içeriği mg gallik asit eşdeğeri olarak hesaplanmıştır.

Kontrol numune: 1 mL çözücü + 1 mL FCR + 1 mL 7% Na_2CO_3



Şekil 3. Toplam fenolik madde tayini için gallik asit kalibrasyon eğrisi

2.3. Antioksidan Aktivite Tayini

Antioksidan aktivite, DPPH radikalini süpürme etkisi açısından Blois' in 2002 metoduna göre belirlenmiştir [12]. Bunun için bitki metanol ekstraktı (1 mL) ile DPPH çözeltisi (4 mL, 0.001M) iyice karıştırıldıktan sonra oda sıcaklığında karanlık bir ortamda 30 dk inkübe edilmiştir. İnkübasyondan sonra çözeltilerin 517 nm'de absorpsiyonları ölçülmüştür. Kontrol olarak 1 mL çözücü içeren deney tüpüne 4 mL DPPH eklenerek aynı işlemler gerçekleştirilmiş olup inhibisyon yüzdesi aşağıdaki ifade edilen (1) nolu eşitlik doğrultusunda hesaplanmıştır.

$$\% \text{ inhibisyon} = [(Abs_{kontrol} - Abs_{numune}) / Abs_{kontrol}] \times 100 \quad (1)$$

2.4. Element Analizi

Toplanan bitkilerin element analizi için, bitki örneklerinden 0.6-1.0 g arası tartılarak mikro dalga yardımıyla çözünürleştirme işlemi yapılmıştır. Bunun için tartılan numuneler basınca dayanıklı politetrafloroetilen (PTFE) kaplara aktarılmış ve üzerine HNO₃/H₂O₂ (10.0/2.0) asit karışımı ilave edildikten sonra Tablo 1'de belirtilen koşullarda Speedwave MWS-3 Berghof marka mikrodalga fırınında parçalama işlemi gerçekleştirilmiştir. Gerekli prosedürlerden sonra element analizi Model Optima™ 7000 DV ICP-OES (Perkin Elmer, Inc., Shelton, CT, ABD) cihazıyla yapılmıştır [3,13].

Tablo 1. Mikrodalga cihazının çalışma koşulları

	1	2	3	4
T (°C)	150	190	100	100
Ta (dk) ^a	10	10	10	10
t (dk) ^b	5	10	10	5

^aİstenilen sıcaklıkta bekleme süresi

^bİki ardışık sıcaklık arasındaki süre

ICP-OES cihazının çalışma koşulları ise Tablo 2'de verilmiş olup kalibrasyon grafiklerine ait denklem ve korelasyon katsayıları Tablo 3'te belirtilmiştir.

Tablo 2. ICP-OES cihazının çalışma koşulları

Parametreler	
Güç(W)	1450
Plazma gaz akış oranı (Ar) (L·dk ⁻¹)	15
Yükseltgen gaz akış oranı (L·dk ⁻¹)	0.2
Nebülizör gaz akış oranı (L·dk ⁻¹)	0.8
Numune akış oranı (L·dk ⁻¹)	1.5
Görünür modu	Aksiyal-radyal
Entegrasyon zamanı (s)	1.0
Temizleme gazı	Azot
Kesme gazı	Hava

3. Bulgular

P. spicata bitkisinin biyolojik aktivite analizleri kapsamında antioksidan aktivite DPPH radikaline proton transferiyle azalan absorbansın (517 nm) ölçülmesi esasına göre hesaplandı. Üzümlük ve Gölgekonak tuzlu alanlarından toplanan örneklerin metanol ekstraktlarının DPPH değerleri sırasıyla 79.6% ve 86.6 %; toplam fenolik içerik ise 73.0 ve 49.5 mg_{gallik}/mL_{ekstrakt} olarak hesaplanmıştır (Tablo 4).

