DOI:10.5281/zenodo.13950685

ÇEVRE BİLİMLERİ VE MÜHENDİSLİĞİ ALANINDA ORİJİNAL ARAŞTIRMA VE DERLEMELER

EKİM, 2024

EDİTÖR
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Çevre Bilimleri ve Mühendisliği Alanında Orijinal Araştırma ve Derlemeler

Editör

Dr. Öğr. Üyesi Emrah Yılmaz

İmtiyaz Sahibi
Platanus Publishing®

Editör
Dr. Öğr. Üyesi Emrah Yılmaz

Kapak & Mizanpaj & Sosyal Medya
Platanus Yayın Grubu

Birinci Basım
Ekim, 2024

Yayımcı Serti ika No
45813

Matbaa Sertifika No
47381

ISBN
978-625-6634-23-7

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Bölüm 1

Bor Minerallerinin Endüstriyel Kullanım Alanları ve Türkiye'deki Önemli Bor Yatakları

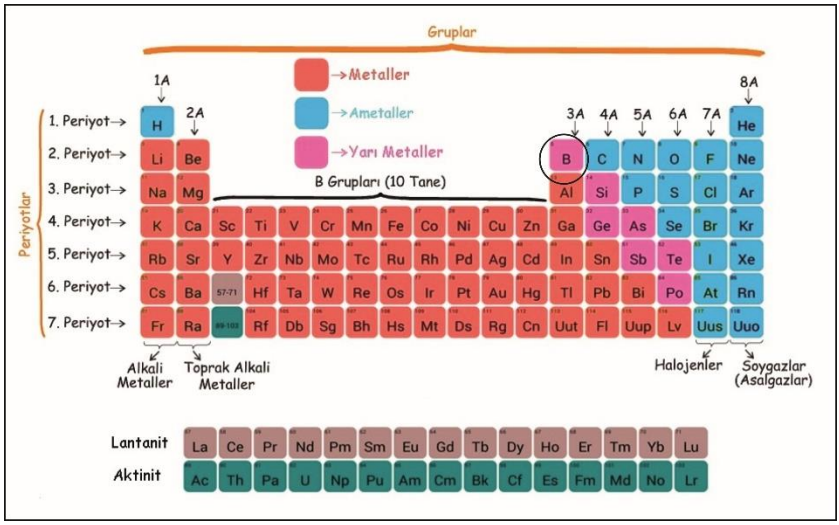
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1.GİRİŞ

1.1. Bor Minerallerinin Genel Özellikleri

Bor, yarı metal sınıfında atom numarası 5 olan ve periyodik tabloda "B" ile gösterilen kimyasal bir elementtir (Şekil 1.1). Periyodik sistemin 3A grubunda bulunan bor elementinin 8B, 10B, 11B, 12B, 13B izotopları bulunmaktadır. Ancak en kararlı olan izotopları 10B ve 11B izotoplarıdır.



Şekil 1.1. Bor elementinin periyodik tablodaki yeri (http 1)

Yer kabuğunda %0.001 oranında ve deniz suyunda 3-5 ppm düzeyinde bulunan bor mineralleri boraks (tinkal), üleksit, kernit, kolemanit, hidroborasit ve pandermit olmak üzere gruplandırılmaktadır (Çelik, 1993). Bor minerallerinin kimyasal bileşimi ise boroalimünyum-silikat mineralleri, borosilikat mineralleri ve borat mineralleri olmak üzere üç gruba ayrılmaktadır (Zhu ve Wang, 2007).

Tablo 1.1. Önemli bor minerallerinin fiziksel ve kimyasal özellikleri (Uz, 1990)

Mineral	Formülü	Kristal Sistemi	Sertliği	Yoğunluğu
Boraks	$Na_2B_6O_7.10H_2O$	Monoklinik	2-2,3	1,72
Kernit	$Na_2B_2O_4.4H_2O$	Monoklinik	2,5	1,91
Üleksit	$NaCaB_5O_9.8H_2O$	Triklinik	2,5	1,96
Kolemanit	$Ca_2B_6O_{11}.5H_2O$	Monoklinik	4-4,5	2,42
Pandermit	$Ca_4B_{10}O_{10}.7H_2O$	Triklinik	3-3,5	2,4
Hidroborasit	$Ca_2B_6O_{11}.5H_2O$	Monoklinik	2-3	2,17

Boraks (Tinkal): $Na_2B_6O_7.10H_2O$ bileşiminde olan mineral Monoklinik kristal sisteminde kristalleşmekte olup kristaller kısa prizmalar şekillidir. Sertliği 2-2,3, yoğunluğu 1,72 gr/cm^3 olan boraks minerali kırılgan yapıya sahip olup taze yüzeyleri camsı ve saydamdır. Oldukça az bir zamanda beyaz (tebeşirimsi) renge dönüşür. Su içerisinde kolaylıkla çözünen mineral bu özelliğiyle diğer bor minerallerinden kolaylıkla ayrılmaktadır. Boraks (tinkal) minerali yataklarda seviyeler oluşturabilir ya da kil, üleksit ve tinkalkonitle beraber bulunabilir (Temur, 2007).

Üleksit: Triklinik sistemde kristalleşen üleksit, $NaCaB_5O_9.8H_2O$ bileşiminde olup büyük kristallere kıyasla ipek görünümlü lif demetleri oldukça yaygındır. Sertliği 2,5, yoğunluğu ise 1,96 gr/cm^3 olan mineralin iri olan kristalleri saydamdır. Killi kısımlarda üleksit kümelerinin birikmesi sonucu pamuk yumağına benzetildiği için ***"pamuk topu"*** olarak adlandırılmıştır. (Kistler ve Helvacı, 1994). Birbiri içerisine geçmiş halde çapraz lifler şeklinde damarlar oluşturmaktadır. Ses ve ısı yalıtımında, seramik, cam ve gübre endüstrisinde, boraks ve borik asit üretiminde yaygın bir şekilde kullanılan Üleksit, Türkiye'de Bigadiç, Kırka ve Emet'de, dünyada ise Arjantin'de bulunur (Eti Maden, 2019).

Kolemanit: Bor mineralleri içerisinde en yaygın bulunan kolemanit minerali $Ca_2B_6O_{11}.5H_2O$ bileşiminde olup Monoklinik sistemde kristalleşmektedir. İnce ve parlak kristaller halinde bulunan mineral kütle halinde bulunduğunda masif tabakalar veya tane yığışımları şeklinde ortaya çıkar. Sertliği 4-5, yoğunluğu 2,42 gr/cm^3 olan kolemanit minerali beyaz, gri veya sarımsı gri renklidir. Su içerisinde yavaş, asitte kolaylıkla çözünen mineral, ısıtıldığında çatırdayarak toza dönüşmektedir. Kolemanit mineralinin başta cam ve seramik sanayii olmak üzere metalürji, cam elyafı, gübre, deterjan ve kozmetik sektörü gibi birçok kullanım alanı mevcuttur (Eti Maden, 2019).

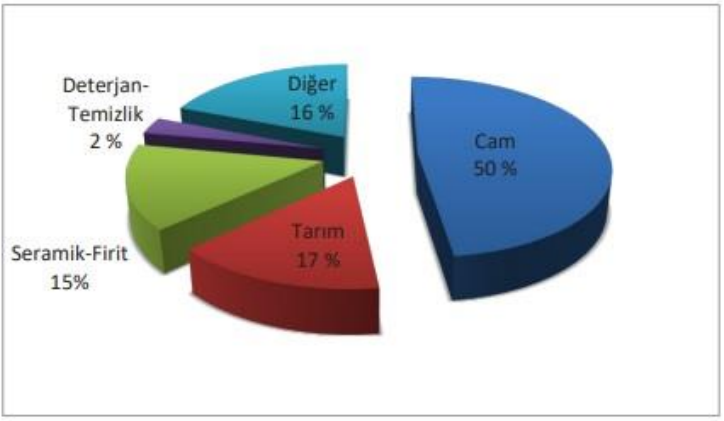
Kernit: Kernit minerali, $Na_2B_2O_4.4H_2O$ bileşimindedir. Monoklinik sistemde kristalleşen mineral, dilimleri boyunca parçalandığında öz şekilleri bozulup kolaylıkla ufalanarak ince liflere ayrılmaktadır. Sertliği 2,5-3, yoğunluğu 1,91 gr/cm^3'tür. Hava ile teması sonucunda üzeri beyaz toz haline dönüşmektedir. Beyaz renkli ve inci parlaklığında olan kernit minerali, su içerisinde borakstan daha az oranda erimektedir (Kistler ve Helvacı, 1994; Ediz ve Özday, 2001).

Hidroborasit: $Ca_2B_6O_{11}.5H_2O$ bileşimindeki hidroborasit minerali Monoklinik sistemde kristaşmekte olup ışınsal ve iğne şeklindeki kristaller şeklinde bulunmaktadır. Sertliği 2-3, yoğunluğu ise 2,17 gr/cm^3 olup, yaklaşık 5-30 cm çapında yumru şeklindedir. Bu yumrular, rastgele dağılmış vaziyette iğnemsi kristallerden oluşmaktadır. Hidroborasit minerali, beyaz renkli olmasına rağmen

içerdiği arsenik oranına göre kırmızı ve sarı renklerde de görülmektedir (Yiğitbaşıoğlu, 2004).

Pandermit: Pandermit minerali $Ca_4B_{10}O_{10}.7H_2O$ bileşimindedir. Triklinik sistemde kristalleşen mineralin rengi beyaz olup, sertliği 3-3.5, yoğunluğu 2.4 gr/cm^3' tür. Görünüşü kalsite benzemektedir (Temur, 2007).

2. BOR MİNERALİNİN ENDÜSTRİYEL KULLANIM ALANLARI



Şekil 2.1. Bor minerallerinin başlıca kullanım alanları (Eti Maden, 2022)

Cam Sanayii: Cam sanayii, Bor minerallerinin en yaygın kullanım alanıdır. Camdaki genleşme katsayısını düşürerek camın darbe direncinin artışına neden olan bor oksit, cama daha yüksek mekanik mukavemet ve çekme kalitesi sağlayarak fiberglas üretiminde önem arz etmektedir (Woods, 1994; Parks ve Edwards, 2007).

Uzay Sanayii: Dayanımlarının yüksek ve yoğunluklarının düşük olması nedeniyle bor lifleri ve bor karbürler roket, uçak ve uzay araçlarının devrelerinin ve gövde parçalarının üretiminde kullanılır (Temur, 2007).

Nükleer Sanayii: Nükleer reaksiyonların denetlenmesine yardımcı olan bor izotoplarından 10B ve 11B izotoplarının radyoaktif parçacıklara karşı yalıtım özelliği bulunmaktadır. Nükleer enerji üretim süreçlerinde nükleer kalkan oluşturan kontrol çubukları imalatı için bor karbürler, borlu çelikler ve titanbor alaşımları kullanılmaktadır (Bilgiç ve Dayık, 2013).

Deterjan: Sabun ve deterjan üretiminde bor minerallerinin önemi giderek arttığı için nüfus artışına da paralel olarak, yakın gelecekte bu sektörde talep edilen bir hammadde olma yolundadır (Temur, 2007). Bor, sodyum perborat şeklinde aktif oksijen kaynağı olarak ağartıcılarda kullanılmaktadır (Köroğlu vd., 2003).

Ek olarak, amonyak oluşumunu önlediği için kokuyu azaltmak amacıyla hayvan çöplerine ve bebek bezi kovalarına da eklenmiştir (Woods, 1994; Parks ve Edwards, 2007).

Tarım: Bor, tarım sektöründe çiçek açma, polen döllenmesi vb. gibi bitki gelişimini sağlayan gübre üretiminde kullanılmaktadır. Toprakta bor miktarının fazlalığı (2-4 ppm) toksik etki gösterirken, az olması (0.5-1 ppm) ise bitkilerde eksikliğe sebep olmaktadır (Tolun, 1988; Ediz vd., 2001). Ayrıca, bor mineralleri, yabancı otları yok ederek toprakta bitki yetişebilmesi için toprağın hazır hale gelmesinde de kullanılmaktadır (Demirtaş, 2006).

Elektronik ve Bilgisayar Endüstrisi: Bor, bilgisayarların mikro chipleri, CD sürücüleri, bataryaları, pilleri, laser printer tonerleri vb. birçok malzemede kullanılmaktadır. Yakın gelecekte borun önemi, iletişim sanayii ve bilgisayar ağlarında daha da artacaktır (Tombal vd., 2016).

Sağlık: Bor, sağlık alanında, antibakteriyel ve antiseptik özelliği sebebiyle losyon, diş macunu, yara temizleme solüsyonu, merhem, göz damlaları gibi maddelerin ürtetiminde kullanılmaktadır. Ayrıca, son zamanlarda bor, nükleer tıp alanında Bor Nötron Yakalama Tedavisinde (BNCT) kanser, dermatoloji, yara iyileştirme vb. tedavilerinde kullanılır (http 2).

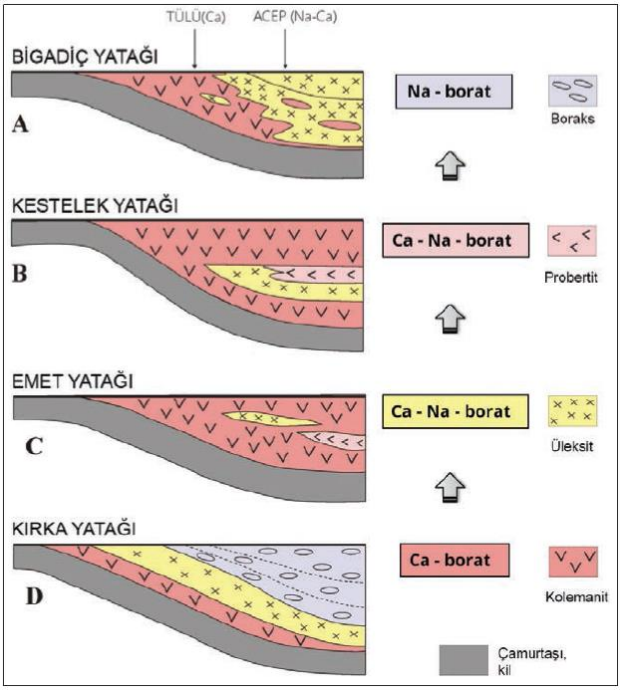
Metalurji: Bor minerallerinin maddi (parasal) olarak payının fazla, ancak miktar olarak az olduğu alan metalürjidir (http 2). Erime derecesinin düşük olması ve metal oksitleri eritme özelliğinden dolayı kıymetli metallerin ayrılmasında, pirinç, bakır, bronz, demir ve çelik ile ilgili lehim işlerinde, kaynakçılıkta kullanılmaktadır (Temur, 2007).

Çimento: Yüksek dayanamıyla borlu çimento, barajlarda, tünellerde, beton yollarda, köprülerde, yüksek binaların inşasında kullanılır. Bor ile malzeme üretilirken malzemenin mukavemeti artırılarak ve pişme sıcaklığı düşürülerek enerji tasarrufu sağlanır ve bakteri-mantar oluşumu engellenir. Ayrıca ısı ve ses yalıtımı da sağlanmaktadır (http 2).

3. TÜRKİYE'DEKİ ÖNEMLİ BOR YATAKLARI

1970'li yıllarda Türkiye'de bor madenciliğinin önemi anlaşılmaya başlanmış, özellikle son 15 yılda hem bor madenciliği hem de ülke ekonomisine olan katkısı bakımından büyük ilerlemeler kaydedilmiştir (Temur, 2007).

Türkiye'de Balıkesir (Bigadiç, Sultançayır), Kütahya (Emet), Bursa (Kestelek) ve Eskişehir (Kırka) illerinde yaklaşık olarak 40.000 km^2'lik bir alanda dağılım gösterir.



Şekil 3.1. Türkiye borat yataklarındaki bor minerallerinin dağılımı (Helvacı, 2015)

Balıkesir-Bigadiç Bor Yatağı: Bigadiç Bor Yatağı, Balıkesir iline bağlı Bigadiç ilçesinin 12 km kuzeydoğusunda yer almakta olup dünyadaki en büyük üleksit ve kolemanit yatağıdır (Helvacı, 2015). Bigadiç bor havzası KD-GB doğrultulu havzalardan biri olup 50-90 km genişliğinde bir zon boyunca mostra vermektedir. Üst Maastrihtiyen-Paleosen yaşlı, türbiditik matriks içinde, Mesozoyik kireçtaşı, çört, spilitik volkanitler, serpantinleşmiş peridotit blokları ve mikritik kireçtaşı merceklerinin oluşturduğu Bornova Fliş Zonu üzerinde yer almaktadır (Erdoğan, 1990; Okay ve Siyako, 1993; Yücel Öztürk vd., 2014). Borat mineralleri, havlit, propertit ve hidroborasitten oluşan alt borat zonu ile inyonit, pandermit, meyerhofferit, hidroborasit, terçit, havlit, rivadavit ve tünellitten oluşan üst borat zonu olmak üzere iki farklı zonda oluşmuştur (Özpeker, 1969; Helvacı,1995; Helvacı ve Orti, 1998; Yücel Öztürk vd., 2014). Bu iki zon diyajenez esnasında montmorillonite, zeolite ve klorite dönüşen kalın tüf seviyeleriyle ayrılır. Rezervi 1024 milyon ton, tenörü ise %35 olan Bigadiç borat yatakları kurak iklim şartlarında yerel volkanizmaya bağlı olan termal kaynaklarla beslenen havzada oluşmuştur (Helvacı, 2015).