Tablo 3. Elementlerin kalibrasyon grafiklerine ait denklem, korelasyon katsayısı (R²) değerleri

Element	Dalgaboyu (nm)	Denklem	R ²
As	193.696	f(x) = 10657x + 346.52	0.9980
Co	228.616	f(x) = 258750x + 2156.4	0.9980
Cr	267.716	f(x) = 426198x + 4130.2	0.9987
Cu	327.393	f(x) = 755145x + 9532.2	0.9984
Fe	228.204	f(x) = 512703x + 3704	0.9987
K	766.490	f(x) = 23939x + 3824.9	0.9972
Li	670.784	f(x) = 3E+07x + 83728	0.9986
Mg	285.213	f(x) = 141701x + 322792	0.9988
Mn	257.610	f(x) = 20414x + 485.24	0.9989
Mo	202.031	f(x) = 69409x + 932.24	0.9983

Na	589.592	$f(x) = 114008x + 176759$	0.9993
Ni	231.604	$f(x) = 185263x + 2170.2$	0.9978
Pb	220.353	$f(x) = 30582x + 1141.2$	0.9972
Sb	206.836	$f(x) = 18506x + 373.74$	0.9988
Ti	334.940	$f(x) = 3E+06x + 365$	0.9984
V	292.464	$f(x) = 291244x + 9635.4$	0.9987
Zn	206.200	$f(x) = 121192x + 2729.4$	0.9992
Be	313.107	$f(x) = 9E+06x + 72084$	0.9984
Cd	228.802	$f(x) = 562992x + 8124$	0.9985
Se	282.8	$f(x) = 11123x + 256.49$	0.9988
Sr	407.771	$f(x) = 6E+07x + 550778$	0.9984

Tablo 4. *P. spicata* bitkisine ait metanol ekstraktlarının biyolojik aktivitesi

Bölge	Toplam Fenolik (mg _{gallik} /mL _{ekstrakt})	% DPPH
Üzümlük	73.0	79.6
Gölgeli konak	49.5	86.6

Üzümlük ve Gölgelikonak tuzlu alanlarından toplanan *P. spicata* bitkisinin element analizi ICP-OES cihazı ile 3 tekrarlı olarak gerçekleştirilmiş olup ortalama değerler Tablo 5'te sunulmuştur.

Tablo 5. Kurutulmuş *P. spicata* bitkisinin ICP-OES ile elde edilen element değerleri

Bölge	Element konsantrasyonu (mg L ⁻¹)					
	As	Be	Cd	Co	Cr	Cu
Üzümlük	*	*	*	0.02	0.18	0.23
	Mg	Mn	Mo	Na	Ni	Pb
	136.80	2.0	*	442.50	0.38	0.07
	Ti	V	Zn	Fe	K	Li
	0.17	0.07	0.7	28.75	255.10	0.15
	Sb	Se	Sr	0.01	*	*
Gölgelikonak	As	Be	Cd	Co	Cr	Cu
	*	*	*	0.05	0.34	0.39
	Mg	Mn	Mo	Na	Ni	Pb
	216.60	3.04	*	513.10	0.69	0.40
	Ti	V	Zn	Fe	K	Li
	0.29	0.13	0.46	69.11	314.80	0.32
Sb	Se	Sr	0.02	*	*	

*Miktarı tespit edilememiştir.

Tablo 5'te belirtildiği üzere Üzümlük ve Gölgelikonak *P. spicata* bitkisinin makro element derişimleri sırasıyla, 442.50 mg L⁻¹Na, 255.10 mg L⁻¹ K, 136.80 mg L⁻¹ Mg, ve 513.10 mg L⁻¹Na, 314.80 mg L⁻¹ K, 216.60 mg L⁻¹ Mg olarak tespit edilmiş ve her iki bölge için bu derişimlerin Na>K>Mg sırasında olduğu belirlenmiştir.

4. Değerlendirme ve Sonuç

Bitkiler, içerdikleri aktif bileşikler (flavonoid, alkaloid,terpenoid, tanen, berberin, kinin) nedeniyle birçok hastalığın tedavisinde kullanılmaktadır [14]. Yapılan kaynak taramasında

Plumbaginaceae familyasına ait bitkilerin fenolik içeriği ve antioksidan aktivitesinin araştırıldığı kısıtlı sayıda çalışmaya rastlanılmıştır.

Bu çalışma kapsamında *P.spicata* bitkisine ait metanol ekstraktlarının antioksidan aktivite ve toplam fenolik içeriği tespit edilmiş, ayrıca bitki toksisitesini etkileyen metal içerik analizleri de yapılmıştır. Fidan'ın 2018 yılında yaptığı çalışmada Siirt Akdoğmuş tuzlu bölgesinden topladığı aynı tür bitkinin etanol ve su ekstraktlarındaki toplam fenolik değerleri sırasıyla 30.65 ve 6.39 mg mL⁻¹ olarak tespit edilmiştir. Çalışmamızda farklı bir çözücü (%80 metanol) kullanılmış ve elde edilen değerler 73.0 (Üzümlük) ve 49.5 (Gölgelikonak) mg mL⁻¹ şeklindedir. Bu değer çalışılan bitki örneğinin önemli bir fenolik bileşik kaynağı olarak değerlendirilebileceğini göstermektedir. Fidan (2018)'in çalışmasında antioksidan aktiviteyi %DPPH bakımından %93.91 (etanol) ve %41.73 (su) olarak tespit ederken çalışmamızda yaklaşık %80 (metanol) olarak tespit edilmiştir. Bu değer, çalışılan bitkinin serbest radikal süpürme aktivitesi açısından önemli olduğunu göstermektedir.

Tıbbi bitki ve formülasyonlarının mineral ve eser element içerikleri yaşamsal organların düzgün işleyişinde önemli rol oynarken tahmini güvenli günlük alım miktarının üzerinde toksik olabilmektedir. Bu sebeple element içeriklerinin tespiti ile ilgili çalışmalar sıklıkla yapılmalıdır. Bu çalışmayla Siirt ilinin iki bölgesinden (Üzümlük ve Gölgelikonak) toplanan Plumbaginaceae familyasının bir türü olan *P.spicata* tuzcul alan bitkisinin toprak üstü kısımlarındaki 21 elementin (Na, K, Mg, Fe, As, Be, Cd, Cr, Cu, Co, Mn, Li, V, Mo, Ni, Sb, Ti, Pb, Sr, Se ve Zn) konsantrasyonu ICP-OES cihazı ile belirlenmiştir (Tablo 5). Element analiz sonuçları farklı coğrafi bölgelerde yetişen aynı şifalı bitki türlerinin farklı seviyelerde metal biriktirdiğini göstermiştir. Bunun yanı sıra bazı element içeriklerinin Türk Gıda Kodeksi ve WHO/FAO'nun meyve/sebze ve bazı gıdalarda izin verilen değerlerin Fe (200 mg kg⁻¹), Zn (5-50 mg kg⁻¹), Cr (2 mg kg⁻¹), Co (0.02-1 mg kg⁻¹), Cu (10 mg kg⁻¹), Pb (10 mg kg⁻¹) [15,16] altında kaldığı belirlenirken kadmiyum ve arsenik tespit edilememiştir.

Bu sonuçlar değerlendirildiğinde çalışılan bitkinin önemli bir antioksidan kaynağı olduğu ve içerdiği ağır metal içerik bakımından toksik etki yaratmayacağı söylenebilir.

Teşekkür


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Measurement of Colloidal Forces between Glass Sphere and Colemanite Surface in NaCl Aqueous Electrolytes

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Abstract - The main objective of the present work was to analyse the interactions of colemanite crystal surface with surrounding fluids and colloidal particles. Specifically, in this research, the interactions between colemanite surface and glass colloidal probe were studied using the atomic force microscopy (AFM). The colloidal forces were measured in $1.0 \times 10^{-3} \text{ molL}^{-1}$ NaCl aqueous solutions at pH values from ~ 7 to 10 to explore a transition from attractive to repulsive forces when the surface charge potential for colemanite changes from positive to negative at isoelectric point (IEP) located near pH ~ 10.2 . As expected, at pH 10 when the colemanite and glass colloidal probe surfaces are similarly charged, a repulsive force was observed. On the other hand, at pH values of 7, 8 and 9 when the surfaces oppositely charged, attractive forces were observed.

Keywords: AFM (Atomic Force Microscopy), colemanite, crystal, colloidal forces

1. Introduction

Atomic force microscopy and its capability of adhesion and colloidal force measurements have become an important characterization device in numerous fields of fields such as surface science, materials engineering, chemistry, biochemistry, and biology. Additionally, the adhesion, colloidal, molecular and atomic forces that can be quantified with the AFM technique provide foundation for theoretical analysis and modeling of these forces [1-3].