Balıkesir-Sultançayır (Susurluk) Bor Yatağı: Sultançayır (Susurluk) Bor Yatağı, Batı Anadolu'da yer alan borat yatakları içerisindeki en eski bor yatağıdır. Türkiye'de pandermit ve havlitin ilk işletildiği sahadır. 1865 yılından 1950'li yılların sonlarına kadar Fransız ve İngiliz şirketleri tarafından bu saha kapalı ocak olarak işletilmiştir. Bor yatağından çıkarılan pandermitler Bandırma (Panderma) limanından yurtdışına taşındığı için pandermit minerali dünya literatüründeki ismini bu limandan almıştır (Travis ve Cocks, 1984). Sultançayır bölgesinde yer alan Neojen istif 750 m'yi bulan tortulları içermektedir. İstifin alt kesiminde yer alan jips, pandermit ve kolemanit oluşukları linyitli bir seviyenin üzerine gelen marn, kireçtaşı ve volkanik tüflerin içerisinde bulunur ve istifin üst kesimini ise marn, tüf ve kireçtaşı ardalanması oluşturmaktadır (Helvacı, 1994; Orti vd., 1998; Helvacı, 2003). Sultançayır (Susurluk) Bor Yatağında, jips baskın mineral olarak bulunur. Ayrıca kalsit, simektit, zeolit ve klorit yatakta bulunan diğer minerallerdir (Orti vd., 1998; Gündoğan ve Helvacı, 1993; Helvacı, 1994; Helvacı ve Alonso, 2000).

Bursa- Kestelek Bor Yatağı: Kestelek Bor Yatağı, Bursa ili Mustafakemalpaşa ilçesinin Kestelek köyünde yer almaktadır. Bor yatağında egemen mineral esas olarak kolemanit, üleksit ve propertittir. Ender olarak da hidroborasit gözlenmektedir (Helvacı, 2015). Rezervi 8 milyon ton, tenörü ise %35'tir. Kestelek bölgesinde bulunan Neojen tortulları Mesozoyik ve Paleozoyik yaşlı temel üzerine uyumsuz olarak gelmektedir. Tabanda konglomera ve kumtaşıyla başlayan çökeller, linyit seviyeleri içeren marn, kil tüf, kireçtaşı ve aglomerayla devam eder. Ortamın daha sonra tektonik duraylılık kazandığı zamanda çökelen boratlı zondaki tüf, marn, kireçtaşı ve bor yatakları meydana gelmiştir. bölgedeki istif bu dönemden sonra gevşek çimentolu konglomera, kumtaşı ve kireçtaşı ardalanmasıyla tamamlanmıştır (Özpeker, 1969; Helvacı, 1994; Helvacı, 2003).

Kütahya-Emet Bor Yatağı: Emet Bor Yatağı, Kütahya ili Emet ilçesinde Hisarcık ve Espey bölgesinde yer almaktadır. Batı Anadolu'nun, başta kolemanit olmak üzere önemli miktarda borat mineralleri içeren Neojen havzalarından biri olan Emet Bor Yatağı'nda kolemanit egemen mineraldir. Rezervi 887 milyon ton, tenörü ise %35'tir. Emet bölgesinde yer alan Neojen istif, Paleozoyik yaşlı mermer, kalkşist, kloritşist ve mikaşist gibi metamofik kayaçlar üzerine uyumsuz olarak gelmektedir. Bölgedeki istif tabandan tavana; çakıltaşı, kumtaşı, marn ve tüf mercekleri içeren ince tabakalı alt kireçtaşı, asidik ve ortaç volkanit-tüf-aglomera, kömür ve jips bantları içeren çakıltaşı-kumtaşı-kiltaşı-marn ve kireçtaşının oluşturduğu kırmızı birim, bor yataklarını ihtiva eden kiltaşı-tüf-tüfit ve marn, kiltaşı-marn ve çört merceklerini içeren üst kireçtaşı, bazaltlardan oluşmaktadır (Helvacı ve Firman,1976; Helvacı ve Orti, 1998; Helvacı, 2003).

Eskişehir-Kırka Bor Yatağı: Kırka Bor Yatağı, Eskişehir ilinin Seyitgazi ilçesine bağlı Kırka bölgesinde yer almaktadır. Kırka bor yatağının egemen mineralı esas olarak boraks olmasına rağmen buna daha az oranda üleksit ve kolemanit eşlik etmektedir (Baysal, 1972; İnan vd., 1973; Helvacı, 1977; Sunder, 1980; Palmer ve Helvacı, 1995; Floyd vd., 1998; Helvacı ve Orti, 2004; Seghedi ve Helvacı, 2014; Helvacı, 2015). Rezervi 519 milyon ton, tenörü ise %25 olan Kırka Bor Yatağı, 1960'lı yıllarda bulunan dünyanın en büyük bor yatağıdır. Yatak üç bölümden oluşmaktadır. Bunlardan ikisi tamamen kolemanitten oluşmakta olup sadece tavan kısımlarında birkaç cm kalınlığında üleksitli kısım bulunur (Yalçın ve Baysal, 1991). Üçüncüsünde ise bor minerallerinde tabandan itibaren kolemanit-üleksit-hidroborasit-üleksit-borakstan oluşan bir zonlanma görülmektedir (Yalçın, 1988).

4. SONUÇLAR

Doğada bütün canlıların yaşamlarını devam ettirebilmeleri için kıymetli elementlerden biri olan bor mineralleri, cam sanayiinden, uzay ve deterjan sanayiine, elektronik, sağlık, tarım metalürji ve nükleer teknolojilere kadar oldukça yaygın ve giderek artan uygulamalara sahiptir. Türkiye, Dünya'nın en büyük bor madenine sahiptir. Özellikle Kırka'daki boraks, Bigadiç, Emet ve Kestelek'teki üleksit ve kolemanit üretimi ile Türkiye'nin dünya pazarlarına egemen hale geleceği söylenebilir.

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Bölüm 2

Leonardit ve Çevresel Uygulamaları

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1. Leonardit

Leonardit, kahverengi ve kömür benzeri görünüme sahip oksitlenmiş bir linyit türüdür. Genellikle bir kömür madeninde olgunlaşmış kömür tabakasının üzerinde yüzeye daha yakın bölgede bulunur. Humik ve organik maddeler üzerine yaptığı çalışmalara ithafen A. G. Leonard'ın adını taşıyan leonardit, %30-80 humik asit (HA) içerir ve organik gübre veya toprak düzenleyici olarak kullanılabilir (Ayuso, 1996). Dünyanın birçok yerinde bol miktarda doğal leonardit kaynağı bulunmaktadır. Linyit kömürü, turbadan sonra en düşük ranklı kömürdür. Kömürleşme derecesine rank adı verilir. Linyitin enerjisi düşüktür ve %25-30 karbon içerir. Leonardit ise, linyitin yüzey korunmazlığında, kömürleşme sürecinden etkilenmeyerek oksitlenmesiyle oluşan veya humustan süzülen humik asitle (HA) zenginleşmiş tortuların oluşturduğu düşük ranklı bir kömürdür. Mikro ve makro bitki besleme maddeleri açısından zengindir. Linyit havzalarının üst bölgeleri, geçirdikleri oksitlenme süreci ve humus tortulaşmasına bağlı olarak, leonardit özelliği taşıyabilirler. Leonardit çoğunlukla linyit yataklarında bulunmakla birlikte her linyit yatağı leonardit içermez. Ülkemizde birçok linyit yatağı bulunmaktadır. Bunların başlıcaları; Soma, Kütahya, Uşak, Muğla, Konya, Trakya bölgesi, Bolu, Yozgat, Çanakkale bölgelerindeki linyit yataklarıdır (Engin ve ark., 2012). Hem dünyada hem de Türkiye'de bulunan leonardit kaynaklarının içerik karakterizsyonu birbirinden farklı bulunmuştur (Pekcan ve ark., 2018; Ratanaprommanee ve ark., 2017)

Leonardit, özellikle HA olmak üzere yüksek miktarda humik madde içeren doğal organik bir maddedir. Tarım toprakları yapılaşma, turizm ve sanayileşmenin yanı sıra daha fazla ürün talebiyle yoğun tarımsal kimyasal kullanımı ve gübrelemenin olumsuz etkisi altındadır. Toprak bozulması, insan faaliyetleri nedeniyle toprak sağlığı ve kalitesinde düşüş, 21. yüzyılın önemli küresel sorunlarındandır. Geçtiğimiz birkaç on yılda, yoğun çiftçilik ve uygunsuz toprak uygulamaları, toprak organik maddesinde (TOM) ve verimlilikte düşüşle kendini gösteren toprak bozulmasına yol açmıştır. Humik maddeler (iyi ayrışmış ve oldukça kararlı organik materyaller, yani humik asit, fulvik asit ve huminler) toprak organik maddesinin önemli bir kısmını oluşturur, toprak verimliliği ve toprağın fiziksel bütünlüğü üzerinde olumlu bir etkiye sahiptir ve besin maddelerinin bulunabilirliğini artırır (Stevenson, 1979; Akinremi ve ark., 2000). Leonardit, bir milyar yıldan fazla süren bir ayrışma süreciyle oluşan ve humik asit içeren doğal oksitlenmiş bir maddedir. Doğal biyomineraller, özellikle leonardit, son zamanlarda humik asit kaynağı olarak cazip hale gelmiştir.

Humik maddeler azot, fosfor ve kükürt rezervuarları olarak kullanılabilir; toprak yapısını, havalanmayı ve drenajı iyileştirir, tamponlama ve değişim kapasitelerini artırır (Stevenson, 1979; Stevenson, 1982). HA uygulamalarının bitki büyümesini, tohum çimlenmesini ve meyve kalitesini iyileştirdiği bildirilmiştir (Mackowiak ve ark., 2001). Ancak bu araştırmaların çoğu farklı humik madde kaynakları veya seviyeleriyle yetiştirilen bitkileri ve toplam humik madde miktarı ile bitki büyümesi arasındaki ilişkiyi incelemiştir (He ve ark., 2009; Xu ve ark., 2009 ve Liu ve ark., 2008). Sadece Serenella ve ark. (2002), yüksek aromatik ve karboksil C içeriğine sahip düşük moleküler boyutlu HA'nın ve peptidik ve karbohidratik karbonlara sahip yüksek moleküler boyutlu HA'nın bitkilerin metabolik parametrelerini olumlu yönde etkileyip etkilemediğini araştırmıştır. Düşük moleküler boyutlu humusun kök hücrelerinin plazma membranına ulaşabildiği ve taşındığı, yüksek moleküler boyutlu bir fraksiyonun ise emilmediği ve yalnızca hücre duvarı ile etkileşime girdiği bulunmuştur. Vaughan (1974) ve Vaughan ve Malcom (1985), humik maddelerle hücre uzamasını, HA'larla güçlü Fe komplekslerinin oluşumuna bağlamış ve bu da duvarla bağlı bir hidroksiprolinin azalmasına neden olmuştur.

Leonardit'in veya ondan üretilen HA'ların toprak iyileştirici veya bitki destekleyici olarak doğrudan kullanılmasının, toprağın özelliklerini ve bitki büyümesini iyileştirmesi beklenmektedir. Humik ve fulvik asitler genellikle tarımsal üretimde kullanılır ve yaygın olarak agronomik potansiyele sahip oldukları bilinmektedir (Ece ve ark., 2007). Toprak organik maddesinin bileşenleri olan humik maddeler (humik ve fulvik asitler), çoğunlukla toprak pH'ı gibi kimyasal gübrelerin olumsuz etkilerini ortadan kaldırmak için kullanılır (Chen ve Aviad, 1990; Akıncı ve ark., 2009; Katkat ve ark., 2009). Humik maddeler (humik ve fulvik asitler), toprak organik maddesinin önemli bir kısmını oluşturur, toprak verimliliği ve toprağın fiziksel bütünlüğü üzerinde olumlu bir etkiye sahiptir ve besin maddelerinin bulunabilirliğini artırır (Stevenson, 1979; Akinremi ve ark., 2000). Humik maddeler, çevredeki toplam biyotanın çürümesiyle oluşan dirençli, koyu renkli heterojen organik bileşiklerdir (Stevenson, 1994). Benzersiz yapıları onları endüstri, tıp, çevre koruma ve tarımda uygulamaları olan çok yönlü bir malzeme haline getirir. Topraktaki HA varlığının, toprağı iyileştirme, stabilitesini geliştirme ve erozyona karşı direncini artırma (Spaccini ve ark., 2002), gelişmiş biyolojik aktiviteyi sağlama (Canellas ve ark., 2002; Canellas ve ark., 2008; Nardi ve ark., 2000; Zandonadi ve ark., 2007), daha yüksek ürün verimi elde etme (Antošová ve ark., 2008; Brownell ve ark., 1987; Eyheraguibel ve ark., 2008) ve toprak ıslahında kullanılabilme (Fava ve ark., 2004; Stehlíčková ve ark., 2009; Von

Wandruszka, 2000) kabiliyetleri nedeniyle sürdürülebilir tarım için gerekli olduğu giderek daha da netleşmektedir.

Kömür benzeri bir görünüme sahip olan leonardit (Şekil 1.1), genellikle yüzeye yakın linyit yataklarıyla ilişkili olarak bulunur. Linyit elektrik üretiminde kullanılır fakat leonardit düşük ısıtma içeriği nedeniyle yakıt olarak kullanılamaz. Bu nedenle, geçmişte leonardit madenciliğin atık ürünü olarak kabul edilirdi. Yapılan araştırmalar sonucu leonarditin yüksek HA içerdiği bulundu (Kohanowski, 1970; Ayuso ve ark., 1996; Dudley ve ark., 2004). Leonardit, yüksek katyon değişim kapasitesi (Pertuit ve ark., 2001; Kalaitzidis ve ark., 2003; Dudley ve ark., 2004) yüksek su ve besin tutma kabiliyeti, birçok bitki besin elementi içermesi (Simandl ve ark., 2001; Kalaitzidis ve ark., 2003) ve yüksek humik asit ve organik madde içeriği (Conxita ve Angels, 2005) gibi özelliklerinden dolayı tarım için önemli bir malzemedir.

Son zamanlarda, leonarditin ticari ölçekte tarımda kullanımı genişlemektedir. Ancak, özellikleriyle ilgili bilgiler oldukça sınırlıdır. Leonarditin %48,60 Organik madde, %26 karbon (C), %2,80 azot (N), ve diğer bazı bitki besin elementleri (P, K, Ca, Mg, Fe, Cu, Mn, Zn) içerdiği bildirilmiştir (Sonmez ve Öktüren Asri, 2024). Conxita ve Angels, (2005) leonarditin %79 humik asit (HA), %55,2 C, %3,4 H, %0,8 N, %2,4 S, %38,1 O, 2,87 meq/g CEC, 3,12 meq/g $COOH^-$ grupları ve 2,07 meq/g OH^- grupları içerdiğini bildirmiştir. Bitki besin maddelerinin yanı sıra leonardit belirli miktarda ağır metal de içermektedir. Alfredo ve ark., (2005) leonarditin 34,9 mg/kg arsenik (As), 0,83 mg/kg kadmiyum (Cd) ve 22,0 mg/kg kurşun (Pb) içerdiğini bildirmiştir.

Leonardit, toprak kalitesini ve bitki büyümesini iyileştirebilen değerli bitki besinleri, organik madde ve humik asit içermesine rağmen, aynı zamanda toprak kirliliğine, fitotoksisiteye ve bitki ve hayvan ürünlerinde istenmeyen kalıntılara neden olabilen potansiyel olarak toksik elementler de içerir. Bu nedenle, leonarditin tarımsal amaçlarla kullanımı dikkatli yapılmalıdır. Leonarditin dünya genelinde çok sayıda kaynağı bulunduğundan, leonarditin kalitesi ve besin bileşimi yerden yere büyük farklılıklar göstermektedir. Bu nedenle, leonarditin tarımsal verimlilikte avantajlarından yararlanmak ve uzun vadede çevre üzerinde olumsuz bir etki yaratmaması için kimyasal içeriği analiz edilmelidir. Toprakta kullanılmadan önce besin içeriğinin ve ağır metal seviyelerinin bitki büyümesi üzerindeki etkilerinin değerlendirilmesi için hem saksı hem de tarla deneyleri yapılmalıdır.