Since 1989, several techniques of force value acquisition and analysis have arisen, and an increasing number of systems revealing unexpected forces have been analyzed. AFM force-distance curves are routinely used in several kinds of measurement including the determination of material's elasticity, material or system Hamaker constant, surface charge density, degrees of surface hydrophobicity, and many others [5]. Several previous studies demonstrated the capability of the AFM method to investigate dynamic force microscopy methods [4, 5], to examine the interfacial forces [6], and to quantify colloidal forces [3, 7]. In mineral processing, the colloidal force measurements provide a better understanding of the colloidal and molecular mechanisms of mineral-mineral and mineral-gas bubble interactions, often leading to better design of mineral processing technologies such as flotation process and selection of solution chemistry for treatment of minerals.

2. Background

2.1. Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) is an imaging technique used to determine topography and surface characteristics. It is also be used for force measurements such as electrostatic, adhesion, van der Waals, colloidal, capillary, magnetic and other forces.

AFM consists of a cantilever with a sharp tip or a colloidal probe at its end that is used to not only scan the surface but also measure the forces of interactions with a substrate in various environment. The cantilever with a sharp tip is typically silicon or silicon nitride with a tip radius of curvature on the order of nanometers.

When the tip is brought into proximity of a sample surface, forces between the tip and the sample lead to a deflection of the cantilever according to Hooke's law [4].

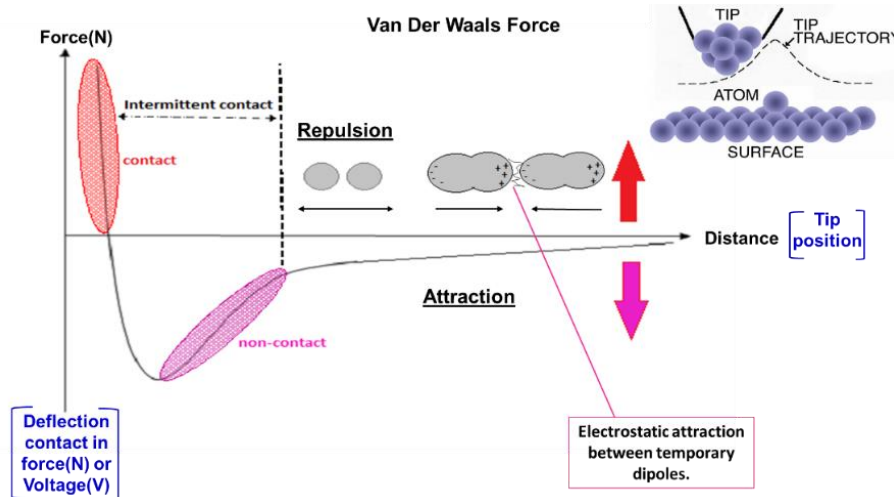


Figure 1. Schematic of a typical force-separation curve and parts of an approach-retraction cycle of the tip.

As shown in Figure 1, the AFM tip away from the sample, the cantilever is not affected by interatomic forces and keeps its equilibrium position. When it brought closer to the sample surface, attractive forces act upon the tip to bend the cantilever towards the sample [8].

But, when the tip is pushed towards the surface repulsive forces dominate, deflecting the cantilever backward. The thick lines indicate the normal ranges of operation for contact and non-contact modes and the long horizontal arrow represents the usual amplitude for intermittent contact [9].

2. Materials and Methods

2.1. Chemicals and devices

The colemanite sample was obtained from Eti Mine Works as lump-sized crystals from Kestelek deposit of Turkey which was cleaved 15×15×5 mm and polished for the AFM measurements. The glass probe (DNP-S10 model) was purchased from Bruker.

The experiments were performed using a Nanoscope E AFM (Digital Instruments Inc.) in a fluid cell (Figure 1). X-ray diffraction (XRD) measurements were carried out with Bruker D8 Discover diffractometer. All colloidal forces were measured in 1.0×10^{-3} molL⁻¹ NaCl aqueous solutions at pH values from ~7 to 10.

2.2. AFM analysis procedure

Interaction forces between glass colloidal probe (which used with 10-micron borosilicate glass) and colemanite crystal substrate at various pH values were measured by atomic force microscopy (AFM). All of the force curves were analyzed with the SPIP software (Image Metrology, Lyngby, Denmark), which translates the cantilever deflection-piezo extension/retraction data to force-separation profiles.

3. Results and Discussions

In this study, we studied to analyse the interactions of colemanite crystal surface with surrounding fluids and colloidal particles.