Şekil 1.1 Leonardit

1.1. Leonarditin Kimyasal Bileşimi

Leonardit, normalde linyit madeninde bulunan oldukça oksitlenmiş bir kömürdür. Yüksek humik asit içeriğiyle, toprak kalitesinin iyileştirilmesi, bitki büyümesi ve verimin artırılması ve ağır metallerin kompleksleşmesi ve detoksifikasyonundaki potansiyel rolü nedeniyle leonarditin yapısının ve bileşiminin aydınlatılmasına dair birçok çalışma vardır. Leonarditteki organik madde, çeşitli işlevlerde (örneğin karboksilik grup) dahil edilmiş önemli miktarda oksijen, kükürt ve azot heteroatomları içerir. Bunlar derişimleri leonarditin elde edildiği kömür yataklarının özelliklerine bağlı olarak değişiklik gösterir (Pookmanee ve ark., 2016).

Leonardit örnekleri besin içerikleri açısından analiz edildi; azot (N), fosfor (P), potasyum (K), kalsiyum (Ca), magnezyum (Mg), demir (Fe), çinko (Zn) ve manganez (Mn) (Department of Agriculture, 2005). Leonarditin kimyasal bileşimleri dünyada yataklardan yataklara değişiklik göstermekte olup organik madde ve humik asit miktarı yaklaşık %39 ile %85 değişiklik göstermektedir (Jackson, 1994; Yolcu ve ark., 2011). Bulunla birlikte tüm leonardit örneklerinde bulunan bitki besin elementleri (N, K, S, Ca, Mg, Fe, Zn ve Mn) fosfor hariç oldukça yüksek olduğu tespit edilmiştir (Yolcu ve ark., 2011).

XRD analizi ile leonardit içerisindeki alçıtaşı, kalsit ve kaolinit gibi çeşitli mineral bileşimlerini de (Tablo 1.1) rapor etmiştir (Ratanaprommanee ve ark., 2017).

Tablo 1.1 XRD ile leonarditte bulunan minerallerin karakterizasyonu

No	Mineral bileşimi
1	Alçıtaşı [$CaSO_4.2H_2O$]
2	Kalsit [$CaCO_3$]
3	Kaolinit [$Al_2Si_2O_5(OH)_4$]
4	Muskovit [$KAl_3Si_3O_{10}(OH)$]
5	Kuvars [SiO_2]
6	Demir sülfür [FeS_2]

1.2. Leonarditin Yararları

Leonardit yüksek organik madde ve humik asit içeriğinden dolayı hem tarımda hem de çevrede çeşitli uygulamalar için çok yönlü bir malzemedir (Tablo 1.2). Leonardit, toprak iyileştirici, organik gübre, atık su, organik bileşikler ve ağır metallerin arıtımı için filtre malzemesi vb. olarak kullanılabilir. Topraklardaki organik maddelerin faydası iyi bilinmektedir ve organik maddelerin tarımsal topraklara uygulanması, toprağın fiziksel, kimyasal ve biyolojik özelliklerini olumlu yönde etkiler (Flaig ve ark., 1977). Organik maddece fakir topraklarda leonardit ve HA uygulamasının etkisi zengin olana göre çok daha fazladır.

Leonardit, toprak için düzenleyici ve bitki için biyo-katalizör ve biyo-uyarıcı görevi görür. Diğer organik ürünlerle karşılaştırıldığında, leonardit özellikle bitki büyümesini (biyokütle üretimi) ve toprağın verimliliğini artırır. Leonarditin bir diğer avantajı da uzun vadeli etkinliğidir. Çünkü hayvan gübresi, kompost veya turba kadar çabuk tükenmez. Leonardit tamamen ayrıştığı için azot gibi besinler için bitkiler besin rekabetine girmez. Bu, topraktaki organik maddelerin mikroorganizmalar tarafından hızla tüketildiği ve humus oluşumu olmadan tamamen mineralleştirildiği eksik ayrışmış kompostta geçerli değildir.

Tablo 1.2 Leonarditin yararları

Tür	Yararlar
Tarımsal	Toprak iyileştiriciler
Atık su	Organik ve metal filtre
Petrol sondajı	Sondaj katkı maddesi
Dökümhane	Katkı maddeleri yeşil kum
İyon değiştirici reçineler	Stabilizatör

2. Humik Maddeler

Toprak organik maddesi; canlı, cansız ya da çürümüş (dekompoze) olan tüm organik maddeleri içeren bir terimdir. Tamamen çürümüş olan organik yapılar humus olarak adlandırılmaktadır. Humus kaynakları (humik maddeler ve humik olmayan maddeler) organik gübreler ve kompost gibi çeşitli organik maddelerdir. Kompost gibi organik gübrelerin önemli bileşenlerinden biri humik asittir. Humik asit, toprakta ve organik gübrelerde doğal olarak bulunmasının yanı sıra; linyit, leonardit, turba, kömür, çiftlik gübresi ve kompost gibi çeşitli kaynaklardan elde edilebilir. Organik maddeler arasında leonardit en yüksek humik ve fulvik asit (%40-85) içeriğine sahiptir (Jackson, 1994; Yolcu ve ark., 2011) (Tablo 2.1).

Tablo 2.1 Çeşitli doğal malzemelerin humik ve fulvit asit içerikleri (Jackson, 1994).

Doğal Kaynak	Humik ve Fulvit Asit içeriği (%)
Leonardit	40-85
Siyah turba	10-40
Sapropel turba	10-20
Torf	10-30
Kahverengi kömür	10-30
Gübre	5-15
Kompost	2-5
Toprak	1-5
Çamur	1-5
Arıtma Çamuru	1-5
Sert Kömür	0-1

Humik asit, yüksek moleküler ağırlıklı, koyu kahverengi, alkali çözeltilerde çözünen uzun zincirli bir moleküldür (Stevenson, 1982). Humik asit, humik maddelerin başlıca bileşenlerinden biridir. Humik maddeler, mikroorganizmaların biyolojik aktiviteleri yoluyla bitki ve hayvansal maddelerin kimyasal ve biyolojik bozunması ile oluşur. İnorganik kısımların bozunması minerelizasyon organik kısmın bozunması ise hümifikasyon olarak adlandırılır (Engin ve Cöcen, 2012). Humik maddelerin bitki büyümesi üzerindeki etkileri, kaynağa ve konsantrasyona, ayrıca humusun moleküler ağırlığına bağlıdır. Düşük moleküler boyutlu fraksiyonu bitkinin hücre zarına kolayca ulaşır ve bitki büyümesi üzerinde olumlu bir etki sağlar. Ayrıca hücre zarının besin alımı özellikle nitrat alımı üzerinde etkilidir. Humik asidin canlı metabolizması üzerindeki etkisi henüz tam anlaşılamamış olmakla birlikte humik maddelerin hem solunumu hem de fotosentezi etkileyebileceği anlaşılmaktadır (Nardi ve ark., 2002).

Organik maddede bulunan humus, toprak verimliliğini, ürün verimini ve mikrobiyal aktiviteleri teşvik eden temel faktördür. Humik maddeler, faydalı toprak organizmaları için iyi bir enerji kaynağıdır. Humik maddeler ve humik olmayan (organik) bileşikler, toprak biotası için enerji ve mineral gereksinimlerinin çoğunu sağlar. Faydalı toprak organizmaları, fotosentez yeteneğine sahip değillerdir, bu nedenle toprakta veya toprakta bulunan artık maddelerin içerdiği karbonla hayatta kalmak zorundadırlar. Karbon bağlarında depolanan enerji, bu organizmalar içindeki çeşitli metabolik reaksiyonlar için enerji sağlama işlevi görür (Giannouli ve ark., 2009).

2.1. Humik Asitlerin Yararları

Güncel bilimsel çalışmalar, toprağın verimliliğinin büyük ölçüde humik asit içeriği tarafından belirlendiğini göstermektedir. Yüksek katyon değişim kapasitesi (KDK), oksijen içeriği ve ortalamanın üzerinde su tutma kapasitesi, humik asitlerin toprak verimliliğini ve bitki büyümesini iyileştirmek için kullanılmasının en önemli nedenleridir.

Humik asitlerin en önemli özelliği, çözünmeyen metal iyonlarını, oksitleri ve hidroksitleri bağlama ve gerektiğinde bunları yavaşça ve sürekli olarak bitkilere salma yetenekleridir. Bu özellikler nedeniyle, humik asitlerin fiziksel, kimyasal ve biyolojik yararlarına aşağıda kısaca değinilmiştir.

Fiziksel Yararlar: Humik asitler toprağın yapısını fiziksel olarak değiştirir.• Toprak yapısını iyileştirir: Humik asitler toprak parçacıklarını fiziksel olarak birbirine bağlayarak hava ve su akışına yardımcı olan, hafif, kumlu topraklarda yüksek su ve besin kaybını önleyen kararlı agregalar oluşturur.

• Toprağın su tutma kapasitesini artırır ve böylece kuraklığa direnmeye yardımcı olur.

Kimyasal Yararlar: Humik asitler toprağın özelliklerini kimyasal olarak değiştirir.

• Bitkilerin besin ve su alımını iyileştirir ve optimize eder.

• KDK'yı dolayısıyla toprağın tamponlama özelliklerini artırır.

• Metal iyonları için doğal bir şelatlayıcı sağlar.

• Bitki büyümesi için gerekli olan organik ve mineral maddeleri içerir.

• Bitki besinlerinin bulunabilirliğini artırır.

• Topraklardaki toksik maddelerin bulunabilirliğini azaltır.

Biyolojik Yararlar: Humik asitler biyolojik olarak mikrobiyal aktiviteleri dolayısıyla bitki büyümesini uyarır.

• Mikroplar tarafından bitki hormonu üretimini dolayısıyla kök büyümesini ve besin alımını uyarır.

• Bitki bağışıklık sistemini güçlendirir böylece hastalık ve zararlılarla daha iyi başa çıkar.

• Tohumların çimlenmesini ve canlılığını artırır.

• Verim kalitesini iyileştirir.

Humik Asitlerin Ekolojik Yararları: Humik asitlerin bir çok ekolojik yararı vardır. Çevre sorunları ve çevrenin korunması için karlı ve etkili çözümler sunar.

Yüksek humik asit içeriğine sahip topraklar nitrat sızıntısını azaltabilir böylece yeraltı suyuna olası kirlilik riskini düşürebilir. Yüksek KDK maddesi olarak humik asit, ağır metaller, pestisitler ve toksik kimyasallar gibi toprak kirleticilerini etkisiz hale getirme ve detoksifiye etme konusunda yüksek bir potansiyele sahiptir. Humik asitler, toprak yapısal birimleri içinde bir çimento görevi görür ve toprak agregalarını stabilize eder, bu nedenle toprak erozyonuna karşı mücadelede etkili bir araçtır.

3. Leonardit ve Humik ve Fulvik Asit ile İlgili Örnek Araştırmalar

Leonardit kullanımının tarihi 1960'lı yıllara dayanmaktadır. Yüksek humik ve fulvik asit içeriği, bitki için zararlı olan toksik madde derişiminin düşük olmasının yanı sıra bitki besin maddeleri ve toplam organik madde açısından zengin olması nedeniyle tarımda kullanımı birçok araştırmaya konu olmuştur. Bu araştırmalarla hem tarım toprağı hem de bitkiler için leonarditin kullanım şekilleri, etkileri ve potansiyel yararları ile ilgili bilgiler elde edilmiştir. Fakat son yıllarda yayınlanan makalelerde leonarditin tarım dışı uygulamalarda kullanıldığı araştırmalar göze çarpmaktadır. Bu çalışmalardan bazıları burada kısaca özetlenmiştir.

Enerji sistemlerinde kullanım için verimli kalorifik değere sahip olmayan linyit ve leonardit gibi malzemelerin elektrolizi ile hidrojen üretimi incelenmiştir. Nispeten düşük kalorifik değere sahip linyitlerin kullanımına ek olarak, enerji üretmek için geleneksel sistemlerde düşük ısıtma değeri nedeniyle yakıt olarak kullanılması mümkün olmayan leonarditin, elektroliz işlemi yoluyla hidrojen üretiminde kullanılabileceği gözlemlenmiştir (Yörük ve ark., 2025). Bozunmaya karşı dayanıklı petrol bazlı plastiklerin yerine biyobozunur bir plastik olan poliaktik asit kullanımı artmaktadır. (Şen, 2024), gıda ambalajlama uygulamaları için

Leonardit (LEO) ve borik asit (BOR) katkılı polilaktik asit filmlerinin hazırlanması ve karakterizasyonunu araştırmıştır. LEO ve BOR/LEO katkılı filmlerde LEO miktarı arttıkça çekme dayanımı ve elastik modülü değerleri buna bağlı olarak artmış, filmlerin kalınlığı ve yırtılma testindeki maksimum kuvvet değerleri azalmış, kopma uzaması değerleri ise dalgalanmıştır. Bir başka çalışmada Leonardit ve bazalt tozlarından sentezlenen membran 0,1 M Ag_2SO_4 çözeltisi ile muamele edilerek gümüş nano partikül ile kaplı seramik membran elde edilmiştir. Bu yeni malzemenin DNA parçalanması, *E. coli* giderimi ve antibiyofilm etkileri için geliştirilmiş antimikrobiyal özellikleri araştırılmıştır (Saleh ve ark., 2023). Suda bulunan Cr(VI)'nın toksik ve zararlı etkileri nedeniyle arıtılması çok önemlidir. Leonardit tozu sudan Cr(VI)'nın adsorpsiyonu ve fotokatalitik redüksiyonunda kullanılmıştır. pH 2'de 10 mg/L'lik başlangıç Cr(VI) konsantrasyonu ile 3 g/L dozda leonardit ile %100 adsorpsiyon giderme verimi elde edilmiştir. Aynı adsorpsiyon koşullarında 0,75 g/L leonardit tozu ile %100 fotokatalitik redüksiyon verimi elde edilmiştir. Ayrıca Leonardit tozunun, 5 kez tekrar kullanıldıktan sonra fotokatalitik süreçte aktivitesinin %70'ini koruduğu bulunmuştur (Arslan ve ark., 2022). Leonarditin 550 ºC'de 5 saat süre ile azot gazı altında pirolizinden siyah toz şeklinde char (LNDC) elde edilmiştir. LNDC ve setiltrimetilamonyumbromür (CTAB) kullanılarak LNDC-CTAB kompleksi sentezlenmiştir. Daha sonra $FeSO_4.7H_2O$ ile muamele edilerek NLDC-CTAB-nZVI nano parçacıkları elde edilmiştir. Yeni malzeme stirenle kirlenmiş toprak ve suyun kullanılmıştır. NLDC-CTAB-nZVI/PS'nin 20 dakikada %98 stiren giderimi sağladığı, stiren daha az toksik bir benzaldehit ara ürününe parçalandığı ve LNDC-CTAB-nZVI/PS sisteminin bitki büyümesi üzerine etkisi ortaya konulmuştur (Angkaew ve ark., 2024). Ozuzun ve Uzal, (2021) leonarditten elde ettikleri humik asitin portland çimento sistemlerinde yeni bir süper akışkanlaştırıcı olarak önemli bir potansiyele sahip olduğunu bildirmişlerdir.

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Bölüm 3

Thermochemical Pretreatment Methods For Producing Bioethanol From Food Wastes

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1. Introduction

In Turkey, 30.3 million tonnes of waste are produced yearly. The average daily waste collected, per person is 1.03 kg. While 85.9% of these wastes produced in our country are sent to waste processing facilities, 60% landfill facilities, 13.5% to municipal waste dumps and 0.6% is burned open, buried and dumped and dumped (WEB-1). According to the results of the waste produced in Turkey it is buried in a large part of the landfill. Approximately one-third of the food produced worldwide is wasted and 3.3 billion tons of CO_2 emissions occur annually from these wastes (WEB-2; Panahi et al., 2022; Moscoviz et al., 2021). Disposal of waste by regular storage has some drawbacks. These are the problems of continuous maintenance and control of the leachate, odor, and storage areas that are formed by the high moisture content of these wastes. Another one is the need for landfills and new storage areas (Yan et al., 2011). It is more organic than about 50% of household waste, and a large part of it, is food waste. Food waste is mostly produced from houses, restaurants. Food waste in domestic wastes can be used both as a refinable and new product-energy source using different techniques such as composting, biogas production, bioethanol animal feed production (Lindkvist, et al., 2023; Fersiz et al., 2017; WEB-3; Hafid et al., 2017a; San Martin et al., 2016). The laws of the European Union limits reducing of food waste, use of more sustainable biomass, landfilling only waste that cannot be recycled and recovered (WEB-4; WEB-5, WEB-6). Therefore, Turkey needs take measures in this area and need create an action plan. The methods, used in this sense are composting of these wastes, anaerobic digestion, biodiesel, biohydrogen and bioethanol production (Hafid et al., 2017a).

Increasing energy demand due to rapid population growth and industrial and technological developments has increased fossil fuel consumption (Vardar et al., 2022; Ayan and Senturk, 2023).

Fossil fuels, especially oil, are the most important energy resource. Transportation system and most of industrial works depend on nonrenewable energy resources. Nations across the world have started to seek alternative energy resources because of the decreased fossil fuel reserves, their high costs and the fast increasing environmental problems (Pieragostini et al., 2014; Searchinger et al., 2008; Gouveia and Oliveira 2009). For this reason, interest in renewable energy sources has increased.

Biofuels, especially bioethanol and biodiesel, are primary renewable energy resources. The use and production of biofuel are important for the global energy crises. Furthermore, it has been a solution for many environmental problems like

air pollution and reducing CO_2 accumulation (greenhouse effect) (Pieragostini et al., 2014; Vavouraki et al., 2014; Hill et al., 2006; Najafi et al., 2009). The EU commission made a decision in 2008 requiring supporting the fuel used in the member states for transportation by biofuel at a ratio of 10% until 2020 (WEB-5).

Bioethanol is a transparent and colourless liquid with a distinctive odour. Bioethanol can be utilised in internal combustion engines, provided that it is blended with gasoline at a ratio of 10% without the necessity for any modifications. (Balat, 2009). Bioethanol production has found wide application in Europe and America (Mussatto et al., 2010).

Bioethanol is produced from the first generation biofuels like sugar beet and canola and the second-generation biofuels lignocellulosic (grass, wood chips, wood dust, domestic waste) (Broda et al., 2022; Vavouraki et al., 2013). It is an alternative fuel to be used after blended with gasoline at certain ratios after produced through fermentation of the first and second-generation products. Bioethanol production through fermentation generally consists of four main stages. These steps are pretreatment and hydrolysis of biomass, fermentation of free sugar, and ethanol production (Abu Tayeh et al., 2014). Hydrolysis of biomass is a rate-restricting step because lignocellulosic matters are hardly biodegradable compounds. Therefore, pretreatment methods are used to accelerate biodegradation (Kim et al., 2014; Kristiani et al., 2013). These methods are physical (ultrasonic), physicochemical (pyrolysis, steam treatment, liquid hot water, ammonia treatment, CO_2 treatment), chemical (acid, alkaline, oxidative, ozone and organic solution treatment) and biological treatment (Sun and Cheng 2002; Carrasco et al., 2011; Sa'nchez and Cardona 2008; Bayrakci and Koçar 2014; Mathew et al., 2014; Miyazawa and Funazukuri 2005; Hamelinck et al., 2005; Pèrez et al., 2008).

The increase in first generation biofuel would cause increase in food prices, animal feed shortage and competition for field required in agricultural production. Bioethanol production from food containing sugar and starch is not desired because such food contains nutritional value (Pieragostini et al., 2014; Thangavelu et al., 2014). Thus, choosing the raw material to be used is very important. High organic matter content and high carbohydrate content indicates that domestic waste and food waste are a good source for bioethanol production. The latest research has concentrated on transforming wastes such as carbohydrate-rich food waste into valuable materials using a variety of bioprocesses (ethanol, succinic acid and hydrogen etc) (Vavouraki et al., 2014; Wang et al., 2008; Han and Shin 2004). There are many advantages to using food waste in bioethanol

production. The aforementioned advantages can be summarised as follows: the substrate is low-cost, available in abundance and renewable. This has increased interest in research into the potential for the conversion of food waste to bioethanol(Hafid et al., 2017b). Food wastes consist of carbohydrate (starch, cellulose, hemicelluloses), lignin, other organic (protein, fat, acid etc) and inorganic matters. pH and calorific value are high (Fersiz and Veli 2015). These wastes are valuable fermentation sugar source and convertible into valuable products (liquid and gaseous biofuel etc) (Vavouraki et al., 2013). Nevertheless, the production of bioethanol from food waste represents a crucial step in the effective pretreatment process, enabling the increased generation of fermentable sugar as a precursor to fermentation.

In order to achieve this, a range of pretreatments, including thermal, chemical and biological, are employed to disrupt the inherent structural complexity of food waste, thereby enhancing the accessibility of enzymes for hydrolysis. Pre-treatment of thermochemical pre-treatment of food waste is highly preferred because it can be easily applied when considering the work done. Hafid et al., 2017a, used pre-treatment of food waste using HCl and H_2SO_4 and obtained a 42.4-fold increase in fermentable sugar production and 0.42 g g^{-1} ethanol yield. In another study, acid pre-processing of food waste with 1% HCl at 100°C for 94 minutes increased the concentration of dissolved sugars by 120% over raw food waste. (Vavouraki et al., 2013). In a separate investigation, the preliminary treatment of culinary waste via a 90°C process utilising both 1.5% HCl and 1.0% H_2SO_4 for a 3-hour incubation period resulted in 49.41 g l^{-1} and 50.32 g l^{-1} of potentially fermentable sugars, respectively (Hafid et al., 2015). As a result, in this study, thermochemical pretreatment processes were used to release fermentable sugar in food wastes and optimum solid concentration, temperature, time, and acid and base amounts were determined. The kinetics of the process were evaluated with respect to the operational conditions. The potential of utilizing food wastes in ethanol bioprocessing was investigated.

Materials and methods

2.1. Features of wastes in the use

The food waste (FW) used in this study was collected from Kocaeli University cafeteria. Wastes were broken into a certain particle size via the Waring 8011 make blender after hard parts had been removed in them and dried at 55 ^{o}C. The dried wastes were grinded via the coffee grinder. The mixed FW was kept in sealed plastic bags and stored in desiccators prior to utilisation. It was stored in a dehumidified environment during the experiment.

2.2. Analytical methods

Homogeneous samples were collected to be characterized of pH Total solid (TS), total volatile solid (TVS), moisture. The analyses were based on the Standard Method (APHA, 2005) (Table 1). The protein content was determined by applying the Kjeldahl method, utilising a conversion factor of 6.25. The sum of the total carbohydrates present in FW was calculated through a two-step sulfuric acid hydrolysis process, in accordance with the procedures set forth by the National Renewable Energy Laboratory Laboratory Analytical Procedure (NREL-LAP) (Hill et al., 2006). The percentage of lipid content was determined by the hexane/isopropanol (3:2) method (Najafi et al., 2009). At the conclusion of the designated time period, hydrolysis samples were collected and subjected to a centrifugation process at 10,000 rpm for a duration of ten minutes. A filtration process conducted through vacuum filtration, utilizing Whatman No. 1 filter paper as the filtration medium, followed this step. Reducing sugar (RS) concentration of the hydrolysate produced from thermochemical hydrolysis of the food waste was determined by using the DNS (3,5- dinitrosalicylic acid) method (Miller, 1959). All experiments and associated analyses were conducted in duplicate.

Table 1: Characteristic of FW Used in the Experiments.

ParameterConstituent	**Value**[a]
pH	6.5
Moisture, %	65
Total solids (TS)	35
Volite solids[b] (VS), %	97
Protein[b], %	9.6
Carbohydrate[b], %	63.3
Oil[b], %	18

[a] Results belong to two replicates
[b] composition of food wastes per gram of dry mass

2.3. Thermochemical pretreatment

The blended food waste underwent a series of treatments, beginning with a hot distilled water treatment, followed by thermochemical pretreatment using H_2SO_4 and NaOH at a concentration of 1-2-3% (vol/vol). The operational parameters of the experimental unit, including the loading of food waste (5-10-20 g l^-

[1]), temperature (50-100-120 °C), and hydrolysis time (150 min), were examined with the objective of achieving the highest degree of hydrolysis of the food waste. All treatment methods were carried out in 250 ml shake flask. Volume was specified as 100 ml for the study. This was achieved via a hot water bath for 50 °C, under a condenser for 100 °C and in an autoclave for 120 °C. Upon completion of the hydrolysis process, the medium was subjected to centrifugation at 10,000 rpm for a period of 10 minutes, followed by filtration through vacuum filtration using Whatman No. 1 filter paper. Variations in reducing sugar (RS) compounds were investigated through the samples collected during the experiment. Moreover, a control set shall be prepared with distilled water without adding any chemical to see effect of hydrolysis (Table 2).

Table 2: TC and RS Values of without Pretreatment Food Waste.

	mg TC g^{-1} dry FW	**mg RS g^{-1} dry FW**
Without treatment FW	220	67

2.4. RS efficiency

RS efficiency was determined by using the following Eq. (1).

$$\text{Efficiency } \% = \frac{C_f - C_i}{C_i} * 100 \quad (1)$$

C_f: RS concentrations after pretreatment (mg g^{-1} dry FW)

C_i : RS concentrations before pretreatment (mg g^{-1} dry FW)

3. Kinetics of thermochemical pretreatment

The hydrolysis of biomass into soluble substrates is a first-order reaction, whereby the rate of reaction is dependent upon the concentration of the particulate biomass and is independent of temperature and pH (Vlyssides et al., 1997; Vlyssides and Karlis 2004).

$$\frac{d(RS)}{dt} = k_1(RS_\infty - RS) \quad (2)$$

Where RS= Reducing Sugar concentration (mg g^{-1} FW); RS_∞= maximum theoretical RS_∞= concentration (mg g^{-1} FW) defined as $RS_p - Rnh$; RS_p = particulate *RS* concentration; RS_{nh}= non-hydrolysable RSp concentration; k_1 = first order rate constant (1 min^{-1}). Integration of Eq. (2):

$$\int_0^{RS} \frac{d(RS)}{RS_\infty - RS} = \int_0^t k_1 dt \quad (3)$$

yields;

$$\ln\left(\frac{RS_\infty}{RS_\infty - RS}\right) = k_1 t \quad (4)$$

or

$$RS = RS_\infty(1 - e^{-k_1 t}) \quad (5)$$

alternatively, the natural logarithm may be modified.;

$RS = RS_\infty(1 - 10^{-kt})$ where

k= 0.434k1 (6)

$$F_1 = 1 - 10^{-kt} \quad (7)$$

$$F_2 = (2.3kt)\left[1 + \frac{2.3kt}{6}\right]^{-3} \quad (8)$$

Equations (7) and (8) can be transformed in series as follows (Croft et al. 2000).

$$F_1 = (2.3kt)\left[1 - \frac{1}{2}(2.3kt) + \frac{1}{6}(2.3kt)^2 - \frac{1}{24}(2.3kt)^3 + \cdots\right] \quad (9)$$

$$F_2 = (2.3kt)\left[1 - \frac{1}{2}(2.3kt) + \frac{1}{6}(2.3kt)^2 - \frac{1}{21.6}(2.3kt)^3 + \cdots\right] \quad (10)$$

The initial three terms of the aforementioned series of equations exhibit a high degree of similarity, with only minor discrepancies observed in the subsequent terms. These differences have a negligible impact on F_1 and F_2. Hence F_1=F_2 written using Eq. (7), (8) and (6);

$$RS = (2.3kt)\left[1 + \frac{2.3}{6}kt\right]^3 RS_\infty \quad (11)$$

By rearranging Eq. (11) the following expression is obtained;

$$\left(\frac{t}{RS}\right)^{1/3} = \frac{1}{2.3k(RS)^{1/3}} + \frac{(2.3k)^{2/3}}{6RS^{1/3}}t \quad (12)$$

Eq. (12) is linear if $(t/RS)^{1/3}$ is plotted versus t. A and B parameters are calculated from Eq. (11) using linear regression. Eq. (13) and (14) gives the relationship with *k* and RS_∞ as;

$$A = (2.3.k(RS_\infty))^{-1/3} \quad (13)$$

$$B = \frac{(2.3k)^{2/3}}{6RS_\infty{}^{1/3}} \quad (14)$$

$$(t/RS)^{1/3} = A + Bt \quad (15)$$

From Eq. (13) and (14)

$$k_1 = 2.61\frac{B}{A} \quad \text{or} \quad k = 4.8387\frac{B}{A} \quad (16)$$

4. Results and discussion

4.1. Acidic and alkaline hydrolysis

Efficiency of acidic and alkaline concentrations (1-2-3% H_2SO_4 and NaOH) were investigated at in pretreatment of FW. Hydrolysis was conducted at 50-100-

120 ºC for 150 minutes. The results are seen in Figure 1. Increasing reaction temperature and retaining time raised RS values in all FW solutions. Lower RS values were obtained in hydrolysis experiments using NaOH and all solid matter concentration (5-20 g l^{-1}) compared to the hydrolysis experiments involving acid (Fig.1). The reason may be maillard reactions caused by high temperature and the increased pH (Vavouraki et al., 2013). It was seen that the pretreatment involving 2% of H_2SO_4 was more effective compared to base concentrations. Higher RS values were obtained.

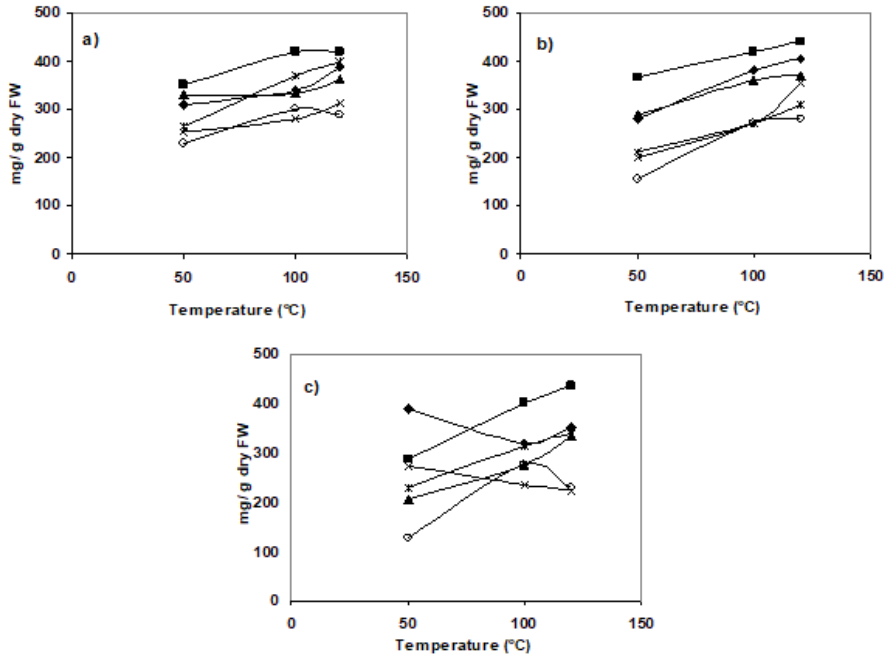


Figure 1. The extent of RS as a function of chemical concentration and temperature at 150 min a) 5 g l^{-1} FW, b) 10 g l^{-1} FW, c) 20 g l^{-1} FW. (◆) 1% H_2SO_4, (■) 2% H_2SO_4, (▲) 3% H_2SO_4, (×) 1% NaOH, (✱) 2% NaOH, (◇) 3% NaOH

4.2. *Kinetics of thermochemical pretreatment*

The datasets derived from thermochemical pretreatment experiments, as detailed in the preceding section, were subjected to kinetic analysis with respect to biomass hydrolysis (Eq. 15). The correlation coefficients of hydrolysis kinetics of the food waste at different temperatures and pHs are found. Hydrolysis rate constant (k) and correlation coefficient (R^2) are given Figure 2 and Table 3.

Additionally, Figure 2 illustrates the influence of pH on the hydrolysis rate constant at varying temperatures of food waste. It was as certained that the

values of the hydrolysis rate constant (1 min^{-1}) at 100 and 120°C are greater than those at 50°C.

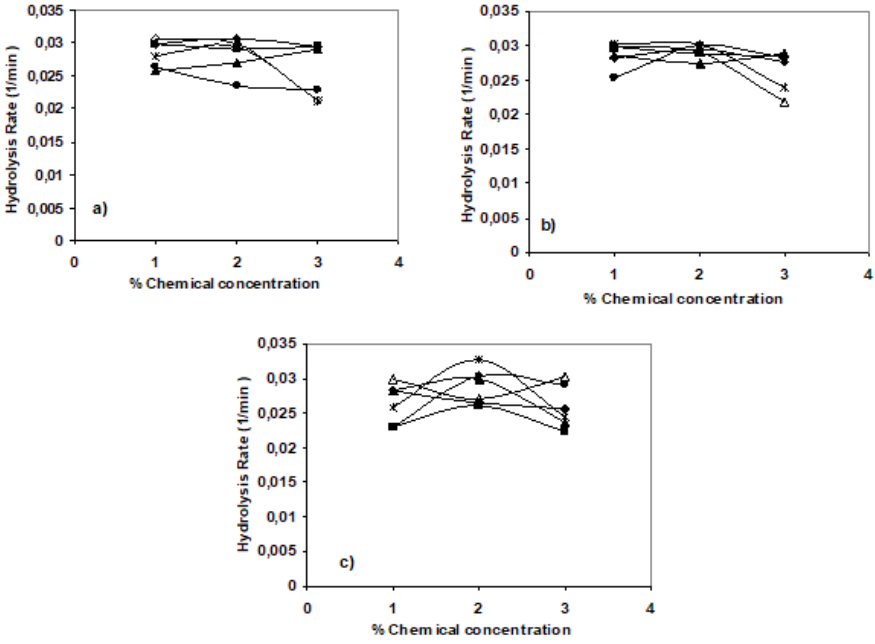


Figure 2. Hydrolysis rate constants for FW as a function of chemical concentration and temperature. a) 5 g l^{-1} FW, b) 10 g l^{-1} FW, c) 20 g l^{-1} FW. (◆) 50ºC H_2SO_4, (■) 100ºC H_2SO_4, (▲)120ºC H_2SO_4, (△) 50ºC NaOH, (✳) 100ºC NaOH, (✳) 120ºC NaOH.