Before force measurements topographic AFM images of the tested colemanite surfaces presented in Fig.2.

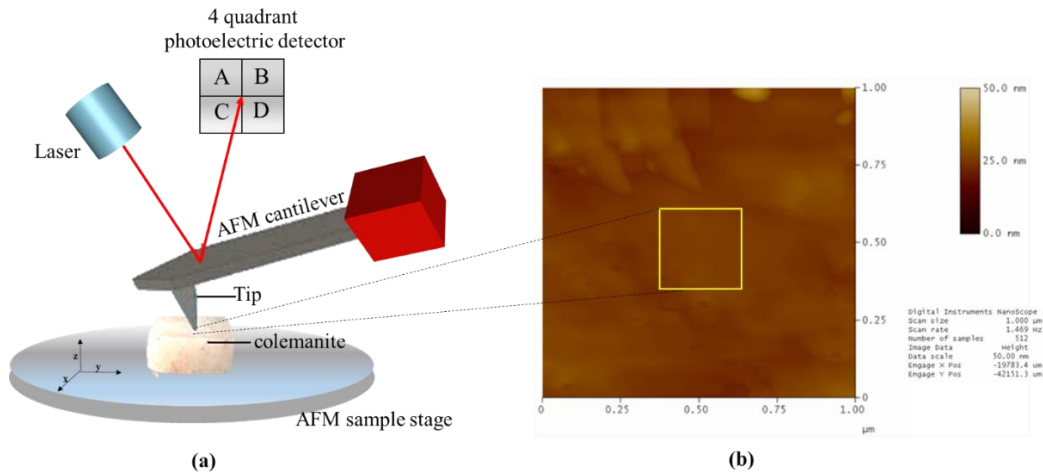


Figure 2. (a) Schematic diagram of AFM (b) 3D AFM height images of colemanite crystal with a smooth surface.

As shown in Fig. 2 (a) the sharp tip scans over the colemanite surface and the deflection of the cantilever is quantified through a laser beam reflected off the backside of the cantilever and received by the photoelectric detector. Finally, the measured cantilever deflection allows the computer to generate a map of the surface topography [10].

The obtained topography image corresponds to the measured height values, $z(x,y)$ (Figure 2(b)) The height value is associated to a pair of surface coordinates (x,y) [11]. XRD patterns of colemanite is shown in Fig. 3.

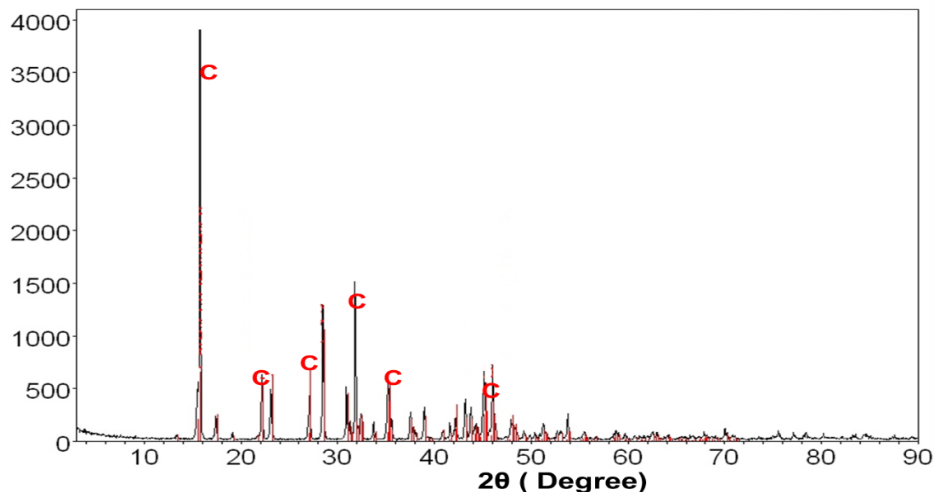


Figure 3. X-Ray diffraction (XRD) patterns of the colemanite.

As shown in Fig. 3 the expected peaks for colemanite, revealing that the sample has a high purity.

The colemanite is a semi-soluble mineral. For this reason, it has a low solubility in water, but it dissolves readily in acid [12]. The colemanite cannot be practically measured below pH 6 due to

dissolution of mineral in HCl. In order to obtain reliable AFM results, all measurements in should be either range from pH 6 to 11.