Table 3: Calculations of Hydrolysis Rate Constant k and R^2.

FW (w/v)	Temperature (°C)	Chemical Concentration	k	R^2
5 g l^{-1}	50	1% H_2SO_4	0.0299	0.973
		2% H_2SO_4	0.0307	0.976
		3% H_2SO_4	0.0295	0.981
	100	1% H_2SO_4	0.0298	0.971
		2% H_2SO_4	0.0291	0.971
		3% H_2SO_4	0.0295	0.969
	120	1% H_2SO_4	0.0258	0.985
		2% H_2SO_4	0.0270	0.971
		3% H_2SO_4	0.0290	0.973
10 g l^{-1}	50	1% H_2SO_4	0.0283	0.977
		2% H_2SO_4	0.0295	0.977
		3% H_2SO_4	0.0276	0.978
	100	1% H_2SO_4	0.0298	0.972
		2% H_2SO_4	0.0289	0.968
		3% H_2SO_4	0.0284	0.971
	120	1% H_2SO_4	0.0286	0.970
		2% H_2SO_4	0.0275	0.972
		3% H_2SO_4	0.0288	0.972
20 g l^{-1}	50	1% H_2SO_4	0.0283	0.975
		2% H_2SO_4	0.0265	0.963
		3% H_2SO_4	0.0256	0.985
	100	1% H_2SO_4	0.0229	0.972
		2% H_2SO_4	0.0261	0.977

		3% H_2SO_4	0.0224	0.955
		1% H_2SO_4	0.0283	0.974
	120	2% H_2SO_4	0.0299	0.970
		3% H_2SO_4	0.0237	0.954
		1% NaOH	0.0308	0.979
	50	2% NaOH	0.0299	0.977
		3% NaOH	0.0212	0.972
		1% NaOH	0.0280	0.967
	100	2% NaOH	0.0295	0.972
5 g l^{-1}		3% NaOH	0.0212	0.972
		1% NaOH	0.2633	0.962
		2% NaOH	0.0236	0.955
	120	3% NaOH	0.0230	0.954
	50	1% NaOH	0.0299	0.974
		2% NaOH	0.0291	0.969
		3% NaOH	0.0220	0.990
		1% NaOH	0.0302	0.974
10 g l^{-1}	100	2% NaOH	0.0301	0.971
		3% NaOH	0.0240	0.947
		1% NaOH	0.0254	0.946
	120	2% NaOH	0.0300	0.972
		3% NaOH	0.0282	0.966
		1% NaOH	0.0300	0.973
	50	2% NaOH	0.0271	0.988

		3% NaOH	0.0304	0.975
		1% NaOH	0.0258	0.963
20 g l^{-1}	100	2% NaOH	0.0327	0.981
		3% NaOH	0.0244	0.954
		1% NaOH	0.0230	0.934
	120	2% NaOH	0.0303	0.975
		3% NaOH	0.0291	0.971

4.1. Hydrolysis of food waste

Arrhenius Eq. (17) gives relationship between temperature and reaction rate (Croft et al., 2000; Atkins and Paula 2001).

$$lnk = -\frac{\Delta H}{RT} + lnC \qquad (17)$$

Here, k = rate coefficient, T = Temperature (K), R = universal gas constant (8.314 J $Kmol^{-1}$), ΔH = activation energy (kJ mol^{-1}).

Figure 3 illustrates that the activation energy for the hydrolysis of food waste by bases is higher than that for acids, indicating a higher energy requirement for the hydrolysis of food waste by bases than by acids.

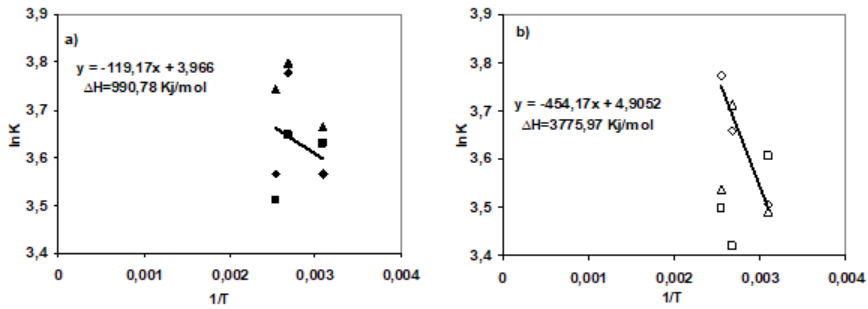


Figure 3. Activation energy for 20 g/l FW as a function of H_2SO_4–NaOH concentration and temperature a) Acidic and b) Alkaline. (✦) 1% H_2SO_4 (■) 2% H_2SO_4, (▲) 3% H_2SO_4, (◇) 1% NaOH, (□) 2% NaOH, (△) 3% NaOH.

4. Conclusions

Because FW has very high sugar content, FW was used as raw material in this study. Thus, valuable organic matters inside FW were recovered and the complex organic matters, which make bioethanol production harder, were converted into the compounds, which are usable more easily. In this study, it was observed that the increased reaction time and temperature raised RS values. It was observed that the pretreatment involving the use of H_2SO_4 is more effective compared to that involving the use of NaOH. It was seen that the acidic concentration of 2% gave better results. The values of maximum mg RS g^{-1} FW, 10 g l^{-1} were achieved by the temperature of 120 ^oC, 150 minutes of reaction time and at the acidic concentration of 2%. The raised temperature and retention time increases the pretreatment efficiency. An increase of 527% in RS value occurred compared to the waste, which had not undergone to pretreatment. It was therefore concluded that the thermochemical pretreatment represents an effective approach. The hydrolysis kinetics of the food waste results were found to be consistent with first-order reaction kinetics. A comparison of the hydrolysis rate constants for acidic and alkaline concentrations reveals that the hydrolysis of acids occurs at a faster rate than that of bases.

Acknowledgments

This work has been supported by Kocaeli University Scientific Research Projects Coordination Unit undergrant number BAP-2014/025.

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Bölüm 4

Galvanotechnic Industrial Site Waste Management

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Introduction

The increase in waste types and waste quantities in Turkey due to rapid economic growth, urbanisation, population growth and increase in welfare level has revealed the necessity of an integrated approach that includes all wastes instead of establishing a separate management system for each waste type. This approach has been supported by the Regulation on General Principles of Waste Management published in the Official Gazette dated 05.07.2008 and numbered 26927 and has been implemented until today (Anonymous, 2008). Initially, the practices were started to be carried out primarily by industries and municipalities that generate waste on a large scale and spread to all facilities in time. Seeing wastes not as rubbish but as recycled products make a great contribution to the national economy and in addition, the need for natural resources is reduced and our natural resources are protected. First, it is aimed to transform wastes into economic and raw material resources. On the other hand, all kinds of measures have become the priority to bring wastes into the economy and convert them into energy (Atçı and Ergülen, 2020). Waste management is a form of management that includes reduction of waste at its source, separation according to its characteristics, collection, temporary storage, interim storage, interim storage, recovery, transport, disposal and post-disposal control and similar operations (Ordu and Kaplan, 2016). The general principle in waste management should be to reduce waste at its source and to recover and reuse the inevitable wastes at the highest possible rate. Waste management is extremely important in terms of corporate sustainability policies implemented by businesses. In waste management, which considers waste as a resource, it is recommended that efforts should be made to prevent the formation of waste, and if this is not possible, to reduce it (Tezel and Yıldız, 2020).

Material and Method

Organised Industrial Zones are special zones whose establishment and operation principles are determined by the Organised Industrial Zones Law. According to the related law, Organised Industrial Zones are goods and service production zones, which are established for industry in a systematic manner and within certain systems by equipping pieces of land with approved boundaries with the necessary infrastructure services and social facilities and techno parks that can be allocated on demand, in order to ensure the structuring of industrial activities in appropriate places, to direct urbanisation, to prevent environmental pollution, to

benefit from information and information technologies, to ensure the establishment and development of production industries in a certain order, and to be operated according to the provisions of this law (Anonymous, 2000).

Waste types arising from factories operating in different sectors in Organised Industrial Zones also vary. These wastes can be listed as coating and metal processing wastes, reactive wastes, textile wastes, dyes, resins, waste oils, contaminated packaging, organic chemicals, etc. apart from domestic wastes. These wastes are accepted as hazardous wastes due to their effects on human health and the environment and should be disposed of without mixing with domestic wastes (Gündüz and Varınca, 2007).

The purpose of the establishment of İkitelli Organised Industrial Zone is to ensure that small and medium-sized industrialists, whose activities cause waste, emissions, noise, etc., which are harmful to human and environmental health, continue their activities without polluting the environment by gathering them in areas outside the settlement areas, in accordance with the principles of urbanism and with all kinds of infrastructure prepared. The industrial zone, which consists of a total of 27,301 workplace units in independent parcels, is 95 per cent completed, but 80 per cent operational (Anonymous, 2024).

Galvanotechnic Industrial Site is in Istanbul Başakşehir district, İkitelli Organised Industrial Zone and has been operating since 1995. It is an industrial site established by metal coating companies operating independently in different locations. There are a total of 190 companies in the site, 103 of these companies are in the galvanising sector and operate both as manufacturers and galvanisers, and some companies operate in the production and sale of chemicals. The number of companies that are not connected with galvanisation activities is quite small. Metal coating facilities with the largest production capacity of our country are in the site. The industrial site has 118.000 m^2 land and a total closed area of 92.000 m^2. The constructions are earthquake resistant (Ataş, 2006).

Metal plating processes are carried out to protect the metal against corrosion, to minimise surface roughness, to obtain maximum hardness and strength on the surface and to obtain a pleasant appearance. For this reason, mechanical polishing processes and electroplating methods are applied. In the electrolysis coating method, the chemical change of the coating metal is utilised by using organic and chemical materials electrolytically.

The steps of the metal coating process in the facilities located in Galvanotechnic Industrial Site are as follows: Firstly, raw materials are accepted to the facility

in appropriate numbers according to the order. Raw materials are sent to the cabinet or hanger assembly unit for coating according to their size. The small sized metal parts that come to be coated are taken into the boxes called cabinets with 8 corners and perforated surface and made ready for coating. Small metal parts are taken to the coating pools and transported between the pools by means of the cabinets. The large-sized raw materials coming to be coated are arranged on hook-shaped hangers and made ready for coating. Large metal pieces are taken into the coating pools and transported between the pools by means of hangers.

Then, pre-cleaning of oil, dirt and rust on the surfaces of small-sized raw materials placed in the cabinet unit is carried out. Temperature is an important criterion in the degreasing process. Generally, degreasing is carried out at a temperature between 60-70 °C. The chemical consumed in this unit is caustic cyanide. Small metal parts coming from the hot degreasing unit and large metal parts with completed hanger assembly are taken to the acid bath unit. The acid is used to remove oxidised, grease/oil contaminated and discoloured parts on the metal surface due to corrosion. The cleaning process with acid is called acid etching. In the acid etching process, the rust, oil and oxide layer on the surface is cleaned with acid without damaging the metal surface. The chemical consumed in this unit is hydrochloric acid.

Metal parts whose surfaces are cleaned with acid are taken into the caustic bath. The caustic solution neutralises the acidic film layer formed on the surface of the metal parts because of acidic cleaning and removes oxidised, rusty and oily parts that are insoluble in acid. In principle, the cleaned metal parts are kept in the caustic bath until the next zinc coating process, so that the contact of the metal surface with air is cut off and the oxidation of the cleaned metal surface is prevented. The cleaned metal parts are taken into the zinc bath and their surfaces are coated with zinc. The purpose of zinc coating is to provide protection by increasing the resistance of metal parts against corrosion, rust and abrasion.

Passivation: It is the name given to the prevention applied to prevent rusting. Iron metal is a metal with very low resistance to air, moisture, liquids and acids. The possibility of oxidation and rusting by chemical reaction is high. The purpose of passivation is a passivation process to prevent the surface from entering this chemical reaction. Passivation after zinc coating ensures that the coating is permanent. Yellow, green, white or black passivation types are applied.

After all cleaning and coating units except the hot degreasing unit, the metal parts are placed in a washing bath containing water to clean the chemical substances on their surfaces. Immersion method is used in the cleaning process. After

the last washing process after the passivation process, the metal parts are taken to the drying unit. Metal parts whose coating and washing processes are completed are taken to the drying machine and dried. After the drying process, the coated metal parts are taken to the warehouse. The finished product is made ready for sale according to the customer's order and stored until the shipment is made.

The results were generalised, and a waste management plan was created by evaluating 10 facilities selected as a sample from a total of 103 metal coating facilities located in the Galvanotechnic Industrial Site (Mete, 2019). Capacity, production, consumption etc. amounts of the selected facilities are as follows.

Facility 1;

Coating production quantity: 7.500.000 pieces/year

Chemicals used in the process:

-Nitric acid: 4.500 kg/year

-Sulphuric acid: 3.000 kg/year

-Phosphoric acid: 110.500 kg/year

Bathroom volume: 7 m^3

Number of people working at the facility: 8 persons

Amount of electricity consumption: 72.25452 kwh/year

Facility 2;

Coating production quantity: 6.960 kg/year

Chemicals used in the process:

-Copper anode: 2.846 kg/year

-Nickel anode: 591 kg/year

-Copper cyanide 766 kg/year

-Zinc cyanide 17 kg/year

-Sodium cyanide 342 kg/year

-Nickel sulphate 337 kg/year

-Sodium hydroxide 259 kg/year

-Sulphuric acid: 95 kg/year

Bathroom volume: 10.265 m^3

Number of people working in the facility: 6 persons

Amount of electricity consumption: 95.000 kwh/year

Facility 3;

Coating production quantity: 12.606 kg/year

Chemicals used in the process:

-Nickel anode: 7,174 kg/year

-Nickel sulphate 4.094 kg/year

-Sulphuric acid: 662 kg/year

-Sodium cyanide 751 kg/year

-Sodium hydroxide: 305 kg/year

-Copper cyanide 599 kg/year

Bathroom volume :14.97 m^3

Number of people working in the facility: 1 person

Amount of electricity consumption: 105.000 kwh/year

Facility 4;

Coating production quantity: 9.635 kg/year

Chemicals used in the process:

-Zinc acid: 9,635 kg/year

-Sodium cyanide 1,734 kg/year

-Sodium hydroxide: 1,349 kg/year

-Zinc oxide: 1,300 kg/year

Bathroom volume: 101 m^3

Number of people working at the facility: 9 persons

Amount of electricity consumption: 29.760 kwh/year

Facility 5;

Coating production quantity: 483.145 m^2 /year

Chemicals used in the process:

-Sodium carbonate 240 kg/year

-Sodium sulphate 3.890 kg/year

-Zinc sulphate 630 kg/year

-Sodium cyanide 9.850 kg/year

-Aluminium sulphate 460 kg/year

-Sodium hydroxide: 8.050 kg/year

Bathroom volume: 57.54 m^3

Number of people working at the facility: 9 persons

Amount of electricity consumption: 60.792 kwh/year

Facility 6;

Coating production quantity: 8.433 kg/year

Chemicals used in the process:

-Nickel anode: 5.913 kg/year

-Nickel sulphate 3,370 kg/year

-Nickel chloride 591 kg/year

-Chromic acid 2,520 kg/year

-Sulphuric acid 25 kg/year

-Sodium carbonate 75 kg/year

Bathroom volume : 40.41 m^3

Number of people working at the facility: 11 persons

Amount of electricity consumption: 207.432 kwh/year

Facility 7;

Coating production quantity: 27.000 m^2 /year

Chemicals used in the process:

-Sodium hydroxide: 100 kg/year

-Nitric acid: 500 kg/year

-Sulphuric acid: 600 kg/year

Bathroom volume: 9.057 m^3

Number of people working in the facility: 3 persons

Amount of electricity consumption: 80.000 kwh/year

Facility 8;

Coating production quantity: 21 tonnes/year

Chemicals used in the process:

-Sodium cyanide 500 kg/year

-Copper cyanide 500 kg/year

-Nickel chloride 150 kg/year

-Nickel sulphate 300 kg/year

-Nickel anode: 500 kg/year

Bathroom volume: 13.05 m^3

Number of people working at the facility: 11 persons

Amount of electricity consumption: 95.000 kwh/year

Facility 9;

Coating production quantity: 198.000 pieces/year

Chemicals used in the process:

-Nickel anode: 1.500 kg/year

-Chromic acid: 600 kg/year

-Sodium hydroxide: 150 kg/year

-Nitric acid 250 kg/year

-Nickel sulphate 200 kg/year

Bathroom volume: 17.54 m^3

Number of people working in the facility: 6 persons

Amount of electricity consumption: 120.000 kwh/year

Facility 10;

Coating production quantity: 207.900 m^2 /year

Chemicals used in the process:

-Zinc oxide: 315 kg/year

-Sodium carbonate 108 kg/year

-Sodium hydroxide: 1.258 kg/year

-Sodium chloride 154 kg/year

-Sodium cyanide 453 kg/year

-Aluminium sulphate 219 kg/year

-Zinc anode: 7.052 kg/year

Bathroom volume: 25.878 m^3

Number of people working in the facility: 3 persons

Amount of electricity consumption: 155.000 kwh/year

All the relevant facilities have an Environmental Impact Assessment (EIA) Not Required decisionwithin the scope of the Environmental Impact Assessment Regulation and an Environmental Permit Opinion Letter within the scope of the Environmental Permit Regulation.

Non-hazardous wastes generated in Galvanotechnic Industrial Site are collected in the storage areas, which are common collection areas in each block of the site and sent to the licensed company contracted by the relevant municipality.

Hazardous wastes from the facilities in the Industrial Site are individually sent to licensed recovery and disposal facilities contracted by the facilities.

There is a cafeteria in the management building of Galvanotechnic Industrial Site. In addition, no vegetable waste oil is generated since there is no individual cooking in the facilities. Vegetable waste oils from the cafeteria in the administration building are sent to the licensed recovery company because of the contract made with the licensed company. No medical waste is generated since no medical procedures are performed in the facilities. An average of 1 kg waste battery is generated annually from the daily use of the personnel in the facility. The waste generated is sent to a licensed recycling company (Mete, 2019).

Based on the example of 10 facilities, the monthly average amount of waste generated in Galvanotechnic Industrial Site is as follows.

Process wastes.

15 01 01 Paper and Cardboard Packaging: 3.090 kg/month

15 01 02 Plastic Packaging: 2.575 kg/month

15 01 10* Packages containing residues of dangerous substances or contaminated with dangerous substances: 5.150 kg/month

15 02 02*: Absorbents, filter materials contaminated with hazardous substances (oil filters, cleaning cloths, protective clothing, if not otherwise specified: 2.060 kg/month

15 01 11*: Metallic packaging containing hazardous porous solid structure (e.g. asbestos), including empty pressurised containers: 515 kg/month

Office generated waste.

08 03 17* Waste printing toner containing hazardous substances: 50 kg/month

16 02 13* Discarded equipment containing hazardous parts other than those specified in 16 02 09 to

16 02 12: 50 kg/month

20 01 21* Fluorescent lamps and other waste containing mercury: 75 kg/month

16 06 05 Other batteries and accumulators: 103 kg/month

Results

When the changes in the hazardous wastes generated in Galvano Technical Industrial Site in the last 3 years are analysed; increases in some waste types are observed. The number of oakum clothes is increasing every year since gloves are not used consciously and are not of sufficient quality. Contaminated packaging, chemical drums and pressurised tubes in pressurised tube waste types show an increase according to increasing production and consumption capacities. Wastes such as fluorescents, cartridges and toners from the facilities remain at the same amounts. Companies individually accumulate their hazardous wastes in temporary storage areas and send them to be licensed recovery/disposal facilities.

When the changes in the non-hazardous wastes generated in Galvanotechnic Industrial Site in the last 3 years are examined; no change in quantities has been observed due to the small amount of packaging wastes generated by production. Non-hazardous wastes are collected in the common areas of the industry.

No process change is considered for waste minimisation and prevention in plant processes. However, to minimise the amount of hazardous waste, refillable cartridges used in the office are preferred. For the batteries used in the facility; rechargeable batteries are preferred. Fluorescent lamps with long life are used. LED lights can be preferred instead of fluorescent lights for fluorescent waste generated by the office to reduce waste. Used chemical drums can be sent to recycling facilities instead of disposal facilities. Awareness raising trainings are

given on separate collection of hazardous and non-hazardous wastes and not mixing them.

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Bölüm 5

Health and Safety Culture in Workplace Environments in Turkiye – A Survey

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1. INTRODUCTION

The importance of living and working environment for human health is undeniable. Turkiye, due to increasing industrialization, population growth, and agricultural activities, not only has to combat environmental pollution but also needs to improve these intense and challenging working conditions, taking precautions against risks arising from hazards and dangers. The dimensions of environmental pollution have increased due to the diversity of industrial activities. There is a variety of environmental pollution ranging from wastewater containing antibiotics, heavy metals, and biological contaminants originating from heavy industries such as textiles, pharmaceuticals, electronics, and the iron-steel industry, to soil and air pollution (Ata R., Tore G.Y., 2019; Ata R, Tore G.Y, Shah M.P., 2021). When wastewater, air, and soil pollution are not adequately treated, it leads to the contamination of water used for agricultural irrigation, thus causing adverse effects on human health due to a toxic food chain, resulting in a variety of diseases, primarily cancer and endocrine system disorders. To treat these endless varieties of pollution from water, air, and soil, various treatment techniques have been implemented, and Turkish regulations have been updated in this regard (Ata R, Tore G.Y., 2019; Ata R., Merdan G.F., 2022).

Since 2005, the continuously published and updated legislation related to the environment and health has ensured a certain progress in health and safety issues in the country. The next step after compliance with the necessary legislation will be to advance to a higher level and to establish a Health and Safety (HS) Culture. It is a well-known fact that a culture surrounding environmental and health issues begins in the working environment. Establishing this awareness and culture of environment and health in workplaces is the path to reflecting this to the public.

Health and Safety Culture in Workplace Environments (HSC-WE) is a system of shared values and behaviors that encompass an organization's beliefs, attitudes, norms and practices. HSC-WE is about taking the necessary precautions to protect the safety and health of employees in the workplace environment and constantly applying these measures in the workplace and determines how employees will behave in the face of dangers in the workplace, how much they will comply with safety policies and to what extent they will assume their responsibilities. HSC-WE not only reduces risks for the accidents and diseases, but also increases employee morale, increases productivity and positively affects the overall performance of work environment.

HSC-WE are influenced by organizational culture. Organizational culture is a commonly used concept to describe shared organizational values that influence

workplace members' attitudes and behaviors. An independent safety culture cannot be divorced from organizational culture, which defines the conditions or environment under which a workplace operates. (Cooper, M.D., 2000).

HSC-WE is shaped not only by rules and regulations but also by the values and behaviors of the organization. This culture should encompass not only the physical health of employees but also their psychological well-being. Adopting this culture within the organization can increase employee satisfaction and help prevent workplace accidents and occupational diseases (Conklin T., 2017).

Elements that constitute HSC-WE;

1. Management Commitment: The basis of HSC-WE is management's commitment to this issue. Top management's determination and leadership regarding occupational safety gives an important message to employees and shapes their attitudes towards safety.

2. Training and Awareness Raising: Raising awareness and training of employees about HSC-WE is critical to preventing accidents. Regular training programs and briefings ensure that employees understand and follow safety procedures.

3. Communication: Open and continuous communication plays an important role in developing a safety culture. The ability of employees to freely share their concerns, suggestions and feedback regarding security strengthens the security culture.

4. Participation and Cooperation: Employees should be encouraged to actively participate in occupational safety processes. Safety committees, employee representatives and regular meetings increase employees' responsibilities regarding HSC-WE.

5. Continuous Improvement: HSC-WE should be constantly monitored and improved. Regular inspections, risk assessments and performance measurements help maintain and improve safety standards.

6. Legal compliance: It involves ensuring compliance with local and international HS regulations, establishing a program to stay informed of regulatory changes, and updating and adapting policies accordingly (Conklin T., 2017; Acar M.N., 2024).

The importance of worker hygiene and health in HS is great. In this context, GMP, GLP systems should be established and continuously developed in the work environment, and the validation of heat, humidity and thermal conditions

in the work environment should be carried out by experts at certain periods (Ata R. 2023).

HSC-WE protects the HS of employees. Work accidents and occupational diseases cause serious costs for both employees and employers. A strong HSC-WE prevents such incidents and minimizes workforce losses and compensation costs. Knowing that employees work in a safe environment increases their morale and motivation. A safe workplace reduces employees' stress levels and increases job satisfaction. Safe working conditions ensure that business processes proceed uninterruptedly and smoothly. Reducing work accidents prevents disruption of business processes and increases productivity. HSC-WE protects and strengthens the reputation of businesses. Regulatory compliance helps businesses avoid fines and penalties. Identifying and evaluating existing risks in the workplace to improve HSC-WE is the first step in creating a safe working environment. Risks need to be managed, measures to be taken must be determined and these measures must be constantly updated. A proactive approach should be adopted in developing HSC-WE, instead of taking precautions after accidents occur, proactive measures should be taken to prevent accidents. Establishing safety committees in the workplace and functioning of these committees effectively contributes to the development of safety culture. These committees provide a platform where employees can voice their safety concerns and suggestions. Systems that reward and encourage safe behavior increase employees' awareness of occupational safety and reinforce positive behavior. Regular workplace inspections and monitoring activities help maintain and improve safety standards. Necessary corrective and preventive measures should be taken according to the inspection results.

In conclusion, HSC-WE is an indispensable element for the sustainable success to protect the health and safety of employees while also positively affecting the performance of the business. Continuously monitoring and improving HSC-WE provides long-term benefits for both employees and businesses.

1.1. Purpose and Significance of the Study

As detailed in the introduction section, according to statistical data from the Social Security Institution, the sectors of construction, medical, chemical, and energy industries classified as highly dangerous and dangerous show high rates of work-related accidents, fatalities, injuries, and occupational diseases. Therefore, the investigation of HSC-WE in these prominent sectors concerning work accidents and occupational diseases has gained importance in this thesis. International literature studies have also recommended the exploration of HSC-WE in these sectors (Cakıt E, et al., 2019).

While reducing work accidents and diseases may be easier in developed countries, developing a HSC-WE in developing countries is a challenging task that requires continuous and renewed efforts from legislators, organizations, and employees. In this context, while globally applicable frameworks and tools exist, it is necessary to establish national frameworks and tools. Therefore, this study aims to contribute to the creation of national frameworks and tools by presenting the HSC-WE, particularly after Law No. 6331, in prominent sectors such as medical, construction, chemical, and energy, highlighting work accidents and diseases in our country alongside existing studies in the literature."

2. MATERIAL AND METHOD

In this study, a non-experimental, cross-sectional quantitative research design was preferred to investigate the HS culture in sectors such as medical, construction, chemical and energy, which carry a high risk in terms of occupational accidents in Turkey. Cross-sectional research allows the evaluation of the current situation by collecting data in a certain period of time and allows the examination of multidimensional concepts such as HS culture in a large group of participants (Dolma & Dolma, 2017). This method contributes to a broad understanding of existing risks and safety awareness, especially in health and safety research (Sandelowski, 2000).

2.1. Data Collection Instruments

In this study, to evaluate the perceptions of employees in sectors with high physical risks related to work, a 55-question survey was applied to employees in sectors such as medical, construction, chemistry and energy under three main headings. These headings are "Demographic Information", "Safety Attitude and Safety Awareness", and "Safety Behavior", respectively. The aim of the survey is to measure the safety attitudes and awareness levels of employees, as well as to examine whether there has been an improvement in the safety culture and a decrease in work-related injuries after the Health and Safety Law No. 6331. Under these headings, there are 6 demographic questions, 21 questions on safety attitude and safety awareness, and 27 questions on safety behavior, respectively. The survey also includes an open-ended area where participants can express their free ideas and present their opinions and suggestions.

The majority of the survey used a Yes/No scale, with a 5-point Likert scale being preferred for more specific situations. These scales allow for a more detailed assessment of participants' perceptions and attitudes regarding safety culture (Likert, 1932). The survey questions were prepared based

on my experience as an Health and Safety (HS) review of previous studies on HS Culture (Sandelowski, 2000). Participants were asked to consider the situation within the framework of the HS Law No. 6331, particularly after 2012. This is important for understanding the effects of the implementation of the law on employees' safety attitudes and behaviors (Çalışkan, 2015).

2.2. Survey Technique

The survey technique was preferred as the data collection method in the study. It includes questions aimed at evaluating employees' perceptions of safety culture, HSE-WE and the effects of these practices. The questions are based on the development of HS Culture after the Law No. 6331 and the effects of this development on work performance, and the concepts of safety awareness, safety attitude and safety behaviors in the safety culture literature (Cooper, 2000).

2.3. Data Analysis

The obtained data were analyzed using SPSS Windows version 23.0 package program. The significance level in statistical analyses was accepted as $p<0.05$. In the analysis of the data, the relationships between demographic characteristics (age group, education level, etc.) and security attitudes, awareness and behaviors were evaluated. Skewness and Kurtosis methods were used to test the conformity of the obtained data to normal distribution. Skewness and Kurtosis are two important statistical measures used to evaluate whether the data is normally distributed. (Kalaycı, 2014).

When the skewness value moves away from zero, it indicates that the distribution is biased to the right or left. In a normal distribution, the skewness value is generally accepted between -2 and +2 (Kalaycı, 2014).

In addition, Cronbach's Alpha coefficients were calculated to test the validity and reliability of the survey. Cronbach's Alpha is a coefficient that measures the internal consistency and reliability of the survey, and values of 0.70 and above are generally considered sufficient (Nunnally, 1978).

Exploratory Factor Analysis was applied to better understand, interpret and test the question items of the survey. Factor analysis allows the variables in the data set to be grouped under basic factors or sub-dimensions and makes data structures more meaningful (Field, 2013). The Kaiser-Meyer-Olkin (KMO) Test and the Bartlett Sphericity Test were used to assess the applicability of this analysis. The KMO test measures whether the sample size is suitable for factor analysis, while the Bartlett Sphericity Test evaluates

whether the correlation matrix between the question items is suitable for factor analysis (Kaiser, 1970; Bartlett, 1954). The results of these tests play a critical role in determining whether the data are sufficient for factor analysis and the reliability of the findings to be obtained because of the analysis.

Based on the survey results, the sectoral differences of HS Culture and its effects on employees were examined.

2.4. Demographic Characteristics and HS Culture Relationship

The age groups and education levels of the employees were also analyzed and the relationships between HS culture and demographic variables were evaluated. Research shows that age and education level influence safety culture and safety behaviors (Neal & Griffin, 2004). It has been frequently emphasized in the literature that employees with higher education levels may be more sensitive in terms of safety awareness and attitudes (Vinodkumar & Bhasi, 2010). Similarly, the effect of the age factor on HS behaviors was also evaluated within the scope of the research.

2.5. Change in HS Culture After The Law No. 6331

An important dimension of the research is to address the changes observed in HS culture after the Law No. 6331. This law was enacted to strengthen HS practices in workplaces and prevent occupational injuries. The survey results reflect the perceptions of employees regarding the development of HS culture in the sectors where the law is implemented and evaluate the effectiveness of the law based on these perceptions (Özkan & Lajunen, 2011).

This research was conducted to understand the current status of HS culture in high-risk sectors in Turkey and to evaluate the safety attitudes, awareness and behaviors of employees, and aimed to obtain reliable results with the help of quantitative data collection techniques and statistical analyses.

2.6. The Universe and Sample of the Research

In this study, sectors with high risks in terms of occupational injuries throughout Turkey were determined as the universe. In particular, the medical, construction, chemical and energy sectors were defined as sectors that stand out in terms of the frequency of occupational injuries and work-related illnesses. These sectors were determined as critical areas where HS culture should be developed due to their high risk and danger (Berg & Hällgren, 2017; Yorio et al., 2014).

The sample consisted of 220 employees selected by random sampling method within this universe. Random sampling is a method in which everyone has an

equal probability of being selected for the sample, and thus the sample provides a high accuracy in representing the universe (Cochran, 1977). The employees were randomly selected from various companies operating in the medical, construction, chemical and energy sectors. This selection was made to make comparisons between sectors and to ensure the generalization of the results.

The sample size and selection method were meticulously determined to increase the validity and reliability of the research. The sample of 220 people provides sufficient representative power and is an appropriate size to evaluate sectoral differences and examine the sectoral effects of HS culture (Fink, 2013).

2.7. Ethical Aspects of the Study

This study was produced from Rumeli University Master's Thesis. The study was approved by Istanbul Rumeli University Scientific Research and Publication Ethics Committee on 28.12.2023.

3. RESULTS AND DISCUSSIONS

3.1. Demographic Portrait of Participants

The demographic characteristics of the participants of the survey on HS culture were examined. The analysis of demographic characteristics provides information about the general profile of the data set, allowing a better understanding and interpretation of the research findings. The frequency distribution of the demographic characteristics of the participants is presented in Table 1 below.

Table 1. Distribution of Demographic Characteristics of Participants

Characteristics		**N**	**%**
Gender	*Mail*	149	67,72
	Femail	71	32,28
Age Range	*18-29*	61	27,72
	30-45	97	44,09
	46-55	58	26,36
	65 üstü	4	1,81
Education	*Primary education*	57	25,91
	High school	94	42,72
	Undergraduate / Associate degree	60	27,27
	Graduate	9	4,09
Working Seniority	*0-5 years*	54	24,55
	6-10 years	116	52,73
	11-19 years	36	16,36
	20 years and more	14	6,36

When the data on demographic characteristics of the employees participating in the survey are examined; In terms of gender distribution, 67.72% of the participants were male and 32.28% were female. This distribution reflects the diversity of the sectoral workforce and provides important data for evaluating gender-based differences in HS culture (Morrison et al., 2018).