Figure 4 shows the colloidal forces measurements between glass probe and colemanite crystal. It can be seen this figure that interaction forces undergo a change in four different pH values.

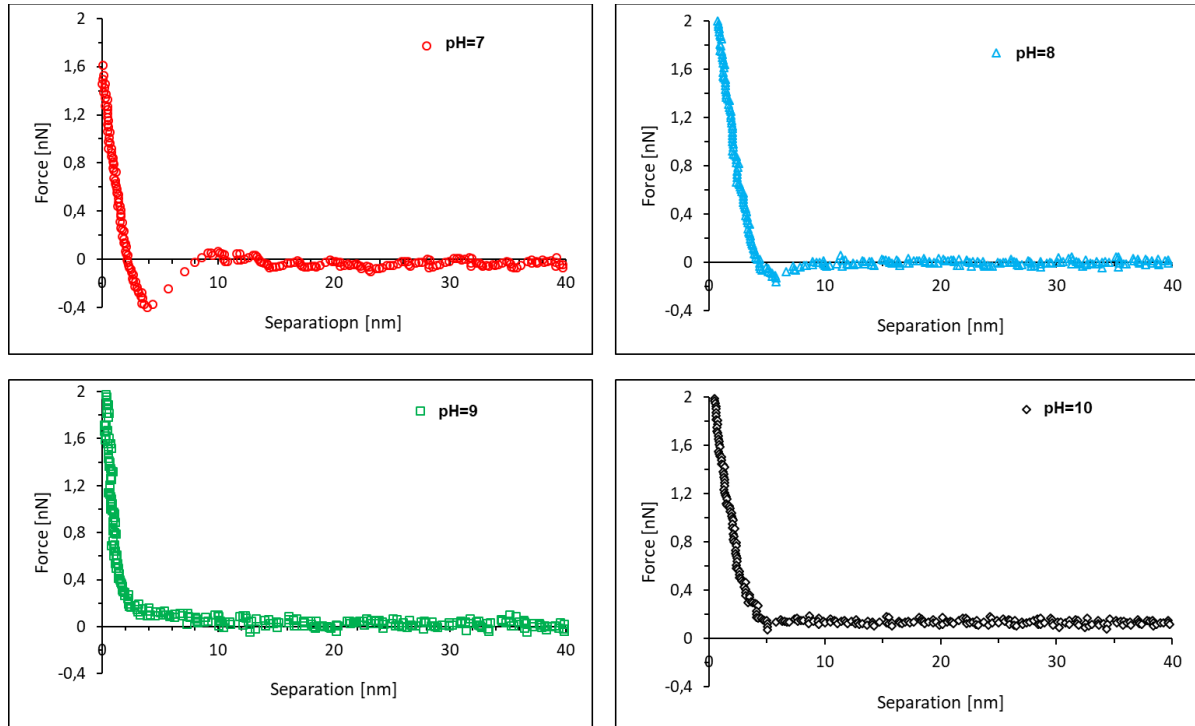


Figure 4. The force versus separation curves obtained for a glass probe tip interacting with Kestelek crystals in $1.0 \times 10^{-3} \text{ molL}^{-1}$ NaCl suspension at 4 different pHs.

The point of zero charge (PZC) of colemanite is about range of 10.2-10.5 [13]. As expected attractive interactions between negatively charged glass probe and positively charged colemanite crystal dominate at pH 7 and 8. These attractive forces weakened at pH 9 and changed to repulsive at pH 10. The transition from attractive to repulsive is associated with reversal of the surface charge for colemanite crystal from positive to negative at pH 10.

4. Conclusions

The colloidal forces between colemanite crystal and glass probe were investigated by AFM. In $1.0 \times 10^{-3} \text{ molL}^{-1}$ NaCl at pH 7, attractive forces have been recorded between the AFM glass probe and colemanite surface. Attractive electrostatic forces result from the interaction between the negatively charged glass probe and positively charged colemanite surface. In the alkaline solution of NaCl pH 8 and 9 weak attractive forces were observed while pH 10 only repulsive forces were observed between the AFM tip and colemanite crystal. As a result, at the pH values (7, 8, 9 and 10) where the AFM measurements were conducted, the nature of the interaction forces depends on the surface charge of colemanite.

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