In terms of age range, the most of the participants were between the ages of 30-45 (%44.09). 27.72% of the participants were between the ages of 18-29, 44.09% were between the ages of 30-45, 26.36% were between the ages of 46-55 and 1.81% were over the age of 65. This is significant for examining the effect of age group on experience and safety attitude (Kelloway & Francis, 2013).

When the educational status was examined, it was determined that 42.72% of the participants were high school graduates, 25.91% had primary school, 27.27% had undergraduate or associate degree and 4.09% had postgraduate education. The effects of education level on HS culture can be analyzed with this data (Sweeney & McFarlin, 2002).

When evaluated in terms of the duration of employment, 52.73% of the participants have been working for 6-10 years, and it is important to evaluate the effect of this experience on safety attitudes and behaviors (Parker et al., 2003).

This demographic data will be used to better understand the participants' attitudes and behaviors on HS culture while interpreting the findings of the study. In addition, analyses on the effects of certain demographic groups on safety culture and behaviors can increase sectoral and vital awareness.

3.2. Evaluation of Reliability and Exploratory Factor Analysis of the Survey

The factor analysis and internal consistency tests of the survey applied to evaluate the HS culture were examined in detail. The Kaiser-Meyer-Olkin (KMO) test and Bartlett Sphericity Test results, which were performed to evaluate the reliability and validity of the survey, show that the data set is suitable for factor analysis.

The value obtained because of the KMO Test was found to be 0.870. This value reveals that the sample size and data are homogeneously distributed. A KMO value above 0.60 indicates that the factor analysis is suitable, and the data are suitable for factor analysis (Field, 2013).

The p value of the Bartlett Sphericity Test was calculated as $p < 0.01$. This result indicates that there is a significant correlation between the variables in the data set and that it is appropriate to analyze the relationships between the factors.

The p value of Bartlett's Sphericity Test being found to be less than 0.05 indicates that the correlations between the factors are strong and the factor analysis is valid (Hair et al., 2010).

Cronbach's Alpha Coefficients were calculated to test the internal consistency and reliability of the survey. In terms of Factor Loadings and Cronbach's Alpha Coefficients, in the analyses made in terms of the factors of the main question items of the survey, "Safety Attitude and Safety Awareness" (HSE-F2) and "Safety Behavior" (HSE-F3), it was determined that questions 12-21 for HSE-F2 and questions 5-12 for HSE-F3 had high factor loadings. These results show that these questions are good representatives of the relevant factors and provide internal consistency of the factors (Brown, 2003).

Cronbach's alpha value for HSE-F2 factor was found as 0.721 and for HSE-F3 factor as 0.710. These values show that both factors have high internal consistency, and that the data obtained from the survey are reliable. A Cronbach's alpha coefficient higher than 0.60 confirms that the reliability of the survey is ensured, and the measurement tool used is valid (Gürbüz & Şahin, 2014).

The factor values corresponding to the question items and the Coranbach's Alpha values of the factors are given in Table 2.

Table 2. Factor Values and Coranbach's Alpha Values of Factors

Factor Nr / Type	Survey Question Item Number	Factor Load	Coranbach's α Values
HSE-F2 Safety Attitude and Security Awareness	Question 12	0,671	0,721
	Question 13	0,666	
	Question 14	0,639	
	Question 15	0,626	
	Question 16	0,601	
	Question 17	0,599	
	Question 18	0,576	
	Question 19	0,572	
	Question 20	0,556	
	Question 21	0,506	
HSE-F3 Safety Behavior	Question 5	0,660	0,710
	Question 6	0,611	
	Question 7	0,606	
	Question 8	0592	
	Question 9	0,565	
	Question 10	0,546	

Question 11	0,506
Question 12	0,496

In the survey, HSE-F2 consists of 21 questions, HSE-F3 consists of 27 questions and factor 3 consists of five questions. As can be seen in Table 2, the fact that the α coefficients of all factors are greater than 70 reveals that the question items in the factors are consistent among themselves and represent the factors in question well.

3.3. Normality Test

In order to decide whether parametric or non-parametric tests will be used in the statistical analysis study applied to the survey data,

"H0 = Data is normally distributed." The hypothesis was accepted.

Skewness and Kurtosis methods were used to test the normality assumption. If the Skewness and Kurtosis coefficients are between -2 and +2, the data is normally distributed (Kalaycı, 2014). Table 3. shows the Skewness and Kurtosis values of the HSC-WE dimensions used in the research.

Table 3. Skewness and Kurtosis values of HSE safety culture dimensions

	HSE - F2	HSE - F3
Skewness	-1,006	0,369
Kurtosis	1,134	-0,211

As seen in Table 3., it was determined that the data was in accordance with the normal distribution assumption and parametric tests could be applied, since the Skewness and Kurtosis values were between -2 and +2.

3.4. HS Culture Tendencies of Participants

In this study, in order to determine the HS Culture tendencies of the participants, the descriptive statistical values of the "Safety Attitude and Safety Awareness" (HSE-F2) and "Safety Behavior" (HSE-F3) factors of the main question items of the HS Culture survey, which are the mean, mode and median values contributing to the HS Culture tendency measures, were calculated and are given in Table 4.

The average score of female participants regarding Safety Attitude and Safety Awareness (HSE-F2) was determined as 4.18. This value shows that women's tendencies towards HS culture are generally high. The median value is 3.6, indicating that most women gather around this score. The mode value is 4, indicating that these women evaluate it most frequently as "Exceeds expectations".

The average score of male participants regarding Safety Attitude and Safety Awareness (ISG-F2) was 3.45, indicating that the median value was determined as 3.4. It shows that the most men gather around this score. The mode value is 3, indicating that men mostly evaluate it as "Meets expectations".

The average score of female participants regarding Safety Behavior (HSE-F3) regarding their tendencies towards ongoing practices and HS Culture in the workplaces they work was calculated as 3.78. The median value is 3.2, indicating that there is a wider distribution around this score. The mode value is 3, indicating that women most frequently evaluate it as "Meets expectations". The mean score for male participants is 3.86, and the median value is 3.8. The mean score for men is slightly higher than for women, indicating a similar trend with the mode value of 3. The standard deviation values of the data indicate the variation in the participants' answers. The standard deviation values for women and men reveal how much the answers differ. These analyses help determine how HS culture practices differ by gender and general trends. Differences in women's and men's perceptions of HS culture can enable the development of various strategies.

Table 4. HSC-WE Tendencies of Participants

Factor (Sub-Dimension)	Gender	Safety Attitude and Security Awareness	Safety Behavior
Mean	Female	4,18	3,78
	Male	3,45	3,86
Median	Female	3,6	3,2
	Male	3,4	3,8
Mod	Female	4	3
	Male	3	3
Std. Deviation	Female	0,68	0,62
	Male	0,72	0,64

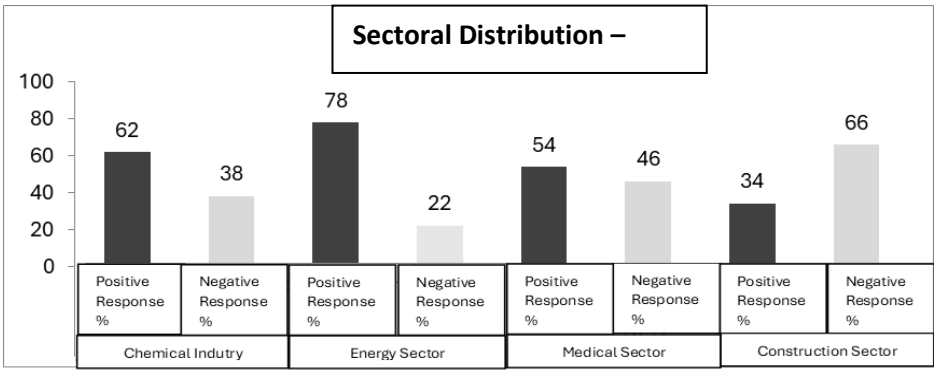
3.5. The density of sectors on the sub-factors that make up the HS Culture

The distribution of the "HSE-F2 (Safety Attitude and Safety Awareness)" and "HSE-F3 (Safety Behavior)" factors used to measure the HS culture in the survey applied in the study by sectors is given in Table 5 and Graph 1.

Table 5. Sectoral Distribution of Responses to Survey Questions

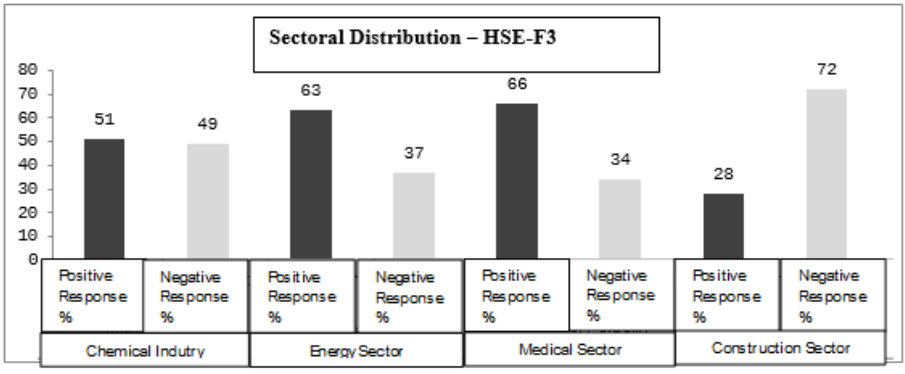
Factor	Chemical Industry		Energy Sector		Medical Sector		Construction Sector		Other Sector	
	Positive Response %	Negative Response %	Positive Response %	Negative Response %	Positive Response %	Negative Response %	Positive Response %	Negative Response %	Positive Response %	Negative Response %
HSE-F2	62	38	78	22	54	46	34	66	38	62
HSE-F3	51	49	63	37	66	34	28	72	27	73

As can be seen in Graph 1, the Energy Sector is at the top with 78% of the positive responses to questions on "HSE-F2 (Safety Attitude and Safety Awareness)", followed by the Chemical Sector with 62%, the Medical Sector with 54% and the Construction Sector with 34%. It was determined that the sector with the most negative responses was the Construction Sector with 66%.



Graph 1. Sectoral Distribution of Security Attitude and Security Awareness

As can be seen in Graph 2, the Medical Sector is at the top of the list with 66% of positive responses to questions regarding “HSE-F3 (Safety Behavior)”, followed by the Energy Sector with 63% and the Chemical Sector with 51%.



Graph 2. Sectoral Distribution regarding Security Behavior

Likewise, it was determined that the sector in which negative answers were given most to the questions regarding "HSE-F3 (Safety Behavior)" was the construction sector with 72%.

3.6. Correlation Analyzes

The results of the Pearson Correlation Analysis between OSH and the factors that support its measurement, namely “HSE-F2 (Safety Attitude and Safety Awareness)” and “HSE-F3 (Safety Behavior)”, and again between HS and the Level of Education of the participants are given in Table 6.

Table 6. Correlation Analysis Between HS Culture in Workplace Environments and Factors

Factors	HSE-F2 (Safety Attitude and Safety Awareness)	HSE-F3 (Safety Behavior)	Education Level
HSE - F2 (Safety Attitude and Safety Awareness)	1,000	0,623**	0,456**
HSE-F3 (Safety Behavior)	0,623**	1,000	0,321*
Education Level	0,456**	0,321*	1,000

* p<0,05,. ** p<0,01

As seen in Table 6, the Pearson correlation coefficient between HSE-F2 (Safety Attitude and Security Awareness) and HSE-F3 (Safety Behavior) was calculated as 0.623. This shows that there is a moderate positive relationship between these two factors. In other words, it is seen that individuals with high security attitude and awareness tend to have high security behaviors. The correlation coefficient between HSE-F2 (Safety Attitude and Security Awareness) and Education Level is 0.456 and this value is significant at 99% confidence level. This finding shows that security attitude and awareness tend to change positively with increasing education level. The correlation coefficient between HSE-F3 (Safety Behavior) and education level is 0.321 and this value is significant at 95% confidence level. This result shows that security behaviors can be partially positively affected with increasing education level, but the relationship is weaker.

These analyses provide important information in understanding the relationships between various dimensions of HS culture and the education levels of the participants. It is seen that the relationship between the education level and safety attitude and awareness is strong, which emphasizes the role of education in developing HS culture. There is a weak and positive relationship between primary

school level employees and total HS culture. This relationship is statistically significant but shows a low correlation (r-value: 0.320, p-value: 0.015 ($p < 0.05$)).

A moderate positive relationship was observed between high school level employees and total HS culture. This relationship is statistically significant and shows that HS culture increases with the increase in education level (r-value: 0.410, p-value: 0.002 ($p < 0.01$)). There is a moderate-high positive relationship between undergraduate level employees and total HS culture. This relationship is significant and shows that the level of education has a significant effect on HS culture (r-value: 0.495, p-value: 0.000 ($p < 0.01$)). There is a highly positive relationship between graduate level employees and total HS culture. This relationship is statistically very significant and shows that the level of education makes a strong contribution to HS culture (r-value: 0.575, p-value: 0.001 ($p < 0.01$)). A positive relationship was observed between the increase in the level of education and total HS culture. Especially the high correlation between graduate level employees and HS culture shows that higher levels of education increase the capacity to better understand and implement HS culture. These findings support that expanding the scope of training programs and encouraging education in workplaces will contribute to the improvement of HS culture.

Table 7. Correlation Analysis Between HS Culture and Education Level

Education Level	Pearson Correlation (*r*)	p-value
Primary School	0,320	0,015*
High School	0,410	0,002**
Undergraduate Education	0,495	0,000**
Postgraduate Education	0,575	0,001**

* p<0,05,. ** p<0,01

4. CONCLUSIONS

The Cronbach Alpha value of the survey answered by 220 participants working in the fields of Medical, Construction, Chemical and Energy production, which are prominent sectors in terms of occupational accidents, was determined as 0.721 for the Safety Attitude and Safety Awareness factor, which are sub-dimensions of the HS culture, and 0.710 for the Safety Behavior factor. The first part of the survey included questions on demographic information of the participants. The fact that the Kaiser-Meyer-Olkin (KMO) test value (0.879) of the data

matrix obtained from the second and third parts of the survey was greater than 0.60 indicates that the data matrix is suitable for factor analysis. According to the participants, the factor "Safety Attitude and Safety Awareness" and the factor "Safety Behavior" were found to have close importance values. In terms of gender among demographic variables, a greater difference was observed in the opinions of female participants regarding the factor "Safety Attitude and Safety Awareness" compared to the factor "Safety Behavior". On the other hand, it was determined that the "Safety Behavior" factor had a more positive effect on male participants than female participants. The survey results revealed that female participants had higher Safety Attitude and Safety Awareness, while male participants had higher Safety Behavior. The correlation analysis conducted showed that there was a significant and positive relationship at a reliability level of 95% between HS Culture and the sub-dimensions "Safety Attitude and Safety Awareness" in all sectors, and a significant and positive relationship at a reliability level of 99% between HS Culture and "Safety Behavior". This supports that HS culture consists of Safety Attitude, Safety Awareness and Safety Behavior. The correlation analysis between the education levels of participants in all sectors and HS culture also statistically reveals that as the education level increases, Safety Attitude and Safety Awareness, and therefore Safety Behavior, increases positively. In this study, it was determined that the sector with the highest "Safety Attitude and Safety Awareness", which is an important factor of HS Culture, is Energy, and the sector with the lowest is Construction. This situation can be attributed to the fact that companies in the Energy sector are generally companies with international connections or partnerships and therefore are more familiar and compliant with HS practices, while the education level of employees in companies in the Construction sector is relatively lower.

This study, which reveals the perspective of HS Culture in the Medical, Construction, Chemical and Energy Sectors, has made a significant contribution to the literature in terms of occupational accidents. When the findings obtained as a result of this research are compared with the studies conducted in the literature, Cronbach Alpha values of 0.70 and above are generally considered acceptable in studies on HS culture (Nunnally, 1978). It is stated that factor analysis is appropriate when the KMO value is above 0.60 (Kaiser, 1974). The findings obtained in this study support that a reliable analysis is provided. The differences between "Safety Attitude and Safety Awareness" and "Safety Behavior" between sectors have also been addressed by various studies. For example, better safety behaviors can be observed in sectors where "Safety Attitude and Awareness" are high (Zo-

har & Luria, 2005) and these findings are consistent with the literature. Differences between genders have also been examined in the literature. It has also been observed in some studies in the literature that women have higher safety attitudes and men show higher safety behaviors (Gunningham & Sinclair, 2000). The fact that Safety Attitude, Awareness and Behavior increase with increasing education level is a finding emphasized in the literature. It has been shown that educated individuals adopt and implement HS culture better (Burke et al., 2006). The differences between the energy and construction sectors have been addressed in the literature as differences in safety culture on a sectoral basis. The higher safety culture in the energy sector can be explained by the fact that this sector is compatible with international standards and generally has more advanced safety practices. The low safety culture in the construction sector is generally associated with lower education levels and less advanced safety practices.

When this thesis study is evaluated in terms of whether it meets the hypotheses established at the beginning of the study, it is assumed that safety attitude and safety awareness are related to organizational commitment and organizational culture, and it is found in the literature that a strong organizational culture positively affects HS culture (Hofmann & Stetzer, 1996). Leadership commitment and management participation generally play a critical role in the development of HS culture (Zohar & Luria, 2005). The hypotheses on training and employee participation are also compatible with the findings obtained in the study. The innovative aspects of this thesis study are that it is a study conducted with a wide range of sectors including Medical, Construction, Chemical and Energy sectors, and it allows for the comparison of HS culture in different sectors, as well as offering a different approach from the studies generally conducted in the literature limited to a single sector. In addition, revealing the significant and positive relationships between HS Culture and its sub-dimensions with a detailed correlation analysis supports the statistical accuracy of these relationships and strengthens the literature on this subject. It is also emphasized in the literature that HS culture should be researched and disseminated in all sectors (Hofmann & Stetzer, 1996). In this sense, this study has made a significant contribution in terms of occupational accidents and research should be conducted in other sectors. At the same time, this thesis study has also led to the research of HS Culture in terms of occupational diseases in these sectors. In addition, dissemination of such studies to all sectors will contribute to the increase of HS Culture. Detailed research can be conducted on safety culture, especially in high-risk sectors (e.g. mining or automotive). Comparing HS cultures in different countries can be useful in understanding the

effects of cultural and legal differences. By conducting similar studies at the international level, the differences between national and international standards can be examined. The findings obtained in this thesis study and the recommendations in line with these findings allow for more comprehensive and in-depth research in the field of HS culture and can increase the knowledge base in this field.

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Bölüm 6

The Impacts of Domestic Wastewater on Concrete Structure: A Case Study in Turkey

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1. Introduction

The ability of building materials and structures to perform their functions for many years without deterioration is referred to as durability. In civil engineering, strength is equally important in addition to durability. Historically, ancient buildings primarily utilized natural stone materials, which were constructed based on the principle of comparing compressive strengths. However, the volumes and weights of these structures were often substantial (Naspolini et al., 2020; Williams et al., 2010; Zhang et al., 2016). Over time, the materials used in construction have evolved.

Modern materials have been developed to withstand flexural and tensile stresses, in addition to compressive strength, with concrete now often replacing natural stone in applications requiring high compressive strength. The design and construction of a building can be viewed as an optimization problem that considers five key principles: durability, strength, functionality, economy, and aesthetics. Structures must be designed to safely support service loads, as well as loads resulting from events such as earthquakes. Additionally, they should resist both external and internal corrosive effects throughout their intended service life, be economical, and fulfill various requirements, all while exhibiting a unique and aesthetic appearance. Achieving these goals necessitates proper construction management and ongoing supervision throughout the building's service life.

Reinforced concrete structures are typically designed for a service life exceeding 100 years. However, despite our country being one of the largest cement producers in Europe, with the necessary technology and expertise for construction projects, many buildings are constructed illegally, without proper oversight, and in a haphazard manner. This situation often results in reinforced concrete structures failing to achieve their intended strength and becoming unstable in a short period of time.

Deterioration of buildings due to mechanical factors, air, water, and chemical substances can significantly reduce the strength and durability of materials. Therefore, it is crucial to detect and address such deterioration promptly to prevent potential hazards. The effects of deterioration can be categorized as physical, mechanical, chemical, and biological. Mechanical effects encompass compressive, tensile, impact, and flexural strength. If the mechanical stress on a building component exceeds the material's service limit, it may lead to structural failure and even collapse (Paula et al., 2014; Prata et al., 2019).

The collapse and damage of buildings during earthquakes exemplify the detrimental effects that concrete deterioration can have. The following types of deterioration commonly occur in concrete:

a) Freezing and thawing

b) Depreciation

c) Overexposure to chemical substances

d) Chemical reactions within the concrete

e) Corrosion of steel and other materials in concrete

1.1. Causes of Deterioration in Concrete

The ability of building materials to fulfill their functions over extended periods without deteriorating is known as durability. Concrete is one of the most widely used building materials today. The durability of concrete can be defined as its ability to maintain its initial properties and designed functions under various environmental and service conditions. Durable concrete refers to concrete that remains unaltered in its shape, quality, and functionality over time, in response to environmental conditions. After the service life period, the safety and cost-effectiveness of the concrete structure may deteriorate. Specifically, the stress capacity of damaged concrete may fall below the service stress, or the costs for repair and maintenance may exceed those of reconstruction (Ucker et al., 2013; Arunvivek et al., 2015; Low et al., 2007; Borger et al., 1994; de Matos et al., 2020).

The design and construction of a building can be viewed as an optimization problem that considers five key principles: durability, strength, functionality, economy, and aesthetics. Structures must be designed to safely support service loads as well as loads resulting from events such as earthquakes. They should also withstand external and internal corrosive effects during their intended service life, be economical, meet requirements, and exhibit a unique and aesthetic appearance. Achieving these goals necessitates proper construction management and ongoing supervision throughout the building's service life.

The deterioration of buildings due to mechanical factors, air, water, and chemical substances can lead to a reduction in the strength and durability of materials. Therefore, it is crucial to detect and address such deterioration in a timely manner to prevent potential hazards. These effects can be categorized as physical, mechanical, chemical, and biological. Mechanical effects include compressive,

tensile, impact, and flexural strength. If the mechanical stress on a building component exceeds the material's service limit, it may lead to structural failure and even collapse (Marzouk et al., 2016). The collapse and damage of buildings during earthquakes exemplify the detrimental effects that concrete deterioration can have.

Water or moisture presence is one of the factors responsible for concrete deterioration, in addition to mechanical effects. However, deterioration can result from several factors beyond mechanical effects. Water can transport hazardous substances into concrete and lead to chemical reactions. The extent of water movement in concrete depends on the type, diameter, and distribution of voids, the presence of micro or macro cracks, and whether the voids are continuous (McGivney et al., 2008; Aboelkheir et al., 2019). Controlling voids and preventing cracking in concrete is essential for long-term durability.

Other internal factors that can lead to concrete deterioration include the alkaline-aggregate reaction, the formation of delayed ettringite, and differences in the thermal properties of aggregate and cement mortars. The risks associated with these effects are unavoidable if measures are not taken to detect and counteract the gradual decline in the durability of concrete over time, which will ultimately lead to a decrease in compressive strength (Ghrair et al., 2018; Dabbebi et al., 2018; da Costa et al., 2020; Farid et al., 2019).

1.2. Corrosion of Steel

Corrosion, commonly referred to as rusting, is a chemical reaction that typically occurs in metals when they are exposed to water and oxygen. All metals, except gold, naturally revert to their lowest energy state, the oxide state. In reinforced and pre-stressed concrete structures, steel is commonly embedded in the concrete (Scrivener et al., 2011; Salvador et al., 2016).

When properly designed, high-quality, impermeable concrete can effectively shield steel reinforcement from physical and chemical factors. However, the reinforcement in reinforced concrete can be susceptible to corrosion through various means. Atmospheric substances can cause corrosion in exposed reinforcement. Additionally, steel embedded in concrete can corrode due to chlorine ions present in the aggregate and from water infiltrating the concrete as a result of carbonation. Using different metals for concrete reinforcement or the concurrent use of coated and uncoated steel, treated with substances like epoxy for corrosion protection, may lead to contact corrosion.

When steel reinforcement corrodes, its cross-section reduces, and its ductility diminishes. The rust generated from the reaction expands, creating internal compressive stress in the concrete and forming a gap between the concrete and the reinforcement. The area of the concrete reinforcement affected by rust, often referred to as the rust margin, can crack, leading to an increase in capillary gaps over time. Consequently, the exposed reinforcement becomes less resistant to external factors, accelerating the corrosion process and resulting in increased section loss. In prestressed elements, even a small loss of cross-section can have severe consequences, potentially leading to the failure of the prestressing tendon. Most critically, the bond between the reinforcement and concrete can become nearly nonexistent (Taylor et al., 1997; Miller et al., 2016; Dos et al., 2017; Sandrolini et al., 2001; Farid et al., 2019).

2. Method

The aim of this study is to investigate the effects of sewage (domestic wastewater) and landfill leachate—chemicals that adversely affect the strength and durability of concrete and reduce its service life.

Another cause of damage to concrete is the chemical reaction of the mixing water, evaporation of the unreacted portion, leakage, and binding of some water in the gel voids, which can lead to the freezing of water within the concrete. Table 2.1 illustrates the various approaches to assessing the degree of damage caused by frost at different temperatures. It is important to note that dry concrete is not affected by frost; rather, frost damage occurs only when concrete becomes fully saturated with water. The extent of air voids in concrete significantly influences its resistance to frost. If sufficient air voids are incorporated, the concrete can become frost-resistant; however, this may result in a decrease in compressive strength. This indicates that not all types of high-strength concrete effectively resist external factors. The ACJ 201 specifies the amount of air that should be introduced into concrete (refer to Table 2.2).

For this study, water samples were collected from untreated water and landfill leachate at the Istanbul Metropolitan Municipality's Domestic Wastewater Treatment Plants. These samples were then transported to the Sakarya University Engineering Faculty's Civil Engineering Building Materials Laboratory and placed in curing tanks. Details of the sample sources can be found in Tables 2.2 and 2.3.

Additionally, a curing tank was constructed using ordinary water. Fifty-four specimens of C20 and C30 grade concrete were produced at Adapazarı concrete plants, with each grade evenly distributed between the two curing tanks. The compressive strengths of these cube specimens were measured on the 7th, 28th,

56th, 90th, and 180th days using a 200-ton concrete compression press, and the findings were subsequently compared.

Table 2.1. Concrete age required to prevent concrete from freezing.

Maximum Aggregate Particle Size (mm)	**Total Air Content of Concrete (%)**	
	Moderate Effect (Concrete not exposed to severe moisture and freeze-thaw salts)	Heavy Effect (Concrete exposed to constant moisture and freeze-thaw salts)
9.5	6	7.5
12.5	5.5	7
19	5	6
25	5	6
37.5	4.5	5.5

Table 2.2. Recommended air content of freeze-thaw concrete

type of cement	**Water/Cement ratio**	**The time required for fresh concrete to avoid damage from frost, depending on curing temperature (hours).**			
		5 ^{O}C	10 ^{O}C	15 ^{O}C	20 ^{O}C
Normal Portland cement	0.4	35	25	15	12
	0.5	50	35	25	17
	0.6	70	45	35	25
Rapid-setting cements	0.4	20	15	10	7
	0.5	30	20	15	10
	0.6	40	30	20	15

Table 2.3. Baltalimanı Wastewater Preliminary Disposal Analysis Results

Parameter	**Deep Sea Discharge Limit**	**Maximum Values (mg/lt)**
T ºC	35 ºC	25.8 ºC
pH	6-10	7.6
Saltinity	-	4.7
CKM	400 mg/lt	6.5
KOI	250 mg/lt	574
BOI_5	350 mg/lt	174
AKM	10 mg/lt	478
Oil- gress	2 mg/lt	103
Sulfur		3.5
SDS		3.84
Sulphate		542
Top-N		95
NH_4-N		29.9
NH_4		56
Top-Cu		0.97
Top-Zn		1.04
Cr^{+6}		6.15
CrO^4		0.87
Ni^{+2}		2.19

Table 2.4. Landfill Leachate Characteristics

Parameters	Number of analysis	Mean	Minimum	Maximum
pH	42	7.4	6.2	8.2
Alkalinity, mg/L $CaCO_3$	42	9673	6300	12000
KOI, mg/L	42	23424	12350	47800
BOI_5, mg/L	36	15371	6820	38500
NH_3-N, mg/L	42	2128	1230	2690
AKM, mg/L	40	1994	940	4720
P, mg/L	37	2.6	0.1	6.4
Color, PtCo	41	19555	7400	44700
Chloride, mg/L	42	3428	725	8500
Fe, mg/L	42	73,9	4.91	365,3
Mn, mg/L	39	4.28	0.27	21.1
Cu, mg/L	39	0.20	0.10	0.42
Zn, mg/L	41	1.07	0.25	3.61
Pb, mg/L	40	0.86	0.18	3.57
Cd, mg/L	39	0.09	0.03	0.21
Cr, mg/L	39	0.32	0.07	0.91
Ni, mg/L	39	0.75	0.36	2.23

3. Results

After the concrete specimens cured in different waters were removed and cleaned on the 28th, 56th, 90th, and 180th days, their compressive strengths were determined using a 200-ton capacity press. The results are presented in Tables 3.1, 3.2, and 3.3.

Analysis of the sewage and landfill leachate during the experimental studies revealed that the water contained various chemicals, including sulfur, sulfate, salt, oil, organic matter, alkalinity, and ammonium nitrate (NH_4NO_3). These substances contribute to varying degrees of damage to both concrete and steel. The concentration of the substances used for curing influenced the intensity and duration of the damage observed.

A detailed examination of the test results shown in the tables indicates that these waters reduce the compressive strength of concrete over time. This effect is particularly pronounced in low-strength concretes, with C20 concrete exhibiting a greater reduction in strength after 180 days compared to C30 concrete.

Table 3.1. Compressıve Strength Of Concrete Cured In Sewage Water (kgf/cm^2)

Concrete Grade	Day							
	28	mean	56	mean	90	mean	180	mean
C20	246 250 243	246	314 308 292	305	339 334 341	338	361 410 385	385

C30	265 267 261	264	343 338 322	335	367 362 370	366	402 421 407	410

Table 3.2. Compressıve Strength Of Concrete Stored In Waste Water (kgf/cm^2)

	Day							
Concrete Grade	28	mean	56	mean	90	mean	180	mean
C20	297 305 316	306	330 320 331	327	362 346 340	349	275 287 396	320
C30	340 350 321	337	360 358 362	360	374 387 384	382	369 320 389	359

Table 3.3. Compressıve Strength Of Concretes Stored In Normal Water (Kgf/Cm^2)

Concrete Grade	**Day**							
	28	mean	56	mean	90	mean	180	mean
C20	302 308 316	309	334 343 334	337	352 358 352	354	368 365 363	365
C30	334 339 336	336	366 370 358	365	362 392 389	380	366 388 374	376

4. Conclusion and Recommendations

Some concrete and reinforced concrete building elements may be used continuously or occasionally, depending on their functions. These elements can come into contact with water containing various chemicals, some of which can damage both the concrete and its reinforcement. The effects of this damage can vary from weak to moderate to severe, depending on the type and concentration of chemicals present in the water (Scrivener et al., 2011; Salvador et al., 2016).

The liquids may contain harmful substances such as sulfates, sulfites, chlorine, ammonia, oils, organic materials, carbonates, acids, and similar agents that can cause damage to concrete. For instance, the presence of sulfates in the environment can lead to salt expansion within the concrete, potentially causing explosions. Chlorine ions can contribute to the corrosion of steel reinforcement and the gradual disintegration of concrete. Additionally, high alkalinity in water can also harm concrete. Calcium carbonate in water reacts with carbonic acid to form calcium bicarbonate, which dissolves calcium hydroxide in cement, rendering the concrete more porous (Salvador et al., 2016; Taylor et al., 1997; Miller et al., 2016; Dos et al., 2017; Sandrolini et al., 2001).

Sulfur compounds and sulfur present in water become detrimental to concrete when hydrogen sulfide, produced over time in hot conditions, reacts with atmospheric oxygen to form sulfuric acid. The effects of sulfuric acid on concrete can be highly destructive, depending on its concentration in the water.

Organic substances such as animal and vegetable oils (e.g., margarine, soybean oil), ammonium compounds, bleaches, detergents, and fertilizers in water can have either slow or rapid polishing effects on concrete (Farid et al., 2019; Scrivener et al., 2011; Salvador et al., 2016; Hover et al., 2011).

The effectiveness of certain chemicals increases with the pH level of the water. Waters with a pH value below 6.5 are considered acidic, which enhances the effectiveness of chemical substances. Conversely, water with a pH above 6.5 must contain bicarbonate to be effective. Extremely high pH values (>13) can lead to alkaline aggregate reactions, as alkali-silica reactions can develop in environments with elevated hydroxyl ions (Ghorbani et al., 2019; Gholhaki et al., 2018).

Examination of the sewage and landfill leachate used in experimental studies indicates that these waters contain chemical substances such as sulfate, sulfur, salt, oil, organic matter, alkalinity, and ammonium nitrate. These substances affect concrete to varying degrees, resulting in damage depending on their concentration. The effects are generally slow and long-lasting (Wei et al., 2017; Ahmed, 2017).

Test results reveal that wastewater reduces the compressive strength of concrete over time (Su et al., 2003; Su et al., 2000; Esfahani et al., 2018), and it can be concluded that these effects will escalate with time. Specifically, the reduction observed at 180 days was slightly more pronounced in the C20 concrete compared to the C30 concrete. Therefore, concretes that come into contact with wastewater and chemically contaminated water are likely to lose strength and durability over time. To mitigate this issue, it is crucial to prevent concrete from coming into contact with such waters.

Acknowledgments: This study, titled "Investigation of the Effects of Sewage and Landfill Leachate on Concrete Strength," was derived from the master's thesis prepared by Dr. Mehmet Hayrullah Akyildiz at Sakarya University, Institute of Science, Department of Civil Engineering, Structural Engineering, under the supervision of Dr. Mansur Sumer.

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